

## **Session 46: Consequences of Acidification of Land and Ocean**

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### **Summary**

Acidification of Planet Earth's terrestrial and oceanic biospheres is happening now and caused by two very different anthropogenic sources'.

Land acidification is caused by nitric and sulphuric acids and whilst its significance emerged during the 1970's it is still an issue in the developed world and a growing issue in developing countries (e.g. Asia) resulting in changes to species diversity, net primary productivity, an imbalance of inorganic nitrogen ions and a stripping of calcium and magnesium ions in soils and eutrophication of fresh water bodies. Feedback reactions between the land and aquatic systems are not well understood or researched.

Ocean acidification is a direct and certain consequence of CO<sub>2</sub> emissions to the atmosphere and its consequences on the global ocean have only recently emerged (e.g. Riebesell et al. 2000; Zeebe and Wolf-Gladrow 2001, Caldeira and Wickett 2003, Sabine et al. 2004, Feely et al. 2004, Royal Society 2005, Kelypas et al. 2006; Turley and Findley 2009) The oceans have already taken up around 27-34% of the CO<sub>2</sub> produced by humankind since the industrial revolution (Sabine et al. 2004). Whilst this has limited CO<sub>2</sub> in the atmosphere, this has come at the price of a dramatic change to ocean chemistry. In particular, and of great concern to scientists all around the world, is the measureable change in ocean pH and carbonate and bicarbonate ion concentration (Royal Society 2005; WBGU 2006; Monaco Declaration 2009, IAP Statement 2009) .

Evidence indicates that ocean acidification is a serious threat to many adult and juvenile organisms and may have implications to food webs and ecosystems and the multi-billion dollar services they provide. For instance, erosion is likely to outpace growth of tropical coral reefs at 450-480 ppm CO<sub>2</sub>, already there are reports of 19% decrease in growth of Great Barrier Reef corals.

By the time that atmospheric CO<sub>2</sub> reaches 450 ppm, it is projected that large areas of the polar oceans will have become corrosive to shells of key marine calcifiers and it will be strongest in the Arctic (this session - Orr et al.). Already loss of shell weight in planktonic Antarctic calcifiers has been observed (this session – Howard et al.). Decreasing pH could also make oceans noisier in the audible range with potential implications for marine life, scientific, commercial, and naval applications using ocean acoustics (this session – Ilyina et al.).

The speed of change in ocean chemistry is very rapid (Fig 1), faster than previous ocean acidification extinctions in Earth's history, from which it took 100,000's of years for recovery of marine ecosystems (Archer et al. 1998). We know with very high certainty that ocean acidification will continue tracking future CO<sub>2</sub> emissions to the atmosphere so the only way of reducing the impact of ocean acidification is their urgent and substantial reduction.

**Introduction:** The oceans and the land are major parts of the Earth's carbon cycle with estimates of the pre-industrial ocean carbon reservoir of about 38000Gt, compared with about 700 Gt in the atmosphere and under 2000Gt in the terrestrial biosphere (Fig 1). Over the last 200 years oceans have been buffering climate change by absorbing around 25-30% of the CO<sub>2</sub> emitted into the atmosphere from the burning of fossil fuels, cement manufacturing and land use change. This has resulted in the measurable alteration of surface ocean pH, concentrations of CO<sub>2</sub>, bicarbonate ions and carbonate ions (CO<sub>3</sub><sup>2-</sup>) as well as the reduction of the saturation state and shoaling of the saturation horizons of CaCO<sub>3</sub> minerals (Figs. 2 and 3). Since pre-industrial times ocean pH has decreased by a global average of 0.1 and unmitigated CO<sub>2</sub> emissions will cause ocean pH to decrease by as much as 0.4 by the year 2100 and 0.77 by 2300. These will be the most rapid and greatest changes in ocean carbonate chemistry experienced by marine organisms for 10's Ma (Fig. 4). The terrestrial biosphere is an integral part of the global carbon cycle, in general most believe that in the past it has been acting as a sink, absorbing a significant fraction of anthropogenic CO<sub>2</sub>. However the fraction depends on many factors such as biological and socio-political processes e.g. whether the area is in a developing vs. developed country and to what extent mitigation activities are occurring. Land acidification has resulted in changes in species diversity, net primary productivity, proportions of inorganic nitrogen ions in the soil and eutrophication of fresh water bodies.

