Overview

The Carbon Mitigation Initiative (CMI) at Princeton University is a university-industry partnership sponsored by BP and Ford Motor Company. The goal of the project is to find solutions to the carbon and climate problem that are safe, effective and affordable. Now entering our 9th year, our researchers are speeding progress in the areas of carbon science, carbon capture, carbon storage, and carbon policy.

The Capture Group assesses technologies for capturing CO₂ emissions from fossil fuels used in electricity, hydrogen, and synfuels production. Other research areas include studies of alternative fuel combustion, renewable energy, and energy storage.

The Storage Group studies potential risks of injecting CO₂ underground for permanent storage. Models of subsurface carbon dioxide behavior and laboratory studies of well cement degradation are helping the group evaluate that risk.

The Science Group collects data from the oceans, the atmosphere, ice cores, and the land biosphere to study how natural sources and sinks of carbon have varied in recent and ancient times, and how they will respond to future climatic change.

The Integration Group synthesizes research discoveries and explores the policy implications of carbon mitigation strategies. It also works to communicate issues of carbon and climate to industry, government, NGO's and the general public.

Led by CMI Co-Directors Stephen Pacala and Robert Socolow, the group has grown to include over 60 researchers. Together we are building a comprehensive view of the challenges of carbon mitigation - and how they can be overcome.

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Executive Summary

The eighth year of the Carbon Mitigation Initiative was marked by BP's decision to commit to the funding of CMI through 2015, a five-year extension that has enabled a deepening of commitment when otherwise we might have begun to close down.

This past year was also marked on campus by an extraordinary outpouring of support from students, faculty, administration, and alumni for Princeton to become the world's leading university in climate and energy research. An early manifestation is the Energy Grand Challenge, a campus-focused effort to provide new courses, internships, and collegial opportunities for Princeton’s students. CMI has been viewed as a template for broadly based interdisciplinary collaborations and industry-university partnerships.

This eighth annual report provides brief reports from the Carbon Mitigation Initiative’s thirteen research groups. Two of these groups were added in the past year, one in nanomaterials and one in ocean biogeochemistry. The reports are presented under our four umbrellas: Carbon Capture, Carbon Storage, Carbon Science, and Carbon Integration.

The CARBON CAPTURE effort is conducted by the Williams Group, the Law Group, and the Arnold Group. The Williams Group, in response to a request from the U.S. National Academies to provide assistance to its study, America’s Energy Future: Technology Opportunities, Risks, and Tradeoffs, developed a consistent set of technical and economic analyses for the conversion of coal and biomass to both electricity and synthetic fuels, with and without CO2 capture. This unified view revealed configurations with unexpectedly favorable costs when power and fuels are produced together, in a world of high prices for both oil and CO2 emissions.

The group also completed a major study on wind with compressed energy storage, whose results point to the promise of this still largely undeveloped storage technology, especially in situations where the wind is remote from the load and natural gas is available to supplement wind at the source.

A new area of investigation is the coal-CO2 slurry as a means for fuel delivery to high-pressure gasifiers. Such a system may have advantages over both water-coal slurries (lower latent heat of vaporization) and dry-feed systems (simpler, less costly pressurization).

The Law Group is conducting fundamental research on the combustion chemistry of biofuels, including higher alcohols such as propanol and butanol, at the high pressures of internal combustion engines. The group continues its notable collaboration with researchers at the Ford Research Laboratory on computational issues of fuel chemistry – providing reduced-order oxidation mechanisms for incorporation in Ford’s computer codes. The result is improved large-scale engine simulations, such as are required to predict engine knock.

During a two-week visit to China in the fall of 2008, Law discussed with Chinese colleagues the establishment of an infrastructure for fundamental combustion research in China to support its technological needs in energy sustainability and climate issues. He gave a total of six lectures and seminars on various topics on fuels, energy, and the environment. As well, in his role as a past
president and a director of the International Combustion Institute, he conducted a site visit on behalf of the 33rd International Combustion Symposium, which will be held at Tsinghua in 2010.

The Arnold Group is developing new electrochemical energy storage technologies for portable power and load leveling and regulation on the grid, compatible with modern forms of energy generation. With the goal of extending the cycle life of lithium-based batteries and carbon-based supercapacitors, they are exploring the relationship between the external mechanical forces on the storage materials and their resulting electrochemical performance.

The CARBON STORAGE effort is conducted by the Celia Group, the Scherer-Prevost Group, and the Peters Group. They all address leakage of CO₂ after storage below ground. An exciting landmark in the numerical modeling by the Prevost-Scherer Group was the completion of an improved flash calculation that simulates the phase changes that would occur during leakage of CO₂ up a well. The group also acquired new experimental capabilities for examining corroded cements.

The Celia Group made steady progress with a hybrid analytical-numerical model of reservoir-scale leakage and is creating a web-based version at the request of BP and the Environmental Protection Agency. Celia, the 2008 Darcy Distinguished Lecturer for the National Ground Water Association, presented a lecture titled "Geological Storage as a Carbon Mitigation Option" on 52 different occasions, across 12 countries and 4 continents.

The Peters Group, funded by DOE, focuses on geochemistry, in particular acid-driven mineral dissolution and precipitation. It is a leading player in a proposal to the National Science Foundation to develop a national experimental CO₂ storage research facility deep below ground.

The CARBON SCIENCE effort is conducted by the Pacala Group, the Sarmiento Group, the Bender Group, the Sigman Group, and the Morel Group. With many overlapping interests, the Pacala Group (terrestrial biosphere) and the Sarmiento Group (oceans) are jointly developing a Carbon Observing System. New work indicates an unexpected increase in the land sink after 1990, concentrated in the tropics. Early results from forward modeling suggest that, in the absence of CO₂ fertilization, a massive release of carbon from the biosphere to the atmosphere will occur if atmospheric CO₂ is allowed to reach double its preindustrial concentration. Their results make use of gas measurement and analysis from the Bender Group.

The Sigman Group and the Bender Group explore paleoclimate. Results from the Sigman Group continue to point to the importance of polar ocean circulation in glacial/interglacial cycles, and are beginning to resolve conflicts between global warming simulations and paleodata. The Bender Group is analyzing ice deposits near the surface in Antarctica that it believes may contain air older than the oldest air trapped at the bottom of Antarctic glaciers.

The Morel Group has embarked on a new CMI science program addressing ocean acidification, integrating laboratory and field studies. Their early studies of phytoplankton growth suggest that while a reduction in unbound iron on its own should reduce the growth rate, the concomitant increase in dissolved CO₂ may counteract this inhibition by making growth more iron-efficient.
The **CARBON INTEGRATION** effort is conducted by the **Pacala-Socolow Group** and the **Oppenheimer Group**. The **Pacala-Socolow Group** has proposed a new approach to the allocation of a global CO₂ emissions target among the nations of the world, based on a reinterpretation of concept of “common but differentiated responsibilities” (language in the current international agreements), so that the phrase refers to individuals rather than nations. In this formulation, obligations are the same for individuals with similar life-styles, independent of the per-capita emissions of the country in which they live. Follow-on work is aimed at modeling CO₂ emissions generated by activities strongly correlated with wealth, including travel by air and meat-eating. Other work documents a remarkable increase in the level of installation and operation of SO₂ scrubbers at China’s coal plants, which conventional economic models would not expect to occur until China had reached a substantially higher per capita income.

A new area of activity is the direct capture of CO₂ from the atmosphere by chemical and physical means. Here, CMI is leveraging a new study being conducted by the Panel on Public Affairs of the American Physical Society.

This group is also responsible for CMI outreach. In the past year, CMI has partnered with the National Energy Education Development Project to bring the “stabilization wedges” concept to teachers.

The **Oppenheimer Group** has initiated a project on the history of environmental assessments, beginning with an assessment of the problem of stratospheric ozone depletion. Through analysis of published and archival documents and interviews with key scientists, policy makers, and members of industry, the history of scientific assessment of ozone depletion is being reconstructed. An intriguing dimension of this work is “negative learning” – the phenomenon where scientists stick for long periods of time to the wrong path, rather than converging on the truth inexorably via successive approximations. The expectation is that insights gained from this project will improve our understanding of the scientific learning process and will be transferable to scientific assessment of global climate change.

At the time of this writing, just before our eighth Annual Meeting, the United States has a new president and a new stance on climate change. Close friends are in the Obama Administration in leadership roles, notably John Holdren, the President’s nominee for Science Advisor. (With his new job, Holdren relinquishes his leadership role in the Energy Technology Innovation Project at Harvard University, within which a BP-funded energy policy effort has been conducted under CMI.) The many Americans long distressed at the desultory policies of the previous administration bearing on climate change are now hopeful that the U.S. can reinvigorate a flagging global effort to improve scientific understanding, accelerate technology deployment, and test and refine bold policies. CMI has never been as much needed.

For previous annual reports, see http://www.princeton.edu/~cmi/summary/
Carbon Capture

The Carbon Capture area of CMI consists of the Williams Group, The Law Group, and the Arnold Group. The researchers are developing new strategies to enable the transition to low-carbon energy sources. Research over the past year has been mainly in the following areas:

- Systems analyses for synthetic fuels production
- Proposed CCS Early Action Initiative
- Collaboration with colleagues at Politecnico di Milano
- CO₂ coal slurry-feed gasification
- Energy in China
- Wind energy and energy storage technologies
- Modeling the combustion of alternative fuels

Systems Analyses for Synthetic Fuels Production

The Williams Group carried out systems analyses for synthetic fuels production include both generic systems studies and a case study of hypothetical coal/biomass polygeneration systems that might be deployed in Illinois.

Generic Systems Studies

A major analytical activity during 2008 was a systematic investigation of mass, energy and carbon balances, fuel-cycle-wide GHG emissions, prospective capital and production costs, and economic outlook as a function of GHG emissions price and oil price, for 16 alternative plant configurations for making Fischer-Tropsch (F-T) liquids in gasification systems from coal or biomass alone, and from coprocessing coal and biomass. The work, the first results published from which appear in the Proceedings of the 2008 Pittsburgh Coal Conference, analyzed both RC (recycle) systems that maximize the production of liquid fuels by recycling unconverted syngas and OT (once-through or “polygeneration”) systems that burn unconverted syngas to generate electricity. Energy and cost adders for CO₂ capture and storage (CCS) relative to systems that vent CO₂ (V) were estimated.

A major impetus for this work was a request from the National Research Council (NRC) to develop a detailed spreadsheet model to help the Alternative Fuels Panel and other Panels of the NRC’s 18-month study entitled America’s Energy Future: Technology Opportunities, Risks, and Tradeoffs being carried out to help guide the Obama Administration on energy policy. The PEI analysis was intended to help the authors of that study understand, on a self-consistent basis, how alternative synfuel and power technologies relate to one another in terms of mass, energy and carbon balances, fuel-cycle-wide GHG emissions, and economic prospects. Previous Capture Group experience with synfuels production analysis and the timely addition to the group in March 2008 of Dr. Guangjian Liu, an
experienced Aspen Plus modeler from the BP Clean Energy Center of Tsinghua University enabled the Capture Group to take on this effort to respond to the NRC request.

For the NRC spreadsheet, the researchers created Aspen Plus models for more than 30 different plants that convert bituminous coal and/or biomass via gasification to electricity and/or liquid transportation fuels (primarily F-T liquids) with and without CCS. Rather than investigate the promise of novel technologies, this study focused on potential gains to be found in new combinations of technologies that are proven at commercial scales or are near commercial. Detailed mass, energy and carbon balance simulation results were imported into a common framework (Microsoft Excel) used for calculating capital costs, fuel-cycle-wide GHG emissions, internal rates of return, and break-even oil prices (for liquid fuels), as functions of GHG emissions price, crude oil price, and financing costs. This dual Aspen/Excel methodology has proved to be a powerful tool for carrying out a detailed, self-consistent evaluation of many disparate plant configurations.

The findings of this study were summarized in a paper prepared for 9th Biennial GHG Control Technologies meeting (November 2008) and presented there by Williams. The main findings are:

- For the same coal input levels, an OT synthesis plant can provide F-T liquids at a much lower production cost (and therefore a lower breakeven crude oil price) than can a RC synthesis plant. This advantage (illustrated in Figure 1 for coal-only systems) arises largely because OT plants can generate electricity at far higher efficiencies than stand-alone coal power plants by harnessing waste heat from F-T synthesis, leading to a relatively high credit for the electricity co-product.

- Polygeneration systems can provide decarbonized electricity at a cost of GHG emissions avoided that is $\frac{1}{3}$ to $\frac{1}{2}$ of that for stand-alone power plants. This avoided cost difference arises because F-T systems generate a pure CO$_2$ stream (accounting for $\sim \frac{1}{2}$ of feedstock carbon) as an inherent aspect of the synthesis process, so that CO$_2$ capture costs are very low (Figure 2). (Capture costs for the RC configuration, also shown in Figure 2, are lower than for the OT system, but economics for the RC design are not as favorable for the conditions analyzed.)

- Biomass/coal co-processing in polygeneration plants with CCS can lead to significant reductions in F-T liquids GHG emission rates very cost-effectively under a serious carbon mitigation policy (Figure 3). This benefit, arising largely because of the negative carbon emissions from biomass deployed in CCS systems, makes it feasible to realize near-zero GHG emissions for liquid fuels with much less biomass input than with biofuels such as cellulosic ethanol.

- Because polygeneration plants have two revenue streams (from liquid fuels and electricity) they can be very powerfully competitive in economic dispatch competition (Figure 4). As long as oil prices are not too low, polygeneration plant operators can bid to sell electricity in dispatch markets down to prices far less than what existing coal power plants can bid—offering thereby a market approach for replacing carbon-intensive coal power with decarbonized power. To illustrate, Figure 4 shows that, at a GHG emissions price of $80$ a tonne of CO$_{2\text{eq}}$, the minimum dispatch cost for CBTL-OT-CCs is $\frac{1}{4}$ of that for existing coal power plants when the oil price is $20$ per barrel, and zero when the oil price is $40$ per barrel.
Figure 1. Breakeven Crude Oil Price vs. GHG Emissions Price for Alternative F-T Liquids Systems Fueled with Coal

All systems shown assume the same level of coal input and produce F-T liquids in the form of finished diesel (61%) and finished gasoline (39%). For the CCS cases, the CO₂ is stored in a deep saline formation located 100 km from the conversion plant. In this figure, as well as in Figures 3 and 7, the selling price for the electricity co-product is assumed to be $60/MWh (US average grid price in 2007) + a GHG emissions charge at the 2007 U.S. grid-average GHG emissions rate (636 kg CO₂eq/MWh).

Figure 2. CO₂ Capture Costs for Alternative Energy Conversion Systems

The capture cost is the difference between the 20-year levelized production cost ($ per GJ) in the CTL cases and $ per MWh in the electricity cases) with CO₂ captured and that with CO₂ vented for the same plant type divided by the CO₂ capture rate (in tonnes of CO₂ per GJ and MWh, respectively). The capture cost includes the cost of compression to 150 bar but not costs for CO₂ transport and storage. The 4th and 5th bars involve post-combustion capture for a supercritical pulverized coal steam-electric plant (PC) and for a natural gas combined cycle power plant (NGCC), respectively.
Figure 3. Break-even Crude Oil Price vs. GHG Emissions Price for Alternative F-T Liquids Systems. The four coal F-T options shown are the same as in Figure 1. The five additional systems involve biomass, assumed in all cases to be delivered at a rate of 1 million dry tonnes per year. Two of these involve only biomass (BTL options) and 3 involve coal/biomass co-processing (CBTL options). Notably, a zero net GHG emission rate is realized for the CBTL-OT-CCS option, which is fueled with 38% biomass.

Figure 4. Minimum Dispatch Cost at Two GHG Emissions Prices for Existing Coal Power Plants (left) and for CBTL-OT-CCS Plants (right). The market determination of when a plant connected to the power grid gets dispatched and thus a plant’s capacity factor depends only on the short run marginal cost (SRMC)...the capital cost is a sunk cost that does not come into play. Power plant operators will bid to provide power in economic dispatch at power prices down to the minimum dispatch cost (MDC), determined by the condition that revenues = SRMC. For existing coal power plants the only revenue stream is from electric power sales, so that the MDC for coal power (MDC CP) = SRMC. For OT F-T liquids systems there are two revenue streams (one from power and one from F-T liquids), so that the MDC can be less than SRMC as long as oil is above a certain minimum price.
If CCS is pursued for biomass, system economics would be more favorable if biomass is co-processed with coal than if it is used in biomass-only systems—because of coal energy conversion scale economies and the low cost of coal relative to biomass. The negative emissions arising from photosynthetic CO₂ storage can offset positive emissions from coal.

