The carbon cycle in the Earth System
(Curator Martin Heimann)

At a glance
The element carbon is a fundamental constituent of life and its global cycle is tightly connected to the habitability of our planet.

Introduction
The carbon cycle in the Earth System constitutes a fundamental, pressing research topic in modern Earth system science. The greenhouse gases carbon dioxide (CO2) and methane (CH4) provide an important forcing factor of the global climate, which, on the other hand, controls the sources and sinks of these gases. In addition, the carbon cycle is currently being seriously perturbed by direct and indirect emissions from human activities. Unraveling and quantifying these interactions and feedbacks is essential to understand the climate history of the Earth, but also to predict its evolution in the future.

On time scales of up to a few thousand years, atmosphere and oceans together with land vegetation and soils have to be considered which rapidly exchange carbon in vast amounts by a multitude of physical, chemical and biological processes. On longer time scales, carbon exchange fluxes with the lithosphere by volcanism and erosion also have to be taken into account. Paleo-records indicate substantial variations of these exchanges as witnessed e.g. by the synchronous variations of the concentrations of the major greenhouse gases (CO2, CH4, N2O) with climate during the ice ages.

Human activities from changes in land use e.g. Deforestation and especially since the beginning of the industrial revolution through the burning of fossil fuels have released large amounts of carbon into the atmosphere. However, only about 40% of this carbon is accumulating as CO2 greenhouse gas in the air, the remainder is taken up by the ocean and the land biosphere. Understanding these sink processes and what regulates their efficiency constitutes a fundamental question in carbon cycle research. Will they continue to operate or even accelerate, or will they saturate under further emissions and rising atmospheric CO2 levels?

The global carbon cycle is not an isolated component of the Earth system. It is embedded in the physical climate environment. Hence there exist a multitude of possible feedbacks from changes in climate on the carbon cycle. E.g. Will warmer temperatures and increased precipitation lead to enhanced land carbon uptake through photosynthesis? Or will warmer temperatures lead to enhanced soil respiration and thus increased releases of CO2, which will accelerate climate warming? What happens to the ocean atmosphere carbon exchanges with a warming ocean and changes in currents and mixing?

The global carbon cycle is also tightly coupled to the cycles of nutrients and water. Interactions between carbon and nutrients, especially nitrogen have a major influence on the ability of ecosystems to store carbon. Furthermore, atmospheric carbon is not restricted to the greenhouse gases CO2 and CH4 alone, but also minor carbon compounds, such as volatile organic carbon compounds (VOC) have to be considered: in many ecosystems, emissions of VOC are
quantitatively comparable to the net carbon uptake (Kesselmeier et al., 2002, Kuhn et al., 2007). VOCs are also important for the formation of atmospheric aerosols, and they impact atmospheric chemistry, air quality, the greenhouse gas and biotoxic ozone and thus also feed back on the physical and biogeochemical processes in the Earth system.

A further, critical process is biomass burning. Unsustainable biomass burning in particular by deforestation and fuelwood use is a substantial net contribution to the atmospheric carbon burden and emissions from fires also affect atmospheric chemistry and aerosols (Andreae and Merlet, 2001).

Substantial coordinated research efforts in all MPIs of the Earth System Research Partnership (Mainz, Jena, Hamburg) are devoted to this theme: by means of process studies in the laboratory and the field, by observations from campaigns and monitoring stations (e.g. Siberia, Amazon) and by simulation studies using comprehensive coupled carbon cycle - climate models.

Furthermore, a new research direction investigates means to manage the global carbon cycle, by reducing emissions (e.g. de-carbonization of energy production, biofuels) and carbon sequestration (e.g. land use management, afforestation, enhanced carbon storage in soils, capturing CO2 from air and sequestration in the deep ocean or in geological formations). This research is tightly linked with other MPIs of the CPTS (e.g. the MPI for Colloidal Research, Potsdam), but also with external partners (e.g. the Potsdam Institute for Climate Impact Research, PIK). Finally, managing the carbon cycle also involves economic, political and societal contexts and thus provides links to the human sciences section of the MPG.