Acidification takes place in the oceans and on the land but the processes and the ions involved are different. Acidification in oceans is primarily caused by CO<sub>2</sub> and physical processes whereas on the land sulphuric and nitric acids are the key ions and biological processes dominate. Experimental work on acidification is often neat, detailed work with few examples of feedback mechanisms either within the specific ecosystem being studied or between the land and the oceans. Transfers of acidifying materials, as wet or dry deposition, between oceans and the land are being carried out but the effects are very difficult to quantify.

**Oceans:** Global circulation models have projected a decrease in the global ocean saturation state of aragonite and its undersaturation of the Southern Ocean within this century (Orr et al. 2005). A large-scale Southern Ocean observational analysis examining the seasonal magnitude and variability of carbonate ion and pH shows an intense winter-time minimum in carbonate ion south of the Antarctic Polar Front and when combined with projected fossil fuel CO<sub>2</sub> uptake will induce aragonite undersaturation as early as the year 2030 (McNeil and Matear, this session). Calcifying planktonic foraminifera and pteropods in the Southern Ocean may already be exhibiting reduced rates of calcification by as much as 38% since the industrial revolution (Howard et al. this session). However, it is the Arctic Ocean which will first experience carbonate ion undersaturation with 10% of surface waters undersaturated in aragonite (a less stable form of CaCO<sub>3</sub>) in 9-5 years and 50% in 30-40 years (Orr et al.). As acidification continues, some surface waters also become corrosive to calcite (the stable form of CaCO<sub>3</sub>) with 50% affected within 70 years. These undersaturated conditions would be chemically corrosive to the shells of all Arctic marine calcifiers which serve as a major food source for walrus, grey whales, bearded seals, and spectacled eiders. Long-term time series measurements in the northern Irminger Sea and in the Iceland Sea show the decline in surface ocean pH and the shoaling of the ASH in the Arctic Ocean by 2m/a (Olafsson et al. this session). Because of the hydrography of the Iceland Sea this means that each year 400 km<sup>2</sup> of seabed and the

animals that live there are exposed to waters inhospitable to marine calcifiers producing aragonitic shells.

Laboratory experiments, field observations of natural CO<sub>2</sub>-rich seawater “hot spots” and studies of previous ocean acidification events in Earth’s history indicate that these changes in ocean chemistry are a threat to the survival of calcifying organisms (e.g. coccolithophores, pteropods, foraminifera, corals, calcareous macroalgae, mussels, oysters, echinoderms and crustacean) and that other biological processes (productivity, internal physiology, fertilization, embryo development, larval settlement and communication) are also vulnerable to ocean acidification (see reviews Turley and Findley 2009; Turley et al. 2009, Fabry et al 2008, Kleypas et al. 2006, The Royal Society 2005). The impact of ocean acidification can be dramatic. For example, the larvae of brittlestar *Ophiothrix fragilis*, a keystone benthic species, shows 100% mortality after 8 days at pH 7.9, just 0.2 below ambient pH (Dupont et al. – this session). In contrast, not all organisms respond the same, others are less vulnerable. For example, tunicates grow and develop more rapidly and show a significant increase in fecundity and there are even species-specific effects of ocean acidification making it difficult to predicted what future ocean ecosystems will look like. Resilience to warming associated with the El Nino-Southern Oscillation has been poorest where CO<sub>2</sub> concentrations are greatest such as in the Galapagos and may explain why true reefs no longer exist there and why many genera of corals went extinct in the eastern tropical Pacific during the late Cenozoic (Manzello et al. 2008). Tropical coral reefs have been shown to be sensitive to carbonate ion concentration, with decreasing aragonite saturation resulting in reduced calcification, such that, by 2050, erosion of the reef may be greater than reef growth (Caldeira et al. this session) and if current trends in carbon dioxide emission continue, coral reefs will likely disappear (Fig 5).

Examination of the effects of decreases in marine calcification, CaCO<sub>3</sub> export and increased carbonate sediment dissolution indicates that total alkalinity increase will start being detectable during the next few decades. Key biogeochemical parameters of the ocean carbon cycle, such as the rain ratio CaCO<sub>3</sub>:POC in biological export production, may be sensitive to ocean acidification with potential feedback to climate. Novel model simulation of marine sediment core data for direct comparison with the marine geologic paleo-climatic record may help reduce uncertainties in future predictions of the impact of ocean acidification on these key biogeochemical parameters (Heinze et al. this session). Sound attenuation in the low-frequency range is primarily due to boric acid relaxation and is a function of seawater pH (Ilyina et al. this session). Decreasing pH could make oceans noisier in the audible range with potential implications for marine life, scientific, commercial, and naval applications using ocean acoustics.