To summarize, coal/biomass polygeneration with CCS systems offer an economically attractive way to decarbonize simultaneously both liquid fuels and electricity under a serious carbon mitigation policy.

**Illinois Case Study for Coal/Biomass Polygeneration with CCS**

The synfuels systems analysis discussed in the previous section was not location specific. To illustrate possibilities more concretely, a case study for Illinois was carried out led by Eric Larson of the Williams group in collaboration with Giulia Fiorese and Stefano Consonni at the Politecnico di Milano (Figure 5). The analysis was for coal/biomass-fueled coal minemouth plants with CO₂ storage in deep saline formations 100 km away. The analysis includes detailed estimates of energy and carbon balances and costs for the biomass supply—assumed to be either corn stover or low-input, high-diversity, perennial grasses (also known as “mixed prairie grasses” or MPGs) grown on degraded lands that are not suitable for food production and have carbon-depleted soils. These feedstocks were selected for focused attention because of growing concerns about biomass grown for energy on lands that could alternatively be used for growing food—concerns about higher food prices and about indirect land use impacts. Growing MPGs in C-depleted soils leads to a build-up of soil and root carbon, which is ecologically desirable and also implies that less biomass input is required at the
polygeneration plant to realize zero net GHG emissions for the liquid fuels than would be required for a system that does not benefit from soil/root carbon buildup. Both plants were designed to provide liquid fuels with a zero net GHG emission rate (GHGI = 0).

The MPG-fueled plants have net output capacities of 13,000 B/D and 410 MW_e. Delivered MPG costs and associated energy use and greenhouse gas (GHG) emissions were estimated as levelized values over a 30-yr period, assuming the field is annually harvested. Fuel-cycle-wide energy requirements associated with MPG production and delivery total 1.0 GJ per dry tonne (dt)—equivalent to 6% of the energy in the delivered biomass. The corresponding GHG emissions amount to 77 kgCO_2eq/dt—equivalent to 4.5% of the CO_2 that would be released if the MPGs were burned. In both instances MPG transport is the dominant contributor (Figure 5). The average cost of delivered MPGs is $132/dt ($7.1/GJ HHV)—about 5 times the assumed delivered coal price on an energy basis. For the plant design using corn stover, net plant output capacities are 7,700 B/D and 290 MW_e,—much less than for MPGs because there is no credit for soil/root C buildup. The estimated delivered yield is 3.8 dt/ha/yr. The average delivered cost is $63/dt ($3.6/GJ HHV)—about half of that for MPGs.

There are many possibilities for plant sites considering that coal underlies 65% of Illinois, the Mt. Simon aquifer underlies much of Illinois, and the fact that MPG and corn stover are abundant (with estimated state-wide supplies of ~ 2 and ~ 20 million dt/yr, respectively) and relatively uniformly distributed (Figure 6).
Using the above discussed biomass cost estimates and the synfuel economic analysis methodology developed in support of the NRC study discussed earlier, the overall economics for these polygeneration plants were explored in relation to the economics for four large coal-only systems. One measure of economic performance, the breakeven crude oil price (BECOP), is shown as a function of the GHG emissions price in Figure 7 for these alternative systems. The BECOPs are essentially the same for MPGs and corn stover even though the delivered biomass cost is about twice as large for MPGs both because the biomass feed rate required to realize a zero net F-T liquids GHG rate is much less for MPGs and because of scale economies. At $0/t CO_{2eq}$ the least costly F-T liquids option is a coal once-through plant that vents its CO$_2$ with no cost for GHG emissions, the BECOP for the coal/biomass polygeneration plants with CCS is 2.5 X as large. But at $60/t CO_{2eq}$, the coal/biomass polygeneration plants with CCS are the most cost-competitive synfuel options—with a BECOP below $40 a barrel and essentially at the same level as for the much larger coal once-through system that vents CO$_2$ when the GHG emissions price is zero.

The same approach to analyzing supply availability in Illinois was used to estimate corn stover and MPG availability and cost in a swath of 23 central US states that in 2007 accounted for 94% of US corn production and ~12 million ha of CRP enrollments (86% of US total). The 23-state potential energy production from coal plus MPG and corn stover is 1.4 million B/D of zero-GHG emitting FTL fuels plus 400 TWh of decarbonized electricity (equivalent to 20% of US coal power generation in 2007).

The biomass potential for co-processing at coal/biomass polygeneration plants might well be greater than these calculations suggest—even in these 23 states. These states contain a USDA-estimated 135 million hectares (~70% of U.S. total) of abandoned or degraded agricultural land that might be considered for growing MPGs. Other prospectively important biomass supplies include other crop
residues and woody biomass supplies such as urban wood wastes and forestry residues: mill residues, logging residues, diseased tree kills, fuel treatment thinnings, and productivity enhancement thinnings.

To summarize, coal/biomass polygeneration with CCS systems supplied with biomass that is not grown on cropland offer both the potential for providing synthetic fuels that would be highly competitive under a serious carbon mitigation policy and for making significant contributions to overall supplies of low-carbon liquid fuels.

Proposed CCS Early Action Initiative

It is widely recognized that the most significant obstacle to the routine pursuit of CCS is successful demonstration of CO₂ storage at “megascale” (storing at least a million tonnes of CO₂ per year) in a variety of geological media—with emphasis on deep saline formations, which account for most of the geological storage opportunity. Demonstrations are needed both to address scientific and technical issues regarding CO₂ storage at commercial scales and to ascertain, to the satisfaction of a wide range of stakeholder groups and opinion-shapers, whether CCS is viable as a “gigascale” carbon mitigation option. To address these needs, an agreement was reached at the July 2008 G8 Summit in Japan that the G8 would commit by 2010 to sponsor 20 large-scale fully integrated CCS demonstration projects worldwide with the aim of establishing the basis for broad commercial deployment of CCS after 2020. The US agreed to sponsor at least 10. But the ensuing global economic deterioration and concerns about the growing budget deficit have cast a shadow on the prospects for major near-term carbon mitigation actions such as the G8-proposed integrated CCS projects.

To address this dilemma, Williams developed a proposal for a CCS Early Action Initiative (CEAI) that exploits the CMI finding that coal/biomass polygeneration systems with CCS represent a low cost approach to electricity decarbonization. The proposed CEAI is motivated by the likelihood that, for early CCS projects, government will have to pay for a significant fraction of the incremental CCS cost, and the premise that federal funds will be scarce for purposes other than for dealing with the economic crisis.

Under the proposed CEAI the Departments of Energy and Defense would collaborate in carrying out 10 megascale integrated CCS projects based on commercial or near-commercial technologies that would involve CO₂ storage in deep saline formations. Both Departments have much to offer to the proposed CEAI. A major role for DoE is essential to ensure technical success. The DoD would be a motivated partner in light of the Air Force’s goal of meeting ½ of its North American jet fuel demand from secure domestically produced synthetic fuels by 2016—a goal that could plausibly be realized under the proposed CEAI. Also the DoD is committed to alternative energy implementation in all sectors and has already established a strong track record.

Under the CEAI the federal government would provide incentives for 10 megascale integrated CCS projects, each of which would meet the criteria for DOE’s restructured FutureGen competition: (i) produce at least 300 MWₑ of decarbonized power; (ii) store at least 1 million tonnes of CO₂ per year in
deep saline formations; (iii) use domestic coal for at least ¾ of the feedstock; (iv) use at least ½ of the coal to make electricity as a product; and (v) come on line by 31 December 2015. Furthermore, under the CEAI, qualifying projects could include not only coal electricity projects but also polygeneration projects that produce, along with decarbonized electricity, synthetic fuels with GHG emission rates that are not more than for the displaced conventional fossil fuels. In order to avoid the “carbon debt” issue recently brought to light by Tim Searchinger and Dave Tilman, projects that co-process biomass feedstocks would be limited to those not grown on good cropland.

In order to minimize the cost to the government, and ultimately society, the winning CEAI projects would be those that satisfy all the above criteria at the least costs of GHG emissions avoided. One part of the incentive for winning projects is government paying over a period of 5 years for the incremental CCS cost. In addition, winning projects that provide synthetic jet fuel would be offered by the Air Force 20-year procurement contracts at purchase prices consistent with synfuel production costs under competitive market financing conditions.

Williams’ analysis in support of his CEAI proposal shows that if all winning CEAI projects were small polygeneration plants (producing ~ 300 MWₑ + 10,000 B/D of F-T liquids) co-processing less than 10% biomass, the estimated present value of the subsidy cost would be $5.8 billion, $4.5 billion, or $0.4 billion (equivalent to 38%, 26%, or 2% of the capital costs for these plants) if the levelized crude oil price over the 20-year subsidy period is $50, $60, or $80 a barrel. For higher levelized oil prices the subsidy would be negative, because the procurement of synthetic jet fuel would save the government money relative to having to buy jet fuel derived from crude oil.

An alternative approach to early CCS action was put forth in the Dingell/Boucher climate change discussion draft released in October 2008. That plan would offer subsidies of $90/t, $70/t, and $50/t for CO₂ emissions avoided over a period of 10 years for the 1st, 2nd, and 3rd sets of 3 GWe each of decarbonized coal power plants deployed in the US. The relevant comparison to the proposed CEAI (were all winning CEAI projects to be small polygeneration plants) is the subsidy required for the first 3 GWe (equal to the plausible total electric capacity for 10 small coal/biomass polygeneration plants under the proposed CEAI)—about $10 billion, equivalent to almost 80% of the capital costs if all the deployed plants were to be IGCC-CCS plants.

Although the primary purpose of the proposed CEAI is to exploit polygeneration as an instrument for gaining early megascale CCS experience at a low cost to government, the CEAI would also help catalyze market interest in deploying coal/biomass polygeneration systems, which face significant institutional hurdles as a result of having to process two very different feedstocks (coal and biomass) and having to market two very different commodity products (electricity and synfuels).

**Collaboration with Colleagues at Politecnico di Milano**

In addition to the Illinois case study described above, the Williams Group collaboration with colleagues at Politecnico di Milano has involved an investigation of the new Shell dry-feed partial water quench gasifier in an IGCC-CCS application and development of a new methodology for
optimizing heat integration for power generation via steam cycles that is likely to be especially important in evolving optimal designs for polygeneration plants.

**Shell IGCC+CCS: Partial Water Quench vs. Standard Syngas Cooling**

Numerous studies indicate that bituminous coal-based electric power with CCS is significantly less expensive using integrated gasification combined cycles (IGCC) instead of standard pulverized coal (PC) steam electric plants. However, for lower rank sub-bituminous coals and lignites which comprise fully half of the world's coal reserves, the advantages of gasification are much less clear. This year Tom Kreutz, in collaboration with Emanuele Martelli and Stefano Consonni at Politecnico di Milano, completed a techno-economic analysis of an idea recently patented by Shell: combining a dry-feed gasifier with a partial water quench of the raw synthesis gas.

The Shell coal gasification process (SCGP) is of particular interest because, as opposed to coal-water slurry gasifiers, it is able to convert coals of all rank into electricity and other energy carriers. However, the SCGP typically employs costly high-temperature heat exchangers to cool down the raw syngas by generating high-pressure steam prior to syngas cleaning and chemical processing. The SCGP offers significantly increased plant efficiency in traditional plants that vent CO₂, but syngas coolers are not well matched to plants with carbon capture. A relatively moist syngas is required to promote the water-gas shift (WGS) reaction and achieve high levels of carbon capture; in a standard Shell IGCC+CCS design, most of the steam generated in the costly syngas coolers is needed for syngas humidification. Shell's new partial water quench design cools the hot raw syngas by direct water injection, both humidifying the syngas and eliminating the costly syngas coolers.

In order to quantify the tradeoff between reduced efficiency and lower capital cost associated with the partial water quench, Kreutz and Politecnico di Milano colleagues completed a techno-economic comparison in the context of bituminous coal-fed Shell IGCC+CCS. Their detailed thermodynamic modeling indicates that the efficiency penalty caused by the partial water quench is relatively small, ~1 percentage point in LHV efficiency. On the other hand, the plant capital cost falls by 4-14%, and the levelized cost of electricity drops between 2.5 and 9%. In short, the partial water quench appears to be a promising strategy for use of dry feed gasifiers in plants with CO₂ capture.

**Optimization of Integrated Steam Cycles**

In a gasification system with co-production of fuels and electricity, the steam cycle is fed by a large number of inputs (heat recovery from various sources at different temperatures) and may supply a large number of auxiliary processes. As part of his Ph.D. thesis at Politecnico di Milano, colleague Emanuele Martelli has developed a new methodology to optimize the configuration and the operating parameters of complex steam cycles. The novel and most relevant feature of the method is its capability to identify the optimal configuration of the heat exchanger network as part of the solution of the optimization algorithm, rather than pre-determining the configuration ahead of optimizing the operating parameters. The original linear model, created in Microsoft Excel, has been extended to allow for automatic optimization of the steam cycle pressure levels, requiring significantly more complex non-linear optimization techniques; the code has been re-written in both MATLAB and a dedicated package for solving sets of non-linear equations. The methodology has been applied to a
number of studies, both at Politecnico and at Princeton by Tom Kreutz, and has proven to be a robust design tool, especially in complex polygeneration plants with high levels of heat integration.

**Separation of CO₂ from Syngas via Phase Change**

The Williams Group has also continued to assess the performance (in terms of power consumption and fraction of CO₂ captured) of cryogenic pre-combustion capture in IGCCs, deepening the analysis on the “external refrigeration scheme” developed in the CMI framework during 2007. Following interactions with BP Alternative Energy group, new schemes with propane/butane as the working fluid have been considered as substitutes for the ammonia chiller originally proposed. Also, an ammonia refrigeration scheme without de-superheating at compressor discharge has been investigated. Preliminary results show that the external refrigeration scheme already considered in 2007 offers slight margins for improvements.

**CO₂-Coal Slurry-Feed Gasification**

Carbon policy enactment might *directly* inspire new approaches to gasifier and energy system design—as illustrated by the idea, currently being investigated by the Williams Group, of using coal-CO₂ slurries for gasifier feed systems.

Pressurized, O₂-blown, entrained-flow gasification has proven to be a promising approach for converting coal and biomass to clean, low carbon energy carriers such as electricity, H₂, synthetic natural gas, and synthetic liquid transportation fuels. Pressurization confers many advantages, both thermodynamic and economic. However, it also exacts costs (thermodynamic and economic), especially for gases, which are much more energy-intensive and costly to compress than liquids. For this reason, an entire class of coal gasifiers (e.g. GE and Conoco-Phillips E-Gas technologies) employs a coal-water slurry that can be pumped at low energy penalty and cheaply to high pressure prior to injection into a high-pressure gasifier. Dry feed gasifiers (e.g. Shell and Siemens), in contrast, pressurize the feedstock via relatively costly and complex lockhoppers that require compressed gas. For this reason, dry-feed gasifiers are typically operated at lower pressures than their slurry-feed counterparts.

CCS at coal conversion facilities offers a potentially attractive alternative: an abundant supply of liquid (i.e. supercritical) CO₂ for preparation of a CO₂–coal slurry for coal pressurization and transport into the gasifier. Such a system may have advantages over both water-coal slurries (due to a lower latent heat of vaporization for CO₂) and dry-feed systems (simpler, less costly pressurization). This idea was investigated by EPRI in the mid 1980’s, but the relative advantages remain unclear.

An investigation of this concept is underway in an effort led Tom Kreutz of the Williams Group in collaboration with visiting colleague Michiel Carbo from ECN in The Netherlands. The investigation will explore the pressure and temperature space of the slurry preparation, storage, transport and injection, seeking to understand the complex issues associated with mixing supercritical CO₂ with
hot, pulverized coal, and to see whether there are promising system designs offering notable thermodynamic and economic benefits.

While full-time at ECN, Carbo is also finishing his Ph.D. at Delft University of Technology. He has designed and analyzed in detail many important sub-systems at coal IGCC+CCS plants—including water-gas shift (WGS), H₂ separation membrane reactors, novel WGS designs, and off-design gas turbine operation.

