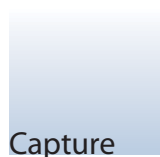




Carbon Mitigation Initiative

Seventh Year Report

February 2008



Capture



Storage



Science



Integration



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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 8th 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 and analysis of renewable energy.



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 Carbon Mitigation Initiative (CMI) at Princeton University has concluded its seventh year. We continue to enter the global discussion of global climate change through several portals, and our effectiveness as participants increases with our experience and staying power. Dramatic changes in Washington in 2007 made our work more valued close to home, and a much broader acceptance of tough global mitigation goals around the world made our work more pertinent than ever.

The **Capture Group** has sparked a new and deepening discussion of the potential of co-gasification of coal and biomass to transform the biomass energy agenda. Deeply technical collaborations with our counterparts in Italy, China and BP were remarkably fruitful. The **Storage Group** has made great progress in modeling both well-scale and basin-scale issues for carbon storage, and is beginning to provide practical tools for quantitative assessments of leakage risks in realistic CCS settings. The **Science Group** is completing the final steps in creating a Carbon Observing System, continues to narrow uncertainties in estimates of natural carbon sources and sinks, and is making an increasingly strong case for the role of the Southern Ocean in glacial-interglacial changes. The **Integration Group** began a new effort whose goal is to break the North-South policy logjam by reframing mitigation as requiring equivalent actions for individuals with the same lifestyles, wherever they live and specifically irrespective of the per capita income of their country. Our outreach effort in 2007 included our playing a version of the wedges with 400 people as the featured event at the Town Hall of the AAAS annual meeting, the largest science meeting in the United States each year.

Our Co-Directors continue to promote exploration of the climate-energy nexus both within the university and in the wider community. Steve Pacala, now the Director of the Princeton Environmental Institute (PEI), is working to consolidate environmentally-oriented science and policy initiatives across campus with Princeton's new "Grand Challenges" program. He has also led creation of a non-profit organization called "Climate Central" to serve as an objective source of information on climate and energy for the media, the policy and business communities, and the general public. And, he was elected to the National Academy of Sciences. Co-Director Rob Socolow now heads the Energy, Climate, and Security Grand Challenge at Princeton. In 2007, among his invited talks were remarks at a plenary meeting of the U.N. General Assembly on climate change and at a retreat for the Executive Directors of the World Bank. He also served on the committee: "Grand Challenges in Engineering," of the National Academy of Engineering and now serves on the National Academies' committee, "America's Energy Future," which, with the next President as its perceived client, is reviewing near-term options that can begin a transformation of the U.S. energy system.

Finally, Princeton in 2007 was graced by the presence of visiting faculty member Ian Vann, the first BP-Vann Fellow. Students raved about his undergraduate course, ENV 311 - *Business of Oil and Gas: A Global Perspective*, where they could share his real-world experiences and insights.

Vann's appetite for serious discussion across a wide range of topics enriched the lives of faculty and students with interests in all aspects of the energy agenda,

The following pages document the major research results of the past year and near-term plans. For a comprehensive summary of the CMI program over the first 5 years and blueprint for the future, the 2006 annual report can be downloaded from our website:

<http://www.princeton.edu/~cmi/summary/documents/annreport06.pdf>

The Capture Group

The Capture group's research over the past year has been mainly in the following areas:

- (i) Analyses to help catalyze early action on CCS in the United States
- (ii) Making fuels and electricity from mixed prairie grasses and coal
- (iii) Participating in the Working Group on Coal to Liquids of the Western Governors' Association
- (iv) Energy in China
- (v) Collaboration with colleagues at Politecnico di Milano
- (vi) Wind energy and compressed energy storage
- (vii) Combustion of alternative fuels

Toward Early CCS Action in the US

Activity aimed at catalyzing early CCS action in the US has focused on CO₂ enhanced oil recovery (EOR) opportunities in Texas and Williams' Congressional testimony laying out a strategy for speeding the adoption of CCS as a routine activity for coal energy conversion systems.

The gasification energy/CO₂ EOR nexus for Texas

In 2006, when TXU made proposals to build many new conventional power plants fueled with low-rank coals in Texas, Bob Williams started a study that ultimately showed that the surge in demand for new coal power presents an opportunity for early CCS action by recovering CO₂ at new power plants for enhanced oil recovery (EOR). In the meantime, public opposition to the planned new coal capacity led on 26 February 2007 to an announcement of a buyout of TXU by the Texas Pacific Group (TPG) and Kohlberg Kravis Roberts to be accompanied by cancellation of plans for all but 3 of the originally planned TXU plants. The ensuing controversy about the remaining 3 plants led David Bonderman (TPG head) to call for a meeting on 5 March 2007 with Dallas Mayor Laura Miller and the members of her committee of Texas mayors that opposed the construction of the remaining three plants to discuss their differences. Williams' draft analysis was already being circulated in Texas, and, as a result, Mayor Laura Miller invited Williams to attend the meeting with Bonderman as one of her two technical advisors for the meeting. At the meeting Williams had the opportunity to discuss briefly the "gasification energy/CO₂ EOR nexus for Texas." However, the controversy about the remaining planned TXU plants continues.

After the meeting Tom Kreutz joined Williams in continuing the analysis of IGCC power with CO₂ capture and use for EOR. A challenge posed by coal power in Texas is that the least costly gasifiers on the market cannot economically be used with the low-rank coals that would be used

in Texas [Texas lignite or Powder River Basin (PRB) sub-bituminous coal]. So Williams and Kreutz set out to model IGCC power plants that would be fired with a blend of low-rank coal and petcoke (which is abundantly available in Texas) designed to “look like” (from the gasifier’s perspective) the high-rank (bituminous) coal that these low-cost gasifiers are designed to use. They found that a blend of 43% PRB coal and 57% petcoke would be well suited for use with the least costly gasifiers. And for these plants they carried out an economic analysis suggesting favorable economics for IGCC plants sited near CO₂ EOR opportunities—to the extent that the power generation cost for such plants with CCS would be no higher than for coal steam-electric plants fired with PRB coals but with CO₂ vented. These results were presented at the 6th Annual USDOE Conference on Carbon Capture and Sequestration (May 2007); a paper is being prepared for presenting these results in a journal.

The “gasification energy/EOR nexus for Texas” idea seems to be catching on. In late spring of 2007, Goldman Sachs announced plans to build 1200 MW_e of petcoke IGCC capacity at Lockwood, Texas, with CO₂ capture and use for EOR—the first 600 MW_e unit is expected to come on line in 2011 and the second 600 MW_e unit in 2013.

Testimony to the Select Committee on Energy Independence and Global Warming

Williams was invited in September 2007 to submit written testimony to the Select Committee on Energy Independence and Global Warming of the US House of Representatives in conjunction with its Hearing on the Future of Coal under Carbon Cap and Trade. Committee Chairman Edward Markey asked Williams to address, as one part of his testimony, a set of questions as to what Congress might do to speed up the widespread deployment of CCS technologies for coal energy conversion systems.

Williams pointed out that, although no energy conversion plant with CCS has been built, there are no technical barriers to carrying out CCS projects for gasification-based energy conversion systems—because all the technological components are proven. He indicated that the only significant barriers are (i) the need for a valuation of CO₂ emissions of at least \$30 per tonne of CO₂ in order to make CCS investments profitable and (ii) institutional issues relating to CO₂ storage (access to underground pore space, liability concerns, etc.)—reflecting the fact that a regulatory framework is not yet in place for CO₂ storage. He described a strategy for getting started with CCS as early as 2013 for all new coal energy conversion facilities. Two key elements of his (seven-part) proposal are a low-carbon obligation for coal power (that would spread over all coal power generation via a trading mechanism the incremental cost of CCS for the growing number of plants that would be decarbonized over time) and establishment of a quasi-public corporation to assume responsibility (including liability) for CO₂ storage in federally certified storage media for the very first plants—plants that would be built before the needed regulatory framework for CO₂ storage is put into place (hopefully, by ~ 2015).

Making Fuels and Electricity from Mixed Prairie Grasses and Coal

A major activity of the Capture Group has been exploring coal/biomass to liquids (CBTL) with CCS systems that produce synfuels + electricity. A new focus this year was using mixed prairie grasses (MPGs) grown via low-intensity techniques on carbon-depleted soils (as proposed in a 2006 *Science* article by David Tilman and collaborators) as the biomass feedstock. Energy and carbon balances as well as capital costs have been estimated, taking into account for the latter recent escalations in construction costs. Costs for the synfuels and electricity produced have been estimated as a function of the economic value of GHG emissions. This activity has been led by Williams and Larson in collaboration with Stefano Consonni and Giulia Fiorese at the Politecnico di Milano, extending earlier analysis led by Williams and Larson on systems with CCS that make synfuels + electricity from coal plus switchgrass (a monoculture energy crop). In this collaboration Giulia Fiorese, one of the Politecnico graduate students who visited PEI during 2007 (see Collaboration with Politecnico di Milano, below), had the major responsibility for developing a comprehensive model to evaluate the logistic chain of biomass supply, its costs and the overall carbon/energy balances of gasification energy with CCS systems that make synfuels and electricity from coal and MPGs.

This MPG strategy would help address biodiversity loss concerns for monoculture energy crops while significantly increasing the negative emissions potential of biomass by complementing geological storage of photosynthetic CO₂ (the focus of earlier work on switchgrass) with root and soil carbon buildup during MPG growth. A system producing 17,000 barrels per day (1032 MW) of Fischer-Tropsch (F-T) liquids + 452 MW_e of electricity was designed with just enough MPGs to reduce the net GHG emission rate for the F-T liquids to zero, while allocating to electricity a GHG emission rate for a stand-alone IGCC plant with CCS (see Figure 1). For a crop consisting of a mixture of 16 prairie grass species it was estimated that zero net GHG emissions could be realized when 21% of input energy is in the form of MPGs (see Figure 1). (If no credit could be realized for the soil/root carbon buildup, the GHG emission rate for the F-T liquids would instead

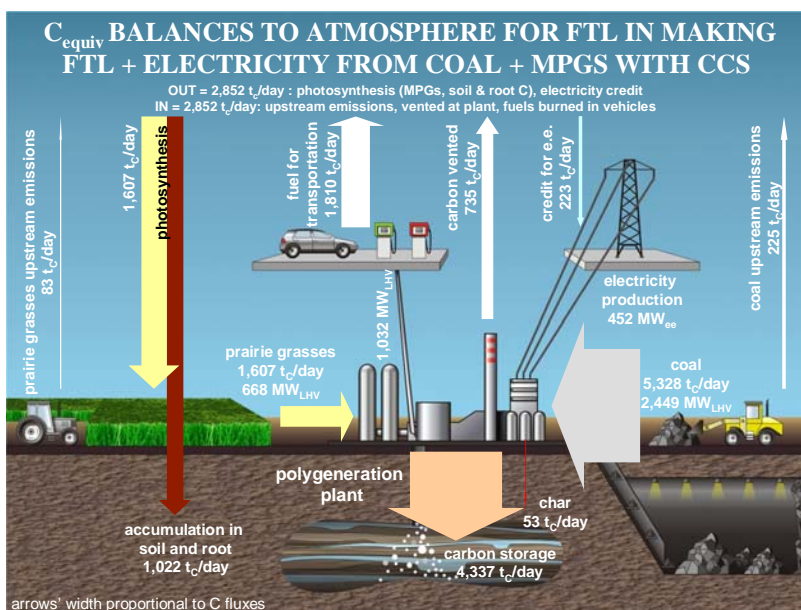


Figure 1. Carbon and Energy Balances for a System Making Low GHG-Emitting F-T Liquid Fuels and Electricity from Coal and Mixed Prairie Grasses (MPGs) Grown on Carbon-Depleted Soils.

The system captures and stores as CO₂ 85% of the C not contained in liquid products. Assuming 16 MPG species, the estimated 30-year average soil/root C storage rate is 0.6 tC for each tC in harvested biomass. Some 10⁶ dry tonnes of MPG are required annually. For a hypothetical case study plant located in Southern Illinois, the estimated MPG yield is 10.4 dry tonnes per hectare per year on lands now planted in corn, and the average MPG transport distance is 43 km. The captured CO₂ is transported 53 km by pipeline for storage in the Mt. Simon aquifer.

be 46% of the rate for the crude oil-derived products displaced.)

For a such a system sited in southern Illinois using MPGs grown on land currently planted in corn, the amount of liquid fuel energy provided would be 3.3 times the amount of ethanol energy that could be produced from the corn now grown on this land (see Figure 2). Alternatively, this same land might be planted in switchgrass for conversion (via use of technologies yet to be demonstrated commercially) to cellulosic ethanol; so doing would reduce the GHG emission rate by an almost order of magnitude relative to that for corn ethanol, but the liquid fuel yield would be about the same (see Figure 2).

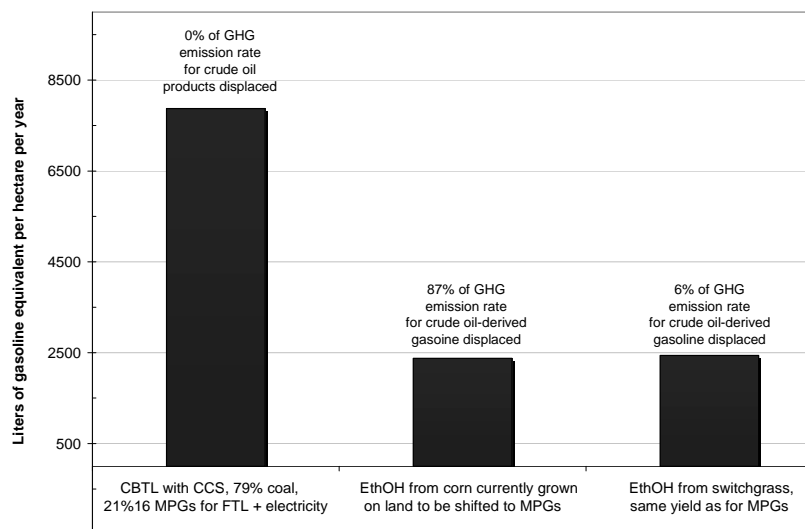


Figure 2. Liquid Fuel Yields for Alternative Technologies. The bar on the left is for the zero net GHG-emitting coal/biomass F-T liquids with CCS case shown in Figure 1 based on use of 16 mixed prairie grasses (MPGs) at a site in southern Illinois where MPGs are grown with low intensity inputs on land now growing corn. The second bar is for ethanol from corn (current corn yield on this land: 7.6 dry tonnes (dt) per hectare per year, 0.47 liters of ethanol per dt). The third bar is for cellulosic ethanol (0.38 liters per dt) derived from switchgrass grown at the same yield as estimated for MPGs (10.4 dt per hectare per year).

A paper describing a case study for the State of Illinois is being prepared, to show under which conditions and which strategies are needed to make the production of FT fuels from co-gasification with CCS competitive with other strategies to mitigate GHG emissions.

If the 19 million acres currently used to grow corn in the US for ethanol were converted 100% to CBTL with CCS using MPG biomass, some 22.5 billion gallons of ethanol-equivalent liquid fuel could be produced annually—more than the total amount of advanced biofuels targeted for production in the US by 2022 under the Energy Independence and Security Act of 2007—some 21 billion gallons per year. Moreover, if all this fuel were used in US light-duty vehicles (LDVs), the result would be 10% lower oil use and a 10% lower GHG emissions intensity for LDVs in that year, assuming no other low carbon fuels would be used to displace oil. For perspective, this emissions reduction potential can be considered in the context of the Low Carbon Fuel Standard that Governor Arnold Schwarzenegger launched via executive order for California in January 2007—which calls for reducing the average carbon intensity of fuels for light-duty vehicles in California at least 10 percent by 2020.

“Carbon debt” concerns have recently been raised about US plans to expand corn ethanol production from 6.4 billion gallons in 2007 to 12 or 15 billion gallons per year over the next

decade. Rapid reduction in U.S. corn growing for food is expected to lead to bringing new lands into food production elsewhere in the world that would release large quantities of carbon to the atmosphere from standing biomass and soil carbon now stored in these lands. Calculations indicate that typically several decades to hundreds of years of biofuel production would be required to “pay off” the carbon debt associated with these carbon releases. This carbon debt problem might be mitigated if corn lands now used for alcohol production could be shifted to CBTL with CCS systems using MPGs. This would be of interest to farmers, however, only if the shift would lead to incomes that are at least as great as for growing corn for ethanol production.

In our economic analysis, the breakeven crude oil price was first estimated to be ~ \$70 per barrel for coal to liquids (CTL) plants for the plant scales considered. It was assumed that the CBTL plants would have to sell their products at the same prices as CTL plants. This condition determines the synfuel producer’s willingness to pay (WTP) for biomass—a price that depends sensitively on the market value of GHG emissions. At low GHG emission prices CBTL technology would not be economic, but at CO₂-equivalent GHG emission values greater than ~\$30-\$35/tCO₂, favorable economics would be realized for systems getting credit for soil/root carbon buildup at WTP levels that would lead to farmer incomes from growing MPGs that are greater than from growing corn. This emissions value is of the order of the minimum GHG emission value needed to induce CCS for new coal power plants. Thus a carbon policy stringent enough to induce CCS for coal power plants would make MPG-based CBTL technology economic in a world with oil prices of the order of \$70 a barrel.