A failure to cut carbon dioxide emissions deeply and soon risks widespread extinctions in the marine environment, with difficult-to-predict consequences for marine ecosystems generally (Caldeira, this session). The geologic record indicates that ecosystem recovery would likely take hundreds of thousands of years (Archer et al. 2005).

**Land:** The increased emissions to the atmosphere from human alterations of the carbon, sulphur and nitrogen cycles have multiple effects on terrestrial and aquatic ecosystems, including acidification, soil fertility loss, downstream eutrophication and a

loss of fish stocks and diversity (Fig. 6; Table 1). Acidification occurs when inputs of acid deposition composed primarily of sulfuric and nitric acids exceed the capability of ecosystems to neutralize these strong acid inputs (Rodhe, et al, 2002). Acid deposition has caused widespread degradation of surface waters, forests and grasslands in central and northern Europe and eastern North America (Phoenix et al, 2006). There has been a substantial change in the elemental composition of emissions and studies in the developed countries (USA and Europe), where air quality legislation has been in place for some time, indicate a steep decline in sulphur dioxide emissions with inputs shifting from being dominated by sulfate acids to nitric and organic acids. An increase in the deposition of reduced and oxidized forms of nitrogen is occurring in the USA. Ammonia emissions are becoming a larger contributor to increasing nitrogen deposition due to increases in animal production, agricultural intensification and biomass burning. Estimates of up to  $7.3 - 9.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  (dry + wet N deposition) to a tropical pasture site in Brazil as a result of biomass burning have been made. These estimates exceed predictions by global chemistry and transport models by at least a factor of two. Anthropogenic activities, like biomass burning and industrial emissions are altering N deposition in Brazil, not only increasing the N deposition but also changing the dominant form of nitrogen from  $\text{NO}_3^-$  to  $\text{NH}_4^+$ . These perturbations in the nitrogen wet deposition processes have important implications in the nitrogen cycle in Brazil with possible deleterious consequences to ecosystem functioning. More broadly, than the example cited above, this shift in the dominant form of anthropogenic input has important implications for element interactions, as S and N play fundamentally different roles in terrestrial and aquatic biogeochemistry (Lara et al, 2001; Artaxo, et al, 2003; Trebs, et al, 2006).

Nitrogen and sulfur deposition remain above critical loads in many countries. Improvements in alkalinity and pH in surface waters has occurred in many regions in response to sulfur dioxide emissions controls, but full recovery may be limited by ongoing depletion of exchangeable soil base cations and continued deposition of inorganic nitrogen. Nitrogen deposition-induced episodic acidification now occurs in regions such as the northeastern US with a long history of acid deposition, and also in the Western US where nitrogen deposition is low, but buffering capacity is even lower. One legacy of decades-long acid deposition has been significant loss of soil buffering capability. A recent experiment in the Tatra Mountains of Slovakia found increases in nitrogen inputs to alpine grasslands that previously had a history of very high inputs of acidic deposition resulted in depletion of both exchangeable base cations and soluble aluminum, and an increase in extractable iron concentrations. There was a concurrent nitrogen deposition-induced reduction in the biomass of vascular plants, associated with a decrease in shoot calcium and magnesium concentrations. Recent studies indicate that decreases in soil calcium and magnesium levels are negatively impacting ecosystem functions at higher levels in the trophic system egg shells of eggs are becoming brittle leading to decreases in clutch size of certain bird species. A trajectory of environmental change from atmospheric nitrogen deposition in highly oligotrophic terrestrial and aquatic ecosystems in the Colorado Rocky Mountains begins with eutrophication and changes in species assemblages, but ends with episodic and chronic acidification. Chronic acidification of alpine waters is projected to occur within several decades at levels of  $7-8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Jeziorski et al, 2008)

Impacts on vegetation systems seems to be completely dominated by the soil buffering capacity. Nitrogen deposition-induced episodic acidification now occurs in regions in

the northeastern USA. Alpine systems are impacted, showing a decrease in biomass of vascular plants and changes in species assemblages as well as chronic acidification of alpine waters over the long term (Long et al, 2009). Modelling studies show an increasing risk of acidification in 2050 mainly in eastern Asia, as well as smaller parts of Latin America and Africa. The application of a simple model to estimate the time development of acidification effects in Asia shows that sensitive soil types in areas of South, Southeast, and East Asia, including parts of southern China, Burma, Hainan, Laos, Thailand, Vietnam, and the Western Ghats of India, may potentially acidify to a significant degree on a 0–50 y timescale. Increases in emissions from biomass and fossil fuel burning are reported for Brazil, India and China (particularly south west China) with concerns about the risk of acidification. To date, impacts on human health in Asia seem more worrisome than impacts on ecosystems (Kuylenstierna, et al., 2001, Hicks, et al, 2008). However, as emissions are expected to continue to increase, the situation needs to be carefully monitored.