**Energy in China**

**Liquid Fuels from Coal and Biomass**

Because of the Williams Group’s unexpected opportunity to contribute to the National Research Council study *America’s Energy Future* (discussed above), some previously planned work was postponed. The postponed work included finalizing of two manuscripts for publication reporting on collaborative research undertaken with Professor Li Zheng’s group at the BP-Tsinghua Clean Energy Center. Professor Li hosted a 12-month visit by Cathy Kunkel (ended in September 2007) that launched an effort to explore the prospects for extending to China the concept of making low GHG-emitting synthetic fuels from coal + biomass (CBTL) with CCS. During the visit period Kunkel, supervised by Larson and interacting with Prof. Li and others at Tsinghua, gathered data and carried out preliminary analyses relating to CBTL strategies for low-carbon liquid fuels supply from two coal-rich regions in China: agricultural Shandong Province, where crop residues are a potential biomass feedstock, and Inner Mongolia, where mixed native prairie grasses may be a potential biomass resource.

Before she left China, Kunkel began the process of preparing manuscripts reporting on these two geographically diverse case studies, but was unable to commit time to the effort after she left China to pursue a year of graduate study in physics at Cambridge University (UK). Kunkel is now pursuing a PhD with the Energy and Resources Group at the University of California, Berkeley. In the coming year Larson will restart the work to complete the manuscripts for publication.

For the Shandong case study, the focus was on developing a comparative analysis of alternative crop-residue-based cooking fuel strategies for rural households—motivated largely by concerns about severe adverse health impacts of indoor air pollution from the direct burning of coal or crop residues for cooking. The analysis is comparing health impacts, cooking fuel costs, and GHG emissions for six cooking fuel strategies: (i) direct coal burning, (ii) direct crop residue burning, (iii) burning pelletized crop residues in cleaner-burning stoves, (iv) burning dimethyl ether (DME) produced from crop residues via gasification, (v) burning DME produced from crop residues + coal via gasification, and (vi) burning DME from coal via gasification. For the options involving coal, both CO₂ venting and CCS approaches are being considered. This analysis includes developing models of the logistical costs of crop residue collection and delivery under conditions for Shandong Province.

The case of Inner Mongolian mixed prairie grasses used for coal/biomass-based synfuels production involved developing an extensive biogeophysical database for Inner Mongolia that includes current
grassland yields, potential yields if degraded lands are restored, the locations of major coal deposits and potential underground CO$_2$ storage sites, and other relevant data. Grasslands account for about 40% of China’s land area, and 30% of China’s grasslands are in Inner Mongolia—much of which are heavily degraded and the restoration of which is a high political priority in China. Although yields on restored grasslands in Inner Mongolia are low (~1.5 tonnes per hectare per year on average), preliminary calculations suggest plausibly attractive economics for farmers growing grasses for energy relative to what is being done with the land at present—if the oil price is high and the value of CO$_2$-equivalent GHG emissions is high (at least ~ $30/t CO$_2$).

**Wind Energy and Compressed Air Energy Storage**

The Williams Group’s analyses of wind/compressed air energy storage (wind/CAES) systems have focused on mitigating the variability of wind and enhancing utilization of the transmission lines needed to access remote, high-quality wind resources by coupling wind farms to compressed air energy storage systems. During 2005-2008 this research was led by Samir Succar under Williams’ supervision.

A milestone in this research was the completion of a major PEI report on CAES: *Compressed Air Energy Storage: Theory, Resources, and Applications for Wind Power*, which was released in April 2008. That report focuses on the geologic requirements for underground air storage, the geographic distribution of wind and storage resources, and the prospective economics of wind/CAES systems relative to coal IGCC without and with CCS.

The central findings of this report are that while additional data are needed to fully assess total storage capacity available in North America, geologies suitable for CAES are widespread and well correlated with the location of high-quality wind resources. This correlation is very auspicious for a low-carbon US energy future because exploitable high-quality wind resources in the US could theoretically satisfy the entire US electricity demand—if ways can be found to deal cost-effectively with the intermittency and remoteness challenges, which CAES systems might enable if sufficient suitable storage capacity can be identified and exploited.

Finally, the report finds that wind/CAES systems prospectively offer attractive economics for generating low-carbon power under the conditions characterizing a serious carbon-mitigation policy. First, baseload wind/CAES systems would become cost competitive (on the basis of levelized electricity costs) with coal IGCC at carbon price levels needed to make CCS economic for such systems. Second, once built, wind/CAES systems would be highly competitive in economic dispatch competition relative to other baseload electric power technologies.

The release of this report and subsequent completion by Succar of his PhD dissertation in Electrical Engineering on this topic conclude a major portion of this work. In September Succar joined the Natural Resources Defense Council in New York, where he is focusing on issues related to the integration of renewable with conventional energy systems. But Succar will continue as a visiting research scholar at PEI and will continue collaborations with Williams and others. Succar and Williams plan to write several papers for peer-reviewed journals based on the CAES report and Succar’s thesis. In addition, during the coming year, Kreutz, Williams and possibly also Succar will
pursue an analysis exploring the prospects for displacing existing coal-intensive power with
decarbonized power in economic dispatch competition by adding to electric grids both coal/biomass
polygeneration with CCS and wind/CAES systems.

Improving Energy Storage Technologies

One of the emerging seed areas within the CMI project involves the development of energy storage
technologies to complement the existing efforts on carbon reduction, capture and storage during
energy generation. These technologies are of critical importance for portable power but also for
providing load leveling and regulation on the grid. Although this is a very broad area that involves
expertise in a number of topics, the Arnold Group has taken a combined approach involving both the
assessment and optimized usage of existing technology and the development of new technologies to
meet emerging demands for energy storage that are compatible with modern forms of energy
generation.

In the area of assessment and optimization, the researchers have recently begun working to detail the
relevant metrics of energy storage including the response time (i.e. how fast a given technology can
store energy and how fast it can release that energy) and the energy density (i.e. how much energy
can be stored) for a number of existing technologies including pumped hydro, compressed air,
mechanical flywheels, batteries, and supercapacitors. Given a better understanding of the benefits
and limitations of existing technologies, they have begun to study new materials and methods to
improve performance. To this end, the group has focused on electrochemical energy storage include
batteries and supercapacitors and developing a better understanding of the relationship between the
external forces on the materials and their resulting electrochemical performance. By improving the
mechanical stability of these materials, the researchers seek to improve the cycle life of existing
batteries and supercapacitors, thereby decreasing the need for replacements and decreasing the
overall cost for implementation.

Combustion of Alternate Fuels

The Law Group has been conducting research on the combustion chemistry of alternate fuels and
their combustion characteristics within the high-pressure environment of internal combustion
engines. The researchers are also interested in the explosion hazards resulting from hydrogen leakage
due to the rupture of high-pressure storage tanks.

Outreach in China

Chung Law visited China for two weeks in the fall, and gave a total of six lectures and seminars on
various topics on fuels, energy, and the environment. These include the plenary lecture entitled “The
role of combustion in climate change and energy sustainability,” at the annual Combustion
Conference held in Xi’an, the plenary lecture entitled “From atomic to cosmic: a panoramic view of
combustion,” at the 7th Asian-Pacific International Conference on Combustion and Energy
Utilization, held in Beijing, and a seminar on “Clean and efficient combustion for transportation:
research agenda and recent progress,” at the BP Center at Tsinghua University, of which he is a guest
Combustion of Methyl Decanoate – A Surrogate Biodiesel Fuel

Methyl decanoate \((n-C_{37}H_{77}C(=O)OCH_3)\), abbreviated as MD, is a large methyl ester that can be used as a surrogate for biodiesel. In an experimental and computational study, the combustion of MD was investigated in nonpremixed, nonuniform flows. Experiments were performed employing the counterflow configuration with a fuel stream made up of vaporized MD and nitrogen, and an oxidizer stream of air. The mass fraction of fuel in the fuel stream was measured as a function of the strain rate at extinction, and critical conditions of ignition were measured in terms of the temperature of the oxidizer stream as a function of the strain rate. A detailed mechanism of 8555 elementary reactions and 3036 species had been developed previously to describe combustion of MD. Since it is not possible to use this detailed mechanism to simulate the counterflow flames because the number of species and reactions is too large to employ current flame codes and computer resources, a skeletal mechanism was deduced from this detailed mechanism using the “directed relation graph” method. This skeletal mechanism has only 713 elementary reactions and 125 species. Critical conditions of extinction and ignition were calculated using this skeletal mechanism and they were found to agree well with experimental data. In general, the MD mechanism provides a realistic kinetic tool for simulation of biodiesel fuels.

Self-Acceleration and Fractal Propagation of Flames

In previous studies the group has conclusively demonstrated that the propagation of a flame in a combustible medium could be accompanied by the development of fine-scale wrinkles over the flame surface. The propensity for such a destabilized mode of propagation is further enhanced in high-pressure environments characteristic of internal combustion engines used for transportation. The presence of wrinkles increases the total flame surface area and as such would increase the flame propagation rate. Furthermore, the continuous generation of the wrinkles implies the increase in the flame speed can be accelerative, and could lead to the eventual transition of the flame propagation mode from being laminar to turbulent and finally to detonative. The transition to detonation is the crucial factor in the onset of explosions either due to the rupture of high-pressure hydrogen storage tanks or as a mechanism for engine knock.

Work this year conclusively demonstrated that such an accelerative mode of flame propagation is indeed possible. Furthermore, if the instantaneous flame radius \(R(t)\) at time \(t\) is expressed as \(t^\alpha\), then it was found not only that \(\alpha > 1\), which indicates self acceleration, but also that \(\alpha\) attains a constant value of 4/3, which implies that the flame propagation is self-similar, with a fractal dimension of 2.25.
Noting that the fractal dimension for turbulent flame propagation is 2.33, this result therefore suggests the interesting possibility that a propagating laminar flame, which is deterministic in nature, can transition to a turbulent flame, which is probabilistic in nature. Furthermore, the existence of self-acceleration also implies the possibility of transition to detonation.

An interesting offshoot of this study is its potential application to the astrophysical phenomenon of supernovae. Here the reactions are nuclear in nature, although it is believed that it is the transition to detonation of the nuclear flame that leads to the star’s extraordinarily rapid rate of attainment of explosion.

**Collaboration with Ford Colleagues on Engine Simulations**

The collaboration with Ford researchers (James Yi) on engine simulation has continued. The Law Group’s contribution has been the development of reduced-order oxidation mechanisms of engine fuels that are needed in the computer codes for large-scale engine simulations. The challenge here is that the oxidation mechanisms of engine fuels are extremely complex, being described by hundreds to thousands of reacting species and thousand to tens of thousands of reactions. Consequently, the associated computational burden is simply too large to make computations practical, even with anticipated advances in computer hardware and algorithms. This in turn implies that engine combustion cannot be simulated with realistic chemistry.

In order to circumvent this difficulty, the researchers have developed a suite of mathematical algorithms that allows the systematic and accurate reduction of these mechanisms to a level that is amenable to computational simulation. During the past year they have reduced the mechanisms for n-heptane and iso-octane, which are the constituents of surrogate gasoline fuels. They have supplied these mechanisms to their Ford colleagues, who are now implementing them in their engine codes.

**Future Plans**

**Gasification of Low-Rank Coals**

Tom Kreutz of the Williams Group will take the lead in pursuing two new activities relating to the gasification of low-rank coals. The first is a study of coal/CO₂ slurries for both coal pressurization prior to gasification and long-distance transport of coal. This concept might offer strategic benefits if CO₂ is readily available—e.g., if CCS is pursued routinely for coal energy systems. Coal transport via such slurries will be investigated as an alternative to rail transport. Such slurries might represent a low-cost approach for realizing high gasification pressures. This strategy might facilitate gasification of low-rank coals, for which water-slurry feeding is uneconomic.

The second project will be an extension of the dry-feed gasification model to include: use of low-rank coals via heat-integrated fluidized bed drying, novel water-gas shift strategies (developed at ECN by visiting colleague Michiel Carbo) and implications for the choice of partial water quench vs. syngas cooler designs for the gasifier, detailed modeling of acid gas removal via physical solvents, and integrating the optimization methodology of Emanuele Martelli for the bottoming (steam) cycle.
Systems Analyses for Synthetic Fuels
During the past year several commercial synthetic fuel projects have been announced that will make gasoline via methanol production from coal followed by MTG (methanol to gasoline) synthesis. A related near-commercial set of technologies is the MTO (methanol to olefins) process coupled to the MOGD (Mobil’s olefin to gasoline and diesel) process. In an effort led by Larson and Williams, the Williams group will carry out detailed techno-economic analyses of coal-based MTG and MTO/MOGD technologies and make comparisons to F-T liquids systems. As in the case of previous analyses, they will examine systems without and with CCS, systems that maximize hydrocarbon yield and that provide considerable co-product power, systems that co-process biomass with coal, and systems that use only biomass.

Catalytic hydrogasification, originally developed by Exxon in the 1970s and currently promoted by Great-Point Energy, gasifies coal at a relatively low temperature (700°C) in a fluidized bed in the absence of O₂; it is especially well suited for use with low-rank coals and biomass. Kreutz will take the lead in carrying out a detailed techno-economic comparison of converting coal and biomass to substitute natural gas (SNG) via catalytic hydrogasification and traditional syngas methanation, without and with CCS and considering both systems that maximize SNG yield and systems that provide considerable co-product power.

Integrated Supply/Demand Approaches for Realizing Zero GHG Emissions for LDVs
Deep reductions in GHG emissions for light-duty vehicles (LDVs) can be realized by shifting to advanced end-use technologies and by using ultra-low GHG emitting energy supplies in LDVs based on these advanced end-use technologies. Williams will take the lead in carrying out a detailed techno-economic systems analysis of alternative combinations of advanced end-use and supply technologies and compare the different combinations with respect to both GHG emissions and costs to consumers. For advanced end-use technologies, attention will be focused on alternative LDV options that John Heywood’s group at MIT has recently analyzed in depth. Alternative supply options considered will include zero net GHG-emitting FTL fuels derived from CBTL with CCS polygeneration systems as well as negative GHG emitting power from biomass power plants with CCS—supply systems that the Williams Group has already modeled.

Collaboration with Politecnico di Milano
In 2009, the collaboration between Politecnico di Milano and the Williams Group will continue to focus on the two topics studied during 2008. The new model for the optimization of heat recovery will be improved as part of Emanuele Martelli’s PhD thesis. As for CO₂ separation via phase change, new configurations will be analyzed, possibly considering the integration of low-temperature CO₂ and sulfur separation, as well as applications other than IGCCs.

Energy in China
Eric Larson of the Williams Group will lead an activity aimed at: (i) completing the research carried out in 2007 at Tsinghua University by Cathy Kunkel on CBTL systems based on both crop residues and mixed prairie grasses grown on grasslands in China and (ii) preparing papers on same for submission to peer-reviewed journals.
Williams and Larson will also collaborate with Li Zheng and colleagues at Tsinghua University to analyze prospects for CCS early action in China—focussing on low-cost CO₂ sources at coal gasification plants that make chemicals and synthetic fuels. This effort will bring together and extend prior work at Princeton (by Kyle Meng with Williams and Michael Celia in 2005 focussing on CCS opportunities near plants that make ammonia from coal in China) and at Tsinghua (including a recent optimization analysis of CO₂ source sink matching).

**Backing Out Coal Power with Low-C Power via Economic Dispatch Competition**

Major findings of the Williams Group’s research for this year are that coal/biomass polygeneration with CCS and wind/CAES power systems would be very competitive in economic dispatch, thereby offering market-based options for displacing carbon-intensive existing coal power with low carbon power. Kreutz will lead an analytical effort in collaboration with Williams to estimate the extent to which these technologies might displace existing coal power on electric grids as a function of GHG emissions prices, oil prices, and other parameters by modeling economic dispatch for the PJM ISO or alternative grid for which good data are available.

**Self-Consistent Comparison of Alternative Energy Technologies**

The spreadsheet model developed by the Williams Group to help the authors of the NRC’s *America’s Energy Future* study has proved to be a powerful tool for comparing alternative energy supply technologies on a self-consistent basis. Over the next two years, Kreutz will lead an effort to expand this spreadsheet model to include both the new systems we intend to analyze as discussed above and other high-profile technologies such as nuclear power and renewable energy that were researched by other groups involved in the NRC study. The group hopes to gain a better understanding of how all these energy technologies interrelate and compete in a future with rising GHG emission prices and uncertain oil and feedstock prices.