A shift from corn to MPGs could plausibly get started in this time frame. MPGs can be established as harvestable crop systems in a few years time. And one technological variant of the CBTL concept—based on dry-feed entrained-flow gasifiers—is commercially ready. Beard Energy is planning to construct a 50,000 barrels per day CBTL plant at Wellsville, Ohio, using this approach. Plans are to co-fire the plant with bituminous coal and 30% biomass (dry-weight basis) and to capture CO₂. Captured CO₂ would be used either for enhanced oil recovery in a nearby oil field or stored in a deep saline formation. Beard is targeting bringing on line the first part of the plant in the 2011-2012 timeframe.

The CBTL with CCS concept is attracting considerable attention, to a large extent as a result of CMI studies and many presentations.¹

¹ For example, a December 2006 panel presentation by Williams (“Toward Cost-Competitive Synfuels from Coal and Biomass with Near-Zero Well-to-Wheels GHG Emissions by Simultaneous Exploitation of Two Carbon Storage Mechanisms,” *Alternative Fuels Seminar: Carbon to Liquids*, Center for Strategic and International Studies, Washington, DC) sparked interest in CBTL with CCS technology by NETL Director Carl Bauer, who made a presentation on the same panel. Also, a July 2007 luncheon keynote address by Williams to the Washington Coal Club (“Synfuels From Coal + Biomass with CO₂ Capture and Storage (CCS)”) brought the CBTL with CCS concept to the attention of many interested in coal issues in Washington. The Washington Coal Club convenes a regular seminar attended by coal industry lobbyists, DOE coal staffers, and Congressional staffers interested in coal issues.

The Air Force has set a goal of meeting ½ of its jet fuel needs in 2016 with F-T liquids. A study for the Air Force and the National Energy Technology Laboratory (NETL)² addressed the question: could these F-T liquids be provided with an average CO₂ emissions rate that is 20% less than that for the crude oil-derived products displaced by exploiting both CCS and CBTL technologies? Also, Williams is a technical advisor for a major follow-on NETL study on the CBTL with CCS concept that will be published in early 2008.

In September 2007, Williams was invited to submit written testimony for the Hearing on the Future of Coal under Carbon Cap and Trade before the Select Committee on Energy Independence and Global Warming of the US House of Representatives, Chaired by Congressman Edward Markey. In part of his testimony Williams sketched out the strategic importance of the CBTL with CCS option, discussed the major challenges, and proposed off-budget incentive schemes for encouraging CBTL and competing low-carbon fuels technologies that would substitute the market for the government as the “picker of the winning technologies.”

Coal to Liquids Working Group of the Western Governors Association

In the spring of 2007, Williams was invited to become a member of the Coal to Liquids Working Group of the Western Governors Association (WGA). The mandate of the Working Group was to produce a report advising the WGA about coal to liquids (CTL) technologies as part of a larger WGA effort on alternative transportation fuels.

Issues promoted by Williams that were reflected in the Working Group’s final report were the importance of: (i) using low-cost CO₂ from early CTL plants for megascale CO₂ saline formation storage projects to help ascertain the gigascale viability of CO₂ storage as a carbon mitigation strategy, (ii) using low-cost CO₂ for CO₂ EOR projects, and (iii) coprocessing biomass and coal to make CBTL with CCS as a strategy for realizing low or even zero net GHG emission rates for synfuels. But Williams did not agree with all the report’s findings and especially with its main public policy recommendation on incentives for commercializing synfuels technologies. As a result, Williams was invited to prepare a separate statement that accompanies the main report, highlighting his disagreements with the main findings and especially his view that commercialization incentives should give priority to systems that offer significant GHG emissions mitigation benefits in displacing crude oil-derived fuels.

Energy in China

Activities relating to energy in China have focused on identifying opportunities for early CCS action and exploring the relevance of the CBTL concept to China.

² DOE/NETL and DoD/Air Force, *Increasing Security and Reducing Carbon Emissions of the US Transportation Sector: A Transformational Role for Coal with Biomass*, DOE/NETL-2007/1298, 24 August 2007.

Opportunities for early CCS action

The urgency of widespread deployment of CCS technologies for coal power generation in China is underscored by the huge growth rate for coal power—almost 100 GW of new coal capacity was added in 2006, equivalent to almost 1/3 of total installed capacity for coal power in China in 2004—and the fact that CCS is much less expensive for new power plants than for retrofit strategies at existing power plants.

Our activities in this area over the past year have been largely in conjunction with international meetings.

In April 2007, Larson gave an invited talk in Beijing at a workshop on CCS and enhanced oil recovery (EOR) organized jointly by BP and PetroChina. Larson's presentation emphasized the relatively low costs of CO₂ from coal gasification systems and the potential attractiveness of utilizing such CO₂ for EOR.

In May 2007 Williams participated in a Joint Workshop on the Industrial Alliance for IGCC and Coproduction and CO₂ Capture and Storage in Beijing, cosponsored by the Energy Technological Innovation Project at Harvard and the Institute of Thermo-Engineering Physics of the Chinese Academy of Sciences. Williams was asked to review CO₂ capture activities in the U.S. In his presentation he described the U.S. petcoke IGCC with CCS projects coupled to enhanced oil recovery (BP Carson Refinery project in California and Goldman-Sachs Lockwood Project in Texas) and growing US interest in coal to liquids technology coupled to enhanced oil recovery. He also showed how over the last two years all power generation capital costs and thus CO₂ capture costs have escalated dramatically as a result of the worldwide scarcity of steel, copper, cement, etc., and skilled construction labor. And he highlighted the findings of earlier CMI research (Meng, Williams, and Celia, 2007) that plants making ammonia from coal represent attractive opportunities for early CCS demonstration projects in China.

In November 2007 Williams was invited to participate at the World Bank in a Roundtable on Innovative Strategies to Accelerate the Development of Clean Energy Technologies. The Roundtable was intended to solicit advice relating to the World Bank Group's Clean Energy for Development Investment Framework Action Plan, which outlines some of the key activities the Bank intends to undertake in the area of mitigating greenhouse gas emissions and helping client countries adapt to changes in climate. Williams highlighted the potential opportunities for demonstration projects using the relatively low-cost CO₂ available at plants that make methanol, dimethyl ether, or ammonia from coal. This World Bank group was especially interested in the ammonia plant opportunities highlighted in our earlier work (Meng, Williams, and Celia, 2007).

Is CBTL with CCS relevant to China?

There have been many proposals for building coal to liquids (CTL) plants in China, and for none of these is CCS being planned. As a result, the fuel-cycle-wide GHG emission rate would be approximately twice the rate for crude oil-derived fuels. So finding a way to get CCS underway for coal synfuels is important for mitigating climate change. However, even if CCS were to be

carried out at CTL plants, the GHG emission rates would be no better than for crude oil-derived hydrocarbon fuels replaced.

As an element of our collaboration with Li Zheng's group at the BP-Tsinghua Clean Energy Center in Beijing, we have begun to explore the prospects for extending to China the concept of making low GHG-emitting synthetic fuels from coal + biomass (CBTL) with CCS. Professor Li hosted a 12-month visit by Cathy Kunkel³ at Tsinghua University beginning in the fall of 2006. During this period Kunkel, supervised by Larson and interacting with Prof. Li and others at Tsinghua, gathered data and carried out preliminary analyses relating to these coal/biomass co-processing strategies for low-carbon liquid fuels supply in China—considering as feedstocks both crop residues (from agriculturally-rich Shandong Province) and mixed native prairie grasses (from Inner Mongolia). Both regions have coal resources.

For crop residues⁴ the focus has been on developing a comparative analysis of alternative 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 prairie grasses used for coal/biomass-based synfuels production involves 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 CO₂ 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 they are doing with the land at present—if the oil price is high and the value of CO₂-equivalent GHG emissions is high (at least ~ \$30/t CO₂).

A new dimension of the China grasslands work is interest in these issues on the part of an internationally known ecologist, Jianguo (Jingle) Wu (a faculty member at Arizona State University), who works on the ecology of Inner Mongolian grasslands restoration (and is originally from Inner Mongolia). A meeting took place in Beijing in March 2007 involving Wu, Kunkel, Li Zheng, Gary Dirks (CEO of BP Asia and a personal friend of Jingle Wu), and Steve Wittrig (who manages BP's academic research investments in China). Larson, Kunkel and

³ Princeton '06 graduate with high honors in physics.

⁴ Of which ~ 360 million tonnes are potentially available annually for energy in China.

Williams prepared background materials for the meeting, and at the meeting Dirks expressed strong interest in exploring further the idea of utilizing grassland biomass for liquid fuels. He suggested trying to pique the interest of the Shenhua Corporation, which is planning the construction of several coal-to-liquids plants in China and is already building the first one in Inner Mongolia. Subsequently (in April 2007), as a result of arrangements made by Jingle Wu, Larson and Kunkel met with key researchers at the Institute of Botany of the Chinese Academy of Science (Beijing) and at the University of Inner Mongolia (Hohuhot), the two leading centers for research on restoration of degraded grasslands. The purposes of these meetings were to collect data and establish contacts for possible future collaborations.

During the coming year, Larson will lead efforts to finish and publish the two pieces of analysis that were initiated with Kunkel⁵ and to search for an outstanding candidate to take up residence with Prof. Li's Group to continue the work Kunkel began.

Collaboration with Politecnico di Milano

A visit of Prof. Stefano Consonni and three research associates from Politecnico di Milano in the spring of 2007 helped deepen and expand the analysis of novel technological options for CO₂ capture. Joint work through a triangular connection among BP, Princeton, and the Politecnico has focused on a number of particularly promising technological and system options for CO₂ capture. With this framework in mind, a formal agreement between BP and the Politecnico has been discussed which would take advantage of the capabilities being developed at the new LEAP lab in Piacenza, and could also include also experimental investigations on the thermodynamic properties of supercritical CO₂ mixtures, an area where significant work is needed to substantiate the performance estimates of capture technologies.

One further opportunity to develop collaborative work between Princeton and Milano comes from the contacts established by both Universities with Prof. Li Zheng at Tsinghua. In November, Li and Dr. Christos Papadopoulos joined a group from Politecnico and Princeton in their visits to two of the four large IGCC plants fed with petroleum tar operating in Italy. Talks are underway to define a joint project, possibly funded by the BP Clean Energy Center at Tsinghua, to simulate the off-design behavior of gasification plants – a topic relevant to most systems with pre-combustion capture.

The research currently being pursued in collaboration with Politecnico falls in the five areas described below:

Cryogenic capture

Following preliminary, positive indications emerged from a screening carried out by the Carbon Capture Group in BP Alternative Energy, work has been carried out to simulate and assess the performance (in terms of power consumption and fraction of CO₂ captured) of cryogenic pre-

⁵ Who in the fall of 2007 started graduate work in physics at Cambridge University, UK.

combustion capture in IGCCs (Figure 3). The novelty of the configurations considered and the preliminary results obtained so far have led BP Alternative Energy to suggest an assessment of the prospects for patent protection. Further investigations will resume soon after clarifying this issue, with the continued involvement of Dr. Federico Viganò.

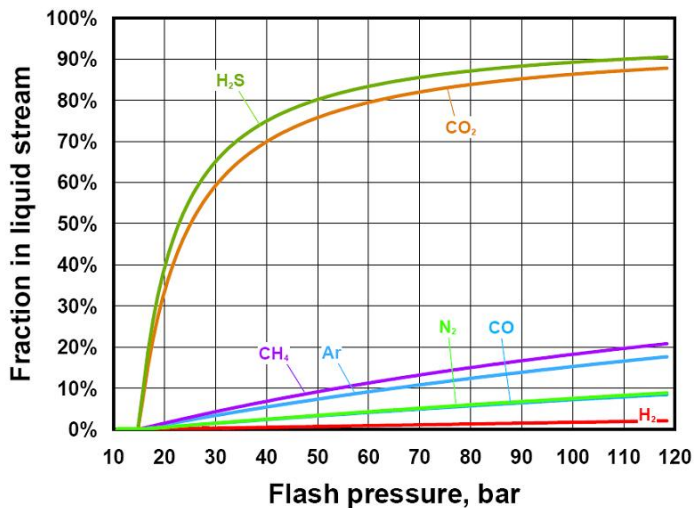


Figure 3. Fractions of each syngas component (as percentage of the total amount of each component) in the liquid stream originated by cooling the syngas to -53°C at the pressure indicated on the horizontal axis. Syngas composition is representative of GE quench gasifier followed by a two-stage shift to convert most of the carbon to CO_2 .

Coal-biomass co-gasification with CCS

If coupled with CCS, the co-gasification of coal and biomass allows the production of fuels with low (possibly zero) content of fossil carbon without being penalized by the small scale suited to systems fed only with biomass. On the other hand, the use of biomass in modern, pressurized entrained flow coal gasifiers is problematic due to the low heating value of biomass and its unfavorable physical features that make it difficult to feed biomass in such gasifiers. A comprehensive analysis of the available technologies and the possible plant configurations that could be adopted for co-gasification has been carried out to identify the most promising options for large scale plants where biomass and coal are co-gasified to produce Substitute Natural Gas (SNG). Despite concerns about its (possibly inadequate) market price, the production of SNG with non-fossil carbon opens the possibility to distribute it through the existing large infrastructure for natural gas at very low cost. Preliminary heat/mass balances and performance estimates have been generated for a large scale plant where the unconverted syngas left downstream of the SNG reactors feeds a state-of-the-art combined cycle.

Assessment of Shell quench gasification and optimization of integrated steam cycles

With a recent patent Shell has introduced a variation of its entrained flow gasification technology meant to be particularly suited to IGCC with CCS. In such new “quench” version, the syngas exiting the gasifier is quenched with a spray of water rather than being cooled in a heat exchanger to generate high pressure steam. The negative impact on efficiency is somewhat compensated by the higher water content of the syngas, which facilitates the water-gas shift to be carried out downstream. The new technology has been modeled in detail and compared with the

“conventional” Shell technology with syngas cooler. Results will be reported in a paper under preparation that will discuss the potential of the new technology for applications with CCS.

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 the Thesis of Emanuele Martelli, a Ph.D. student at Politecnico among the ones who have visited PEI, a new method is being developed to optimize the configuration and the operating parameters of the steam cycle. 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.

Wind Energy and Compressed Air Energy Storage

The Capture Group’s analyses of wind/compressed air energy storage (wind/CAES) have focused on converting intermittent wind power into baseload power and on the prospects for exploiting good but remote wind resources by sending baseload wind/CAES power via long-distance, high-voltage transmission lines to distant power markets. Since 2005 this research has been led by Samir Succar under Williams’s supervision. During 2007 research exploring the prospects for wind/compressed air energy storage (wind/CAES) systems has been on (i) understanding better the market competition between baseload wind power and baseload coal power, and (ii) getting a better understanding of compressed air energy storage technology.

Baseload wind power vs. baseload coal power

Because the least costly CO₂ capture option for coal power is for coal integrated gasifier combined cycle (IGCC) plants (at least for bituminous coals), the wind/CAES systems analysis has focused on the competition between wind/CAES and coal IGCC plants with CCS and coal IGCC plants with CO₂ vented.

In a wind/CAES system, a small amount of fuel (typically natural gas) would be burned in the compressed air stream recovered from storage, the combustion products of which would be expanded in a turbine to produce electricity. The GHG emission rate for a natural gas-fired baseload wind/CAES unit would be very small, ~ 1/10 of that for a coal IGCC with CO₂ vented or ~ 1/2 of that for a coal IGCC with CCS. Also, although wind/CAES cannot compete with today’s new coal power plants in the absence of a carbon mitigation policy, the levelized generation cost (in \$/MWh) would be very close to that for coal power in the presence of a CO₂-equivalent GHG emissions price – about \$30/tCO₂, the minimum needed to induce by market forces a power generator to build a coal plant with CCS instead of one that vents CO₂ - assuming all plants operate at the same “baseload” capacity factor of 85%.

Our research found that the wind/CAES option would have a lower dispatch cost than the coal options more than 90% of the time when the value of CO₂-equivalent GHG emissions is \$30/tCO₂.

Adding more and more wind/CAES to the power grid would lead to lower and lower capacity factors for all the competing coal power options—thus driving up the levelized generation costs for the coal power options.

Notably, the wind/CAES option enables both wind and natural gas to compete in baseload power markets in a carbon-constrained world. The intermittency of wind makes it impossible for a “pure” wind system to provide baseload power. Moreover, high natural gas prices exclude natural gas combined cycle power technology from providing baseload power wherever there is a substantial amount of coal power on the grid. But coupling wind to CAES makes it possible for wind to deliver firm power. And the use of wind to provide compressor energy for CAES enables natural gas to be burned at low enough heat rates in CAES units to be competitive with coal in economic dispatch.

