

2

Forcings and Feedbacks

Craig Idso (USA)

Tim Ball (Canada)

Contributing: *Tom Segalstad (Norway)*

Key Findings

Introduction

2.1 Carbon Dioxide

- 2.1.1 Correlation with Temperature
- 2.1.2 Atmospheric Residence Time of CO₂

2.2 Methane

- 2.2.1 Atmospheric Concentrations
- 2.2.2 Emissions to the Atmosphere
- 2.2.3 Extraction from the Atmosphere

2.3 Nitrous Oxide

2.4 Clouds

- 2.4.1 Albedo
- 2.4.2 Cloud Cover

2.5 Aerosols

- 2.5.1 Total Aerosol Effect
- 2.5.2 Biological
- 2.5.3 Non-Biological

2.6 Other Forcings and Feedbacks

- 2.6.1 Carbon Sequestration
- 2.6.2 Carbonyl Sulfide
- 2.6.3 Diffuse Light
- 2.6.4 Iodocompounds
- 2.6.5 Stratospheric Perturbations
- 2.6.6 Volcanism

Key Findings

The following points summarize the main findings of this chapter:

- Research published in peer-reviewed science journals indicates the model-derived temperature sensitivity of Earth accepted by the IPCC is too large. Negative feedbacks in the climate system reduce that sensitivity to values an order of magnitude smaller.
- Establishing the historic phase relationship

between atmospheric carbon dioxide and temperature is a necessary step toward understanding the physical relationship between CO₂ forcing and climate change. When such analyses are conducted, changes in CO₂ are frequently seen to *lag* changes in temperature by several hundred years.

- Many studies reveal a large *uncoupling* of temperature and CO₂ throughout portions of the historical record. Such findings contradict the IPCC's theory that changes in atmospheric CO₂

drive changes in temperature.

- Atmospheric methane observations over the past two decades reside far below the values projected by the IPCC in each of the four *Assessment Reports* it has released to date. The IPCC's temperature projections, which incorporate this inflated influence, should be revised downward to account for this discrepancy.
- Because agriculture accounts for almost half of nitrous oxide (N₂O) emissions in some countries, there is concern that enhanced plant growth due to CO₂ enrichment might increase the amount and warming effect of this greenhouse gas. But field research shows N₂O emissions will likely fall as CO₂ concentrations and temperatures rise, indicating this is actually another negative climate feedback.
- The IPCC has concluded “the net radiative feedback due to all cloud types is likely positive” (p. 9 of the Summary for Policy Makers, Second Order Draft of AR5, dated October 5, 2012). Contrary to that assessment, several studies indicate the net global effect of cloud feedbacks is a cooling, the magnitude of which may equal or exceed the warming projected from increasing greenhouse gases.
- The IPCC likely underestimates the total cooling effect of aerosols. Studies have found their radiative effect is comparable to or larger than the temperature forcing caused by all the increase in greenhouse gas concentrations recorded since preindustrial times.
- Higher temperatures are known to increase emissions of dimethyl sulfide (DMS) from the world's oceans, which increases the albedo of marine stratus clouds, which has a cooling effect. The IPCC characterizes this chain of events as “a rather weak aerosol-climate feedback at the global scale” (p. 21 of the Technical Summary, Second Order Draft of AR5, dated October 5, 2012), but many studies suggest otherwise.
- Several other important negative forcings and feedbacks exist in nature, about which little is known or acknowledged by the IPCC. Such forcings and feedbacks have been shown by multiple scientific studies to significantly

influence Earth's climate to a degree comparable to that of projected anthropogenic-induced global warming.

- The IPCC claims a positive feedback exists between climate and the carbon cycle on century to millennial time scales such that a warming climate will result in a loss of carbon storage. There is no empirical evidence to support such an assertion. Just the opposite appears to be the case, as global carbon uptake doubled over the past half-century.

Introduction

Scientists increasingly recognize climate is influenced not only by rising atmospheric carbon dioxide levels, but also other forcings and feedbacks. Even James Hansen—who in 1988 testified before a U.S. Senate Committee that “the global warming is now large enough that we can ascribe with a high degree of confidence a cause-and-effect relationship to the greenhouse effect”—was far more circumspect ten years later as lead author of a paper published in the *Proceedings of the National Academy of Sciences, U.S.A.* (Hansen *et al.*, 1998).

Hansen *et al.* examined the forcings of well-mixed greenhouse gases (CO₂, CH₄, N₂O, and CFCs), tropospheric ozone, stratospheric ozone, tropospheric aerosols, forced cloud changes, vegetation and other planetary surface alterations, solar variability, and volcanic aerosols. That examination revealed so many uncertainties in the forcings that the researchers concluded, “the forcings that drive long-term climate change are not known with an accuracy sufficient to define future climate change.” Nevertheless, the IPCC has expressed confidence in projections of future climate, saying the temperature sensitivity of Earth's climate system in response to a doubling of atmospheric CO₂ concentrations “is *likely* to be in the range 2°C to 4.5°C with a best estimate of about 3°C, and is *very unlikely* to be less than 1.5°C [italics in the original]” (IPCC, 2007).