**Improving Energy Storage Technologies**

In the year ahead, the Arnold Group will be continuing work on assessment and optimization of energy storage technologies by integrating their existing knowledge with the other work groups in CMI. On the technology front, the group will continue studies in lithium-based battery systems and carbon based supercapacitor systems. Ultimately, they seek to provide small-scale prototype examples of fully integrated storage with renewable energy generation such as solar cells or wind based power.

**Alternative Fuels Combustion**

The Law Group will continue collaborating with Ford on the simulation of engine processes. The emphasis will be predicting engine knock, which is a primary factor limiting the improvement of combustion efficiency, especially with the development of high-compression engines. The reduced reaction mechanisms for n-heptane and iso-octane will be extended to the more complex and realistic primary reference fuels (PRF) and integrated to the engine simulation codes developed at Ford. Collaboration with the simulation group at the Sandia National Laboratory will also be initiated for HCCI (homogeneous charge compression ignition) engines, again using the highly efficient reaction mechanisms that Law and colleagues have developed. The Sandia group under the direction of Dr. Jackie Chen is world renowned in performing high-fidelity direct numerical simulations (DNS) of combustion processes in engines.
Finally, a comprehensive experimental and modeling research program on the combustion of biofuels has been initiated and will form the major thrust of the group’s current program. In addition to studying the combustion chemistry of ethanol, the group will also initiate research on the higher alcohols such as propanol and butanol, as well as their blends with conventional gasoline fuels.
Publications


Carbon Storage

The Carbon Storage Effort is conducted by the Scherer-Prevost Group, the Celia Group, and the Peters Group. The Storage Group of CMI works to understand the possible risks of CO₂ leakage from underground storage, particularly through existing wells.

Highlights of this year’s progress include:

- Acquisition of new tools for preparing and analyzing well cement samples.
- Completion of an improved flash calculation that allows Dynaflow to simulate phase changes that would occur during leakage of CO₂ up a well.
- Development of a hybrid analytical-numerical model and a new web interface for large-scale injection models.
- Development a novel image analysis method to quantify the accessibility of minerals to formation fluids in sedimentary sandstones
- Submission of a proposal for an underground research laboratory for simulating CO₂ leakage

CO₂ Leakage Potential of Existing Wells

Oil and gas fields offer an appealing opportunity for storage, since their existence proves that a seal can keep hydrocarbons contained for millions of years and much is known about subsurface strata in well-explored areas. However, because oil-producing areas in North America have been punctured by many thousands of existing wells, the seal integrity of well cements is a critical factor in determining whether CO₂ will stay stored, or leak up through these potential conduits to the surface.

The Scherer-Prevost Group is combining experimental data on cement integrity with small-scale simulations to assess the potential for leakage through aging wells. The prediction of leakage rates requires an analysis that takes account of the flow rate, the corrosion rate of well cement, volume changes in the solid products (which might either enlarge or block the flow path), and phase changes in the fluid (including rapid expansion of supercritical CO₂ as the pressure drops). The experimental data that are most important as input for this modeling task are the permeability, diffusion, and mechanical properties of corroded cement and caprock materials.

Analysis of Corroded Cements

During the past year the researchers have focused on methods for preparing and handling cement samples that are uniformly corroded, so that they can be examined by methods such as nuclear magnetic resonance (NMR) that do not have great spatial resolution. They have also acquired
major new experimental capabilities, with the arrival of a system for supercritical drying of cements (which allows preparation of delicate corroded samples for microscopic examination) and an environmental SEM for microstructural examination of wet samples (such as cement in acidic brine).

The diffusivity of water within a porous material can be measured by NMR. The group contracted with a company to provide an NMR system specifically designed for analysis of its cement samples, but it was necessary to cancel the contract when it became clear that they could not deliver the system that was promised, costing precious time. They group is now adapting the equipment available on campus (which is intended for a different kind of measurement) to suit their needs. Preliminary results have been obtained on a corroded sample of special iron-free cement (which yields better NMR results, owing to the absence of magnetic impurities). The measured diffusivity (9.2 x 10^{-9} m^2/s) is within a factor of two of the value obtained by Bruno Huet by fitting his simulations to Duguid’s experimental results. Measurements of well cements are underway.

To examine the microstructure and to obtain composition profiles of corroded samples, it is necessary to dry them without alteration by capillary pressure. This can be achieved by supercritical drying, in which the pore solution is replaced by a liquid with a low critical temperature (such as Freon), then raising the sample to a temperature and pressure above the critical point and extracting the fluid. This is conventionally done with CO_2, but that would cause carbonation of cement (Figure 8), so the researchers adapted their autoclave to use Freon R23; since this is expensive material, the modifications included a system for purifying and recycling the Freon. The system is now operational.

Figure 8. Scanning electron micrograph of heavily corroded iron-free cement after supercritical drying shows the high porosity resulting from the reaction. In this case, the drying fluid was CO_2, so the sample is heavily carbonated. The new system will allow drying from Freon, so additional carbonation will be avoided.
The group has recently received an environmental scanning electron microscope (ESEM) through an NSF grant (with Scherer as PI). This instrument allows examination of wet samples, allowing observation of cement as it corrodes (but not with the high resolution possible with dried samples). It also has detectors that permit accurate compositional profiling, so the researchers can examine the composition of the sequence of corrosion layers in cement. This will provide data to validate and refine the corrosion model developed by Huet.

**Permeability Measurements in Shale**

Shale is the most common cap rock material, so estimates of the diffusivity and permeability of this material are important for modeling leakage. A novel beam-bending technique developed in the Scherer lab permits rapid measurement of permeability, and this method has now been demonstrated to work for shale. When a beam of saturated material is bent, the top is compressed and the bottom is stretched, so a pressure gradient is created in the pore liquid; as the liquid flows to relieve the gradient, the force required to sustain the deflection decreases. By measuring the kinetics of relaxation of the force and fitting the data to the theoretical expression, the permeability can be determined. An example of the results is shown in Figure 9. The good quality of the fit indicates that the permeability, as well as the elastic modulus and viscoelastic relaxation rate, can be obtained by this method. This work will be extended to include a variety of types of shale before and after exposure to carbonated brine.

![Figure 9. Relaxation of force, W, required to sustain a fixed deflection for a plate of shale containing pentadecane.](image)

The relaxation of the load results from flow of the pore liquid (resulting in hydrodynamic relaxation) and deformation of the solid itself (viscoelastic relaxation). The fit to the theoretical curve is excellent, so the permeability can be accurately determined.

**Analysis of Field Samples and Well Data**

Through collaborations with colleagues in industry, academia, and government, the Scherer and Celia groups are using tools and models developed at Princeton to characterize wells in the field.
Teapot Dome Samples

The actual impact of CO₂ injection on well integrity depends on whether cements in existing wells are more or less susceptible to attack than those used in the laboratory. In collaboration with Dr. Barbara Kutchko at NETL, the researchers have continued to examine cement samples obtained in 2004 from a 19 year-old well at the Rocky Mountain Oil Testing Center in Wyoming. Some of the samples show extensive sulfate attack, apparently from reaction with the brine. Clearly, the durability of well cement will be affected by brine concentration, so this factor will have to be taken into account in predicting the risk of leakage. A manuscript is in preparation regarding the condition of the samples from Teapot Dome.

Cement from a Natural CO₂ Deposit

In an effort led by Walter Crow of BP, samples of cement were recovered by taking sidewall cores from a 30-year-old well that had been placed into a natural CO₂ deposit in Colorado. The cement cores showed a degree of carbonation that decreased with increasing distance from the boundary with the CO₂ deposit. This was interpreted to mean that a leak must have been present to bring the CO₂ into contact with the cement. Calculations showed, however, that the pores of the shale cap rock would have been saturated with CO₂ owing to contact with the deposit. As soon as the well was constructed, CO₂ would have diffused from the shale toward the cement, where it could have created the observed carbonation layer in the absence of a true leak from the CO₂ deposit. Carbonation of cement near natural deposits must thus be interpreted with caution, as cement far above the reservoir may be carbonated without a leak along the well.

A series of calculations was run to evaluate the risk of creating leaks in a reservoir as the pressure of injected CO₂ deflects the cap rock: since the stiffness of the rock differs from that of the cement plugs that pass through it, cracks might form in the cement that would permit leakage. Simulations done by Jan Prévost and Zhihua Wang using Dynaflow, indicate that the bending stress in the cap rock is negligible. However, as the cap rock deflects upward, shear stresses are created along the well, if it is anchored in the reservoir. Preliminary results indicate that leakage paths could be created in this way, but further calculations are needed to test the sensitivity of the results to the boundary conditions.

Vertical Interference Test Data

Over the past year, the Celia Group continued to work with Walter Crow, Brian Williams, and others at BP to analyze and interpret results from the Vertical Interference Tests (VIT) that BP has been leading at several old wells. Walter has led the effort to re-enter the old wells and perform the tests, and CEE alumnus Sarah Gasda has been using the code she developed while at Princeton to analyze the results and infer plausible ranges of effective permeability for the cement outside of casing. The test is described in Gasda et al. (2008) and some of the results are described in Crow et al. (2008a,b). In particular, the most recent analysis involves a 30-year old well from a natural CO₂ production reservoir. The wellbore was exposed to a 96% CO₂ fluid from the time of cement placement. A sampling program resulted in the recovery of 10 side-wall cement cores extending from the reservoir through the caprock. The hydrologic, mineralogical and mechanical properties of these samples have been measured and those results are combined with an in-situ pressure-response test to investigate cement integrity over larger length scales.
Although alteration of the cement samples is present in all cores in varying degrees, hydraulic isolation has prevented leakage based on the pressure gradient measured between the caprock and CO₂ formation as well as lack of corrosion and no casing pressure history. Simulation of test data indicates the best match for effective permeability is approximately 1-10 millidarcies which suggests cement interfaces as the primary path for potential migration rather than through the cement matrix.

**Aquifer Simulation with Dynaflow**

In 2007, Bruno Huet and Jean Prévost of the Scherer-Prevost Group developed a reactive transport model to describe the corrosion of cement by carbonated brine. The group expected to produce extensive simulations of corrosion and leakage during 2008, but Bruno left Princeton to join Schlumberger, so that work was brought to a halt. They have not been able to find a qualified person to replace Bruno, and his new position has not allowed him to devote a significant amount of time to this work, so his departure has seriously hindered progress. He has just finished the first paper that will be published to describe the work he did in Princeton, and will hopefully be able to complete at least one more. The manuscript describes the simulations of Duguid’s flow-through experiments, showing good agreement between experiment and calculations.

Focus has now turned to the flash calculation, which predicts the phases present under given conditions of temperature, pressure and composition. This is a major challenge when the system crosses a phase boundary, such as boiling of CO₂ when carbonated brine rises through a crack. In collaboration with Dr Lee Y. Chin (ConocoPhillips), Jean Prévost has developed two modules with different flash calculation algorithms (using either enthalpy or temperature as the primary variable) that are now integrated with the fully coupled Dynaflow simulator. A comparative study is underway for developing an optimal procedure for calculation of the phase behavior of carbonated brine. Numerous test runs indicate that correct phase tracking is critical to obtain accurate and rigorous results. More work in developing a reliable phase tracking algorithm is needed. Preliminary results show that the thermal compositional simulator is capable of handling phase change for CO₂-water mixtures. Debugging and validation of the simulator for analyzing non-isothermal compositional problems is in progress.

**Large-Scale Assessments of Leakage Risks**

During the last year, the Celia Group continued to develop its large-scale modeling framework with a focus on leakage estimation. This included a number of new components to the models, a great improvement in model robustness, development and initial application of a hybrid analytical-numerical model, and development of an initial beta-version of a web interface for the group’s models.
Figure 10. Location of Wabamun Lake study area in Alberta, Canada (a) and existing wells (b).

**Semi-analytical Model for Leakage Estimation**

Our semi-analytical model is designed to model injection of CO₂ into a deep saline aquifer, in a domain that includes multiple layers and multiple (possibly leaky) passive wells. As described in the past, this model uses a set of analytical solutions, driven by standard two-phase flow equations, to solve for the location and evolution of the CO₂ injection plume, all secondary plumes caused by leakage of CO₂ along well segments, the flow of brine both within the formations and along the leaky wells, and the pressure field at all points within the domain. During the last year, the software was completely re-written so that the code is now much more robust and is about ten times more efficient. Some of the relevant mathematics that underlies the algorithms can be found in a recent paper that has just appeared (online) in the journal Environmental Science and Technology.

The researchers continue to apply the code to a specific site in Alberta, Canada (Figure 10), where they have worked with colleague Stefan Bachu to put together a data set. Because the group can run tens of thousands of simulations, they can perform a range of probabilistic risk assessment calculations. The latest publication related to this work is a GHGT-9 paper where risk of leakage as a function of depth of injection is examined. Figure 11 is taken from that paper, and shows

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>Top Depth [m]</th>
<th>Thickness [m]</th>
<th>k [mD]</th>
<th># Wells</th>
<th>Max Inj [Mt/yr]</th>
<th>Wells Contacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belly River</td>
<td>729</td>
<td>56</td>
<td>86</td>
<td>1</td>
<td>2.8</td>
<td>197</td>
</tr>
<tr>
<td>Cardium</td>
<td>1052</td>
<td>15</td>
<td>7</td>
<td>1155</td>
<td>0.1</td>
<td>23</td>
</tr>
<tr>
<td>Viking</td>
<td>1288</td>
<td>30</td>
<td>53</td>
<td>900</td>
<td>1.7</td>
<td>200</td>
</tr>
<tr>
<td>Mannville</td>
<td>1462</td>
<td>65</td>
<td>7</td>
<td>885</td>
<td>1.7</td>
<td>43</td>
</tr>
<tr>
<td>Nordegg</td>
<td>1536</td>
<td>50</td>
<td>4</td>
<td>735</td>
<td>0.7</td>
<td>13</td>
</tr>
<tr>
<td>Wabamun</td>
<td>1610</td>
<td>90</td>
<td>13</td>
<td>138</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>Nisku</td>
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<td>72</td>
<td>70</td>
<td>39</td>
<td>21.4</td>
<td>31</td>
</tr>
<tr>
<td>Keg River</td>
<td>2507</td>
<td>22</td>
<td>4</td>
<td>11</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>Pika</td>
<td>2845</td>
<td>14</td>
<td>16</td>
<td>2</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Basal Sandstone</td>
<td>2965</td>
<td>38</td>
<td>23</td>
<td>1</td>
<td>2.6</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 1: Data for layered domain.** Shaded rows correspond to injection formations.
example leakage results for injections into different layers. The layers and some of their properties are shown in Table 1. Three important points related to the results are highlighted here. First, there is an obvious difference in the number of wells that penetrate the caprock of a formation, as a function of depth. While those numbers might be expected to map directly to leakage amounts, this is not seen in Figure 11, especially when analyzing the Nordegg and Nisku formations. This is because this is only a single injection plume, and the characteristics of the formations make those plumes quite different. This highlights the second important point which is related to formation injectivity.

While the Nordegg formation has more than an order of magnitude more wells penetrating its caprock, as compared to the Nisku, the number of wells contacted after 50 years by a single injection plume is actually less (13 versus 31), and the leakage associated with injection into the Nisku is slightly higher. All of this is driven by limits on injection rates due to an imposed limit that the maximum injection pressure should not exceed 90% of the estimated fracture pressure. This highlights the importance of fracture pressures limiting injection rates and the need for careful strategies to design injection wells. The third point to highlight is the two different estimates for leakage probabilities in Figure 11, each based on a different assumed structure of the input probability distribution for the leaky wells. One uses a standard bi-modal lognormal distribution, while the second attempts to incorporate ‘soft’ information about the wells based on a scoring system proposed by Watson and Bachu, which was mapped into a permeability field. This highlights the continued importance of parameter identification and the critical part that the BP field program plays in quantifying leakage risk.
Numerical Sharp-Interface Model and Hybrid Model

The semi-analytical model used above requires a number of simplifying assumptions, some of which may be inappropriate for a given system. For cases where the simplifications cannot be justified, the team has developed a numerical implementation that maintains the basic assumptions of a macroscopic sharp interface and vertical equilibrium, but eliminates the need for more severe assumptions like homogeneous and horizontal formations. They have now implemented an initial version of this model and tested it in a variety of ways, including an international code comparison.