**Monitoring the global carbon cycle and its “hot-spots”**

A few key regions are critical for the global carbon cycle. On land these are the “green lungs” of the planet, i.e. the boreal/arctic forest and tundra, as well as the tropical rainforest of Amazonia, Congo basin and south-eastern Asia. In these areas the vegetation and soils contain large amounts of carbon, which may be vulnerable to climatic or human perturbations. A sizable fraction of the boreal forest and tundra is furthermore underlain by permafrost, containing additional, very large carbon stocks. In a warming climate thawing of permafrost could thus release large amounts of carbon as CO2 or, in swamps and bogs, as CH4 which would further accelerate climate change. Both regions are also subject to anthropogenic impacts, e.g. by forest logging, biomass burning and deforestation for agriculture and pasture.

Two important marine hot-spots are located in the North Atlantic and the Southern Ocean around Antarctica. In both regions, the formation of deeper waters exports excess carbon from the surface into the deeper layers. Changes in the oceanic circulation in these areas would thus decrease the ocean carbon sink capacity; first studies demonstrate that this is already happening in the Southern Ocean (LeQueré et al., 2008).

Understanding the underlying processes in hot-spot areas therefore is especially important. While this can be achieved by process and modeling studies, e.g.
studying past variations of climate and vegetation, or ocean circulation, a sound, long-term observing strategy in these regions is also needed. As an example, the MPIs of Jena and Mainz have established jointly with the Institute of forest in Krasnojarsk the Zotino Tall Tower Observatory (ZOTTO) in the center of the Siberian taiga forest. This observatory includes a 300m tall mast for the measurement of regional atmospheric signatures of greenhouse gases, reactive chemistry, aerosols and meteorology (Kozlova et al., 2008). A similar observatory is being established in the center of the Amazon forest in the near future. A complementary strategy consists in probing hot-spot areas by means of repeated aircraft campaigns e.g. using the high-altitude-long-range research aircraft (HALO) of the German research community.

Finally, remote sensing from satellite evidently offers a promising approach to monitor the carbon cycle and its key hot-spot areas. However, the sources and sinks of CO2 or CH4 can not be directly seen from space; they have to be inferred either from measurements of optical properties of the surface of the earth (e.g. greenness of the land vegetation, ocean color), or from atmospheric trace gas concentration measurements determined from the absorption spectra of reflected sunlight or the infrared radiation of the upper atmosphere. In each case appropriate numerical models have to be used to convert the spatio-temporal variations of the measured properties into surface sources and sinks. The typically very small variations make their detection with sufficient accuracy a technological challenge, however (Houweling et al., 2004, Frankenberg et al., 2006, Bergamaschi et al., 2007).

Atmospheric chemistry of natural carbon compounds
Terrestrial vegetation, especially tropical rain forest, releases vast quantities of volatile organic compounds (VOC) to the atmosphere, which are removed by oxidation reactions and deposition of reaction products. The oxidation is mainly initiated by hydroxyl radicals (OH), acting as a “detergent” of the atmosphere. The reaction products form a complex mixture, including low volatile gases that condense into particles, which in turn serve as condensation nuclei of clouds (Williams et al., 2007).

Recent research by the MPI for Chemistry has shown that the atmosphere-biosphere interactions of tropical forest ecosystems maintain a remarkable balance (Lelieveld et al., 2008). The natural VOC emissions serve important biological functions, for example by attracting pollinators and repelling herbivores. The biosphere uses the ambient air as a transport medium, and oxidation of these compounds brings about the concentration gradients sensed by insects. The forest atmosphere thus provides a means to distribute VOC for communication and defense purposes, and to dispose of metabolic products while sustaining an auspicious environment without the build-up of toxic compounds.