CAES technology

The extent of the wind/CAES opportunity in mitigating climate change depends on the availability of suitable geologies for CAES. To better understand the issues involved, a major activity during 2006-2007 was to assess CAES technology for potential applications that include but are not restricted to wind/CAES. The draft final report was widely circulated for review during the second half of 2007, and the report is now being finalized based on feedback received. The report discusses both the turbomachinery of CAES (essentially a gas turbine in which the compressor and expander functions are separated in time) and the geologies of underground air storage.

The major CAES storage options are mined hard rock (including abandoned mines), aquifers, and salt (salt domes or bedded salt). The only commercial plants use salt domes, but the world’s first wind/CAES plant (a 268 MW CAES plant coupled to 75-100 MW of wind capacity at Dallas Center, Iowa, a project being developed by the Iowa Association of Municipal Utilities) will involve aquifer storage and is expected to come on line in 2011. The CAES report focuses on aquifer storage, the dominant geological storage option in most US regions that have high-quality wind resources (see Figure 4).

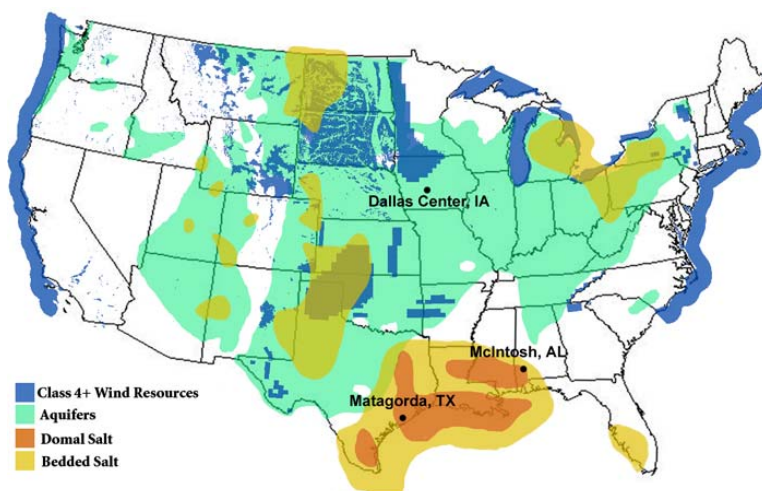


Figure 4. Distribution in the United States of prospective aquifer, domal salt, and bedded salt compressed air storage resources, and of high-quality wind resources.

The theoretical potential for aquifer CAES in the US is huge. However, the true CAES potential for aquifers cannot be determined without doing detailed studies of different aquifer types, focusing on the implications of air storage. There is considerable experience with underground natural gas storage, but most experience with natural gas storage relates to seasonal storage, whereas CAES coupled to wind would be characterized by charge/discharge cycles of the order of a day. Moreover, air has physical and chemical properties that are different from natural gas (including the fact that storing air introduces oxygen underground that can lead to a wide range of chemical reactions and the introduction of aerobic bacteria) that imply rates of injection and recovery that are not only different from those for natural gas, but which also can change over time as a result of chemical reactions and biological activity.

Combustion of Alternative Fuels

Chung Law and Yiguang Ju have carried out fundamental research on hydrogen and dimethyl ether combustion to pave the way for use of alternative fuels in the transportation sector. Law's group also addresses the safety issues in handling and storage of hydrogen gas by analyzing the explosion hazards associated with the sudden release of a high pressure hydrogen jet into air. This year, research was conducted on three projects related to safety and utilization aspects of combustion.

Initiation of explosions

An important aspect of the hydrogen economy is the safety associated with storage and handling of a light and highly reactive gas. This year Law's group has continued its investigation of the initiation of accidental fires and explosions upon the puncture of a high-pressure hydrogen storage tank. The evolution of the gaseous jet issuing from the puncture was computationally simulated, including the associated shock trains that could potentially heat up the gas to initiate the reaction and hence explosion.

Flame front instability

In the early years of the grant, Law's team determined the conditions for hydrogen ignition and hydrogen flame propagation. They found that the flame surface at higher pressures becomes unstable, leading to cellular pulsations. The effect was found to increase the flame speed and burning rate of fuel, a beneficial aspect of hydrogen use in ICE's promoting the power of the engine.

However, hydrogen gas can sometimes be too easily ignited under supercharged conditions, creating undesirable high pressure shock waves in a phenomenon known as engine knock. Law and his group proposed a new strategy to limit knock while maintaining the desirable aspects of hydrogen combustion. They showed that dilution of the hydrogen gas with a heavier fuel such as propane may eliminate the propensity of the flame to be destabilized by reducing the flame sensitivity. This finding implies that use of hydrogen/propane mixtures could reduce the need for supercharging required in an engine, reduce the tendencies for the detrimental events of knock and pre-ignition, and lower the potential for explosion of hydrogen in storage.

This year, the transition of a spark-ignited outwardly propagating flame front from a smooth surface to a wrinkled one was experimentally studied in high-pressure environments simulating those within internal combustion engines, with the anticipation that the increases in the flame surface area would increase the propagation rate that could eventually lead to self-turbulization of the flame. The experimental results on the transition state agree well with theoretical predictions (Figure 5).

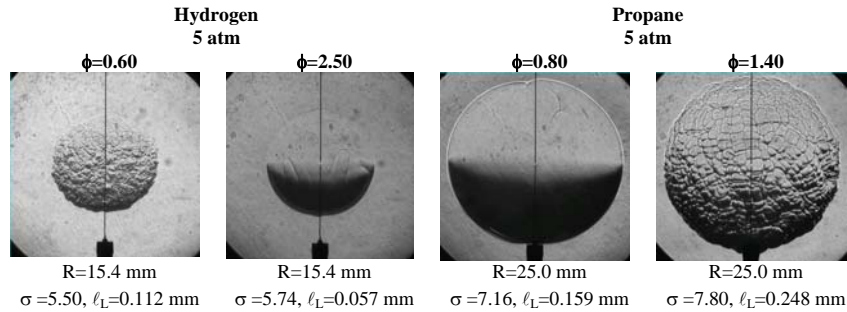


Figure 5. Images of expanding hydrogen and propane flames. Rich hydrogen and lean propane flames remain smooth during flame propagation, while lean hydrogen and rich propane flames become wrinkled and hence could self turbulize.

Collaboration with Ford on engine simulations

Collaboration has been initiated with researchers at Ford (James Yi and Claudia Iyer) to improve the simulation capability of their engine codes. The improvement has been conducted along two directions: facilitation of the engine code itself, and the reduction of the extremely large detailed chemical reaction mechanisms of fuels oxidation to sizes that can be accommodated in engine codes. It is noted that our initial contributions have already resulted in an increase in the computation speed by 33%, without loss of accuracy. Figure 6 shows that there is no detectable difference in the predicted pressure rise during combustion in the engine cylinder when using the revised computer code (ckwyp) that we supplied.

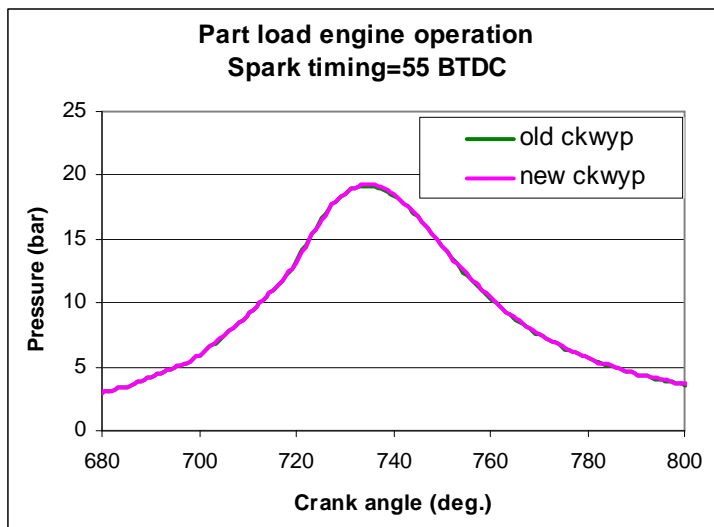


Figure 6. Comparison between the computed pressure rise during engine combustion using the previous and improved computer codes (ckwyp), showing there is no loss in accuracy while gaining 33% speedup in the computation.

Future Plans

Over the coming year the Capture Group's activities will involve both completing ongoing activities and pursuing new initiatives in four primary areas:

- (i) Analysis of a low carbon obligation for coal power in both the U.S. and China via a collaboration with colleagues at Tsinghua University in Beijing.
- (ii) Analysis of prospects for making low GHG emitting fuels and electricity at oil refineries via gasification of coal, biomass, and petroleum residuals with CCS and by subsequent coprocessing of raw syngases and crude oil to make final products.
- (iii) Launching of a new initiative aimed at understanding the prospects for biomass recovery for energy from forests in cost effective and sustainable ways.
- (iv) Collaboration with Ford on simulation of engine processes

A new member of the Capture Group is Prof. Guangjian Liu, who will be physically present in Princeton by the end of February 2008. In December 2007 Liu successfully defended his thesis and was awarded a Ph.D. by the Department of Thermal Engineering at Tsinghua University, where his thesis advisor was Prof. Li Zheng. After getting his Ph.D. he became an Assistant Professor at the North China Electric Power University in Beijing, a position he will return to after a one- to three- year tenure at PEI. At PEI he will be a Visiting Research Associate Scholar, modeling coal and coal/biomass energy systems for a carbon-constrained world using Aspen Plus and other models.

Low carbon obligation for coal power in the U.S. and China

During 2008 Williams and Larson, in collaboration with Profs. Li Zheng and Ni Weidou at the BP-Tsinghua Clean Energy Center in Beijing, will develop a paper outlining the technical feasibility and implications of pursuing a low carbon obligation for coal power in the U.S. and China over the period 2015-2025. Attention will be given to the prospects for providing decarbonized power via polygeneration systems (via CTL technology in China and via CBTL technology in the U.S.). The aim will be to get the article published in an influential high-visibility journal.

Production of low-carbon fuels at oil refineries

A new grant from NetJets in support of research on low carbon jet fuel has been awarded to Profs. Fred Dryer and Ju Yiguang in the MAE Department and Williams and Larson at PEI. In 2008, the researchers will explore the prospects of making, at oil refineries, low GHG-emitting fuels and electricity via cogasification of coal, biomass, and petroleum residuals with CCS, then subsequently coprocessing the raw syngases and crude oil at oil refineries.

Forest biomass for energy and sustainable forestry

As a result of interactions between Williams and David Tilman (University of Minnesota) during Tilman's sabbatical at PEI during the fall of 2007, a new initiative is to be launched to explore using forest-residue/forest-thinning biomass for energy (including considerations of potential

supplies and their costs) in a sustainable manner (including considerations of carbon balances, biodiversity, impacts on primary forest product industry yields, forest fire management, etc.) via a collaboration led by Williams, Tilman, and John Kadyszewski (Winrock International). As a result of a brainstorming session at Princeton in December 2007 (involving Williams, Larson, Tilman, Kadyszewski, and Giulia Fiorese of Politecnico di Milano) it was decided to launch this new initiative by organizing a workshop to be convened at PEI some time during 2008.

Simulation of engine processes with realistic fuel chemistry

Collaboration with Ford on the simulation of engine processes will continue. The emphasis will be on gaining the predictive capability of engine knock, which is a primary factor limiting the improvement of combustion efficiency. Realistic chemistry for the surrogate fuel components such as *n*-heptane and iso-octane will be used. Since the reaction mechanisms for these fuels are typically very large in terms of the number of species and reactions, they will be systematically reduced to smaller sizes, while retaining chemical comprehensiveness. Strategies will also be developed to further facilitate the computation speed in the simulation.

Publications

- Chiesa, P., T. Kreutz, and G. Lozza, "CO₂ Sequestration from IGCC Power Plants by Means of Metallic Membranes," *Journal of Gas Turbines and Power*, **129**: 123-134, 2007.
- Greenblatt, J.B., S. Succar, D. Denkenberger, R. H. Williams, and R. H. Socolow, "Baseload wind energy: Modeling the competition between gas turbines and compressed air energy storage for supplemental generation," *Energy Policy*, **35**(3):1474-1492, March 2007.
- Iisa, K., C.E. Courchene, W.J. Frederick, Jr., M. Realf, E.D. Larson, and S. Consonni, "Mill integration issues for black liquor gasification based biorefineries," *Proceedings of the 2007 International Chemical Recovery Conference*, Quebec City, Canada, 29 May – 1 June, 2007.
- Jomaas, G., J.K. Bechtold, and C.K. Law, "Spiral waves in expanding hydrogen-air flames: experiment and theory," *Proceedings of the Combustion Institute*, Vol. 31, pp. 1039-1046, 2007.
- Larson, E.D., H. Jin, and F.E. Celik, "Large-Scale Gasification-Based Co-Production of Fuels and Electricity from Switchgrass," *Biomass and Bioenergy*, forthcoming (submitted July 2006).
- Larson, E.D., A. Shanker, and T.B. Johansson (guest co-editors), 2006: *Energy for Sustainable Development*, **X** (2), June (130 pages), special issue based on the Workshop on Biofuels for the Transport Sector in Developing Countries organized by the Science and Technology Advisory Panel of the Global Environment Facility, 29 August – 2 September, 2005, New Dehli, India.
- Larson, E.D., 2007: *Biofuel Production Technologies: Status, Prospects, and Implications for Trade and Development*, United Nations Conference on Trade and Development, New York and Geneva (forthcoming).
- Larson, E.D., S. Consonni, R.E. Katofsky, K. Iisa, and W.J. Frederick, "Gasification-based biorefining at kraft pulp and paper mills in the United States," *Proceedings of the 2007 International Chemical Recovery Conference*, Quebec City, Canada, 29 May – 1 June, 2007. (Awarded "Best Paper" at the ICRC)
- Larson, E.D., H. Jin, G. Liu, and R.H. Williams, "Zero-carbon FT liquids via gasification of coal and biomass with CCS," PowerPoint paper, *Proceedings Sixth Annual Carbon Capture and Sequestration Conference*, Pittsburgh, PA, 7-10 May, 2007.
- Meng, K., R.H. Williams, and M.A. Celia, "Opportunities for low-cost CO₂ storage demonstration projects in China," *Energy Policy*, **35**: 2368-2378, 2007.
- Radulescu, M.I. and C.K. Law, "The transient start of supersonic jets," *Journal of Fluid Mechanics*, Vol. 578, pp. 331-369, 2007.
- Radulescu, M.I., G.J. Sharpe, C.K. Law, and J.H.S. Lee, "The hydrodynamic structure of unstable cellular detonations," *Journal of Fluid Mechanics*, Vol. 580, pp. 31-81, 2007.
- WGA Coal to Liquids Working Group (G. Parker, P. Bollinger, G. Schaefer, D. Sheppard, and R. Williams), *Coal to Liquids*, a report of the Transportation Fuels for the Future Initiative of the Western Governors' Association, including a separate statement by R. Williams (appendix), November 2007.
- Williams, R.H., S. Consonni, G. Fiorese, and E.D. Larson, "Synthetic gasoline and diesel from coal and mixed prairie grasses for a carbon-constrained world," PowerPoint paper, *Sixth Annual Carbon Capture and Sequestration Conference*, Pittsburgh, PA, 7-10 May 2007.
- Williams, R.H. and Kreutz, T.G., "An opportunity for enhanced oil recovery in Texas using CO₂ from IGCC+CCS fueled with mixtures of petcoke and low-rank coals," PowerPoint paper, *Proceedings Sixth Annual Conference on Carbon Capture and Sequestration*, Pittsburgh, PA, May 7-10, 2007.
- Yuan, J. Y. Ju, and C.K. Law, "On flame-front instability at elevated pressures," *Proceedings of the Combustion Institute*, Vol. 31, pp. 1267-1274 (2007).

The Storage Group

Almost all realistic scenarios for significant reductions in global CO₂ emissions include a substantial fraction corresponding to Carbon Capture and Storage (CCS). However, in order for geological CCS to take place at the necessary scale, concerns surrounding storage security must be addressed. The Storage Group of CMI works to understand the possible risks of CO₂ leakage from underground storage and to provide information relevant to CCS policy.

The major goals of the Storage Group are:

- (i) To incorporate experimental findings into simulations of brine-cement interactions and identify the important variables affecting CO₂ leakage rates
- (ii) To use the well-scale information from geochemical modeling to complete a large-scale risk analysis of a representative North American oil field and develop rapid and robust tools for leakage risk assessment

In the last year, the group continued its modeling and laboratory experiments, expanded the scope and scale of analyses, and was directly involved in the development of a new field experiment that has now been implemented successfully as part of a CCP project.

Leakage Potential of Existing Wells

Early in the CMI project, the Storage Group identified existing wells in oil and gas fields as a potentially important leakage pathway, especially in North America. 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. Assessing the leakage potential of existing wells, and its impact on risk assessment, has thus become the primary focus of the Storage Group.