A key impediment to past discussions about limiting the impacts of acid deposition in the developing world has been the absence of baseline data, before the emissions began, on soil and river chemistry and species composition and distribution. Now is the time to begin to collect such information. The importance of obtaining integrated site-specific data to make more accurate assessments about soil acidification status is stressed, especially for parameters such as soil chemistry and local deposition rates (especially base cation deposition), sulphur and nitrogen retention in soils and ecosystems, and biomass harvesting and weathering rates from sites representative of different soil and vegetation types and management regimes.

### **Leading questions:**

- Will increased knowledge on the physiology of closely related marine taxa make a significant difference to quantifying impacts of acidification?
- Are there important feedbacks between ocean acidification and climate?
- Are there “tipping points” in ocean acidification and what are they?
- What will future ocean ecosystems look like and will they still provide important ecosystem services?
- How will air quality legislation change the terrestrial buffering capacity in different parts of the world and over what time scales will this change need to be measured?
- To what extent will soil acidification and stripping of calcium and magnesium ions lead to reduced terrestrial net primary productivity and changed ecosystem functioning thereby reducing the terrestrial sink strength?
- Has the terrestrial carbon sink become saturated?
- What would be the impact of proposed geoengineering solutions to climate change on ocean acidification?

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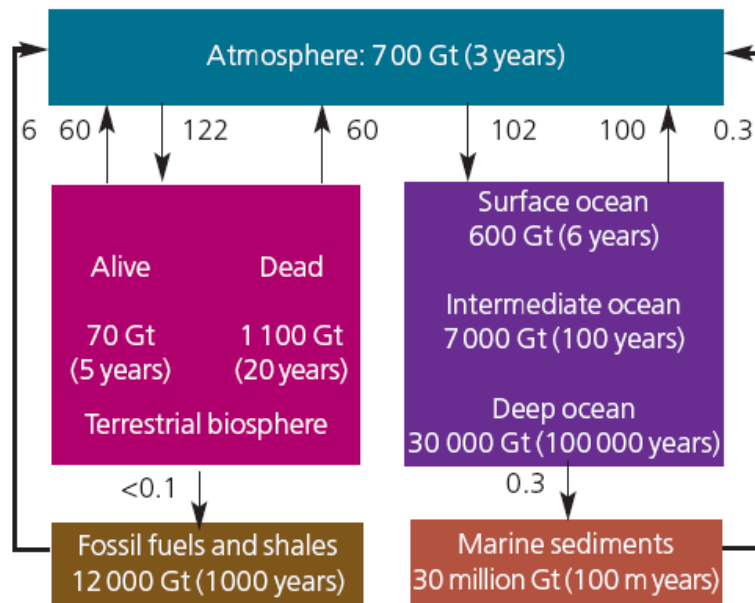
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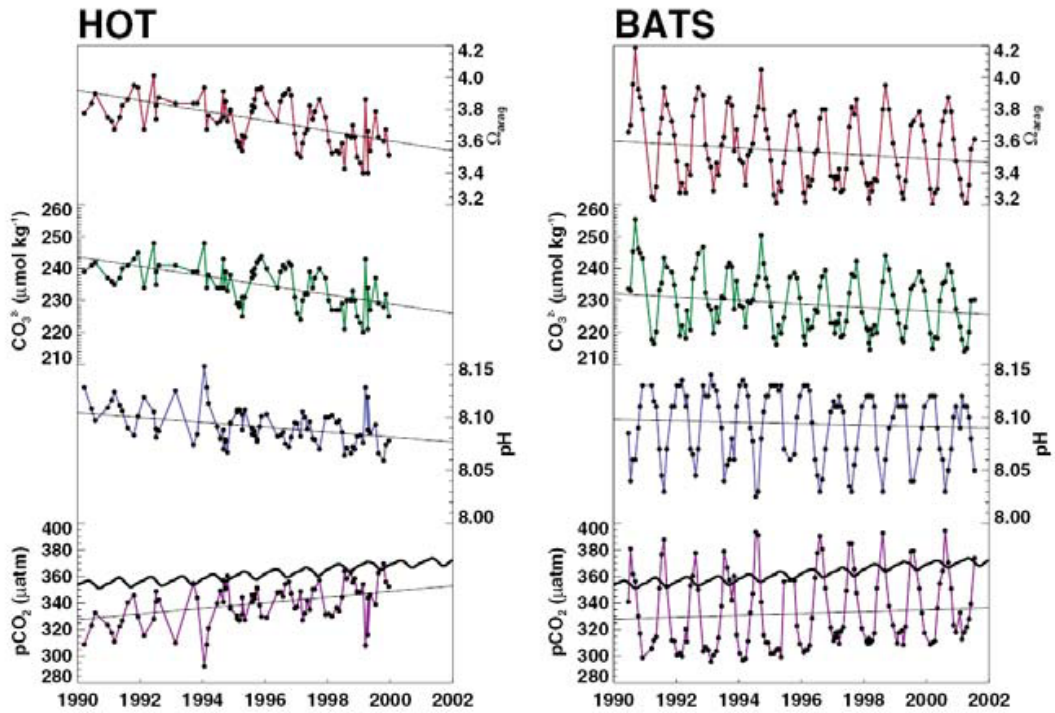
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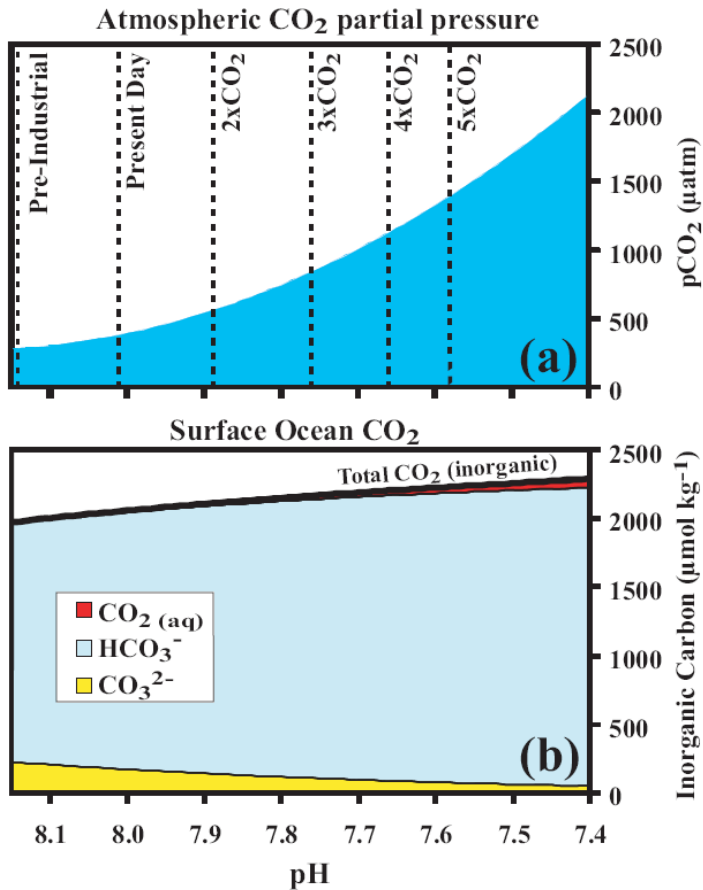
## Figures