Rather than depleting OH radicals and thus the atmospheric oxidation capacity, as was believed for decades, the research suggests that the photochemistry of VOC over the forest recycles OH (Lelieveld et al., 2008). Surprisingly, this process does not contribute to photochemical smog, in contrast to the anthropogenically influenced atmosphere.
**Ocean Biogeochemistry in the Earth System**

Due to its chemical composition and its huge volume, the ocean is the largest reservoir for carbon with a fast exchange rate with the atmosphere. Its carbon inventory is 60 times larger than the atmospheric one and 20 fold the amount stored in the land biosphere. Small dynamical or biogeochemical perturbations within the ocean system can, therefore, cause a relatively large impact on the atmospheric carbon inventory and, thus, on the climate relevant radiation budget.

The ocean is a major sink for anthropogenic CO2 emissions: Already in the late 19th century Arrhenius estimated a long term oceanic uptake capacity of up to 83 % of an atmospheric disturbance. This uptake is primarily effectuated by dissolution of CO2 in the surface water, chemical reaction with the ocean carbonate system and subsequent transport to depth by ocean currents and mixing (Wetzel et al., 2005, Matsumoto et al., 2004).

Historically, the role of the marine biology has been believed to primarily determine the large scale carbon pattern within the ocean by being in a steady state distribution, because the growth of marine algae is limited by available nutrients and not by the abundant dissolved inorganic carbon. More recently, however, increasing emphasis has been placed on the understanding of the interaction of carbon with other biogeochemical components like nitrogen, phosphorus, silicate, sulphur, and oxygen. Nitrogen as N2O and sulphur as DMS, both products of biological processes, are clearly identified to affect the atmospheric radiation budget (Six and Maier-Reimer, 2006, Kloster et al., 2006). A climate-induced stabilization of the water column reduces the marine ventilation and, thus, the marine oxygen inventory. Less oxygen in deeper layers enhances, in turn, the production of gaseous N2 and N2O by denitrification and the subsequent evasion of nitrogen to the atmosphere. The loss of this nitrogen which, in form of nitrate, is an essential nutrient for marine algae, leads to a reduction of the photosynthesis and, consequently, of carbon uptake.

**The terrestrial carbon cycle**

Land ecosystems interact with climate through numerous biogeophysical and biogeochemical feedbacks. Ecosystems modify biophysical parameters of the land surface (e.g. the albedo), form specific spatial patterns, and contribute to the global cycling of carbon and nutrients through biogeochemical exchange with the atmosphere and ocean (Heimann and Reichstein, 2008). Many climate-relevant biological processes such as plant successions, soil evolution, and accumulation of organic residues in wetlands involve alterations of the land surface and the abiotic environment at time scales up to millennia. An understanding of these processes and their intrinsic coupling to the physical components of climate system is progressing rapidly. The challenging issue is an integration of this knowledge into Earth System models which provide the most coherent framework for the global-scale synthesis. An ever-growing computational power makes it possible to simulate feedbacks between climate and biogeosphere with increasing resolution and precision. This opens a promising perspective for improved projections of biospheric and climate dynamics in the future necessary for a better assessment of long-term implications of the climate policies.
The most fundamental question about the interactions between climate and biogeosphere is about an effect of these interactions on the climate system dynamics. Do these interactions stabilize the climate system or do they amplify external perturbations? The more specific questions are as follows:

- What are mechanisms of these feedbacks and how did they operate in the past (Brovkin et al., 2009, Claussen, 2009)?

- What are the biospheric tipping points in the greenhouse climate (Friedlingstein et al., 2006, Raddatz et al., 2007)?

- How these feedbacks are changing from a short-term (seasonal, annual) to the long-term (centennial, millennial) scale?

- What can we learn from ever-increasing resolution and quality of palaeo-archives (Tzedakis et al., 2009)?

The challenge of understanding feedbacks between climate and biogeosphere cannot be met without permanent improvement of the modelling tools. MPI-M has a long-term commitment to foster the further development of Earth System Models, applied widely for fundamental and applied research. Cycling of carbon and nutrients, both on land and the ocean, is an intrinsic part of this model. This model development includes intensive use of observational data on the functioning of local and biogeochemical cycles that recently have become available from global observational programs and databases.