Cement durability experiments

An issue critical to the potential for leakage is the reaction of well cements exposed to carbonated brines that would result from CO₂ injection. The group's early series of flow-through and batch experiments suggest that cements would be highly susceptible to attack from carbonated brines flowing through sandstone reservoirs. In the flow-through experiments, cement was destroyed at a rate on the order of 0.1 mm/week under conditions comparable to sequestration in a sandstone formation at a depth of 1-2 km. More likely rates of attack have been probed using batch experiments, in which the acid must diffuse through the pores of stone to reach the cement. The cement samples exposed to brines in the batch reactors were not as quickly degraded as those in

the flow-through experiments, but in one month reaction rings formed at the cement/stone interface caused permeability to increase by an order of magnitude before subsequently leveling off.

In contrast, the team's experiments showed that the rate of attack was undetectably small when the brine was equilibrated with limestone prior to contact with the cement, because the acidity is reduced and the calcium content of the brine is increased by such exposure. These results imply that sequestration in limestone formations would be much less likely to result in cement corrosion than sequestration in sandstone formations.

Scherer's group also established collaboration with National Energy Technology Laboratory (NETL) laboratory in Pittsburgh to study cement corrosion under high-pressure conditions that more closely approximate the environment in a storage formation. The NETL group's initial results indicate that rates of cement corrosion decrease at elevated pressure, which would improve the outlook for carbon storage in deep saline aquifers. Work is ongoing both to quantify this pressure dependence and to identify the mechanism responsible.

To support modeling of the leakage potential of existing wells, additional data is needed regarding the transport and mechanical properties of corroded cement already exposed to carbonated brines, which should provide a more realistic analogue for the conditions likely to be found in aging wells. Previous results indicated a catastrophic loss of integrity of the cements when the corrosion is well advanced. However, there may be a more subtle deterioration that occurs in limestone formations, where our short-term (i.e., 1-year) experiments indicate little or no attack, that might have significant impact on leakage over the course of a century. Therefore, a new graduate student, Ed Matteo, is undertaking experimental studies of the structure and properties of cement following exposure to carbonated brine. Ed is presently using NMR to measure the transport rate of fluids in the degraded cement, to improve our prediction of corrosion rates.

Modeling brine-cement interactions

The data from cement durability experiments are informing simulations of brine-cement interactions in existing wells to assess the overall potential of CO₂ leakage from underground aquifers. The likely leakage pathways along existing wells involve micro-annuli or other flow paths that tend to occur at the interface between well cement and rock, or between well cement and casing. These flows can be modified or controlled by geochemical reactions that occur on the scale of the leakage pathways, and inclusion of these important small-scale processes in large-scale continues to be a significant computational and conceptual challenge.

In response to this need, the Storage group has been developing a geochemistry module to couple with reactive transport modules in the geomechanical model *Dynaflow*. The resulting multi-phase, multi-component model includes geochemistry appropriate for reaction and degradation of well cements in the presence of carbonated brine solutions, resolves small-scale behavior in the vicinity of wells, and describes the cement reactions as well as phase behavior of the fluid phases.

With this model we can now study system behavior and leakage patterns along different kinds of wells, including relevant multi-phase flow physics, flash calculations, and cement reactivity.

The modular nature of the software is particularly important. The module for non-reactive equilibration of the components (*i.e.*, flash calculation) includes all the CO₂-rich phases, and is supported by a separate module that calculates all the thermodynamic properties of the system. Bruno Huet has assembled the most extensive database in existence for reactions involving components of phases in cement, and can calculate the composition of the solution in equilibrium with any assemblage of cement phases between 0 and 100°C. All of these modules are currently integrated by Jean Prévost into *Dynaflow*, which has exceptional ability to couple geomechanics (including fracture) with geochemistry. However, all of these modules could also be used with other systems, such as Eclipse.

In the last year, enormous progress was made by Bruno Huet and Jean Prévost in developing the reactive transport model to predict the rate of attack of carbonated brine on cement. (Bruno Huet has recently joined Schlumberger in Clamart, France. We hope to continue collaborating with Bruno on the development of the reactive transport code.) The model correctly reproduces the rates of advance of reaction fronts in paste that were measured by Andrew Duguid, now working for Schlumberger in their Carbon Services program in Pittsburgh (Figure 7).

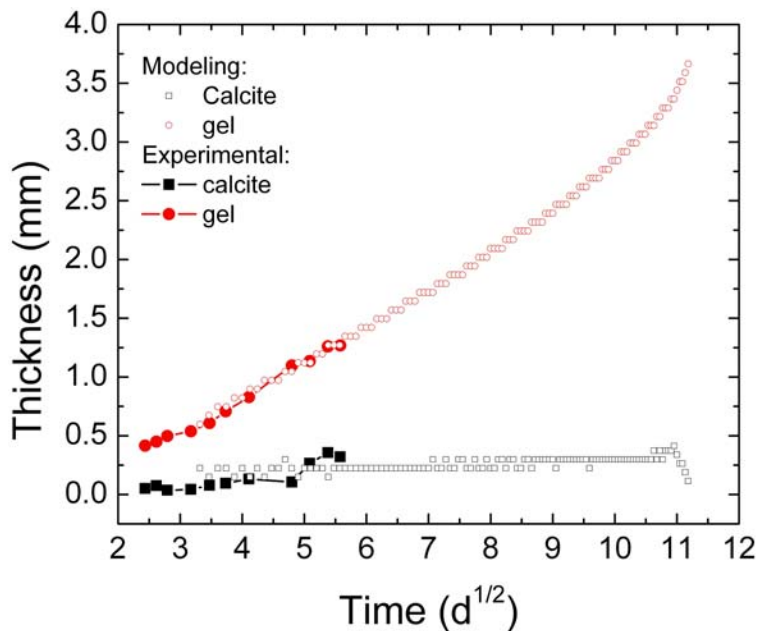


Figure 7. Comparison of thickness of reacted layers measured by A. Duguid and calculated using the reactive transport model developed by B. Huet and J.-H. Prévost.

After combining experimental data with simulation results, the mechanisms of cement reactivity in CO₂-saturated brine are now better understood. Our original interpretation of Andrew Duguid's experiments was that the precipitated layer of calcium carbonate was protective, but the situation is more subtle. The calcium carbonate layer may control the rate of attack initially, causing the linear rate of growth of the corroded layer. However, later in the process the rate of

diffusion through the gel layer begins to dominate. The ability of the CaCO_3 layer to plug the cement porosity (and thereby delay attack) depends on two things: the solubility of calcite in the aqueous phase (which depends on the CO_2 content of the brine) and the rate at which calcium diffuses through the gel layer into the brine. The implications of these mechanisms for the healing of cracks by precipitation of calcite are being examined.

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 CO_2 when carbonated brine rises through a crack. Following widespread consultation among experts in the field (including Lee Chin at Conoco/Phillips and G. Pope's group at UT Austin), it was agreed that none of the existing codes can handle this situation! Prévost and Lee Chin have recently developed the first flash calculation that does handle this problem correctly, and they are now implementing it in the reactive transport program.

Another major goal of our group is to evaluate the risk of *creating* leaks in a reservoir as the pressure of injected CO_2 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. This question is being investigated by Jean Prévost and a new graduate student, Zhihua Wang, using the poromechanical capabilities of *Dynaflow*.

Large-Scale Modeling of Leakage Risks

While the detailed leakage along a well is obviously very important information, it is unlikely that we will know the kinds of detailed information to predict leakage details when analyzing a field injection operation. As shown in Gasda et al. (2004), Celia et al. (2006), and Bachu and Celia (2008), among others, an injection operation in may produce a CO_2 plume that intersects hundreds of existing wells, whose condition is very difficult to determine *a priori*. Therefore the tools needed for large-scale modeling must be able to describe three-dimensional multi-phase flow with leakage along many wells whose properties are highly uncertain.

Semi-analytical models

To accommodate this situation, Michael Celia's group has developed a set of semi-analytical models that are sufficiently fast to allow many realizations to be run, thereby providing Monte Carlo-type of stochastic analysis. The computational efficiency of the models allows thousands of simulations to be run in a probabilistic framework, so that we have a much richer output set for analysis and decision making. The result is a probability distribution for leakage amounts, given statistical parameters for well properties as inputs.

Current applications are focused on the trade-off between injection depth and risk reduction, as well as loss of injectivity as a function of depth of injection. For example, in the Wabamun Lake area of Alberta, where four large power plants produce about 35 Mt CO_2/yr , we have analyzed injectivity and leakage risk across a number of formations in the vertical sequence. The lowest

permeable formation is the Keg River formation, which has only a handful of wells that penetrate its caprock. However, the formation is thin (thickness is about 15 meters) and not very permeable, so maximum injection rate, constrained by fracture pressure limits, is only about 0.25 Mt CO₂/yr. In this case, leakage risk is very low, but injectivity is also very low. The number of wells that penetrate caprock formations progresses from 5 (Keg River) to 40 (Nisku) to 58 (Wamamun) to 731 (Nordegg) to 883 (Lower Manville) to 895 (Viking) with distance toward the surface. Note that our earlier studies of well densities focused on the Viking formation (Gasda et al., 2004). Injectivities in all of these formations are determined largely by formation thicknesses, and in none of the formations do we find injectivities much above 1 Mt CO₂/yr. If the entire 35 Mt CO₂/yr is to be stored here, most or all of the formations would probably be used. As such, all wells in the area would likely be considered in the analysis. We also note more generally that while many formations have apparently large storage capacity, injectivity restrictions may limit their utility. The results from our semi-analytical model runs show that, as long as we assume an uncorrelated permeability structure along each potentially leaky well, we continue to see large reductions in the leakage fluxes as a function of distance toward the land surface. That is, the intervening permeable layers above the injection formation tend to trap most of the CO₂ that leaks from the injection formation. While this is good news, it also highlights the need to generate field data on the effective permeability of well segments, and to analyze the statistical characteristics of the data sets.

We have also performed a series of analyses to identify the limits of applicability for these kinds of simplified models – see Gasda et al. (2008). One of the results of this analysis was to determine when the assumption that formation slope can be ignored during injection is valid. We find that for all of the cases using the moderate permeability value of $5 \times 10^{-14} \text{ m}^2$ (that is, 50 milli-Darcy, which is characteristic of, for example, the Alberta Basin), values of a dimensionless centroid measure, which provides a measure of the amount of asymmetry in the plume, are all less than 0.05. This means that the centroid has moved less than 5% of the overall distance that the plume has moved. We consider this to be a reasonable criterion for when the effect of slope can be neglected, and therefore when we can reasonably use the suite of semi-analytical models we have developed. For the high-permeability case, which we took to be a permeability of 3 Darcy, we observe centroid movements of between 5% and 30% of the plume extent. In those cases, slope can clearly be important, and should not be ignored in the analysis.

Basin-scale simulations

In addition to these semi-analytical models, the Celia group is developing hybrid numerical-analytical approaches to allow for analysis of very large spatial domains. These techniques will allow simulation of an entire sedimentary basin, covering several hundred thousand square kilometers. This is motivated by the question of where displaced brine may move on a basin-wide scale, especially under scenarios of full implementation of a CCS strategy.

Our basin-scale model is based on a multi-scale finite element method, tailored to the specific problem of CO₂ injection and leakage estimation. In particular, we are developing algorithms based on a method referred to as the Variational MultiScale (VMS) method. The general idea is to use a numerical VMS-based approach to capture large-scale flows on regional scales of

hundreds of kilometers, and to use versions of our semi-analytical approximations to form the sub-space Green's functions which are needed to accurately capture the effect of injection and leakage on the local scale. This will allow us to combine the flexibility of considering complex heterogeneous large-scale flow fields with fast and accurate representations of local flow processes. In addition, the VMS methodology inherently leads to decoupled fine scale problems for the equations we consider, a significant advantage in the design and implementation of efficient parallel algorithms.

We continue to collaborate with Stefan Bachu at the Alberta Geological Survey and Alberta Energy and Utilities Board to use the Alberta Basin as a test case. We are interested in how the basin, at about 500,000 km², would behave under a scenario of full implementation of CCS across Alberta. If we can develop this model of the subsurface, then we could couple into it surface facilities, including pipelines and other infrastructure, to see what a fully developed CCS world might look like several decades into the future. Such a model allows for broad environmental as well as economic analysis, and could have a variety of optimization and general trade-off analyses included.

Finally, we note that to maximize the problems that can be analyzed, we are porting all of these codes to a parallel computing environment, where we expect to be able to run large basin-wide simulations. We have already accomplished this with most of our semi-analytical models, and we can now perform thousands of simulations over time periods of days. We know of no other computational tools that can achieve this kind of efficiency.

Upscaling and other science issues

Celia's group continues to work on basic issues associated with upscaling for both flow physics and geochemistry, and on other basic science issues associated with multi-phase flow in porous media. The recent work of Nordbotten et al. (2007; 2008a,b) focuses on how to define a macroscopic pressure in the presence of sub-scale variability. The definitions presented resolve some paradoxes with traditional averaging, including calculations of upscaled relative permeabilities that exceed unity. The work of Li et al. (2006; 2007a,b,c) addresses the question of upscaling geochemical reactions and the fundamental mathematical representation of reactions in the presence of sub-scale variability. This is being complemented by detailed studies of rock structure and mineralogy, led by our colleague Professor Peters and her students. Finally, we note the recent publication of a paper authored by Kyle Meng, Bob Williams, and Michael Celia, focused on early opportunities for CCS in China.

Targeted Field Experiments

Analysis of field 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. This question is beginning to be answered by cements obtained in 2004 from a 19 year-old well at the Rocky Mountain Oil Testing Center in Wyoming. George Scherer of the Storage group worked with

Schlumberger and RMOTC staff to design and execute an innovative drilling project that retrieved one intact sidecore (composed of cement, casing, and formation rock) and several fragmented cement samples from depths of 3000-5000 feet.

Initial analysis of the samples revealed a surprisingly complex microstructure that differed greatly from what was expected for the type of cement described in the cement log for the well. However, through collaboration with NETL it was confirmed that the sample was from the lead cement, which contained fly ash, rather than the cement that was expected to be in the location from which the sample was taken. A report on the analysis is in preparation.

Field estimates of well-bore permeability

In large-scale models of injection and leakage, the most important parameter values, and the ones that have the largest uncertainty, are the permeability values assigned to all of the well segments in the domain being analyzed. To our knowledge, these values have never been measured, nor are there any estimates in the open literature. Therefore we decided to design a field experiment that we believed would allow these critical parameters to be determined. The test is described in Gasda et al. (2007), and is shown schematically in Figure 8, where a constant pressure is imposed at a location along the well annulus and the pressure response is measured at another location along the annulus. In the published paper, we considered limits based on fracture pressures and on instrument accuracy to determine ranges of detectability for the effective well permeability. This test was applied for the first time a few months ago as part of a BP/Schlumberger CCP2 project, and the results are encouraging. Initial analysis of the resulting data shows that we are able to estimate the effective permeability of the cement section outside of the well casing, and that the estimated values are consistent with other measurements. We believe this kind of experiment can provide the greatest reduction of uncertainty in leakage estimates, and we will work to a continuation and expansion of these experiments at different field sites.

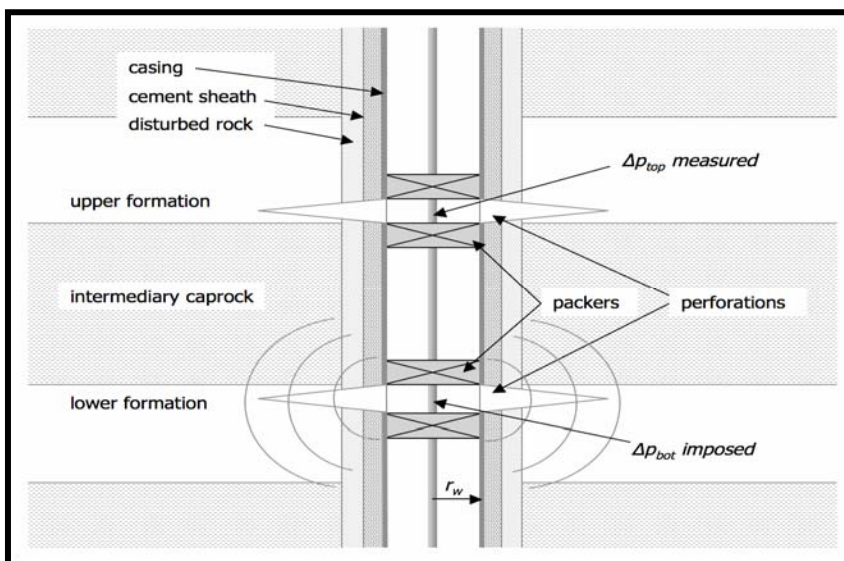


Figure 8. Figure 1 from Gasda et al., 2008b – schematic of downhole pressure test.

Future Plans

Experimental studies and geochemical modeling to be carried out in the next two years should predict the most important variables affecting leakage rates within a well. This information will be combined with statistical information about well properties to provide input for the semi-analytical and coarse resolution models developed by Mike Celia and colleagues for risk assessment.