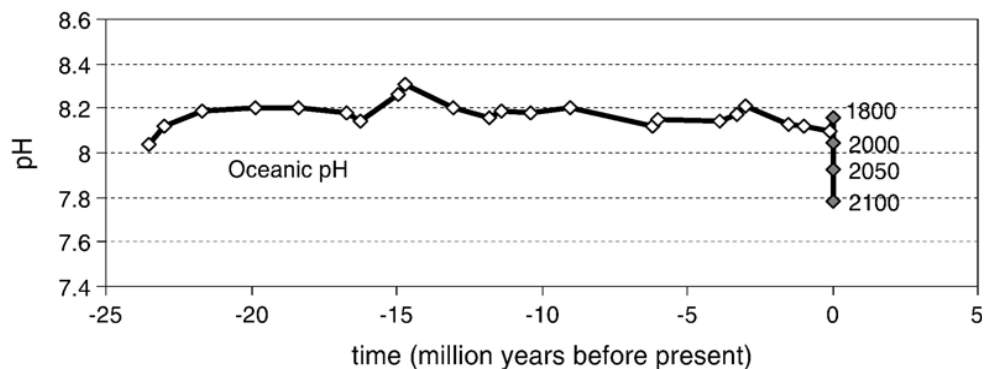
**Figure 1.** Diagram of the global carbon cycle showing sizes of carbon reservoirs (units are Gt (gigatonnes): 1 Gt = 10<sup>15</sup> grams) and exchange rates ('fluxes') between reservoirs (units are gigatonnes per year) in the terrestrial and the oceanic parts of the Earth system. Also shown are 'residence times' (in years) of carbon in each reservoir: however, some mixing between the deep oceans and marine sediments does occur on shorter timescales. Carbon exchanges readily between the atmosphere, the surface oceans and terrestrial biosphere. However, the residence time of carbon in the atmosphere, oceans and biosphere combined, relative to exchange with the solid Earth, is about 100 000 years. Redrawn from Holmen (2000) by the Royal Society (2005).



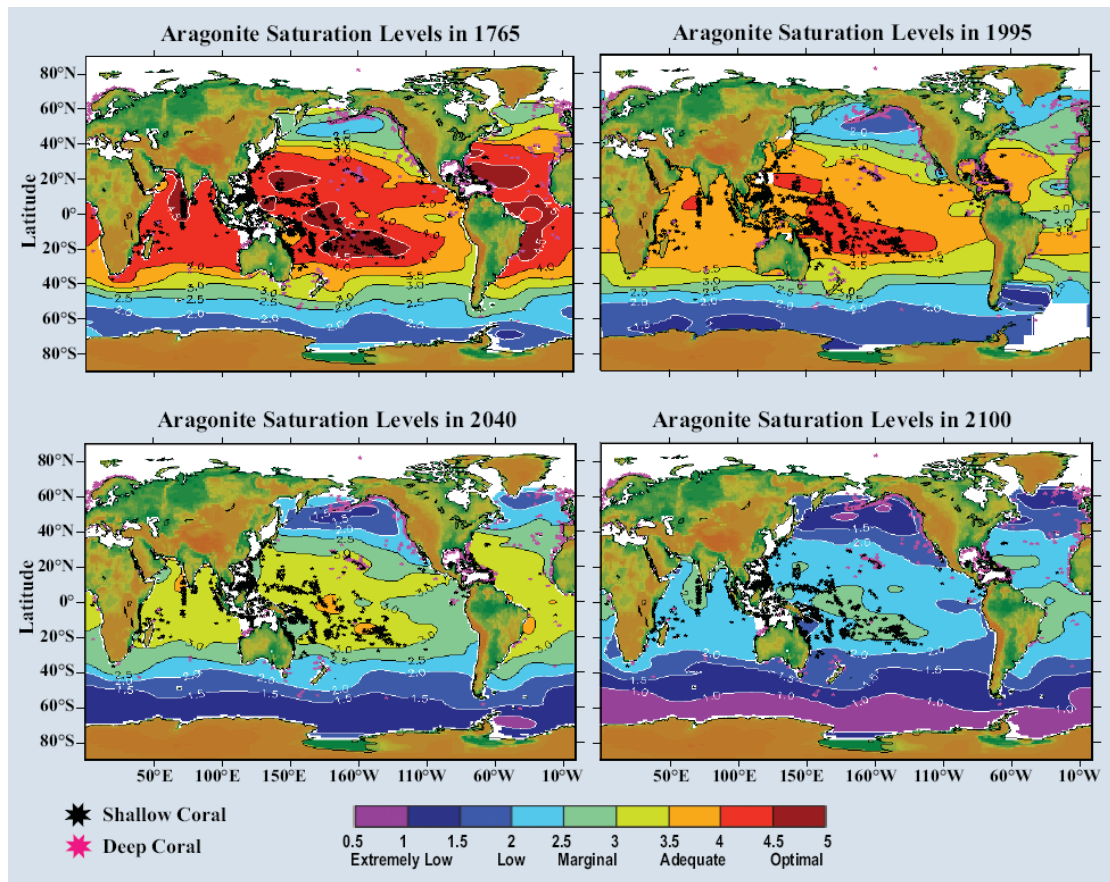
**Figure 2.** Monthly carbon-system parameters at two time-series stations in subtropical gyres: at HOT (Hawaii Ocean Time-series station) in the Pacific and BATS (Bermuda-Atlantic Time-series Station) in the Atlantic. (Kleypas et al., 2006).