The effects of nitrogen on the carbon cycle

Nitrogen and not carbon is the main element that drives life, because nitrogen is the main constituent of proteins and of nucleic acids. Thus, nitrogen is involved in all enzyme reactions and in the transcription of genetic information. The photosynthetic rate of leaves may serve as an example. CO2-assimilation by leaves depends on the activity and the amount of the CO2-reducing enzyme, Rubisco. About 80% of leaf nitrogen is incorporated in Rubisco, and needed for CO2 assimilation. Fertilizer application in agriculture aims at increasing the Rubisco content.

Atmospheric nitrogen, N2, is biologically inert. It must be reduced to NH4+ before it can be assimilated into proteins. In natural systems, the reduction of N2 into NH4+ is carried out by N2-fixing organisms, such as legumes or specialized fungi. However, human activities presently produce about as much reduced N as natural processes, mainly through fossil fuel burning.

During combustion, N2 is oxidized to form NOx which is being emitted to the atmosphere where it interacts with O2, and it is thus the main precursor for tropospheric Ozone, a potent greenhousegas aside of CO2. During this reaction, part of NOx is oxidized to form the nitrate anion, NO3-, which reacts with atmospheric ammonium, a side product from animal husbandry, to form the aerosol ammoniumnitrate which is subsequently being washed out from the atmosphere by rain. Wet and dry nitrogen deposition on plant leaves and soils acts as anthropogenic fertilizer across the Northern Hemisphere (Schulze, 2000, Trebs et al., 2006).
The deposition of nitrogen accelerates plant growth. There is evidence, that the accelerated uptake of CO2 at elevated atmospheric CO2 concentrations is in fact catalyzed by nitrogen. Without N-addition, the CO2 effect disappears. Increased growth means also increased litter production of leaves and roots, and thus increased soil respiration. However, nitrogen increases also the immobilization of carbon as humus substances. In soils the reduced nitrogen is being oxidized by microorganisms to form nitrate again. In this process N2O is being produced as a by-product. Nitrate can only be used by broad leaved trees and herbs, not by conifers. Also fertilizer applications in agriculture lead to an excess of nitrate. Thus, large amounts of nitrate are washed out from ecosystems into anaerobic zones of the groundwater, where nitrate is again being reduced to ammonium, with N2O as by-product (Schulze et al., 2002).

In summary, reduced and oxidized nitrogen interact with the climate system in numerous ways, by aerosol formation, by N2O production, by NOx and NH3 emissions, and by acceleration of plant primary production across all ecosystems.

Chemical-technical approaches to reduce the atmospheric CO2 burden
As the atmospheric CO2 is essentially men-made and a result of industrialization, also countermeasures have to be technological and on industrial scale. Development of a meaningful strategy and feasible technology to handle the atmospheric CO2-problem by chemical-engineering means, potentially even on the global scale and curing the debts of earlier years of industrialization, is a therefore a key issue of modern green chemistry.

In the MPS, such a potential strategy is analyzed. The basic idea is to take the abundant biomass waste from the farming cycle and to turn it into useful stable carbon products which then can act as a carbon deposit. Since waste biomass usually would biologically decompose and liberate its carbon content as CO2, this measure is effectively CO2-negative and generates additional economic benefits via carbon products at the same time. This coupling of carbon products and negative CO2-impact was first described in a scientific paper in 2007 (Titirici et al., 2007) and meanwhile, a variety of pilot plants on the 10 kT biomass/a scale are already under construction, aiming to test the technical applicability of this technology in a communal environment.

The process is a “rediscovery” of a very easy path to convert low value and widely available wet biomass into interesting carbon nanostructures using environmentally friendly steps. It was already described in 1913 by Bergius who reported on the hydrothermal transformation of cellulose into coal like materials (Bergius, 1913). In “hydrothermal carbonization” (HTC), a simple carbohydrate containing precursors, e.g. usually raw plant biomass, is “steam-cooked” in water at around 200 °C in the presence of easily available catalysts and under self generated pressure in order to produce the coal-like materials. This essentially mimics the natural process of peat or coal formation, and simply spoken, one might call HTC “coal making in a day”. The favorable aspects of HTC include the direct use of wet biomass without further processing and the fact that the reaction is exothermic; therefore it can generate, in a well-chosen technical environment, its own processing heat.
Of course this carbon can be burned and used for energy purposes, and wood or charcoal is the oldest energy source known to humankind. However, this direct re-consumption is “only” carbon neutral, but might nevertheless replace fossil coal in some areas, especially in rural areas of the second and third world. To create effective carbon negative sinks for society, real large scale deposits for carbon are to be found. At the MPI-CI, a whole range of important applications for such hydrothermal carbon materials is currently explored. Thus, carbon is not only treated as a CO2 deposit or energy source, but also as a valuable material, adding economic benefits to the sequestration issue. Biomass transformed into carbon materials for long lasting applications indeed can effectively take out atmospheric CO2, at least for the lifetime of the products. For this approach, the notation “carbon negative products” was coined.