One of the test problems involved in the code comparison was a faulted part of the Johannsen formation, off the Norwegian coast. Predictions of plume extent and migration using a relatively simple sharp-interface model compared well with full industry simulators like Eclipse – see Gasda et al., 2009 and Class et al., 2009. Note that this test problem did not include any leakage, so it was a straight-forward injection into a single formation, with the complexity being associated with the geometry of the formation and geological heterogeneity.

A second test problem included leakage along a single existing well in a relatively simple three-layer domain, with two permeable formations separated by an impermeable caprock, as depicted in Figure 12. This problem was motivated by earlier published work in which a similar problem was solved. This test problem was solved using both a semi-analytical approach and a numerical approach. For the numerical solution, the domain was discretized using coarse grid blocks, and represented the leaky well using a sub-scale analytical solution borrowed in part from the semi-analytical solutions.

Figure 12. Schematic of test problem from Class et al. (2009).
This combination of coarse-scale numerical approximation, which captures geometric and parameter heterogeneities, and fine-scale analytical solutions that capture the local leakage behavior, is referred to as a hybrid numerical-analytical solution. This hybrid solution worked very well in the comparison exercise, and is now their preferred method to solve problems with relatively complex geology that also include potentially leaky wells or other concentrated leakage pathways. The test problem set-up is shown in Figure 12, and the set of solutions, including both the group’s semi-analytical (Elsa) and hybrid (VESA) solutions, is shown in Figure 13. Many other details can be found in the manuscripts of Gasda et al. (2009) and Class et al. (2009), which are currently under review for publication in the journal Computational Geosciences.

The researchers are now in the process of putting together a broad modeling framework that can incorporate both numerical and analytical solutions into an overall simulation. They refer to this as a ‘hierarchical modeling framework’ in that users will be given options that range from simple to relatively complex simulation tools, and they hope to report favorably on this new modeling paradigm in future reports.

**Other Uses of Storage Group Models**

In addition to the applications described above, several others have used these models over the last year. Jason Deardorff, a graduate student at the Colorado School of Mines, completed an MS Thesis titled *The Geologic Carbon Sequestration Potential of the Denver-Julesburg Basin of Colorado: Applied Methodologies for Basin Scale and Site-specific Assessment of CO2 Sequestration Potential*. Jason used the group’s analytical models to estimate storage potentials for a number of formations in the Colorado area and is now employed by the U.S. Environmental Protection Agency. Professor Mark Person from Indiana University was inspired by the sharp-interface approach, specifically the paper of Nordbotten and Celia (2006), and used the group’s...
approach to model a number of injection scenarios in the Mt Simon formation in Illinois. Some of that work was presented in December 2008 at the American Geophysical Union meeting (Person et al., 2008).

**Geochemical Reactions in Saline Aquifers**

**Up-scaling Reaction Rates**

Catherine Peters is leading a project funded by the DOE Office of Science, titled “Up-Scaling Geochemical Reaction Rates for Carbon Dioxide (CO₂) in Deep Saline Aquifers,” for which the Peters Group will collaborate with the Celia Group and W. Brent Lindquist (SUNY Stony Brook). The goal is to bridge the gap between our knowledge of small-scale geochemical reaction rates and rates meaningful for modeling reactive transport at core scales. The focus is on acid-driven mineral dissolution and precipitation relevant in the context of geological sequestration of CO₂.

The major challenge with predicting reactive transport in consolidated media is accurate characterization of mineral surface areas. Existing methods of quantifying mineral surface areas for consolidated media at best are imprecise and at worst are not valid because they do not account for armoring clay minerals, matrix cementation, and grain inclusions. Through a combination of Backscattered Electron (BSE) scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of thin sections, the group has developed a novel image analysis method to quantify the accessibility of minerals to formation fluids in sedimentary sandstones (Figure 14). For example, for one of the sandstones studied, the researchers concluded that if a mineral volume fraction is used as a proportional measure of accessible surface area in consolidated sandstones, the reaction rates are likely to be overestimated by three to five times.

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**Figure 14. Elements of a BSE-EDX mineral map.** Reactivity in sandstones is notoriously difficult to characterize due to the high degree of consolidation and cementation. This novel image processing algorithm allows us to quantify the accessibility of minerals to carbonic acids, thereby determining mineral reactivity under acidic conditions.
This novel method is further being applied to provide insight on how uncertain the estimates of surface areas often used in reactive transport and reaction path models are in the context of deep sedimentary formations.

**Impacts of SO₂ Co-Injection**

Peters group is now focussing on a new research question related to the effects of co-injection of SO₂ in the context of CO₂ geologic sequestration. To quantify the extent to which SO₂ will dissolve into and acidify formation brines, the researchers have determined the solubility of SO₂ in brine at high pressures, simulated the diffusive transport of SO₂ from a supercritical CO₂ phase, and modeled the formation of various sulfur-containing acids. Hydrolysis alone will produce sulfurous acid, which is somewhat stronger than carbonic acid. While fully oxidizing conditions are needed to convert all the SO₂ to sulfuric acid, a very strong acid, simulations show that, even in the absence of strong oxidant the SO₂, disproportionation reactions can generate both sulfuric acid and hydrogen sulfide. The sulfuric acid will lead to significant brine acidification, pH<2, if phase equilibrium between the injection plume and formation brine is reached. These findings indicate that SO₂ contact with the brine is likely to be limited by diffusion through the supercritical CO₂ plume, thereby causing a delayed and less severe impact on brine pH.

**Outreach and Other Activities**

**Celia Darcy Lecture**

During Calendar Year 2008, Professor Celia was the Darcy Distinguished Lecturer for the National Ground Water Association. Professor Celia presented the lecture titled "Geological Storage as a Carbon Mitigation Option" to 52 different venues, mostly universities, across 12 countries and 4 continents. Details about the lecture, including a copy of the slides used in the final presentation can be found on Professor Celia’s home page: (http://www.princeton.edu/cee/people/data/c/celia/profile/the-darcy-lecture-outline).

Overall the lecture was attended by about 4,000 individuals, and in each of the lectures CMI, BP, and Ford were acknowledged explicitly. In August Professor Celia also gave a public lecture in Malaysia, which was attended by close to 1,000 people. This was not the Darcy lecture but addressed similar issues related to energy, carbon mitigation, and the role of CCS. Note that the website includes a manuscript associated with that lecture as well as other materials related to CCS and activities at Princeton.

During 2008 Professor Celia visited BP Sunbury in July and BP Houston in October. During the July visit Prof. Celia presented a modified version of the Darcy lecture via web connection to other BP offices. It was also during that visit that Max Watson asked for a simple version of the group’s analytical solutions for performing calculations. He asked for a spreadsheet version, but the team instead created a web-based version of the simplest solutions. The web version is still being tested but can be found at http://monty.princeton.edu/~mark/InjSim2. This web-based version of the group’s simple solutions was further motivated by a meeting at Princeton in September with researchers from the U.S. Environmental Protection Agency, where the desire
for such tools was reiterated. During this meeting, Professors Celia and Nordbotten also gave a web seminar that was broadcast to different EPA offices across the U.S.

In response to the release by the E.P.A. of draft guidelines for CCS injection wells, Professor Celia was part of a committee formed by the National Ground Water Association to respond to the proposed regulations. The committee ultimately put together more than 200 pages of responses, including a set of white papers. NGWA has also been active in meeting with Congressional representatives on issues related to CCS and protection of ground water resources.

**IEA Summer School**

Princeton was well represented with 4 PhD students from the Storage Group - Benjamin Court, Brian Ellis, Ed Matteo, and Juan Nogues - at the 2008 IEA GHG CCS Summer School on Vancouver Island. The IEA Greenhouse Gas R&D Programme (IEA GHG) Carbon Capture and Storage (CCS) Summer School is designed to offer students – primarily PhD students and postdocs - the opportunity to enhance their understanding of CCS implementation and technology, as well as develop network contacts in the CCS Community. Approximately 60 students from over 20 countries and a diversity of disciplines were selected from over one hundred applicants to attend the Summer School.

Dozens of CCS industry experts were invited speakers who presented overviews of capture, transport and storage of carbon dioxide, as well the economic, regulatory, and social aspect of CCS implementation. The Princeton students also applied their knowledge of CCS by working in teams to answer questions related to the implementation of CCS, including

- How can CCS be applied to small and medium scale sources?
- What is required for large scale CCS deployment?
- Can CCS be part of an integrated, sustainable, and secure energy system?
- Is CCS a viable option for developing nations? (selected as "Best Presentation")

The group presentations were the culmination of the week’s activities and exposed the students to working on complex problems within a group that is both interdisciplinary and of an international constituency. The full agenda for the week’s activities, including technical presentations and the group presentations can be found at the following link: [http://www.co2captureandstorage.info/SummerSchool/SS2008_Agenda.html](http://www.co2captureandstorage.info/SummerSchool/SS2008_Agenda.html)

**Future Plans**

The Storage group will continue work to characterize corroded cements, expand field studies, refine and apply the Dynaflow and analytical-numerical models, and develop a hierarchical modeling framework for modeling basin-scale injection scenarios.
Underground Facility for Leakage Testing
A proposal has been submitted to NSF (with Catherine Peters as the lead investigator and Jean Prévost and George Scherer among the PIs) to build a facility for testing of leakage on a large scale. A deep underground science and engineering laboratory (DUSEL) is being constructed in an abandoned gold mine in South Dakota, with the primary goal of carrying out particle physics experiments. Proposals have also been solicited for use of the facility to do experiments in other fields, such as biology and geomechanics. The researchers propose to use the long vertical shafts to create a pressure vessel with a length comparable to the height of the Empire State Building to simulate leakage from a reservoir. The scale would enable following phase changes as super-critical CO₂ expands, and measurement of the change in leakage rate through cement with controlled cracks or annular gaps. This would provide a direct test of the group's simulations of leakage through wells. The proposal was developed in collaboration with colleagues at the Lawrence Berkeley National Laboratory.

Field Studies of Well Properties
In terms of applications, Michael Celia's group will continue to work with Walter Crow, Brian Williams, and others at BP to expand the number of wellbore tests and the associated database of effective permeability values for cemented annular regions of old wells. They will also continue to work with Stefan Bachu and Teresa Watson to further integrate their scoring system, based on 'soft' well data, into probabilistic models for leakage along wells. Finally, they will begin to develop a new field test site that builds on initial work at the Wabamun Lake area (Figure 10 and Figure 11). Because it seems likely that several CCS operations will be developed around the greater Edmonton area, in association with oil sands production, the researchers are interested in how multiple large-scale CCS operations will interact and interfere with one another. That requires modeling on a scale much larger than the domain of Figure 10, which covers 2,500 km² contains roughly 1,300 old wells. If the domain size were expanded by an order of magnitude, the number of wells should increase in proportion, and the overall computational challenge to increase by more than a linear multiple. The team plans to initiate data collection activities for this much expanded domain over the next year, and to develop a hierarchical modeling framework with these kinds of applications in mind. Geological and geometric heterogeneities, fault zones, interacting plumes, and potential leakage along perhaps tens of thousands of wells will all need to be included in the modeling. The team sees this as their next large challenge, one that will allow subsurface models to move toward an integrated assessment of CCS operations on a regional scale.

Evaluating Cement Corrosion and Impacts
In the coming year, the Scherer-Prévost group will continue to focus on their two priorities: (1) characterizing the mechanical and transport properties of corroded cement, and (2) developing the software tools needed to model leakage of CO₂. The modeling work is currently directed toward perfecting the flash calculation, to permit prediction of phase changes as the fluid rises through zones of decreasing temperature and pressure. This research is being performed by Prof. Jean Prévost in collaboration with Dr. Lee Y. Chin (ConocoPhillips). They are still hoping to have meaningful collaboration with Bruno Huet at Schlumberger, but that has not been possible to date. In the past year, the experimental work by Ed Matteo has been largely devoted to
developing experimental methods, which are now being put to use. In the near future they expect
to quantify the diffusion coefficient in cements with various degrees of corrosion damage, and to
determine the indentation strength of those materials. These data are essential inputs for the
modeling of leakage.

**Large-Scale Injection Simulations**

Celia and colleagues plan to continue to develop their semi-analytical and numerical sharp-
interface models to allow for more complex geometry, geology, and fluid behavior, while still
maintaining computational efficiencies. This will include development of analytical solutions
that include diffuse leakage across caprock formations. While they do not believe this is
important in terms of mass transport, it can be quite important when analyzing the pressure
response to injection systems. The pressure response, in turn, is important when identifying the
"Area of Review", an important quantity in the EPA guidelines. Their approach will be to take
advantage of capillary exclusion for the CO₂ but to allow brine to leak across caprock formations.
This reduces the problem to one of single-phase flow with moving boundaries, for which some
analytical solutions can be derived. The researchers will integrate these solutions, with varying
degrees of complexity, into their overall semi-analytical model for injection and leakage.

The group will also expand its numerical sharp-interface model to include more complex
heterogeneity, to allow for sub-scale representation of faults as well as leaky wells, and to
integrate more complex phase behavior along concentrated leakage pathways. The overall
approach is to solve the sharp-interface equations on coarse grids within each layer, and to use
local analytical solutions to capture sub-grid-scale behavior like local upconing around a well or a
fault, with concomitant Peaceman-type corrections for the local pressure field. This kind of
approach represents a multi-scale hybrid numerical-analytical solution, with numerical solutions
used at the large scale and analytical corrections used on the fine scale. The researchers plan to
extend this concept to develop a more general 'hierarchical' modeling framework, where they use
large-scale semi-analytical solutions in parts of the overall domain where they are justified,
numerical sharp-interface models where heterogeneity and other factors require such solutions,
and local analytical corrections to model the effects of concentrated leakage pathways. While
simple in concept, there are a number of computational issues to be worked out, and they will
begin to develop the details of this framework over the next year.
Publications


Person, M., A. Banerjee, J. Rupp, P. Lichtner, R. Pawar, and M. Celia,


Basic Research Relevant to CO₂ Sequestration", Gaithersburg, MD, March 2008.

Peters, C. (PI), G. Scherer (CoPI), M. Celia, J. H. Prevost, T. Onstott, Dept. of Civil & Environmental Engineering, Princeton University; F. Dobson (CoPI), C. Oldenburg (CoPI), B. Freifeld (CoPI), J. Birkholzer, J. Wang, Earth Sciences Division 90-1116, Lawrence Berkeley National Laboratory, “Collaborative Research: DUSEL CO₂, A Deep Underground Laboratory for Geologic CO₂ Sequestration Studies: A proposal for the conceptual design of the facility and experiments”, submitted to NSF.

http://www.deepscience.org/index.html


Scherer, G.W., Jean H. Prévost, and Zhi-Hua Wang, "Bending of a Poroelastic Beam with Lateral Diffusion", submitted for publication

Carbon Science

Researchers in the Carbon Science area work to explain historical changes in atmospheric carbon dioxide levels, the nature and variability of carbon sources and sinks, and the feasibility and impacts of large-scale carbon mitigation. The work is conducted by the Pacala, Sarmiento, Bender, and Sigman Groups.

The science group’s research over the past year has focused on three basic themes:

- Using a Carbon Observing System to monitor changes in carbon cycling
- Field studies of atmospheric and ocean chemistry
- Studies of ancient climate, ocean circulation and nutrient cycling

Carbon Observing System

The Sarmiento and Pacala Groups have continued the development of a “Carbon Observing System” that incorporates observation data from various origins along with different kinds of models (atmosphere, ocean and land) to monitor both short and long time scale changes in the carbon cycle, and to provide predictions for the future. An important component of this work consists of identifying the anthropogenic transient signal against a background of elevated natural (interannual to decadal) variability in the carbon cycle using both models and observations. Recent analyses of observations as well as models forced with the observations suggest that there have been significant changes in oceanic circulation and a reduction in the oceanic carbon sink over the past 2 to 3 decades, and that the land biosphere may have undergone a major increase in uptake starting around 1990.