Cement durability experiments

Ed Matteo and George Scherer will use NMR to measure diffusion coefficients and a variety of techniques to measure permeability changes during leaching. We will also study the change in strength and stiffness as corrosion proceeds. To characterize the structure of the corroded cement, we will use supercritical drying to remove the pore liquid without altering the structure of the material. This is made possible by the fact that supercritical drying prevents the creation of capillary pressure, which causes collapse of the pore structure during ordinary drying. The structure will be studied using nitrogen sorption and transmission electron microscopy. This information will be needed to refine the leakage model and expand our confidence regarding the risk of leakage over the long term. Andrew Duguid's experiments reveal that a layer of calcium carbonate precipitates in the reaction zone, resulting in a decrease in porosity and a temporary slowing of attack. It is possible that this precipitate would heal small cracks, while larger ones would be opened further. This possibility will be explored by forcing flow through cracks of controlled width to see whether there is a threshold size below which the flow is arrested.

Dynaflow development

Jean Prevost, in collaboration with Bruno Huet (now at Schlumberger, Clamart) and Lee Chin (Conoco-Philips), will complete the implementation of a geochemical module in *Dynaflow* that includes the constituents of cement. The geochemistry module has been developed and successfully tested against the experimental data of Andrew Duguid. The effort now is focused on improving the kinetic predictions by coupling a transport module with the geochemistry module. The remaining challenges are 1), the prediction of the change in diffusion rate as the porosity is changed by corrosion, and 2) the quantification of the advective flow driven by volume changes following chemical reactions. We will also assess the importance of pressure on the corrosion rate of cement by comparing results from the high-pressure studies at NETL to predictions from the geochemical module of *Dynaflow*. If necessary, improved pressure dependence will be introduced into the model.

New simulations of cement reactivity

The multiphase flash calculation has been modified to allow for pressure and temperature changes as the plume rises toward the surface, including thermal effects. This will permit us to simulate the behavior of a flow of CO₂-saturated brine escaping through an annulus or crack in a well. Multiple leakage scenarios will be examined, including the impacts of varying brine composition, initial gap width, and depth at which the leak originates. The simulations will also be extended to include corrosion of the steel casing in the well.

At the end of about 2 years from today, we will be able to put bounds on the risk of leakage under unfavorable conditions (brine in a sandstone formation encountering a pre-existing annular gap in typical cement). Should we discover that the brine is quickly neutralized as it flows through the gap, so that the leak is not significantly expanded over the course of a century, then the behavior of the wells under more benign conditions is academic. On the other hand, if our simulations indicate that leaks worsen at a significant rate in sandstone formations, then we will need to see whether there is any such risk under more favorable circumstances (such as limestone formations).

Impact of injection on leakage risks

In addition to geochemical studies, Jean Prévost and Zhihua Wang will examine the potential risk from deformation of the cap rock during pressurization of the formation by injection of CO₂. Owing to the difference in stiffness of the rock and the cement plugs that pass through it, there is a possibility that the cement will crack as the pressure rises, resulting in the creation of leaks. Using the poromechanical capability of *Dynaflow*, they will explore the circumstances under which such damage might occur.

Large-scale modeling

Moving forward, Michael Celia and colleagues plan to continue to put together models that provide quantitative estimates of the most important factors in large-scale CCS systems. These include leakage estimates for the injected CO₂, and both local and basin-wide migration of displaced brine. These analyses require special modeling methods, which will be pursued through targeted combinations of numerical and semi-analytical approaches. Over the next year, the models will be implemented on massively parallel machines available at Princeton. These models will be designed to focus on subsurface behavior, but will ultimately be designed to accommodate information about surface facilities, pipelines, and other practical considerations. The aim is to create a tool that can provide a complete basin-wide analysis of how a full-scale CCS implementation will look, and what it will mean in terms of subsurface perturbations involving both CO₂ and brine migration. In addition to these modeling efforts, we would like to continue to work with field engineers to enhance our experimental methodology, and encourage additional measurements so that we can begin to put together a data base that can inform risk calculations and guide injection decisions.

Publications

- Bachu, S. and M.A. Celia, "Assessing the Potential for CO₂ Leakage, Particularly through Wells, from CO₂ Storage Sites", to appear, *The Science and Technology of Carbon Sequestration*, AGU Monograph, 2008.
- DePaolo, D.J., F.M. Orr Jr., S.M. Benson, M. Celia (*Co-Lead*, *Multiphase Fluid Transport*), A. Felmy, K.L. Nagy, G.E. Fogg, R. Snieder, J. Davis, K. Pruess, J. Friedmann, M. Peters, N.B. Woodward, *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems*, Report from the Workshop Held February 21-23, 2007, Office of Basic Energy Sciences, U.S. Department of Energy, June 2007.
- Duguid, A., M. Radonjic, and G. W. Scherer "The Effect of Carbonated Brine on Well Cement Used in Geologic Formations.", paper TH4-10.2 in *Proc. 12th ICCG*, eds. J.J. Beaudoin, J.M. Makar, L. Raki (National Research Council of Canada, Montreal, Canada, 2007)
- Duguid, A. and G.W. Scherer "Degradation of Oilwell Cement Due to Exposure to Carbonated Brine," *SPE Journal* (submitted)
- Huet, B.M., J. H. Prevost and G.W. Scherer "History matching of cement reactivity in CO₂ saturated brine using the reactive transport code DYNAFLOW", *Geochimica et Cosmochimica Acta*, (submitted).
- Huet, B.M., "Cement reactivity in CO₂ saturated brines: use of a reactive transport code to highlight key degradation mechanisms" (submitted)
- Li, L., C.A. Peters, and M.A. Celia, "The Effects of Mineral Spatial Distribution on Reaction Rates in Porous Media", *Water Resources Research*, **43**, W01419, doi:10.1029/2005WR004848, 2007a.
- Gasda, S.E., J.M. Nordbotten, and M.A. Celia, "Determining Effective Wellbore Permeability from a Field Pressure Test: A Numerical Analysis of Detection Limits", *Environmental Geology*, published online 18 July 2007b.
- Gasda, S.E., J.M. Nordbotten, and M.A. Celia, "Upslope Plume Migration and Implications for Geological CO₂ Sequestration in Deep Saline Aquifers", to appear, *IES Journal A: Civil and Structural Engineering*, 2008.
- Li, L., C.A. Paters, and M.A. Celia, "Reply to 'Comment on Upscaling Geochemical Reaction Rates using Pore-scale Network Modeling' by P.C. Lichtner and Q. Kang", *Advances in Water Resources*, **30**, 691-695, 2007b.
- Li, L., C.A. Peters, and M.A. Celia, "Applicability of Averaged Concentrations in Determining Geochemical Reaction Rates in Chemically Heterogeneous Porous Media", to appear, *American Journal of Science*, 2007c.
- Meng, K., R. Williams, and M.A. Celia, "Opportunities for Low-cost CO₂ Demonstration Projects in China", *Energy Policy*, **35**, 2368-2378, 2007.
- Nordbotten, J.M., M.A. Celia, H.K. Dahle, and S.M. Hassanizadeh, "Interpretation of Pressure in Darcy's Law", *Water Resources Research*, **43**, W08430, doi:10.1029/2006WR005018, 2007a.
- Nordbotten, J.M., I. Rodriguez-Iturbe, and M.A. Celia, "Stochastic Coupling of Rainfall and Biomass Dynamics", *Water Resources Research*, **43**, W01408, doi:10.1029/2006WR005068, 2007b.
- Nordbotten, J.M., M.A. Celia, H.K. Dahle, and S.M. Hassanizadeh, "On the Definition of Macro-scale Pressure in Multi-phase Flow in Porous Media", to appear, *Water Resources Research*, 2008a.
- Nordbotten, J.M., J.P. Noguees, and M.A. Celia, "Appropriate Choice of Average Pressure for Upscaling Relative permeability in Dynamic Flow Conditions", to appear, *SPE Journal*, 2008b.
- Puma, M.J., I. Rodriguez-Iturbe, M.A. Celia, and A.J. Guswa, "Implications of Rainfall Temporal Resolution for Soil-moisture and Transpiration Modeling", *Transport in Porous Media*, **68**, 37-67, 2007.
- Scherer, G.W., J. J. Valenza II, and G. Simmons "New Methods to Measure Liquid Permeability in Porous Materials", *Cement Concr. Res.* **37**, 386-397, 2007.
- Scherer, G.W., "Poromechanics Analysis of a Flow-Through Permeameter with Entrapped Air", *Cement Concr. Res.* (in press).

The Science Group

The Carbon Science group works 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. Since the beginning of the grant, the group has made considerable progress in inversion modeling of carbon sources and sinks. These efforts are the final steps toward a Carbon Observing System that will allow both monitoring of carbon sources and sinks and prediction of their future behavior.

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

- (i) A carbon observing system to monitor the fate of anthropogenic carbon, the mechanisms that determine that fate, and the ongoing response of the natural carbon system to global warming
- (ii) Paleoclimate studies aimed at developing a deeper understanding of the earth system response to changes in biogeochemical and climate forcing
- (iii) A geoengineering "truth squad" that will investigate proposals for carbon and climate mitigation

Each of these is discussed in turn.

Carbon Observing System

Since the beginning of CMI grant, the Sarmiento and Pacala groups have performed a variety of studies to improve the understanding of carbon dioxide surface flux location, intensity and evolution in time and space. Their efforts have resulted in development of new sampling strategies, improvement of model components, and development of inversion methods. This work provides a unique knowledge base to allow 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.

Inversion modeling of land sinks

This year, the group of Professor Jorge Sarmiento continued its work with inversions to improve CO₂ flux estimates for the tropics, where there are very few atmospheric observations to provide constraints for carbon fluxes. We have been able to gain considerable insights into the tropics by incorporating other types of observations. An ocean inversion that is analogous to the atmospheric inversions has been developed to estimate net air-sea fluxes of CO₂ and other tracers using ocean interior tracer observations and ocean general circulation models. Unlike atmospheric inversions, the ocean inversion is not data-limited due to the relatively large number of high quality oceanic observations (over 68,000) and because the spatial footprints of air-sea

tracer fluxes are preserved in the ocean interior as a result of the relatively long time scale of ocean circulation.

The ocean inversion was recently combined with an atmospheric inversion in a joint ocean-atmosphere inversion. The joint inversion finds a remarkably large tropical and southern hemisphere land source of 1.8 ± 1.1 Pg C yr⁻¹. Previous atmospheric CO₂ inversions have not detected this source because the in situ atmospheric observations alone do not effectively constrain fluxes in the tropics and southern hemisphere. The joint inversion removes this reliance on priors by strongly constraining air-sea fluxes, so that, as a consequence, the tropics become a net source.

In the past year, we finalized publications on time-independent air sea fluxes estimated from ocean interior data and models and their implications for terrestrial fluxes when combined with analogous atmospheric data and models. In addition, we employed forward simulations using the MOZART atmospheric transport model to examine whether the large tropical and southern hemisphere land fluxes estimated in Jacobson et al. (2007a, b) are consistent with atmospheric observations of the ¹³C/¹²C isotopic ratio in CO₂ from the NOAA-ESRL flask network. Our preliminary results indicate that the results from the joint inversion generally match the observed latitudinal gradient, supporting the hypothesis of a large tropical and Southern Hemisphere land source. We are currently engaged in sensitivity studies to determine whether this result is robust.

Another major weakness of atmospheric inversions is the reliance on atmospheric transport models. Recent studies have shown that errors in these models can lead to biases in the estimates of the Northern Hemisphere terrestrial land sink on the order of 1 PgC yr⁻¹ (Stephens et al., 2007). In collaboration with the NOAA Earth System Research Laboratory (ESRL), the Sarmiento group has developed a novel budgeting approach to circumvent the traditional weaknesses of atmospheric inversions. This approach exploits the new NOAA-ESRL network (20 sites) of aircraft profiles obtained as part of the North American Carbon program.

The direct carbon budgeting method finds a moderate carbon sink in the coterminous U.S. of -0.51 ± 0.39 GtC.yr⁻¹ over the period 2003-2006. This sink is mainly distributed in the Midwest states, which are characterized by extensive agriculture, and in the Southeast regions where forests are regrowing. An additional sink is located in the south of the boreal region.

Land model development

A major achievement of Steve Pacala's team has been the development of a new dynamic global land model, LM3, in collaboration with GFDL and USGS scientists. New simulations carried out by Elena Shevliakova and Sergey Malyshev suggest a terrestrial source due to land-use activities from 1.1 to 1.3 GtC/year in the 1990s, which is substantially smaller than the previous estimates. The analysis suggests a secondary vegetation sink of 0.35 - 0.6 GtC/year in the 90s and smaller cropland and pasture sources due to deceleration of agricultural land clearing since 1960s. The smaller magnitude of the land use flux in turn implies a smaller magnitude of the missing terrestrial sink, a finding that agrees with results from inversion modeling described above.

In another modeling advance, Sarmiento's and Pacala's groups have designed a data-based prognostic fire model for use in dynamic land models. This model estimates monthly burned area from four climate predictors (precipitation, temperature, soil water content and relative humidity) and one human-related predictor (road density). So far, due to the lack of reliable data over long time periods in other regions, this model has been designed for the boreal forest regions only. However, by exploiting observations of carbon dioxide from space, it is now possible, for the first time, to have a direct proxy for fire emissions in the tropics. Studies are underway to estimate the potential use of this new data to model fire in the tropics.

Pacala's group is also working to understand how changes in climate will affect the geographic distribution of biomes and the mix of species that they contain. The feedbacks from the changes in the species composition are likely to have more significant feedbacks on climate and carbon cycling than the average changes in biomes' properties. In order to represent changes in the species composition in the next generation of land models, the Pacala group has developed a new, analytically tractable demographic model of forest dynamics: the perfect plasticity approximation, PPA. The PPA model will enable scientists to understand the underlying causes of the local, regional, and global relationship between plants diversity and climate.

Finally, in order to understand the impact of global change on terrestrial carbon storage, Stefan Gerber, in collaboration with Michael Oppenheimer and Steve Pacala, is incorporating nitrogen cycling into LM3. A particular focus of the work is improving representation of biological nitrogen fixation (BNF), the most important nitrogen flux globally, compared with other current vegetation models. Experiments with the new model show the critical role of the nitrogen dynamics in terrestrial biomass accumulation. After disturbances, nitrogen limitation with reduced biomass growth can persist over millennia, but the rate of the recovery depends largely on strength of biological nitrogen fixation. Experiments have also been carried out to explore the role of the nitrogen in the so called CO₂ fertilization effect. Preliminary results also point to BNF as one of the critical mechanisms if nitrogen is to limit plant growth in response to increased atmospheric CO₂ (Figure 9).

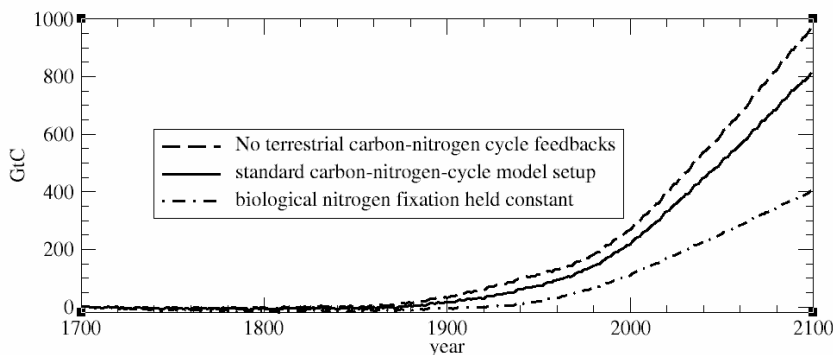


Figure 9. Modeled change in terrestrial carbon storage due to the CO₂ fertilization effect for projected CO₂ increase according to scenario IS92a. The simulation shows how nitrogen acts to limit terrestrial uptake (dashed vs. solid line). The effective sink strength depends on the ability of the terrestrial system to respond with biological nitrogen fixation (solid vs. dashed-dotted lines).

Reconciling models and observations of ocean carbon fluxes

Dr. Keith Rodgers (in collaboration with Rik Wanninkhof at NOAA-AOML) has been using models and observations to identify and quantify the amplitude of the background variability in natural (pre-anthropogenic) oceanic dissolved inorganic carbon (DIC) in the upper ocean. Identifying and understanding the background variability may be an important step to reducing error in measurement-based estimates of the ocean uptake of anthropogenic CO₂ through the CLIVAR/CO₂ Repeat Hydrography Program.

Importantly, for both the Indian Ocean and the Southern Ocean, our simulations indicate that the seasonal-to-interannual changes in column inventories of DIC are closely related to changes in sea surface height from remote satellite measurements. This strongly supports the working hypothesis that much of the elevated natural variability is dynamically-driven, and points the way to the development of a new method that incorporates satellite altimetry measurements to separate the natural variability component of DIC from Repeat Hydrography measurements.

Michael Bender's group continues to measure O₂/N₂ ratios in samples collected around the world, and use the results to calculate ocean and land carbon uptake worldwide. Their results show that, between 1994-2006, the oceans sequestered 2.1 Gt C/year and the land biosphere 0.7 Gt C/year. Also becoming evident in their data is evidence for an acceleration in the rate of ocean carbon uptake, estimated to be about estimated to be 1.0 +/- 0.5 Gt C/year between 1994-2005. This acceleration is the expected consequence of increasing rates of combustion and the increasing atmospheric burden of fossil fuel CO₂.