Research on long lasting HTC-based carbons include optimization of synthetic procedures for black porous carbon as a conditioner to improve soil quality (thus generating “black soil” from depleted soil) (Titirici et al., 2007, Steinbeiss et al., 2009), ion exchange carbons for ion binding or with improved sorption capacity to clean drinking water (Demir-Cakan et al., 2009) but also high end carbon hybrid materials which can be effectively used as an anode in the future generation of lithium batteries (Hu et al., 2009), for example for the “plug-in” city car. It is most interesting to note that changing the material base to carbon-negative sustainable biomass does not compromise the carbon properties. In fact, the literature-described battery capacities are by a factor of 3 higher than the current golden standard of technology, graphite. Also, the ion exchange capacity of the synthetic humin ion exchangers is by a factor two higher than the best commercial, petrochemical ion exchange resins. Other applications that are currently exploited include CO2-specific sorbents for CO2 separation (Zhao et al., 2010) or –returning to energy issues- the development of an indirect carbon fuel cell which turns aqueous dispersions of hydrothermal coal directly into electric energy, which on the long run can act as a potential source of electricity with an overall zero-emission balance of CO2 (Paraknowitsch et al., 2009).

Especially the black humin carbon for soil improvement seem to have the potential for taking up a majority of CO2 on a global scale while generating a biological benefit at the same time, say via higher crop yields of farmland or a potential reforestation of badlands. A serious geoecological analysis of such measures and massive interdisciplinary operations are however needed before turning such concepts into broad scale reality.

**Future research directions**

The study of the global carbon cycle is highly interdisciplinary and progress is expected from scientific and technological advances in all involved research fields. This includes:

(1) process studies for the elucidation of key carbon transformation processes in particular in terrestrial and marine ecosystems, as well as in soils e.g. by means of isotopic labeling techniques, or manipulative experiments;
(2) improved long-term observations from stations in key hot-spot areas, repeated aircraft campaigns and the establishment of new space-borne remote sensing systems;

(3) improved representation of the multitude of carbon transformation processes in comprehensive models of the Earth system.

Beyond disciplinary improvements, advances in our understanding of the global carbon cycle are expected from research in the following areas:

(1) The coupling of the carbon cycle to the other element cycles of nutrients (N, P) and the hydrological cycle;

(2) The investigation of the multitude of climate system - carbon cycle feedbacks on the whole temporal spectrum ranging from days to ice-age cycles and geological epochs using comprehensive Earth system models;

(3) The impacts and interactions of human activities on the global carbon cycle: in particular through land use change and land management practices, but also by increased urbanization as well as losses of biodiversity on land, but also in the ocean;

(4) Management of the global carbon cycle, either by mitigation of emissions, increasing natural sink processes or by technical approaches to capture CO2 from the air.

Lastly, the global carbon cycle and its management cannot be studied in isolation from a natural science perspective only. The perturbation of the global carbon cycle is tightly linked to human development and the need for energy and food resources on land and in the sea. The scientific assessment of any management options thus clearly needs to take into account the multitude of socio-economic drivers and interactions in the modern world. Addressing this in a rational, scientific way poses a huge challenge, that, however, must be met in order to steer the Earth system within acceptable bounds over the next 100 years and beyond.
References


Bergius, F., „Die Anwendung hoher Drücke bei chemischen Vorgängen”, Halle, 1913