Impacts of a Doubling of CO₂

A collaboration between the Pacala Group and GFDL has produced a result that provides important new understanding of the implications of doubling the pre-industrial concentration of atmospheric CO₂ (572 ppm), a level that many view as an appropriate target for mitigation or as a likely outcome of an attempt to cap the concentration at 450 or 500 ppm. The new finding is made possible by a coupled ocean-land-atmosphere earth system model that is able to calculate the equilibrium climate associated with any given level of atmospheric CO₂. Note that virtually all previous calculations with earth system models have been limited to transient runs in which the climate is still changing at the end of the run. The result is contained in a manuscript that has been submitted for publication: “Uncertainty in the Land-Carbon Uptake due to CO₂ Fertilization under Climate Change,” by Elena Shevliakova, Ronald J. Stouffer, Lori T. Sentman, Stephen W. Pacala, Michael J. Spelman, and Sergey Malyshev.
The study focuses specifically on uncertainty associated with the magnitude of CO$_2$ fertilization of the biosphere and contains a review of published empirical evidence that CO$_2$ fertilization may not deliver a sustained terrestrial sink because of several mechanisms of down-regulation. Evidence of the possible failure of CO$_2$ fertilization has been described in several previous CMI annual reports.

With sustained CO$_2$ fertilization, the model predicts that a doubling of the pre-industrial concentration of CO$_2$ would create a terrestrial sink that would eventually absorb over 200 Gt of carbon. This result is similar in magnitude to the values produced by the transient runs reported in the latest IPCC report. However, if CO$_2$ fertilization is down-regulated, then the model predicts that the biosphere will emit over 400 Gt of carbon to the atmosphere, mainly from tropical rainforests and arctic soils. The difference between a gains and losses in these two runs is nearly as large as the total CO$_2$ currently in the atmosphere.

If this extra CO$_2$ is emitted sufficiently slowly, then the oceans will take up most of it. But if it is emitted quickly, then it would require that humanity either mitigate an additional 26 wedges worth of CO$_2$, or allow the atmospheric concentration to exceed a doubling, which would cause more climate change and induce still more emissions from the biosphere. This implies that it might be impossible to maintain the concentration at a doubling without revolutionary new mitigation technology. The group is now planning to attempt the transient calculation to determine how fast the extra carbon would be emitted.

**Temporal Shifts in the Sources and Sinks of Atmospheric CO$_2$**

The Sarmiento Group has discovered an apparent increase in the net land uptake of CO$_2$ of 0.9 (0.8 to 1.0) Pg C yr$^{-1}$ after 1990/91 based on a novel analysis of the atmospheric CO$_2$ growth rate. In this approach, the net land flux is estimated as the balance of relatively well-known components of the carbon budget: fossil fuel emissions, the observed growth rate in the atmosphere, and the oceanic uptake from state of the art ocean models. Due to substantial uncertainties in the temporal variability of oceanic uptake, a suite of ocean models was used. The predominant signal in the inferred net land flux (Figure 15) is the very large interannual variability. However, using a low pass Butterworth filter, it is possible to resolve a clear shift towards greater land uptake after 1990/91 than before it. The net land sink estimated using the six time-varying ocean models increases by an average of 0.9 (0.8 to 1.1) Pg C yr$^{-1}$ after 1990/91. Such an acceleration of the net land carbon uptake had been noted previously for the decade of the 1990s compared with the decade of the 1980s; and this post-1990/91 net land uptake estimate is consistent within uncertainty with the atmospheric oxygen based estimate of 0.51 ± 0.74 Pg C yr$^{-1}$ for the period of 1993 to 2003. However, this analysis suggests a much greater persistence in time of this signal, including that the major Pinatubo anomaly of 1991 to 1993 can account for only 0.27 (0.20 to 0.31) Pg C yr$^{-1}$ of the increase in long-term averages. An analysis of the atmospheric growth rate shows that this post-1990/91 shift in the net land uptake appears to find expression as modulations of the amplitude of the variability itself rather than a simple shift of the mean state.
One possible explanation for this increased terrestrial uptake is an observed increase in shortwave radiation accompanied by an intensification of the hydrological cycle in the early 1990’s. The group’s plan to test this hypothesis is described below in “Future Plans.”

Figure 15. Terrestrial carbon uptake inferred from estimates of fossil fuels, the observed atmospheric growth rate of CO$_2$, and an ocean model [Le Quere et al., 2007], smoothed with a 12 month running mean (gray), a five year low pass Butterworth filter (red), and a ten year low pass Butterworth filter (blue). Positive values indicate uptake and negative values indicate emissions.

**Nutrient feedbacks on the Terrestrial Carbon Cycle**

Stefan Gerber, in collaboration with Lars Hedin, Michael Oppenheimer and Steve Pacala, has completed implementation of nitrogen dynamics in the Princeton-GFDL LM3V land model. The new model resolves processes, dynamics and feedbacks that have not previously been captured and represents a substantial improvement over all previous and existing dynamic global vegetation models. Early simulations with the model suggest that nitrogen limitation acts as brake on the CO$_2$ fertilization effect, and that feedbacks between carbon and nitrogen cycling are strongest in extra-tropical regions.

An urgent question with respect to global change is whether terrestrial systems may act as a significant sink for anthropogenic carbon via a CO$_2$ fertilization response. To test whether nitrogen limitation would restrict the biosphere’s ability to sequester carbon in such a scenario, Gerber and colleagues performed simulations from 1500 to 2000 AD that included past changes in
atmospheric CO₂, land-use transitions and recent climate change. The model with the new nitrogen formulation predicts a terrestrial carbon source of ~11 GtC over the last 150 years (Figure 16), which is in broad agreement with estimations based on ocean inventory and budgeting approaches. Conversely, when feedbacks between terrestrial carbon and nitrogen cycling were neglected, the model predicted a cumulative sink of about 15 GtC. Sensitivity testing showed that nitrogen cycling hampers carbon sequestration in the model by preventing uptake under CO₂ increase but also reduces carbon losses during land-use transitions.

The model is also able to reproduce global patterns of terrestrial carbon storage over individual decades. While the terrestrial biosphere appeared to be a source of about 0.5 GtC yr⁻¹ over most of the historic period, the team found a shift from source to sink around 1970. Comparison of simulated carbon fluxes for the 1980s and 1990s against results from budgeting approaches and inverse modeling results shows good agreement for both decades. Increased carbon uptake in the 1990s appears to occur mostly in the tropics, while extra-tropical regions (mostly Northern Hemisphere) sequester carbon at a similar rate in both decades.

**A Wintertime Window for CO₂ Uptake in the North Pacific**

To evaluate the pathways and timescales associated with the uptake of anthropogenic CO₂ over the North Pacific, the Sarmiento Group forced an ocean model with NCEP reanalysis fluxes over 1948-2003. The model revealed that there are two principal regions of uptake, the first along a band between 35–45°N and 140–180°E, and the second along a band between 10-20°N and between 120°W and 180°E (Figure 17a). For both of these regions, the dominant timescale of
variability in uptake is seasonal, with maximum uptake occurring during winter and uptake being close to zero or slightly negative during summer when integrated over the basin.

The model results indicate a decadal trend toward increased uptake of anthropogenic CO$_2$ (Figure 17), but the trend is due largely to modulations of the uptake maximum in winter. This implies that, for detection of anthropogenic changes in CO$_2$ uptake, in situ measurements will need to resolve the seasonal cycle in order to capture decadal trends in ΔpCO$_2$. As uptake of anthropogenic CO$_2$ occurs preferentially during winter, observationally-based estimates which do not resolve the full seasonal cycle may results in underestimates of the rate of uptake of anthropogenic CO$_2$.

![Figure 17. Uptake of anthropogenic carbon over the North Pacific for the ocean model. (a) Air-sea CO$_2$ fluxes integrated over 1993-2001 (moles/m$^2$) with positive values indicating a flux into the ocean. The figure reveals a clear uptake maximum in the Kuroshio Extension region to the east of Japan, and a secondary maximum to the southeast of Hawaii. (b) The temporal behavior of the basin-integrated uptake of anthropogenic CO$_2$ (Pg C/yr) over the North Pacific, with maximum values in winter and minimum in summer.](image)

**Using Satellite Measurements to Detect Anthropogenic Change in Ocean Chemistry**

One of the principal challenges in detecting anthropogenic change with a Carbon Observing System is that there is elevated natural variability in the Earth’s climate cycle. As a result, detection must be understood in part as a signal-to-noise problem. A key component of separating the anthropogenic perturbation signal from the natural variability signal involves developing a mechanistic understanding of the natural background variability in the carbon cycle. To this end, observations and ocean models have been used to identify mechanisms driving large seasonal to interannual variations in dissolved inorganic carbon (DIC) and dissolved oxygen (O$_2$) in the upper ocean. The Sarmiento Group began with observations linking variations in upper ocean DIC and O$_2$ inventories with changes in the physical state of the ocean. Models were subsequently used to address the extent to which the relationships derived from short-timescale (6 months to 2 years) repeat measurements are representative of variations over larger spatial and temporal scales.
The main new result with this work is that local redistribution of water associated with the passage of planetary waves in the upper ocean (in particular through the action of baroclinic Rossby waves) can make a first-order contribution to the natural variability of DIC and O2 in the upper ocean. This results in a close correspondence between (natural) DIC and O2 column inventory variations and sea surface height (SSH) variations over much of the ocean (Figure 18).

The close correspondence between SSH and both DIC and O2 column inventories for many regions suggests that SSH changes (inferred from satellite altimetry) may prove useful in reducing uncertainty in separating natural and anthropogenic DIC signals (using measurements from CLIVAR’s CO2/Repeat Hydrography program).

Investigating ocean-atmosphere-biosphere interactions

Oxygen in the Atmosphere and Surface Ocean

The Bender Group has continued to study of the O2/N2 ratio of air. The primary objective of this work is to use the atmospheric O2 balance to constrain the partitioning of fossil fuel CO2 sequestration between the land biosphere and the oceans. Atmospheric O2/N2 measurements constrain this partitioning because CO2 uptake by the land biosphere adds O2 to air, while dissolution in the oceans does not. The researchers are currently in the process of updating mass balance calculations based on their atmospheric record, which extends back to 1991. The length of record now allows the group to begin examining whether there is evidence in the O2/N2 data for acceleration of ocean CO2 uptake.

Figure 18. Changes in measured column inventory of DIC (black, mol/m²), O2 (green, mol/m²), and SSH (red, cm) from TOPEX altimetry data along 80°E in the Indian Ocean between March 1995 and September 1995. The close correspondence between the changes in SSH and the changes in DIC inventories indicates that local convergence and divergence of water associated with the passage of ocean (Rossby) waves is driving the DIC inventory variations.
The other objective of this work is to constrain rates of ocean fertility on the scale of the ocean basins. To this purpose, the group recently installed air samplers at Hateruma (Japan) and Cape Point, South Africa. Hateruma will allow intercalibration of results from their global collection network with those from the Japanese network in the western Pacific. Cape Point will help constrain productivity of the large region of high-chlorophyll waters east of South America.

A second project involves studies of local fertility of waters of the Southern Ocean. In this work, the concentration and isotopic composition of dissolved O$_2$ at the sea surface are measured, together with the Ar concentration. The researchers use the results to constrain gross primary production and net community production in the mixed layer which, in the Southern Ocean, generally comprises most of the euphotic zone. The work also includes continuous measurements of the ratio of dissolved O$_2$ to dissolved Ar along cruise tracks, enabling them to continuously constrain net community production (and export production) on oceanographic transits. The work is providing unparalleled detail about variations in upper ocean carbon fluxes in the Southern Ocean, and results generally support the view that light (which depends on mixed layer depth) and iron availability are key variables promoting higher production rates in the Southern Ocean. At the same time, they contradict expectations that silica availability (which enables diatom growth) enhances productivity. The group has added an analysis/modeling component to this work; one early result is to demonstrate that ocean biogeochemistry GCMs correctly simulate productivity in some broad areas of the Southern Ocean, but do a poor job at local scales.

**Impacts of Ocean Acidification on Phytoplankton**

The most certain effect of the ongoing increase in atmospheric CO$_2$ is change in the chemistry of the surface ocean, including an increase in dissolved CO$_2$ concentration, a decrease in pH, and a decrease in the saturation state of calcium carbonate, CaCO$_3$(s). These changes, designated collectively as "ocean acidification," will have a host of effects on the ocean biota -- some subtle, some perhaps dramatic. The work the Morel Group concerns the effects of ocean acidification on the growth of marine phytoplankton, the microscopic plants that form the basis of the marine food chain and are responsible for nearly half of primary production on Earth.

In about a third of the world oceans, primary production is limited by Fe availability. Morel and colleagues have found that decreasing seawater pH decreases the concentration of free Fe, Fe', at equilibrium with organic chelating agents to an extent that depends on the acid-base chemistry of the chelator. In laboratory cultures, the net result of this decrease in Fe' is a decrease in the uptake rate of Fe by phytoplankton (Figure 19). The same result should obtain in the field where Fe is bound to organic chelators of unknown structure. Preliminary field experiments, conducted in the Fe-limited North Atlantic Ocean during summer 2008, support this prediction.

While the effect of acidification in decreasing Fe availability is clear, the net effect on the growth of the phytoplankton is complicated by possible changes in the Fe requirements of the organisms. In particular, an increase in CO$_2$ concentration could alleviate the need to concentrate it intracellularly and make photosynthesis more efficient. This idea is supported by the researchers' laboratory experiments showing a large decrease in Fe-use efficiency (defined as the rate of photosynthesis per mole of cellular Fe) at high pH/low CO$_2$. The team has not observed an
increase in Fe-use efficiency when CO$_2$ is increased above ambient values (pH is decreased). Analyses of Fe-containing photosynthetic proteins in the group’s field samples are consistent with the laboratory observations.

![Image](image_url)

**Figure 19. Impact of pH on iron uptake.** Steady state iron uptake rates, $p$, of two diatoms (A) Thalassiosira weissflogii and (B) Thalassiosira oceanica as a function of total iron concentration, Fe$_T$, and (C) the unchelated iron concentration, Fe$'$, at three different pH values.

**Paleoclimate**

The Sarmiento and Sigman groups continue to develop new models and tools for studying ancient changes in carbon fluxes and climate.

**Long-term Variations in Oceanic and Atmospheric Radiocarbon**

It has become increasingly clear over the last decade that the Southern Ocean plays a critical role in the global carbon cycle, and that it may be expected to play a key role in determining carbon-climate feedbacks under climate change. Recent modeling has suggested a direct mechanistic link between changes in the strength of the winds over the Southern Ocean and perturbations to the exchange of CO$_2$ between the oceanic and atmospheric reservoirs. Given this potentially strong link, and the lack of knowledge about how Southern Ocean winds have changed in the past, the Sarmiento Group has been motivated to test the idea that past changes in atmospheric $\Delta^{14}$C (inferred from paleo-proxies) can reveal past changes in Southern Ocean winds.

Paleo-proxy records reveal large $\Delta^{14}$C variations for both the atmosphere and the ocean on centennial to millennial timescales. One of the most pronounced examples is the onset phase of the Younger Dryas, when atmospheric $\Delta^{14}$C rose by 70 per mil in only 200 years. This change coincided with a large and rapid decrease in the $\Delta^{14}$C of intermediate waters of the North Pacific. Another example is the most recent deglaciation transition between full glacial and interglacial states of the climate system. During this time atmospheric $\Delta^{14}$C decreased by more than 200 per mil over 3000 years (this interval has been referred to by Broecker and others as the “Mystery Interval”, with the mystery being a specific reference to radiocarbon). For both atmospheric and marine reservoirs of CO$_2$, paleo-proxies indicate that many of the significant variations and transients in atmospheric CO$_2$ are mirrored in atmospheric $\Delta^{14}$C on centennial to millennial timescales over the last 50,000 years.
These past changes are important as they correspond to changes in the state of the climate system during times when mechanistic understanding of climate change is at best incomplete. In order to address this problem, Rodgers, Mikaloff-Fletcher, and Slater used an ocean model to test the idea that variations in the strength of the Southern Ocean winds provides a means to explain both the changes in $\Delta^{14}C$ of the atmosphere and the ocean on centennial to millennial timescales. Previous modeling efforts have sought to explain such changes through perturbations of the meridional overturning circulation (MOC) of the North Atlantic, but in models MOC perturbations have thus far proven unable to account for the amplitude of the changes in $\Delta^{14}C$ revealed in the paleo-proxy records.

The model experiments conducted reveal that only relatively modest (20%) changes in the Southern Ocean winds are able to produce changes in both atmospheric $\Delta^{14}C$ and ocean interior $\Delta^{14}C$ that are consistent with the amplitude of the changes found in the paleo-proxy records. The results obtained thus far provide a “test-of-concept” for a Southern Ocean mechanism that serves to motivate further work with more sophisticated models. Future work will also focus on relating these changes to changes in CO$_2$.