Observational data are also being used to evaluate and improve model simulations of ocean CO₂ uptake. An analysis by Sarmiento's group has shown that estimates of contemporary oceanic uptake of anthropogenic carbon cluster quite tightly if models that do not fit radiocarbon and CFC observations are first eliminated, and that there is now a convergence of oceanic uptake estimates of anthropogenic carbon around a value of 2.2 ± 0.3 Pg C yr⁻¹ for the early 1990s. This number is consistent with observation-based estimates made by Michael Bender's group and represents a significant narrowing the estimated size of the ocean sink. The result also suggests that the terrestrial "missing sink" is much smaller than previously estimated.

Linking ocean circulation and biogeochemistry

Yves Plancherel, a graduate student in the Sarmiento group, in collaboration with Dr. Andrew Jacobson at NOAA/ERSL in Boulder, Colorado, is working on developing a statistical tool designed to gain insight into how ocean biogeochemistry is linked to the large-scale ocean circulation. Although further research is necessary to ground-truth preliminary findings, the results obtained thus far with CMI funds were sufficiently encouraging that the Sarmiento group was able to obtain three years of NSF funding awarded to continue this project.

Daniele Bianchi, another graduate student in the Sarmiento group, works on understanding the location and processes that control the upwelling branch of the meridional overturning circulation. This is a central problem in oceanography with implications from climate change to

ocean productivity to deep-sea sequestration of anthropogenic carbon. Observational syntheses suggest that most of the upwelling occurs in the interior ocean, either spread broadly throughout the main thermocline or focused in regions of exceptionally intense mixing. However, a number of state-of-the-art numerical models suggest that the upwelling occurs primarily in the Southern Ocean. We included primordial Helium-3 emanating from mid-ocean ridges as a tracer in a suite of models with different representations of ocean mixing, representing the spectrum of behavior between upwelling occurring primarily in the Southern Ocean and upwelling occurring elsewhere. Preliminary results suggest that the models with upwelling in the Southern Ocean produce tracer distributions that are more consistent with observations.

Bianchi is also working with postdoc Eric Galbraith and Sarmiento to understand the physical and biological controls on open ocean anoxic zones, where water column denitrification takes place.

Paleoclimate

Daniel Sigman's and Jorge Sarmiento's groups continue to develop new models and tools for studying ancient changes in carbon fluxes and climate. Data from sediment cores and results of computer simulations have continued to strengthen the evidence that the Southern Ocean, the continuous band of ocean surrounding the Antarctic continent, plays an important role in glacial-interglacial CO₂ changes

Model development

Eric Galbraith led the work in the Sarmiento group in the continued development of the coarse resolution coupled model CM2.1C (a coarser resolution version of GFDL's climate model CM2.1). This work is motivated by interest in studying coupling between carbon and the physical components (ocean/atmosphere/land) of the climate system under climate change. The goal is to develop a model which runs an order of magnitude faster than the state-of-the-art generation of models developed at GFDL such as CM2.1, which was considered to be one of the premier coupled models presented in the most recent IPCC report. An order of magnitude increase in speed would facilitate the long simulation times needed for paleoclimate studies.

Work over the last year has focused on improving the skill of CM2.1C in its simulation of the pre-industrial climate state. As a means of evaluating model skill, the root-mean-square error of sea surface temperature with respect to observed sea surface temperature is a commonly used diagnostic of the mean bias (area-weighted) in the model representation of surface temperatures. The RMS temperature error of CM2.1C is compared with a number of models that were considered as part of the IPCC report in Figure 10. CM2.1C is now an IPCC-class model with regard to its temperature and salinity errors, as well as other characteristics such as stable ocean overturning, the global surface winds, as well as a respectable representation of El Niño variability.

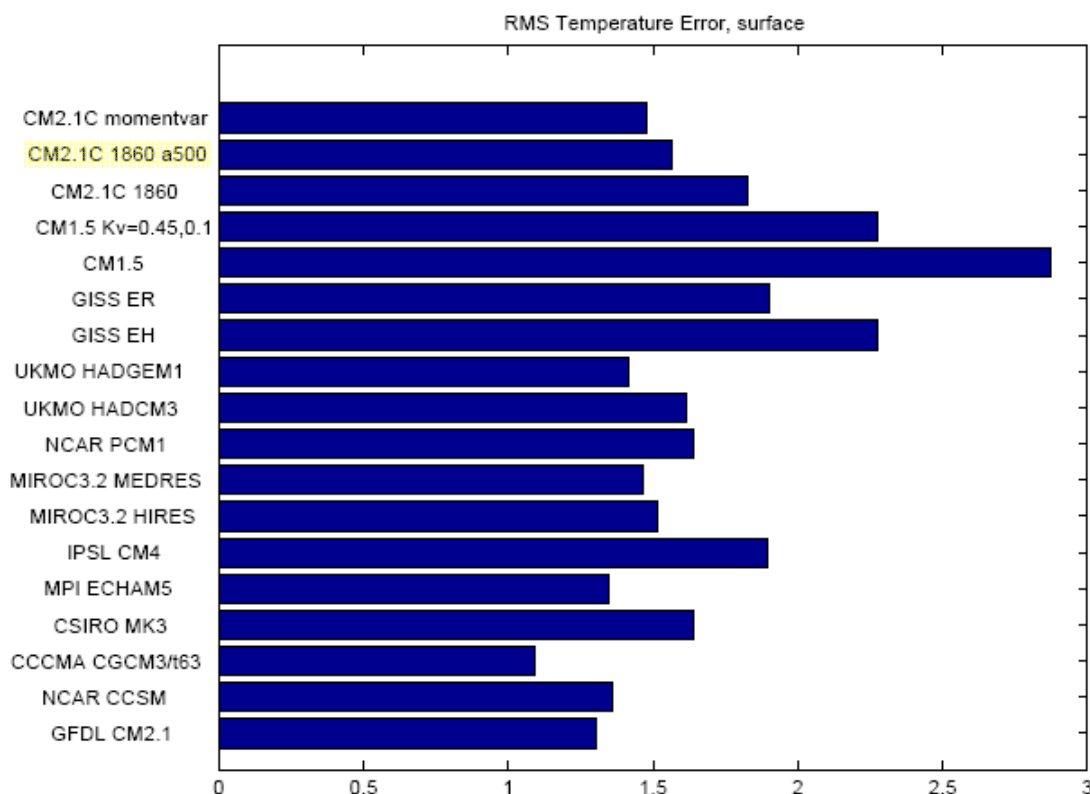


Figure 10. A comparison is shown between the Root Mean Square (RMS) sea surface temperature error for IPCC simulations. The models shown in the chart include the full-resolution CM2.1 model (the last model shown) from GFDL and the coarse-resolution version of CM2.1 (CM2.1C). The first five bars in the chart indicate different stages of improvement in the representation of physical processes for CM2.1C, with the second (**CM2.1C 1860 a500**) representing the control run that is now an IPCC-class model. The models from other institutes include those of the Goddard Institute for Space Studies (GISS), the UK Met Office (UKMO), and the National Center for Atmospheric Research.

In a related modeling effort, Richard Slater has continued the development of the modules used for ocean tracers in the GFDL ocean models. As a test of model skill, a comparison was made between simulated and observed CFC-12 changes along P6 (32°S) in the Pacific Ocean. Both the observations and the model reveal a clear subsurface maximum in the CFC-12 change, establishing that the circulation in the coupled model is able to reproduce to first-order important structures and features in passive tracers in a region known to be significant for the global ocean uptake of anthropogenic carbon, as well as for paleoclimate changes.

Studying glacial-interglacial changes and the Southern Ocean

Daniel Sigman and his collaborators continue to pursue the 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 affect atmospheric CO₂ in the observed sense of its glacial/interglacial oscillation, by, during ice ages, reducing the natural leak of biologically

sequestered CO₂ out of the ocean and into the atmosphere. Moreover, this work 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.

Work by graduate student Brigitte Brunelle on ice age conditions in the Bering Sea of the Subarctic North Pacific indicates reduced nutrient supply from below during the last ice age, strengthening the case for a bipolar (Antarctic and North Pacific) increase in stratification during ice ages. In related work by Eric Galbraith, it has been demonstrated that these polar ocean changes were indeed paralleled by reduced ventilation and increased storage of CO₂ in the deep ocean of the last ice age, and Galbraith has produced new constraints on the timing with which this deep CO₂ reservoir was dissipated at the end of the ice age, eventually accumulating in the atmosphere.

Based upon the measurement results, Sigman's group has recently begun to consider physical mechanisms for the apparent climate/polar stratification link mentioned 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. As described above, an underlying motivation was that both the Antarctic and the subarctic North Pacific were less efficient at ventilating the ocean interior under cold climate regimes of the geologic past, potentially explaining glacial/interglacial variations in atmospheric CO₂. de Boer's work has demonstrated that both ocean cooling in itself and cooling-induced changes in the westerly winds work to reduce Antarctic overturning, such that both have the potential to explain past ventilation changes (Figure 11). At the same time, negative feedbacks arise in the model, placing bounds on the ventilation rate of the ocean interior and its susceptibility to a cooling-driven decrease. These include the role of North Atlantic overturning in the energy balance of the deep ocean.

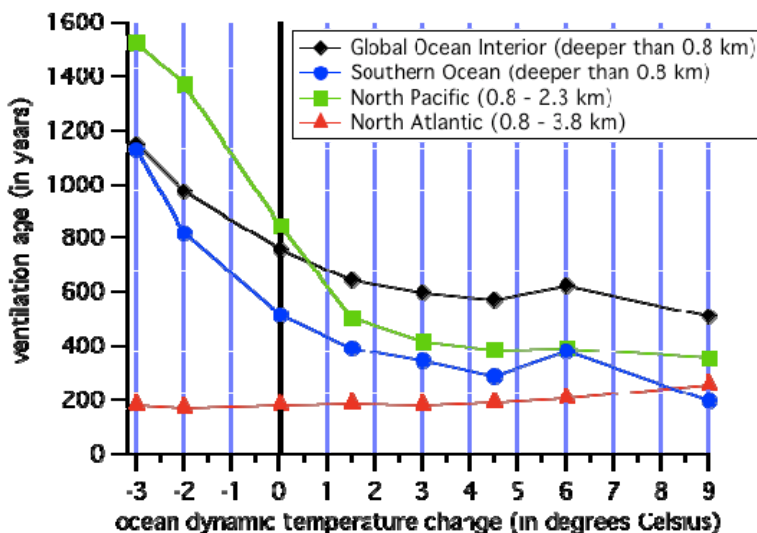


Figure 11. Sensitivity of the deep ocean ventilation age to 'dynamic' ocean temperature change in a version of the GFDL ocean model (after de Boer et al., 2007). In the experiments shown, the temperature input to the seawater density calculation step in the model is changed globally from the standard case. Ventilation age, the mean time since deep water has contacted the ocean surface, is plotted for the global ocean as well as for each of the major deep water formation regions. The experiments predict that a colder ocean than today would have reduced overturning in the Southern Ocean and North Pacific, leading to a globally "older" deep ocean that sequestered more CO₂ from the atmosphere, but increased overturning in the North Atlantic.

In light of the confluences of de Boer's modeling work with paleoceanographic measurements by Sigman's group and other investigators, a new hypothesis has been posed to explain the most recent set of major deglaciations. From the glacial state of Antarctic and North Pacific stratification, orbital forcing and glacial melting in the Northern hemisphere are called upon to decrease the relative driving forces for overturning in the North Atlantic versus the other ocean basins. As North Atlantic overturning ceases, Antarctic overturning increases, releasing CO₂ to the atmosphere and reducing the surface albedo associated with southern hemisphere sea ice. These processes drive global warming, which leads to large scale deglaciation. This hypothesis has many testable aspects and also provides a straightforward conceptual framework for ongoing investigation.

Impacts of climate change on ancient civilizations

Sigman's group is also working to improve our understanding of the climate that directly preceded the era of large scale human alteration of the global environment. Sigman has collaborated with his close colleague Gerald Haug, Professor in the Geological Institute at ETH Zurich, on high resolution studies of marine and lake sediment cores to reconstruct climate changes in the northern hemisphere tropics over the Holocene, the last 10 thousand years during which the Earth has been in a warm ("interglacial") climate state. Sediment records from a lake in southeast China and the Cariaco Basin off the coast of Venezuela indicate that at least some past migrations of the Intertropical Convergence Zone (ITCZ) appear to have stretched across the Pacific. Moreover, there is suggestive evidence that shifts in the ITCZ represented caused environmental changes that contributed to sociopolitical events in dynastic China and the Classical Maya of Central America.

Climate change and ocean productivity

Also in collaboration with the Haug group, Sigman's group is working to understand the response of the ocean's nitrogen cycle to climate change. As part of this effort, high-resolution sedimentary nitrogen (N) isotope records across two major deglaciations were generated from the Cariaco Basin, a low-oxygen basin with a remarkable well-preserved sedimentary sequence. The reconstruction appears to connect competing views on the controls of N₂ fixation, suggesting that N₂ fixation is tightly coupled to ocean N loss but is also sensitive to iron supply and so is stimulated by dust inputs. These results argue for some degree of N cycle response to changing dust input to the ocean, but little opportunity for the large N₂ fixation-driven changes in ocean fertility that have been hypothesized as a part of plans to add iron to the tropical and subtropical ocean.

Impacts of Geoengineering

The CICS Science group is working with GFDL through CICS to maintain a group of scientists able to analyze mitigation options as they arise. While iron fertilization and deep-sea injection do not appear to be gaining traction as viable options, there does continue to be strong interest in them, including amongst private commercial ventures. There are many unresolved questions that are of considerable interest scientifically, and the outcomes will have significant impact on our evaluations of the viability of these options.

Simulations of iron fertilization

During the last year, Sarmiento's group carried out a set of iron fertilization simulations making use of the new generation of ecosystem and iron chemistry models that have been developed over the past decade at Princeton and GFDL. These fertilization model results differ significantly from the major conclusions of our previous research in showing greater sequestration efficiency. The main reason for this discrepancy is that the added iron is retained for a long period of time in the new models, and thus continues to draw down carbon each time it returns to the surface. In previous research, it had been assumed that the added iron would be scavenged very rapidly.

Additional tests that were performed included the addition of a simple global atmosphere for carbon, which reduced the efficiency by about 40% due to decreased uptake elsewhere, and a simulation where the added iron is only allowed to be used once before it is then removed from the system, which reduced the efficiency by up to a factor of 10. Other simulations were performed to help us better understand the mechanisms which differentiate the new generation of models from past and to compare our results more directly with some of the oceanic iron fertilization experiments (IRONEX).

As a complement to the iron fertilization study, Keith Rodgers conducted a modeling study of natural decadal variability in iron concentrations in the Equatorial Pacific. This study indicates that the supply of iron to the upwelling region along the equator may exhibit large decadal variability. Understanding such variability in iron cycling will be valuable when interpreting the representativeness of the background state at the time of particular in situ fertilization experiments, and in assessing the potential of fertilization to reduce atmospheric CO₂ concentrations.

Future Plans

Although there is consensus in the scientific community that the planet is warming, and on the overall budget of carbon, large uncertainties still exist concerning the location of natural carbon sources and sinks, and the mechanisms that control their variability and response to climate change in both the land and ocean. The CMI Science Group has already made significant progress in estimating sink magnitudes and explaining their causes. As we continue to improve our observational and simulation capacities, we will increase confidence in estimates of future CO₂ change and the mitigation effort needed to avoid damaging climate consequences.

We emphasize that the CMI science component is a synergistic activity building on a broad range of research on the Princeton University campus that includes that carried out by NOAA's Geophysical Fluid Dynamics Laboratory (GFDL); the Cooperative Institute of Climate Science (CICS), which is a collaboration between Princeton University and GFDL; and the large basic research programs maintained by all the participants in the CMI science program with support from government agencies such as NOAA, NASA, NSF, and DOE. With help from our partners, we will continue to expand and deepen research in our main thematic areas.

Carbon observing system

A series of papers published during 2007 represent a culmination of a long term effort by Sarmiento's group to determine the long term average of the air-sea CO₂ flux and how knowledge of this influences our understanding of terrestrial CO₂ fluxes. Now the group is focusing primarily on analysis of new observations being obtained by ongoing repeat surveys, with a major emphasis on the detection of the anthropogenic invasion of carbon in the face of very large interannual variability of the natural carbon cycle.

Ocean inventories

With the goal of reducing uncertainty in estimates of the time-evolving uptake of anthropogenic CO₂ from Repeat Hydrography measurements, the Sarmiento group will extend previous work to properly interpret the Repeat Hydrography observations and to quantify the uptake of anthropogenic CO₂ by the ocean. Modeling work will consist of the use of forced ocean circulation experiments with GFDL's MOM4, which includes GFDL's Ocean Biogeochemistry model (TOPAZ) online. An evaluation of model-simulated DIC fields against repeat measurements in the ocean will facilitate a dynamical interpretation of the observations.