**Figure 3.** Changes in ocean carbonate chemistry associated with increasing atmospheric CO<sub>2</sub>. (a) how different atmospheric CO<sub>2</sub> concentrations equate to surface pH, (b) the speciation amongst the different dissolved carbon forms (and see Figure 2). (Kleypas et al., 2006)



**Figure 4.** Past (white diamonds, data from Pearson and Palmer, 2000) and contemporary variability of marine pH (grey diamonds with dates). Future predictions are model derived values based on IPCC mean scenarios (Turley et al. 2006).



**Figure 5.** Projected aragonite saturation states in 1765, 1995, 2040 and 2099 with known locations of warm and cold water corals. Aragonite saturation levels less than one are undersaturated, corrosive waters. ( Feely et al. 2004 and Orr et al. 2005). (Kleypas et al. 2006)

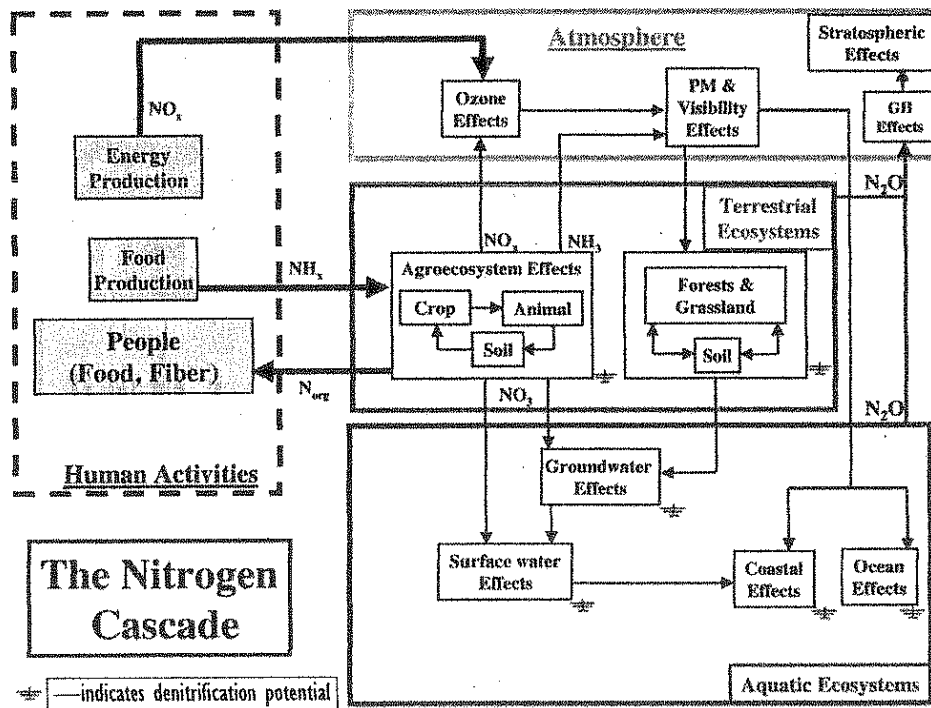
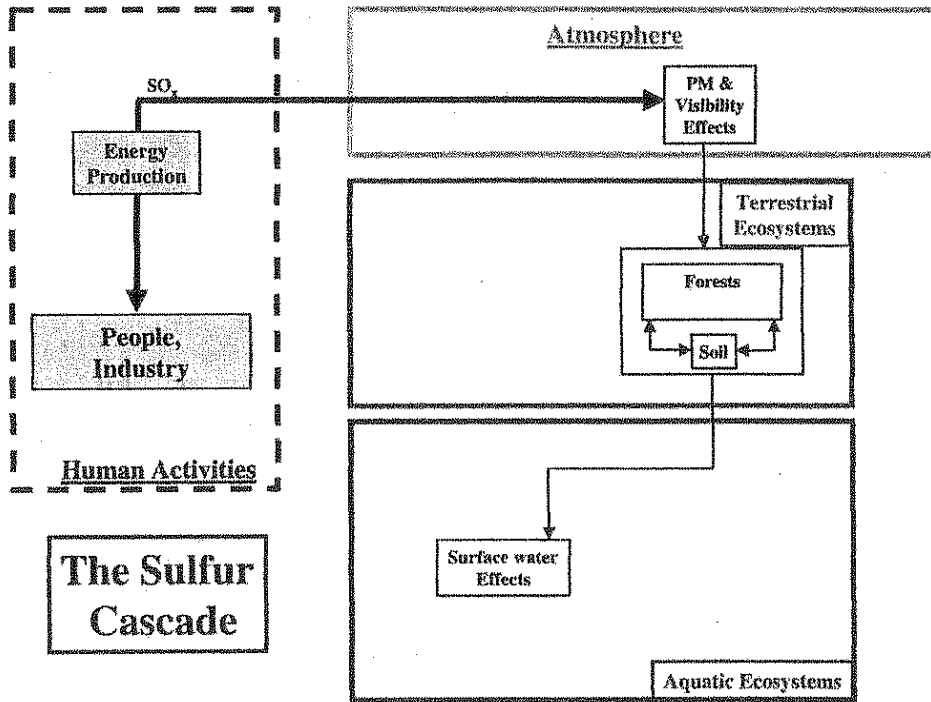