### Studying Glacial-Interglacial Changes and the Southern Ocean

Daniel Sigman and his collaborators continue to pursue evidence for reduced vertical exchange (i.e. “stratification”) in the halocline-bearing polar ocean regions under colder climates of the past 3 million years. A major motivation for this focus is that the reconstructed polar ocean changes have the capacity to lower atmospheric CO$_2$ during ice ages by reducing the natural leak of biologically sequestered CO$_2$ out of the ocean and into the atmosphere.

The work also bears on the expected response of the different polar ocean regions to anthropogenic climate change, with implications for regional weather, fisheries, and the oceanic sink of anthropogenic carbon. Global models of anthropogenic warming have traditionally indicated that polar oceans would become more stratified with warming, whereas the changes reconstructed by Sigman and his colleagues from paleoclimate data show increased stratification in cooler climates. However, this picture of disagreement is starting to change because of recent realizations regarding the response of the Southern Ocean to 20$^{th}$ century wind shifts, which appear to agree with the sensitivities inferred from the paleoclimate data.

In 2008, former Princeton postdoc Rebecca Robinson published the largest set to date of diatom microfossil nitrogen (N) isotope records from the Southern Ocean over the last ice age/interglacial transition, which are intended to reconstruct surface nutrient conditions in the past. These records suggest a remarkable scenario for ice age conditions in the Antarctic Zone of the Southern Ocean, the domain closest to the Antarctic continent. While the entire modern Antarctic surface ocean layer is nutrient-rich, there is a weak decrease in nutrient concentrations toward Antarctica. The downcore N isotope data suggest that this southward decrease became much stronger during ice ages, leading to nutrient-deplete conditions close to the continent (Figure 20). The decrease supports the existence of stronger stratification in the South that limited upward transport of nutrients from deep water, which would also prevent CO$_2$-rich deepwater from contact with the atmosphere. A reasonable modern analogue is the Arctic Ocean, although the cause for this nutrient-deplete, highly stratified condition in the Arctic is different.
If this hypothesis bears up under testing with further modern and ice age data for the Antarctic, it will do much to explain the decline in atmospheric carbon dioxide during ice ages.

![Modern Southern Ocean](image1)

**Figure 20. Modern and ice age modes of ocean circulation in the Southern Ocean**

![Ice Age Southern Ocean (hypothesis)](image2)

Sigman’s group has recently begun to consider physical mechanisms for the apparent climate/polar stratification link described above. Former postdoc Agatha de Boer adapted the current GFDL ocean model (MOM4) for paleoclimate-scale simulations and used this platform to investigate the sensitivities of deep ocean ventilation to fundamental climate parameters, including the mean temperatures of the ocean and atmosphere and the strength of the southern hemisphere westerly winds. In a paper published in 2008, de Boer considered together her model experiments on three important forcings of polar ocean overturning: mean ocean temperature, the atmosphere’s hydrological cycle, and the westerly winds. This leads to the proposal of two end-members of ocean overturning behavior, “thermal” and “haline” limits, in which temperature and salinity, respectively, are the dominant controls on the distribution of deep water formation among the major polar ocean regions (Figure 21).
At the “thermal” limit, convection is shared among the North Atlantic, North Pacific, and Southern Ocean. At the haline limit, convection is restricted to the North Atlantic. The modern ocean appears to lie between these end-members, with similar rates of overturning in the North Atlantic and Southern Ocean, but little formation of interior water in the North Pacific. The effect of a more vigorous hydrological cycle is to produce stronger salinity gradients, favoring the haline state of North Atlantic dominance in deep water formation. In contrast, a higher mean ocean temperature will increase the importance of temperature gradients because the thermal expansion coefficient is higher in a warm ocean, tilting the system toward the thermal limit of globally distributed polar ocean overturning. An increase in westerly winds tends to weaken the salinity gradients more strongly than it does the temperature gradients, also pushing the ocean toward the thermal state of globally distributed overturning. This perspective unifies the behavior from otherwise disconnected model experiments, providing a useful conceptual framework for more specific, hypothesis-driven studies of the climate sensitivities of ocean overturning. From this perspective, the models of global warming predicting increased stratification with anthropogenic warming are likely driven by the hydrological cycle; the paleoclimate data suggest that the models may be overly sensitive to it, relative to the wind and ocean temperature forcings. Alternatively, the models' increased stratification with anthropogenic warming may be a transient phenomenon that is replaced by decreased stratification once the mean ocean temperature comes into equilibrium with the atmosphere.

**Stability of the Ocean Nutrient Reservoir**

Nitrogen (N) is a limiting algal nutrient in the low latitude ocean, and an increase in the oceanic N inventory has been seen as the leading alternative explanation to polar ocean changes for the lower atmospheric CO2 content observed during ice ages. Sediment records have shown clearly...
that the rate of N loss from the ocean was lower during ice ages, and it has also been argued that the input of N from N fixation was greater at those times, raising the possibility of a large increase in N inventory and global ocean productivity during ice ages.

Over the last two years, graduate student Haojia Ren in Sigman’s group has been developing a new method for reconstructing past nutrient conditions in the low latitude ocean, using the N isotopes of organic matter trapped within calcium carbonate microfossils. Her first application of the method is to the question of N fixation (i.e. N input) changes over glacial cycles [Ren et al., in press]. She has found that N fixation in the Atlantic was sharply reduced during ice ages. The N fixation decrease was most likely a response to the known ice age reduction in ocean N loss, due to a long-posed but weakly substantiated feedback involving the phosphorus demands of N fixing organisms. This feedback would have worked to balance the ocean N budget and to curb ice age-to-interglacial change in the N inventory. While this avenue of research has just opened, the results to date indicate that natural and human pressures to a change in the N inventory will be countered by this negative feedback, which will act to stabilize global ocean fertility.

**Mechanisms of Younger Dryas Cooling in Western Europe**

Sigman’s group is also working to improve understanding of the mechanisms by which past ocean changes have interacted with conditions on land. As part of a long term collaboration with close colleague Gerald Haug, Professor in the Geological Institute at ETH Zurich, sediment from a German crater lake was used in a high resolution study of western European climate at the onset of the Younger Dryas cold period ~12,700 years ago. The Younger Dryas cold period was likely fundamentally driven by a sharp reduction in North Atlantic overturning circulation. However, previous climate model studies have suggested that the overturning circulation alone could not fully explain the degradation in European climate.

Data from the lake indicate an abrupt increase in winter storminess at the onset of the cold period, occurring from one year to the next at 12,679 yr BP, providing one of the best dated records of this climate transition. The storminess change is best explained by an abrupt change in the North Atlantic westerlies towards a stronger and more zonal jet due to a cooling of the subpolar North Atlantic. The reconstructed wind shift may explain the temporal coincidence of the overturning decrease with European cooling, providing an important part of the missing link between ocean and land.

**Future Plans**

The Science group will continue to develop and apply models to investigate modern and ancient carbon cycling, make new field measurements, and work to extend paleoclimate observations back in time.
Carbon observing system

Much of the Pacala and Sarmiento Groups’ work with the Carbon Observing Network has focused on distinguishing between the natural variability of the carbon cycle and the anthropogenic transient. Importantly, the researchers have thus far been able to use models to identify processes that contribute to the elevated background variability. In applying this process understanding to the detection problem, it will be possible to reduce uncertainty in the detection of anthropogenic change. Work with the Carbon Observing Network will also continue with process-oriented studies of variability that are an integral part of the detection problem.

Temporal Changes in Terrestrial CO$_2$ Fluxes

An important focus for future work will be on using the LM3V dynamical vegetation model (developed jointly by the Pacala Group at Princeton and GFDL) and statistical analysis to determine the cause of the apparent 1990 shift in the terrestrial carbon sink identified in work with the observations. In particular, the researchers will test the hypothesis that the increased terrestrial uptake is due to an observed increase in shortwave radiation and an intensification of the hydrological cycle in the early 1990’s. In addition, they will investigate the impact of other drivers of variability in the carbon cycle such as surface warming, land use change, fertilization of the terrestrial biosphere by increased atmospheric CO$_2$ concentrations, fires, and natural variability of the climate system that occurs on interannual time scales. In support of this effort, work has begun with the LM3V dynamical vegetation model in stand-alone mode to test its sensitivity to a wide range of parameters. Not only does this constitute an important tuning exercise for developing a set of optimal parameter settings, but it also contributes scientifically to understanding ecosystems processes that could be important for climate studies.

Temporal Changes in Air-Sea CO$_2$ Fluxes

Future efforts in the Sarmiento Group will focus on understanding the processes controlling interannual to decadal variations in air-sea fluxes of CO$_2$ over the Southern Ocean. It has long been argued in the ocean carbon modeling community that variability in global air-sea CO$_2$ fluxes is dominated by variations associated with El Niño in the Equatorial Pacific, but recent studies have argued that anthropogenic transients in the circulation of the Southern Ocean have driven significant perturbations in the exchange of carbon between the ocean and atmosphere in this region.

One component of this work will involve using models to understand mechanistically how the ocean carbon cycle may respond to an increase in the strength of the winds over the Southern Ocean in response to anthropogenic climate change. Böning et al. [2007] have argued that the current generation of ocean models used to model the carbon cycle may not adequately capture the eddy response to changes in surface winds over the Southern Ocean, since none of them have been run at eddy-permitting resolution and their parameterization of eddies in these models may not be adequate. To this end, a series of process-focused sensitivity studies will be performed with the MOM4-TOPAZ model forced with CORE reanalysis surface fluxes and a more sophisticated parameterization of eddy processes. These sensitivity studies will have as their goal
not only a mechanistic understanding of the response of the ocean carbon cycle to perturbations, but also to an appropriate choice of eddy parameterization for the Southern Ocean.

As part of this work, the group will also develop an improved atmospheric boundary condition for CO₂ concentrations for use with ocean modeling studies. Preliminary sensitivity studies indicate that the commonly used CO₂ boundary condition used by the ocean modeling community may lead to spurious signals due to inconsistencies in the filtering of the temporal variations in the data.

Finally, in collaboration with Olivier Aumont at the IRD and Laurent Bopp at the LSCE, the team is currently evaluating simulations conducted with the same ocean circulation model (ORCA2-PISCES) that have been forced with two different reanalysis products, that of NCEP and ERA-40. Initial results indicate important differences in the globally integrated air-sea CO₂ fluxes between the different model runs. In particular, decadal air-sea CO₂ flux variability in the Equatorial Pacific is larger for ERA-40, with these variations sufficiently large to contribute to account for important differences in the globally integrated fluxes. Further analysis indicates that the dynamical variability in the ERA-40-forced run is reflected in a better simulation of sea surface height (SSH) in the Equatorial Pacific than is found for the NCEP-forced run. This serves to highlight that the Equatorial Pacific fluxes (and thereby the global fluxes) in the NOCES suite of NCEP-forced runs may share a bias towards being too small. As this analysis continues, it will be important to investigate the potential implications for estimates of not only global ocean carbon fluxes, but also for terrestrial carbon fluxes.

**Land Modeling**

Representation of nitrogen cycling in LM3 will continue to be improved by adding phosphorus feedbacks and assessing its impact on regional differences in carbon cycling. Both modeled disturbance experiments and the historical simulations show that feedbacks between carbon and nitrogen cycling in the model are strongest in extra-tropical regions. In contrast, carbon dynamics in tropical forests are almost unaffected by nitrogen feedbacks. However, lowland tropical forests often grow on deeply weathered soil and supply of soil derived nutrients - in particular phosphorus - might be more limiting than nitrogen. The researchers plan to amend the model with phosphorus feedbacks to assess if biomass increases throughout the tropics can be sustained under possible phosphorus constraints, and will further conduct research on how to produce a global data set that specifies external supply from weathering.

**Field Measurements**

**Impacts of Ocean Acidification**

The project dealing with the impacts of ocean acidification on phytoplankton will be widened to examine the conditions of nitrogen and phosphorus limitation in addition to that of iron limitation. Continuous cultures have been initiated to quantify the possible effects of increasing CO₂ on the C:N ratio of model phytoplankton under N-limited conditions. New laboratory
experiments will also examine the effect of decreasing pH on the utilization of organic phosphate. Both of these studies will be complemented by field experiments as described below.

**Field Measurements**

The ongoing laboratory studies of the impacts of ocean acidification on phytoplankton will be complemented by field experiments taking advantage of vessels of opportunity. In a cruise to the iron-limited region of the North Pacific (Canadian P-line cruises), new field incubations with a redesigned experimental protocol will be carried out in an attempt to quantify the effect of pH on of Fe uptake and Fe use efficiency in situ. On board experiments with varying pCO2 will be performed during cruises off the California coast in N-limited regions of the Pacific. The effect of pH on the use of organic phosphorus by the ambient flora will be tested in the North Atlantic at Bermuda time series station in the North Atlantic.

**Paleoclimate**

**Extending the Ice Core Record of Paleoclimate**

Michael Bender’s group is reconstructing polar climates and the history of atmospheric greenhouse gas concentrations by analyzing trapped gases in ice cores. Ph. D. theses completed in 2007 and 2008 developed the definitive timescales for the Vostok ice core (back to 400 ka, i.e., 400,000 years before present) and the Dome C ice core (back to 800 ka). The researchers’ current focus is to obtain older ice by drilling in locations where ice appears to be preserved for millions of years because of anomalous conditions in the local climates or bedrock topography. In Mullins Valley, in the Dry Valleys region of Antarctica, their collaborator David Marchant has drilled cores reaching 16-26 m depth underlying volcanic ash deposits dated to 1.5 – 4 Ma (million years). Bender and colleagues will date the trapped gases by their Ar isotope composition using a method recently developed in Bender’s lab; the basis is that the abundance of 40Ar relative to other Ar isotopes increases with time because 40Ar in Earth’s crust, produced by 40K radiodecay, continuously outgases to the atmosphere. They will then tackle the problem of greenhouse gas concentrations in these cores. Ar isotope dating also enables a series of related studies (on the age of permafrost, on old ice in other settings, and on the “dirty ice” at the base of the Greenland glacier) which will give new information about climate history and glacier dynamics.

**A Proxy for Southern Ocean Winds**

The Sarmiento Group will continue to pursue a series of oceanic and atmospheric model simulations that suggests that physical processes over the Southern Ocean may have first order importance in determining the latitudinal gradient of atmospheric radiocarbon. Therefore, atmospheric radiocarbon from direct observations and tree rings could provide valuable insight into processes controlling ocean circulation over the last 1,000 years, a period for which few paleo-proxies are available.

Measurements of radiocarbon in tree rings over the last 1000 years indicate that there was a pre-industrial latitudinal gradient of atmospheric radiocarbon of 3.9-4.5‰ and that this gradient has
temporal variability on the order of 6‰. Previous efforts to explain the variability in the latitudinal gradient have suggested that it is caused by changes in the frequency of ENSO in the tropics. An alternative hypothesis has been tested here, namely that the natural latitudinal gradient of radiocarbon is primarily controlled by ventilation of the Southern Ocean using fluxes from a suite of models based on the Modular Ocean Model version 3, which are used to force an atmospheric transport model. The results from this suite of simulations suggest that the atmospheric latitudinal gradient of radiocarbon is sensitive to wind stress and wind speed in the Southern Ocean. Increased wind stress in this region leads to greater upwelling of strongly radiocarbon depleted Circumpolar Deep Water (CDW) to the surface, leading to a strong decoupling of the air-sea fluxes of $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$ in this region. This decoupling is due to the fact that the $^{14}\text{DIC}$ in CDW is depleted relative to $^{12}\text{DIC}$ due to radioactive decay. As a result, increased wind speed leads to stronger gas exchange and therefore stronger $^{14}\text{CO}_2$ uptake as well as increased $^{12}\text{CO}_2$ outgassing in this region. Taken together, these effects result in a decrease in the $\Delta^{14}\text{C}$ of atmospheric CO$_2$.

These dynamical perturbations to the Southern Ocean are much more efficient than dynamical perturbations in the tropics or the North Atlantic in changing the atmospheric radiocarbon signal. Perturbations of amplitudes similar to those of observed decadal trends in Southern Ocean winds for the NCEP reanalysis (about 25%) are sufficient to account for changes in the latitudinal gradients in atmospheric radiocarbon from the tree-ring proxy records over the last 1000 years.