Additionally, output from the coupled earth system model described in the following section will be used to study the dynamical processes that control natural variability of DIC. An important limitation of forced ocean experiments lies in the surface freshwater boundary condition (namely that sea surface salinity is typically restored to observations), and this is expected to damp variability in ventilation processes. Thus the coupled model simulations will serve as an important complement to the forced ocean simulations for identifying and understanding processes controlling DIC changes in the ocean interior.

Air-sea fluxes

Sarmiento's group is also interested in producing an interannually varying air-sea CO₂ flux data product using satellite measurements and the GFDL Earth System Model (ESM2.1). The recently completed joint atmospheric inversion studies of Jacobson et al. (2007a) and Jacobson et al. (2007b) find that the land regions of the tropics and the Southern Hemisphere are likely to be a large source of CO₂ to the atmosphere. In contrast to other studies, this result suggests that tropical land ecosystems may not be experiencing enhanced growth due to elevated atmospheric CO₂ concentrations. However, the joint inversion result derives mainly from oceanic inversion fluxes, which have no interannual variability and use observations of dissolved inorganic carbon (DIC) and nutrients measured mainly during the early- to mid-1990s. Thus there is a clear need for additional data constraints to evaluate the time-varying component of the problem.

We intend to develop a new gridded interannually-varying air-sea CO₂ flux dataset, relying largely on remotely-sensed satellite data products, the GFDL ESM2.1, and a semi-empirical nonlinear reference scheme (neural networks). The semi-empirical scheme will first be used to determine relationships between variability in simulated air-sea fluxes and model variables that correspond to fields available from remote sensing. The relationships will then be used to produce the air-sea CO₂ flux dataset from the satellite data.

Air-land fluxes

As a complement to recent research in the Sarmiento group to detect interannual variations in CO₂ flux exchanges over North America, work will be conducted by the Pacala and Sarmiento groups towards developing a mechanistic understanding of the detected changes. As a long-term goal, attribution of changes in carbon fluxes will involve distinguishing between a variety of influences, including: (a) land use changes, (b) fertilization associated with increased atmospheric CO₂ concentrations, (c) the action of fires, (d) changes in the mean state of the atmosphere associated with global climate change, and (e) natural variability in the carbon cycle. As an important first step towards attribution, we will work with models and observations to understand the natural variability component, which we define to be the background variability that would be expected to occur in the absence of human intervention. For the purposes of detection, this represents the background noise against which the anthropogenic perturbation is to be detected.

In order to characterize the amplitude and structure of CO₂ flux variations over North America over interannual to decadal timescales, we intend to use the LM3V model (developed jointly by Princeton and GFDL) coupled to GFDL's three-dimensional dynamical atmosphere model AM2. In doing so, we intend to test the hypothesis that interannual variability in CO₂ fluxes over North America is largely driven by internal variability of the atmosphere, whereas decadal variability in CO₂ fluxes is a largely deterministic non-local response to sea surface temperature variations.

Climate and biogeochemistry

An important direction of future research in the Sarmiento group will be to explore the ways in which carbon in the ocean couples to the other components of the climate system in earth system models, and how this can help us understand paleoclimate and predict the future response of the earth system to global warming.

Improved models of nutrient cycling

Recent research at Princeton and GFDL has clarified that the critical parameters that control the air-sea balance of natural CO₂ are the absolute concentrations of preformed and remineralized nutrients in the ocean. This new understanding has led us to a renewed emphasis on improving our simulations of the processes that determine the distribution of these two types of nutrients in the ocean interior, and how climate change modifies those processes. Our new more careful examination of these properties has revealed a number of problems that reflect limitations in both ocean circulation and ocean biogeochemistry models. We are tackling these problems on three fronts:

We have a major new effort underway to develop improved models of ocean circulation by a strategy of new tracer simulations that will enable us to test the models, and by a wide range of sensitivity studies aimed at improving the models, particularly in the critical region of the Southern Ocean.

In addition to our ongoing efforts to develop surface ecology models, we have a new effort underway to more carefully examine ocean interior nutrient, oxygen, and carbon distributions and determine how these can be improved. This research will benefit greatly from the deployment of new methods for high speed convergence of the models to solutions that will enable us to carry out a much wider range of parameter sensitivity studies than has ever been possible before.

Paleoclimate

To increase our understanding of past climatic changes, the Sigman and Sarmiento groups will continue to improve modeling tools and collect new data from ocean sediments.

Model development

Development of a new coarse-resolution coupled climate model of the earth system including the terrestrial as well as oceanic carbon cycles will be continued. This is an essential component of our strategy that will make it possible for us to carry out long (multi-millennial) simulations of the climate, a much more complete set of tests of the many theories for the ice ages that have been developed at Princeton and GFDL, and a wide array of studies of the sensitivity of the carbon cycle to future climate change.

Understanding glacial/interglacial cycles

Available data suggest that a hydrographic front within the modern Antarctic Zone, which today has modest but measurable impacts on the carbon cycle, was far more important during the last ice age. To evaluate this hypothesis, Sigman's group will work in partnership with international collaborators to recover and analyze new sedimentary materials from the different regions of the Antarctic, as well to study different regimes of the modern Antarctic to ground-truth paleoceanographic tools. This effort should also yield records with better age control than previously available, allowing comparison of the detailed timing of Antarctic ocean changes with other records of climate change and with the end-glacial rise in atmospheric CO₂.

Over the past year, graduate student Abby Ren in Sigman's group has developed a new paleoceanographic tool, based on the organic matter internal to the calcium carbonate microfossils of planktonic foraminifera (surface-dwelling animals), to reconstruct nutrient conditions across the ocean outside the most polar regions. While the utility of Sigman's previous tools was limited to the more productive regions of the ocean, this new tool opens up essentially the rest of the ocean to parallel investigation. Although the development work has many aspects and will continue for some time, Sigman's group is now entering the application phase, with the work beginning on several sediment records from across the global ocean. Among the central goals is testing the expected low latitude consequences of the polar stratification hypothesis.

Geoengineering and a carbon sequestration "truth squad"

This will continue to be a low-level effort of examining geoengineering and carbon sequestration proposals using our earth system models. Past research has included examinations of deep sea

CO₂ sequestration and iron fertilization. A major ongoing project that will be completed during the following year is a re-examination of the iron fertilization scenario using new ecosystem models that were finally completed over recent years.

Publications

- de Boer, A. M., J. R. Toggweiler, and D. M. Sigman, "Atlantic dominance of the meridional overturning circulation," *Journal of Physical Oceanography*, in press.
- de Boer, A. M., D. M. Sigman, J. R. Toggweiler, and J. L. Russell, "The effect of global ocean temperature change on deep ocean ventilation," *Paleoceanography*, 22, PA2210, doi:10.1029/2005PA001242, 2007.
- Boyd, P.W., T. Jickells, C. S. Law, S. Blain, E. A. Boyle, K. O. Buesseler, K. H. Coale, J. J. Cullen, H. J. W. de Baar, M. Follows, M. Harvey, C. Lancelot, M. Levasseur, N. P. J. Owens, R. Pollard, R. B. Rivkin, J. Sarmiento, V. Schoemann, V. Smetacek, S. Takeda, A. Tsuda, S. Turner, A. J. Watson, "Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions." *Science*, 315: 612-617, 2007.
- Brunelle, B. G., D. M. Sigman, M. S. Cook, L. D. Keigwin, G. H. Haug, B. Mingram, G. Schettler, and S. L. Jaccard, "Evidence from diatom-bound nitrogen isotopes for Subarctic Pacific stratification during the last ice age and a link to North Pacific denitrification changes," *Paleoceanography*, 22, PA1215, doi: 10.1029/2005PA001205, 2007.
- Crevoisier C., E. Shevliakova, M. Gloor, C. Wirth and S.W. Pacala, "Climate and human drivers of fires in the boreal forests: data constrained design of a prognostic model for burned area," *J. Geophys. Res.* (In Press)
- Deutsch, C., J. L. Sarmiento, D. M. Sigman, N. Gruber, and J. P. Dunne, "Spatial coupling of nitrogen inputs and losses in the ocean," *Nature*, 445, 163-167, 10.1038/nature05392, 2007.
- Dunne, J. P., J. L. Sarmiento, and A. Gnanadesikan, A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor," *Global Biogeochem. Cycles*, 21, GB4006, doi:10.1029/2006GB002907, 2007.
- Galbraith, E. D., S. L. Jaccard, T. F. Pedersen, D. M. Sigman, G. H. Haug, M. Cook, J. R. Southon and R. Francois, Carbon dioxide release from the North Pacific abyss during the last deglaciation, *Nature*, 449, doi:10.1038/nature06227, 2007.
- Gloor, M., N. Gruber, J.L. Sarmiento, C.S. Sabine, R.A. Feely, and C. Rödenbeck, A first estimate of present and pre-industrial CO₂ flux patterns based on ocean interior carbon measurements and models, *Geophys. Res. Lett.*, 30, art. No. 1010, 2003.
- Gruber, N., M. Gloor, S.E. Mikaloff Fletcher, T. Takahashi, S.C. Doney, M. Gerber, A.R. Jacobson, K. Lindsay, D. Menemenlis, A. Mouchet, and J.L. Sarmiento, in revision. Toward consistent estimates of the oceanic sources and sinks for atmospheric CO₂ (Global Biogeochem. Cycles).
- Houlton, B. Z., D. M. Sigman, E. A. G. Schuur, and L. O. Hedin, A climate-driven switch in plant nitrogen acquisition within tropical forest communities, *Proceedings of the National Academy of Sciences*, 104, 21, 8902-8906, doi:10.1073/pnas.0609935104, 2007.
- Jacobson, A. R., S. E. Mikaloff-Fletcher, N. Gruber, J. L. Sarmiento, M. Gloor, and TransCom Modelers, "A joint atmosphere-ocean inversion for surface fluxes of carbon dioxide: I. Methods and global-scale fluxes." *Global Biogeochem. Cycles*, 21, GB1019, doi:10.1029/2005GB002556, 2007.
- Jacobson, A. R., S. E. Mikaloff-Fletcher, N. Gruber, J. L. Sarmiento, M. Gloor, and TransCom Modelers, "A joint atmosphere-ocean inversion for surface fluxes of carbon dioxide: II. Regional results. Global Biogeochem. Cycles, 21, GB1020, doi:10.1029/2006GB002703, 2007.
- Levine, N.M., S.C. Doney, R. Wanninkhof, K. Lindsay, and I. Fung, "The impact of ocean carbon system variability on the detection of temporal increases in anthropogenic CO₂," submitted, *J. Geophys. Res.*
- Meckler, A. N., G. H. Haug, D. M. Sigman, B. Plessen, L. C. Peterson, and H. R. Thierstein, "Detailed sedimentary N isotope records from Cariaco Basin for Terminations I and V: Local and global implications," *Global Biogeochemical Cycles*, 21, GB4019, doi:10.1029/2006GB002893, 2007.
- Mignone, B. K., R. H. Socolow, J. L. Sarmiento, and M. Oppenheimer, "Atmospheric stabilization and the timing of carbon mitigation," submitted to *Climatic Change*.
- Mikaloff Fletcher, S. E.; Gruber, N.; Jacobson, A. R.; Gloor, M.; Doney, S. C.; Dutkiewicz, S.; Gerber, M.; Follows, M.; Joos, F.; Lindsay, K.; Menemenlis, D.; Mouchet, A.; Müller, S. A.; Sarmiento, J. L., "Inverse estimates of the oceanic sources and sinks of natural CO₂ and the implied oceanic carbon transport." *Global Biogeochem. Cycles*, 21, GB1010, doi: 10.1029/2006GB002751, 2007.
- Najjar, R. G., X. Jin, F. Louanchi, O. Aumont, K. Caldeira, S. C. Doney, J.-C. Dutay, M. Follows, N. Gruber, F. Joos, K. Lindsay, E. Maier-Reimer, R. J. Matear, K. Matsumoto, P. Monfray, A. Mouchet, J. C. Orr, G. K. Plattner, J. L. Sarmiento, R. Schlitzer, R. D. Slater, M. F. Weirig, Y. Yamanaka, and A. Yool, "Impact of circulation on export production, dissolved organic matter, and dissolved oxygen in the ocean: Results from Phase II of the Ocean Carbon-cycle Model Intercomparison Project

(OCMIP-2).” *Global Biogeochemical Cycles*, 21: GB3007, doi:10.1029/2006GB002857, 2007.

Ogle, K. and S.W. Pacala, “A modeling framework for inferring tree growth and allocation from physiological, starvation, and allometric traits.” *Tree Physiology* in press.

Pacala, S.W., Coordinating Lead Author. And: R. Birdsey, S. Bridgham, J. Caspersen, R. Conant, K. Davis, B. Hales, R. Houghton, J. Jenkins, M. Johnson, G. Marland, K. Paustian, R. Socolow, R. Tol. and S. Wofsy. “The North American Carbon Budget Past and Present,” In: *The First State of the Carbon Cycle Report (SOCCR): The North American Carbon Budget and Implications for the Global Carbon Cycle*, Departments of Energy and Commerce and NASA, 2007.

Purves, D.W., J.W. Lichstein, S.W. Pacala. “Crown Plasticity and Competition for Canopy Space: A New Spatially Implicit Model Parameterized for 250 North American Tree Species.” <http://www.plosone.org/article/doi/10.1371/journal.pone.0000870>, 2007.

Rodgers, K. B., J. L. Sarmiento, O. Aumont, C. Crevoisier, C. de B. Montegut, N. Metz, “A wintertime uptake window for anthropogenic CO₂ in the North Pacific,” *Global Biogeochem. Cycles*, in press.

Rodgers, K.B., O. Aumont, C. Menkes, and T. Gorgues, “Decadal variations in equatorial Pacific ecosystems and ferrocline/pycnocline decoupling,” *Global Biogeochem. Cycles*, in press.

Shevliakova, S.W. Pacala, S. Malyshev, G.C. Hurtt, P.C.D. Milly, J.P. Caspersen, L. Thompson, C. Wirth and K.A. Dunne. “The Land Carbon Cycle and Vegetation Dynamics in the Dynamic Global Land Model LM3V,” *Global Change Biology*. in press.

Sigman, D. M. A. M. de Boer, and G. H. Haug, “Antarctic stratification, atmospheric water vapor, and Heinrich events: A hypothesis for late Pleistocene deglaciations,” in *Past and Future Changes of the Oceanic Meridional Overturning Circulation: Mechanisms and Impacts*, Schmittner, A., J. H. C. Chiang, and S. R. Hemming, Eds., AGU Geophysical Monograph 173, 335-350, 2007.

Strigul, N., Pristiniski, D., Purves, D.W., Dushoff, J., Pacala, S.W.. “Crown plasticity and large-scale forest dynamics: A new method of modeling vegetation dynamics. “(In review)

Sweeney, C., E. Gloor, A. J. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof, “Constraining global air-sea gas exchange for CO₂ with recent bomb ¹⁴C measurements,” *Global Biogeochem. Cycles*, 21, GB2015, doi:10.1029/2006GB002784, 2007.

Yancheva, G., N. R. Nowaczyk, J. Mingram, P. Dulski, G. Schettler, J. F. W. Negendank, J. Liu, D. M. Sigman, L. C. Peterson, and G. H. Haug, “Influence of the Intertropical Convergence Zone on the East Asian Monsoon,” *Nature*, 445, 74-77, 10.1038/nature05431, 2007.

The Integration Group

The Integration Group pursues research on how the projected economic and environmental impacts of anthropogenic greenhouse gas emissions affect the design of economically sound risk management strategies. Its members also synthesize and disseminate CMI research results, particularly the concept of “stabilization wedges.”

Progress this year has been made in three main areas:

- (i) Outreach to climate stakeholders and development of a post-wedges approach to the North-South divide over carbon mitigation policies
- (ii) Modeling the atmospheric distribution of ethanol in order to understand the impacts of future anthropogenic emissions
- (iii) Analyzing the costs and benefits of a system that can predict a slowdown of ocean circulation in response to climate change

Synthesis and Outreach

The Integration Group continues to reach out to new audiences and develop new perspectives on carbon mitigation. CMI's best known product is probably the "Princeton wedges." The wedges work emerged in 2004 from the effort of the project's two co-PIs, Steve Pacala and Robert Socolow, to reconcile the dissonant evaluations of the urgency of the climate change problem being articulated at that time. On the one hand, environmental scientists were promoting immediate mitigation, while at the same time economists and others involved in integrated assessment were advocating large investments in mitigation in the second half of the century. The wedges work developed the case that humanity already has the tools to "solve" the climate problem if we wish to, at least for the next half-century. Knowing humanity could solve the problem changed the debate: if we can, let's do it, said many leaders. Paraphrasing Lord Browne writing in *Foreign Affairs* in 2004, if the costs and damages are comparable and uncertain, let's get on with the job.