Figure 6. The sulphur and nitrogen cascades.

Table 1. Biogeochemical interactions for sulphur and nitrogen

**14.2a**

### Sulfur Biogeochemical Interactions

*Atmosphere to Forests to headwaters to Rivers to Coastal Waters*

Transfers	Interactions	Consequences
Atmosphere ↓ $(SO_x)$	Reacts with $NH_3$ to form PM2.5 aerosols  Reacts with $Ca^{++}$ & $Mg^{++}$ to form PM10 aerosols  Reacts with NaCl in coastal atmosphere	increases regional haze, changes radiation balance, and impacts human health  increases atmospheric removal rates  increases atmospheric removal rates
Forests ↓ $(SO_x)$	Absorbs to soil surfaces  removes cations from exchange surfaces  increases $Ca^{++}$ , $Mg^{++}$ , $K^+$ , $H^+$ , $Al^{3+}$ in soil solution	stores sulfate; delays surface water acidification  $H^+$ & $Al^{3+}$ acidify soil and decrease forest productivity  $Ca^{++}$ , $Mg^{++}$ , $K^+$ losses decrease forest productivity
Headwaters ↓ $(SO_4^-)$	Transfer of $H^+$ , $Al^{3+}$ to surface waters	Increase in acidity of surface waters; loss of alkalinity and biodiversity
Rivers ↓ $(SO_4^-)$		
Coastal waters ↓ $(SO_4^-)$		

### Nitrogen Biogeochemical Interactions

**14.2b**

*Atmosphere to Forests to headwaters to Rivers to Coastal Waters*

Transfers	Interactions	Consequences
Atmosphere ↓ $(NH_3, NH_4^+)$	$NH_3$ reacts w/ $H_2SO_4$ & $HNO_3$ to form PM2.5 aerosols  $NO$ reacts w/sunlight to form OH which increases $O_3$ $NO$ reacts w/sunlight to form OH which decreases $CO$ , $CH_4$  reacts w/NaCl in coastal atmosphere	increases regional haze, changes radiation balance, and impacts human health  increases GWP and decreases forest productivity  decreases GWP  increases Nr inputs to coastal ecosystems
Forests ↓ $(Nr)$	biota take up Nr  microbes convert $NH_4^+$ to $NO_3^-$ microbes produce $N_2O$ and $NO$  $NO_3^-$ increases in soil solution; cations also increases transfer to cations to headwaters	Increases forest productivity; transfers P to biomass from soil; sequesters C in biomass  Soil acidifies  Increases in tropospheric $O_3$ & GWP; decreases in stratospheric $O_3$  $H^+$ & $Al^{3+}$ acidify soil and decrease forest productivity  $Ca^{++}$ , $Mg^{++}$ , $K^+$ losses decrease forest productivity
Headwaters ↓ $(Nr)$	transfer of $H^+$ , $Al^{3+}$ to surface waters  microbes produce $N_2O$ and $NO$	increase in acidity of surface waters; loss of alkalinity and biodiversity  Increase in tropospheric $O_3$ & GWP; decreases in stratospheric $O_3$
Rivers ↓ $(Nr)$	microbes produce $N_2O$ and $NO$	Increases in tropospheric $O_3$ & GWP; decreases in stratospheric $O_3$
Coastal waters ↓ $(Nr)$	increase in productivity, hypoxia, and eutrophication microbes produce $N_2O$ and $NO$	increase in HAB, loss of biodiversity, etc.  Increases in tropospheric $O_3$ & GWP; decreases in stratospheric $O_3$