Thus the first stage of this work will focus on demonstrating that pre-anthropogenic atmospheric $\Delta^{14}\text{C}$ serves as a proxy for past changes in Southern Ocean winds. This first step, which is strongly supported by preliminary results, will emphasize $\Delta^{14}\text{C}$ as a tracer of physical state variables. The second stage of this work will have as its goal to connect this with variability in the carbon cycle. Radiocarbon has now been included in the biotic ocean biogeochemistry module developed by Eric Galbraith in the Sarmiento group, and this tool will allow us to identify quantitatively the relationship between the responses of $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$ fluxes to wind perturbations over the Southern Ocean. Thus this work that relates $\Delta^{14}\text{C}$ to the carbon cycle will be conducted in close collaboration with Joe Majkut in his study of the effect of ocean eddies in modulating the response of the carbon cycle to wind perturbations over the Southern Ocean.
Publications


Suwa, Makoto, and Michael L. Bender
“Chronology of the Vostok ice core
constrained by O$_2$/N$_2$ ratios of occluded
air, and its implication for the Vostok
climate records,” *Quaternary Science

Suwa, Makoto, and Michael L. Bender
“O$_2$/N$_2$ ratios of occluded air in the
GISP2 ice core,” *Journal of Geophysical
Carbon Integration

The Carbon Integration effort is conducted by the Pacala-Socolow Group and the Oppenheimer Group. Researchers in this area investigate challenges to implementing carbon policy and synthesize and disseminate CMI research results, particularly the concept of “stabilization wedges.”

Highlights of this year include:

- Participation in a number of efforts to inform national carbon and mitigation policy
- Expanded outreach to teachers via a new partnership with the National Energy Education Development Project
- Completion of a paper on a “universal emissions cap” for individuals
- An analysis of rapid investment in environmental technology in China
- Involvement in studies of the challenges of geoengineering
- Initiation of a project on the history of scientific assessments

Synthesis and Outreach

CMI’s Integration effort includes participation in high-visibility national studies of climate change and energy technology strategy, and outreach to new audiences.

This group is responsible for CMI outreach, as well as the dissemination of CMI research results, particularly the concept of “stabilization wedges.” In the past year, CMI has partnered with the National Energy Education Development Project to bring the “stabilization wedges” concept to teachers.

Informing National Climate Policy

Co-Directors Pacala and Socolow are serving in high profile positions to inform national carbon policy. Pacala is chairing a National Academies committee, Methods for Estimating Greenhouse Gas Emissions, which is examining strategies to monitor international commitments on climate change. Socolow is a member of two National Academies committees: America’s Energy Future: Technology Opportunities, Risks, and Tradeoffs (AEF), which is wrapping up, and America’s Climate Choices (ACC), which is just starting work. The AEF committee will soon complete a report to inform the new administration’s energy policy (Secretary of Energy Steven Chu was also a member of the committee). The ACC study is a comparably ambitious new two-year study, which will provide guidance about a year from now as the U.S. engages in negotiations to build a post-Kyoto framework.
The Stabilization Wedges Concept and Game

Roberta Hotinski, formerly the Information Officer for CMI, continues to work for the group as a consultant with primary responsibility for education and outreach based on the “stabilization wedges” concept, which remains enormously popular. She receives weekly requests from researchers, teachers, and non-profit groups seeking to use wedge-related materials, and the wedges website initiated last year (http://www.princeton.edu/wedges) has been viewed by 4000 unique visitors over the past year. Hotinski has continued facilitating wedges workshops around the country and helped CMI develop a new partnership to facilitate outreach to younger students.

Hotinski presented the wedges game in two major venues this year – the Scripps Howard Institute on the Environment at Florida Atlantic University and a congressional briefing sponsored by the American Association for the Advancement of Science in Washington, D.C. The Scripps Howard Institute is a weeklong continuing education program for environmental journalists, which in 2008 had global climate change as a theme. Following an overview of climate change issues by GFDL researcher Keith Dixon, Hotinski presented the stabilization wedges game to 21 journalists from around the country.

The Washington briefing was hosted by the Congressional Research and Development Caucus and sponsored by the AAAS Center for Science, Technology, and Congress. Both co-chairs of the caucus, U.S. Representatives Judy Biggert (Illinois) and Rush Holt (New Jersey), attended the event, which attracted 80 participants (Figure 22). The players were mainly congressional staff members, along with representatives of foreign embassies, energy-related companies, and nonprofit organizations. Hotinski presented the wedge concept and game, which was followed by a presentation on mitigation challenges from Jae Edmonds, chief scientist at the Pacific Northwest National Laboratory’s Joint Global Change Research Institute. Although most participants had heard of the wedges concept, many commented that they were glad to have first-hand experience with the game.

Figure 22. U.S. Representative Judy Biggert and AAAS CEO Alan I. Leshner play the wedges game at the briefing sponsored by AAAS and the Congressional R&D Caucus.

Photo by Harvey Leifert
To meet increasing demand for wedge materials oriented toward younger players, CMI has partnered with the National Energy Education Development Project (NEED) to develop a wedge-focused climate curriculum. The new curriculum, which includes activities for meeting lower CO2 targets and calculating “personal” wedges, will be used in the group’s teacher training this spring. NEED’s experience with training teachers (in 2006 and 2007 the group reached 47,000 classrooms) will greatly leverage CMI’s materials and make the group much more effective in serving the K-12 community.

Hotinski also continues to serve on advisory boards for the Franklin Institute in Philadelphia, which is developing a kiosk featuring the wedges in its new geosciences exhibit, and for the Climate Solutions Project, a proposed large-scale exhibition, discussion forum, and festival centered around solving the carbon and climate problem that will travel around the U.S.

Climate Central
CMI staff are also involved with a new non-profit organization, called “Climate Central,” which has now opened an office in downtown Princeton. Steve Pacala, along with Jane Lubchenco, the newly appointed head of NOAA, were founding board members of the group, and CMI researchers Tom Kreutz and Eric Larson are now serving as staff experts. Climate Central uses such in-house experts and a blue-ribbon network of scientists to synthesize climate information and produce stories for print, broadcast, and the web that are relevant to the policy makers and the general public. As an auspicious start, one of the group’s programs “Montana: Trout and Drought,” appeared on “The News Hour with Jim Lehrer” in October.

Climate Policy Research

The Pacala-Socolow Group has proposed a new approach to the allocation of a global CO2 emissions target among the nations of the world, based on a reinterpretation of concept of “common but differentiated responsibilities” (language in the current international agreements), so that the phrase refers to individuals rather than nations. In this formulation, obligations are the same for individuals with similar life-styles, independent of the per-capita features of the country in which they live. Follow-on work is aimed at modeling CO2 emissions generated by activities strongly correlated with wealth, including travel by air and meat-eating.

The group also hosted a workshop in June devoted to biofuel feedstock, directed by David Tilman and Socolow. They assembled a small group of leaders in the current debate about the full environmental costs of this resource. A joint statement is being prepared for publication.

Other policy-related work includes a study of increased environmental investment in China and work on geoengineering.

The Oppenheimer Group has initiated a project on the history of environmental assessments, designed to be transferable to scientific assessment of global climate change. An intriguing
dimension of this work is “negative learning” -- the idea that the history of science is marked by many wrong turns, rather than by successive approximations converging on the truth.

**Beyond Wedges – Focusing on the Emissions of Individuals**

Shoibal Chakravarty is leading an effort to formulate a new framework for assessing national obligations for carbon mitigation. The new approach frames the principle of “common but differentiated responsibilities” at the level of individuals, not nations. The scheme blends fairness and pragmatism to propose “one rule for everyone,” where all those with the same emissions are treated equally, wherever they live. A “universal individual emissions cap” is defined transparently from a global emissions target. National targets are derived by summing the excess emissions of all “high emitter” individuals in a country—“high emitters” are those whose emissions exceed the “individual emissions cap.”

An emissions distribution for each country is estimated using income distribution data from the World Bank, plus national emissions data and projections from the Energy Information Administration. Using this information, the team has linked income to carbon emissions and determined a universal emissions cap and emissions target for all countries. The approach also provides for lifeline emissions to the world’s poor and shows that energy, poverty and climate change can be addressed simultaneously. For example, reducing global emissions in 2030 from a “Business as Usual” projection of 43 Billion tons of CO₂ to 30 Billion tons (a 30% global cut with respect to BAU for that year and essentially the same global emissions as in 2008) will require the participation of 1.1 Billion people who emit above 10.8 tons of CO₂ per year. This cap corresponds to an average global income of about $39,000 (PPP, in 2000 dollars). Providing lifeline emissions of 1 ton of CO₂ per year in 2030 to the poorest 2.7 Billion people will instead involve 1.3 Billion people and reduce the “individual emissions cap” to 9.6 tons of CO₂ per year.

The proposal is aimed at the critical period of the next 20-30 years where the researchers foresee dramatic change as many countries become richer and a global middle class develops. The policy proposal provides a unified approach to treat both developed and developing countries simultaneously. It begins by putting most of burden of emissions mitigation on the developed countries and slowly shifts the responsibility on the fast growing developing countries as they grow richer. The proposal also benefits by being flexible and easily updated for different global targets.

2008 saw the completion of a paper: “Climate Policy Based on Individual Emissions,” and presentations of its ideas to a range of international audiences, notably including at the Conference of the Parties to the Framework Convention on Climate Change in Bali.

**Geoengineering - Injection of Aerosols Into the Stratosphere**

A new area of activity in the group is the evaluation of the feasibility and impacts of schemes to engineer the earth. In August, Socolow participated in a week-long workshop in Santa Barbara on the injection of aerosols into the stratosphere for albedo enhancement to counteract greenhouse gas warming. The workshop has produced a report that outlines the
required R&D portfolio that could sort how actually to achieve effective aerosol deployment, the merits and risks of this strategy, and the situations in which the case for deployment might be compelling. Socolow is also the co-chair of a new study on the direct capture of CO₂ from the atmosphere by chemical and physical means. Here, CMI is leveraging a new study being conducted by the Panel on Public Affairs of the American Physical Society. His co-chair is William Brinkman, former Vice-President for Research at Bell Laboratories.

**Environmental Investment in China**

Yuan Xu is working with Bob Williams and Rob Socolow to shed light on the extraordinary and unexpected turn toward environmental investment in China since 2006, as manifested in particular in sulfur dioxide scrubbing at coal plants. There has been a remarkable increase in the level of installation and operation of scrubbers to improve regional air quality and reduce adverse impacts on health and agriculture. Conventional economic models would have predicted that such a high level of effort would not occur until China had reached a higher per capita income.

With the help of Chinese written references and some field verification, the researchers documented the rapid deployment of sulfur dioxide scrubbers at coal power plants in 2006 and 2007. Scrubbers were installed in each of these years at plants with more than 100,000 megawatts of total generating capacity, overtaking the rate of construction of new coal power plants. Scrubber installation in each year equaled the entire scrubber capacity in the U.S. The team has described the surprising scale of investment in a paper titled “China’s Rapid Deployment of CO₂ Scrubbers.”

**Lessons from Recent Scientific Assessments**

Michael Oppenheimer and colleagues are continuing their research into “negative learning” and its impact on climate policy. Keynyn Brysse, a historian of science, has just begun a two-year postdoctoral research project to investigate the history of scientific assessments of ozone depletion. This project is part of the new joint initiative between Michael Oppenheimer at Princeton and Naomi Oreskes at UC San Diego.

The role of scientific assessments in the evaluation of knowledge has expanded over the past three or four decades to become an integral factor in shaping government policy on climate change. But how well have these scientific assessments worked, and how might they be made to work more efficiently and effectively in the future? The ozone case, particularly the creation of the Montreal Protocol, is widely regarded as an example of successful policy-making (which came about, some analysts have argued, as a result of widespread scientific consensus). At the same time, it is also an example of at least two scenarios that scientists and policy makers would wish to avoid if possible: an unexpected outcome of great import (the Antarctic ozone hole), and the tendency to follow a path of learning that turns out to be wrong (negative learning). In the case of ozone depletion, scientists initially dismissed from consideration knowledge that turned out to be critical (heterogeneous chemical reactions occurring on the surfaces of polar stratospheric cloud particles and volcanic aerosols).
Why did scientists reject this key group of reactions, what made them reconsider, and what lessons can this example teach us about avoiding such mistakes in future climate research? This case of negative learning, as exemplified by the failure to include heterogeneous reactions in models and theories of stratospheric ozone depletion, will be the first question investigated by Brysse in her study of the history of ozone depletion science. Through analysis of published and archival documents, and through interviews with key scientists, policy makers, and members of industry, the history of scientific assessment of ozone depletion will be reconstructed and used to improve understanding of the scientific learning process, and to improve the process of scientific assessment of global climate change.

**Future Plans**

**Synthesis and outreach**

Rob Socolow will continue to work to inform national energy policy through participation in committees and conferences. He will be a participant in three sessions of the Aspen Institute this spring and summer. One of these is a "Solutions Summit" – with the modest goal of creating "the optimal actionable comprehensive Global GreenPrint for the new administration." He expects also to give considerable time to the National Academies’ Committee on America’s Climate Choices, which lists the following as its organizing questions:

- What short-term actions can be taken to respond effectively to climate change?
- What promising long-term strategies, investments, and opportunities could be pursued to respond to climate change?
- What are the major scientific and technological advances needed to better understand and respond effectively to climate change?
- What are the major impediments to responding effectively to climate change, and what can be done to overcome these impediments?

Socolow will also be a speaker at the opening public event of this new study, a “summit” in late March 2009.

**Stabilization Wedges**

In response to the continued popularity of the wedges, Roberta Hotinski will continue to work with groups outside Princeton to facilitate workshops and help develop wedge-based materials for new audiences. In particular, she will continue to work with the NEED Project to revise and update the new climate curriculum in response to teacher input.

**Individual emissions**

Pacala and Socolow will continue to collaborate with Chakravarty and Massimo Tavoni to develop simplified tools relevant to the assignment of responsibility for carbon mitigation in the post-Kyoto (post-2012) era, with the goal of helping break the "north-south" impasse in
international climate policy. A particular focus will be on high-emitter consumption profiles, for example the link between income and future increases in aviation emissions.

**Direct Air Capture**

The American Physical Society study of direct capture of CO2 from air will be conducted throughout 2009. Socolow, as its co-chair, has arranged for its key fact-finding meeting to be held on March 23-25, 2009, at Princeton, in order to provide cross-fertilization with Princeton researchers. The study will focus specifically on physical/chemical direct-capture technologies, excluding both biological methods for direct capture and issues of CO2 storage after capture (both of which are widely studied elsewhere). Since direct physical/chemical capture of very dilute atmospheric CO2 (about 400 ppm) shares some similarities with the capture of moderately dilute CO2 (about 100,000 ppm) from the exhaust exiting coal and natural gas power plants and industrial facilities, this study will also include the evaluation of emerging “post-combustion capture” technologies. As such post-combustion capture technologies are currently under intense industrial development, their evaluation will provide valuable insight into potential technological barriers and cross-fertilization opportunities for direct capture. The study will also examine the moral hazard raised by direct capture, as even knowing that direct air capture might work could reduce the level of effort on other alternatives.

**Environmental investment in China**

The focus on China’s capacity to initiate its own climate change initiatives will continue. Yuan XU will complete his thesis on sulfur dioxide scrubbers and present his work in China at select audiences. Jie LI will also complete her thesis, which is an exploration of alternative rules for targets at the province level that would enable the achievement of a national carbon mitigation target – an allocation question analogous to that asked about countries meeting a global target in other CMI work. Indeed, income disparities across the provinces of China resemble those across the nations of the world. Both Xu and Li are graduate students in the Science, Technology, and Environmental Policy (STEP) Program of the Woodrow Wilson School of Public and International Affairs, directed by Oppenheimer.

**Lessons from scientific assessments**

Keynyn Brysse has already made contact with several potential interview subjects and is in the process of arranging interviews with key scientists in the spring of 2009. This first round of interviews will form the basis for a paper on negative learning as exemplified by the initial treatment of heterogeneous reactions in ozone depletion science, and also lay the groundwork for further exploration of this rich history.
Publications


Xu, Y., R. Williams, and R. Socolow, “China’s rapid deployment of SO2 scrubbers,” Submitted for publication in Energy and Environmental Science.