Outreach to climate stakeholders

Co-Directors Pacala and Socolow have continued efforts to inform a variety of stakeholders about the wedges concept and the need to start cutting emissions now. Socolow gave invited testimony to the Senate Finance committee about carbon mitigation strategies, and also gave presentations on carbon mitigation at a Conference on the States and Climate Change, to the U.N. General Assembly, and to the World Bank Executive Directors. Socolow is also a member of a National Academies committee, *America's Energy Future: Technology Opportunities, Risks, and Tradeoffs*, which aims to provide authoritative and widely accepted assessments of existing and new energy technologies, their associated impacts, and projected costs. Among other activities, Pacala gave presentations at the Energy Crossroads Conference at Stanford, the International Petroleum

Technology Conference in Dubai, and met with the ambassador from Saudi Arabia. He is also deeply involved in development of a new communications organization called “Climate Central” (see below).

The Stabilization Wedges concept and game

Roberta Hotinski, formerly the Information Officer for CMI, is now working for the group as a consultant with primary responsibility for education and outreach based on the “stabilization wedges” concept (please see previous annual reports or the web page cited below for an introduction to the wedges). The wedges continue to grow in popularity and CMI continually receives new requests for permission to reproduce graphics and use other wedges-based materials. There is also high demand for facilitation of the wedges game at workshops and seminars - Hotinski presented the wedges game at ten events this year (including the AAAS Town Hall mentioned above and a meeting of the European Union’s Science & Technology Advisors), reaching hundreds of participants in the business, education, and policy communities. In addition, she has developed a new website combining existing articles, graphics, and game materials as a resource for others wishing to present the wedges concept on their own (see <http://www.princeton.edu/wedges>), which receives hundreds of hits per month.

There is growing interest from the informal and K-12 education communities in adapting the wedges to more diverse and younger audiences. The wedges have been included in K-12 climate curricula of the Keystone Group and the World Wildlife Federation, and the teacher’s guide developed by Hotinski has been incorporated into multiple compendia of K-12 climate change materials. Hotinski is also serving on advisory boards for the Franklin Institute in Philadelphia, which is considering using wedges in a 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.

Beyond wedges – focusing on the emissions of individuals

To further promote solutions to climate change, Co-Directors Pacala and Socolow have been developing an approach, as simple as “wedges” in its underlying structure, that could conceivably break the current policy logjam. The new focus is on counting the CO₂ emissions rates of individuals, rather than nations, to gain acceptance of the view that those who emit at the same rate, wherever they live, should experience the mitigation effort in similar ways. The goal is to provide a route to a new view of what is “fair,” one that recognizes both that there are wealthy people in poor countries and that poor countries are awash in poverty.

Starting from income distribution data acquired by the World Bank, Pacala and Socolow, along with their post-doc, Shoibal Chakravarty, and collaborators elsewhere, have linked income to carbon to arrive at an emissions curve for all the world’s citizens. Their analysis reveals that, because the 3 billion poorest people in the world together are responsible for only about half a billion metric tons of carbon emissions, the development of the desperately poor is not in conflict with solving the climate problem. In contrast, the 500 million wealthiest people – with incomes above \$30,000 - \$40,000 (USD) per year – live in all the countries of the world and are responsible for about half of global emissions. To stabilize at an atmospheric CO₂ concentration limit of 450

ppm, Pacala and Socolow calculate a personal emissions limit for these rich emitters that falls from about 5 tons to 1 ton carbon per year over 50 years. By basing national caps on the number of emitters above a certain carbon threshold/income level, international policy makers could place the burden of carbon mitigation on those who have benefited economically from high emissions while still taking into account widespread poverty in developing nations.

Climate Central

Co-Director Steve Pacala has also been leading development of a unique non-profit organization, called “Climate Central,” dedicated to providing the public and policymakers with objective, peer-reviewed information about climate change and potential solutions in a manner that the general public can understand. With early funding from the Flora Family Foundation and the 11th Hour Project, Pacala and Jane Lubchenco of Oregon State University have been working to organize and staff the organization.

Intended to be the “Reuters of climate” (in Pacala’s words), Climate Central will have a bureau-like structure (with headquarters in Princeton and the first of several offices in Palo Alto, California) and use the latest communications technology, media expertise, and high quality production facilities to provide rapid response to events as they happen. Berrien Moore, founding director of UNH’s Institute for the Study of Earth, Oceans and Space, has signed on as the group’s executive director, and Heidi Cullen of the Weather Channel and Charlie Lyons, a former writer and producer for ABC News, have also joined the team.

Linking Air Pollution and Climate Change

Michael Oppenheimer’s group continues to investigate the linkages between air pollution and climate change. They are currently studying the impacts of ethanol on air quality and climate.

Air pollutants, ethanol, and climate

Because of energy security and climate change concerns, bio-ethanol is currently being promoted on a global scale as a viable substitute for fossil fuels. However, future increases in atmospheric ethanol can influence the concentration of tropospheric ozone, a potent pollutant, and can impact the oxidizing capacity of the troposphere.

Although ethanol is ubiquitous in the troposphere, we have little knowledge of its sources and sinks, and atmospheric distribution. To address this need, Vaishali Naik and Michael Oppenheimer, in collaboration with scientists at GFDL, applied a well-tested chemical transport model (MOZART-4) to simulate the global ethanol atmospheric distribution and budget, and used atmospheric measurements of ethanol to place constraints on the ethanol budget.

The researchers compared the simulated ethanol concentrations with aircraft, ship-based, and site-specific ground measurements to assess the degree of consistency between atmospheric measurements and our understanding of the ethanol budget. A simulation using known ethanol sources (Figure 12) underestimates the observed concentrations by a factor of 2 in the eastern United States and by more than a factor of three in Mexico City, off the coast of Asia in North

Pacific, and in the remote South Pacific ocean. The high observed ethanol values in Mexico City are attributed to local pollution events that our relatively coarse resolution model was unable to capture. Given the short atmospheric lifetime of ethanol, values measured off the coast of Asia and in the remote Pacific could not be explained by simply increasing continental emissions or reducing the oceanic sink of ethanol. An additional diffuse source of about 10 ppt day^{-1} in the model improved the large observation-model mismatch in these regions, with little improvement in the observation-model comparison over the eastern US and Mexico City. Thus, our analysis suggests that a large secondary source ($\sim 30 \text{ Tg yr}^{-1}$) of ethanol would explain the measured ethanol concentrations in remote regions.

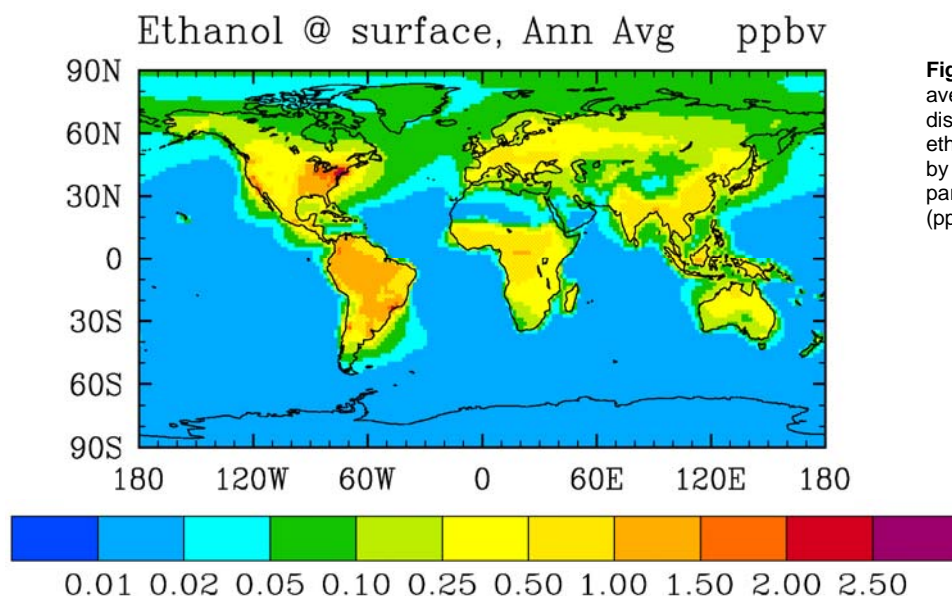


Figure 12. Annual average surface distribution of ethanol simulated by MOZART-4 in parts per billion (ppb).

The researchers suggest that the additional source of ethanol from oxidation of other volatile organic compounds, particularly in remote regions, could dwarf the anthropogenic surface sources of ethanol that are nevertheless important for polluted, populated areas of the world. Further work is needed to better constrain the global ethanol budget to be able to quantify the impacts of projected future increases in ethanol emissions. Areas of research include reliable and new atmospheric measurements with wider spatial sampling of ethanol and its precursors, additional direct measurements of ethanol emissions from plants, and better estimates of ethanol deposition velocity.

Assessing and Improving the Utility of Climate Observation Systems

Klaus Keller, now at Penn State, has been analyzing two interrelated questions. First, how can we understand, detect, and predict potential anthropogenic threshold responses of the climate system? Second, how can we use this scientific information to design sound risk-management strategies?

Predicting changes in ocean circulation

One potential climate threshold response involves an abrupt and/or persistent weakening of the North Atlantic meridional overturning circulation (AMOC), an ocean circulation system that transports heat from low latitudes to the North Atlantic basin and the surrounding regions. The geologic record and model simulations suggest that the AMOC may weaken or even collapse in response to climatic forcing. Such a threshold response could be associated with considerable ecological and economic impacts. The current predictions about the future fate of the AMOC are, however, deeply uncertain.

Over the past year, Keller and colleagues analyzed the effects of potential climate threshold responses (such as an abrupt and/or persistent shutdown of the North Atlantic Meridional Overturning Circulation, AMOC) on economically efficient climate strategies. One particular focus was on the potential value of AMOC observation systems to improve the design of climate strategies. They showed, for example, that the currently implemented and well-tested AMOC observation system may well fail at the task of providing a confident prediction of an approaching AMOC shutdown before the forcing threshold has been crossed. However, investments in an AMOC observation system that *would* enable a confident and early prediction of an AMOC shutdown would likely pass an economic cost-benefit test. In ongoing work, they are also analyzing the risks of recently proposed geoengineering proposals.

Future Plans

Synthesis and outreach

Pacala and Socolow, with several junior collaborators, will continue developing 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. The team developing this analysis includes young investigators from India and China who wish to apply these tools to the states and provinces of their home countries, once our first papers are completed. It is conceivable that this second integration product from CMI will have as large an impact on the conceptualization of CO₂ mitigation as the Princeton's wedges work has had.

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 addition, Dr. Pascale Poussart, PEI's new Assistant Director for Energy Initiatives, will become a full-time member of the team in May and will work to both expand outreach and integrate CMI with other campus initiatives.

Linking energy security and carbon concerns

With the emergence of a second University thrust in energy alongside CMI in the form of the Energy Grand Challenge (discussed above), work on energy and security will be substantially expanded. A notable beneficiary of this expansion will be the fledgling university program on oil, energy, and the Middle East, a collaboration of the Department of Near Eastern Studies, the Woodrow Wilson School of Public and International Affairs, and the Princeton Environmental

Institute. This collaboration will now be headed by a newly hired full professor, Bernard Haykel, a historian of Saudi Arabia and Yemen with strong interests in contemporary events.

Impacts of greenhouse gases on air quality

We anticipate that future work addressing linkages between air quality and greenhouse gas emissions will include both work in collaboration with GFDL on the understudied problem of methane emissions management ("methane wedges") and work on interactions between greenhouse policy and air quality policy. An example of the latter is the current thesis research of a graduate student from China, who is examining how China sets and implements environmental goals. He is learning the details of China's ambitious programs of the past few years to reduce its SO₂ emissions, with the objective of predicting how China will set and implement goals for CO₂ emissions.

Improving assessments of climate change risks

A new initiative has been undertaken by Oppenheimer and colleagues at MIT, NCAR, and UC San Diego, as concern has grown in the climate community about the capabilities of the assessment process. Despite the great success of IPCC, many questions have arisen about its assessment of the future contribution of ice sheets to sea level rise. A notable lesson from recent assessments of both climate and other problems is the underestimation of the likelihood of large or unusual outcomes (ice sheet disintegration, ozone hole), and a tendency to pursue paths of learning for a very long time (despite contraindications) that ultimately prove to be wrong (which they call "negative learning"). In order to better understand the scientific learning process and shape an improved assessment process, Oppenheimer has engaged with colleagues at UCSD in history of science to explore in depth the interaction among uncertainty, scientific learning and scientific assessment, with the case history of the West Antarctic ice sheet as a first study.

Publications

- Baehr, J., K. Keller, and J. Marotzke, "Detecting potential changes in the meridional overturning circulation at 26 °N in the Atlantic," *Climatic Change*, published online, <http://dx.doi.org/10.1007/s10584-006-9153-z>, 2007.
- Baehr, J., D. McInerney, K. Keller, and J. Marotzke, "Optimization of an observing system design for the North Atlantic meridional overturning circulation," *Journal of Atmospheric and Oceanic Technology*, 2007.
- Brennan, K., R. Matear, and K. Keller, "Measuring oxygen concentrations improves the detection capabilities of an ocean circulation observation array," *Journal of Geophysical Research – Oceans*, 2007.
- Chameides, W. and M. Oppenheimer, "CLIMATE CHANGE: Carbon Trading Over Taxes," *Science* 315: 1670 [DOI: 10.1126/science.1138299] (in Policy Forum), 2007.
- Greenblatt, J.B., S. Succar, D.C. Denkenberger, R.H. Williams, and R.H. Socolow. "Baseload Wind Energy: Modeling the Competition between Gas Turbines and Compressed Air Energy Storage for Supplemental Generation," *Energy Policy*. Vol. 35, Issue 3, Pages 1474-1492, 2007.
- Keller, K., C. Deutsch, M. G. Hall, and D. F. Bradford, "Early detection of changes in the North Atlantic meridional overturning circulation: Implications for the design of ocean observation systems," *Journal of Climate*, 20, 145-157, 2007.
- Keller, K., S.-R. Kim, J. Baehr, D. F. Bradford, and M. Oppenheimer, "What is the economic value of information about climate thresholds?" Book chapter in: *Integrated Assessment of Human Induced Climate Change*, Chief Editor: Michael Schlesinger, Cambridge University Press, 2007.
- Keller, K. and D. McInerney, "The dynamics of learning about a climate threshold," *Climate Dynamics*, Published online,
- <http://dx.doi.org/10.1007/s00382-007-0290-5>, 2007.
- Keller, K., A. Robinson, M. Oppenheimer, and D.F. Bradford, "The regrets of procrastination in climate policy," *Environmental Research Letters*, 2 024004 (4pp) <http://dx.doi.org/10.1088/1748-9326/2/2/024004>, 2007.
- Keller, K., G. Yohe, and M. Schlesinger, "Managing the risks of climate thresholds: Uncertainties and needed information," *Climatic Change*, published online, <http://dx.doi.org/10.1007/s10584-006-9114-6>, 2007.
- Keller, K., D. McInerney, and D. F. Bradford, "Carbon dioxide sequestration: When and how much?" *Climate Change*, 2007.
- McInerney, D. and K. Keller, "Economically optimal risk reduction strategies in the face of uncertain climate thresholds," *Climatic Change*, published online, <http://dx.doi.org/10.1007/s10584-006-9137-z>, 2007.
- Mignone, B.K., R.H. Socolow, J.L. Sarmiento, and M. Oppenheimer, "Atmospheric Stabilization and the Timing of Carbon Mitigation," accepted for publication in *Climatic Change*.
- Sheppard, M.C. and R.H. Socolow, *Perspective (Cover Story, Invited): Sustaining Fossil Fuel Use in a Carbon-Constrained World by Rapid Commercialization of Carbon Capture and Sequestration*, *AIChE Journal*, John Wiley & Sons, Hoboken, NJ, Volume 53, No. 12, pp. 3022-3028, 2007.
- Naik, V., D. Mauzerall, L. Horowitz, M. D. Schwarzkopf, V. Ramaswamy, and M. Oppenheimer, "On the sensitivity of radiative forcing from biomass burning aerosols and ozone to emission location," *Geophys. Res. Letters*, 34, L03818, doi:10.1029/2006GL028149, 2007.
- Oppenheimer, M., B.C. O'Neill, M. Webster, and S.,l Agrawala, "Climate Change: The Limits of Consensus," *Science* 317 (5844), 1505. [DOI: 10.1126/science.1144831, 2007.
- Michael Oppenheimer, Brian C. O'Neill, and Mort Webster, "Negative Learning and Global Environmental Change," submitted to *Climatic Change*.
- Socolow, R.H., "Special Report: Approaching Midnight -- Facing new unknowns,". *Bulletin of the Atomic Scientists*, Vol. 63, No. 1, pp. 45-46, 2007.
- Socolow, R.H. and S.-H. Lam. "Good Enough Tools for Global Warming Policy Making," *Philosophical Transactions of the Royal Society*, 365: 897-934, February 2007.
- R.H. Socolow and S.W. Pacala. "A Plan to Keep Carbon in Check," *Scientific American*, Vol. 295, No. 3, pp. 50-57, September 2006. ~ Selected for inclusion in: *The Best American Science and Nature Writing*, 2007, Richard Preston (ed). Boston: Houghton Mifflin Company, pp. 259-267, 2007.
- Yang, C.-J. and M. Oppenheimer, A "Manhattan Project" for Climate Change?" *Climatic Change*, 80:199-20, 2007.