The preceding chapter discussed a host of biases and discrepancies that lessen confidence in the ability of models to project future climate. In Chapter 2, we now review important forcings and feedbacks in the climate system. Failure of the models to account properly for the influence of these forcings and feedbacks further erodes confidence in the model projections of climate. Some of the forcings and feedbacks discussed in this chapter may have the potential to offset completely the radiative forcing

expected from rising atmospheric CO₂.

References

Hansen, J.E., Sato, M., Laci, A., Ruedy, R., Tegan, I., and Matthews, E. 1998. Climate forcings in the industrial era. *Proceedings of the National Academy of Sciences, U.S.A.* **95**: 12,753–12,758.

IPCC. 2007-I. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., and Miller, H.L. (Eds.). Cambridge University Press, Cambridge, UK.

2.1 Carbon Dioxide

When Earth was in its infancy, some 4.5 billion years ago, the atmosphere was predominantly composed of carbon dioxide. At that time, its CO₂ concentration, in terms of the units most commonly used today, would have been at something on the order of 1,000,000 ppm. Ever since, however, the CO₂ content of the air, in the mean, has been dropping.

By 500 million years ago, it is estimated the atmosphere's CO₂ concentration fell to a value of only ~20 times more than it is today, around 7,500 ppm. By 300 million years ago it had declined to close to the air's current CO₂ concentration of 400 ppm, after which it rose to four times that amount at 220 million years before present (Berner 1990, 1992, 1993, 1997; Kasting 1993). During the middle Eocene, some 43 million years ago, the atmospheric CO₂ concentration is estimated to have dropped to a mean value of approximately 385 ppm (Pearson and Palmer, 1999), and between 25 million and 9 million years ago, it is believed to have varied between 180 and 290 ppm (Pagani *et al.*, 1999). This last range is essentially the same range over which the air's CO₂ concentration oscillated during the 100,000-year glacial cycles of the past 420,000 years (Fischer *et al.*, 1999; Petit *et al.*, 1999). With the inception of the Industrial Revolution, the air's CO₂ content has surged upward, now above 400 ppm with the promise of significantly higher concentrations to come.

In addition to its variation over geologic time, the atmosphere's CO₂ concentration exhibits a seasonal variation. It declines when terrestrial vegetation awakens from the dormancy of winter and begins to grow in the spring, thereby extracting great quantities

of CO₂ from the air; and it rises in the fall and winter, when much of the biomass produced over the summer dies and decomposes, releasing great quantities of CO₂ back to the atmosphere.

The air's CO₂ content also varies spatially over the surface of Earth. Most spectacular in this regard are the local concentration enhancements observed over large metropolitan areas due to high levels of vehicular traffic and commercial activities. Idso *et al.* (1998a, b), for example, measured CO₂ concentrations near the center of Phoenix, Arizona that were 50 percent greater than those measured over surrounding rural areas. Significant enhancements of the air's CO₂ concentration also may be observed in the vicinity of burning coal seams and naturally occurring high-CO₂ springs.

Given the radiative properties of atmospheric CO₂, concerns have been expressed for some time that rising levels of CO₂ may lead to a significant warming of the planet. The IPCC supports such a hypothesis of future CO₂-induced climate change, and it also has concluded the modern rise of atmospheric CO₂ is affecting the climate *now*. Writing in its *Fifth Assessment Report* (FAR), the IPCC states

Globally, CO₂ is the strongest driver of climate change compared to other changes in the atmospheric composition, and changes in surface conditions [since the Industrial Revolution]. Its relative contribution has further increased since the 1980s and by far outweighs the contributions from natural drivers. CO₂ concentrations and rates of increase are unprecedented in the last 800,000 years and at least 20,000 years, respectively (Summary for Policy Makers, Second Order Draft of AR5, October 5, 2012, p. 7).

Research suggests, however, that the IPCC's view of atmospheric CO₂ as "the strongest driver of climate change" should be reconsidered if not outright rejected. The studies reviewed here find it is likely rising atmospheric CO₂ concentrations will have little impact on future climate.

References

Berner, R.A. 1990. Atmospheric carbon dioxide levels over Phanerozoic time. *Science* **249**: 1382–1386.

Berner, R.A. 1992. Paleo-CO₂ and climate. *Nature* **358**: 114.

Berner, R.A. 1993. Paleozoic atmospheric CO₂: Importance of solar radiation and plant evolution. *Science* **261**: 68–70.

Berner, R.A. 1997. The rise of plants and their effect on weathering and atmospheric CO₂. *Science* **276**: 544–546.

Fischer, H., Wahlen, M., Smith, J., Mastroianni, D., and Deck, B. 1999. Ice core records of atmospheric CO₂ around the last three glacial terminations. *Science* **283**: 1712–1714.

Idso, C.D., Idso, S.B., and Balling Jr., R.C. 1998a. The urban CO₂ dome of Phoenix, Arizona. *Physical Geography* **19**: 95–108.

Idso, C.D., Idso, S.B., Idso, K.E., Brooks, T., and Balling Jr., R.C. 1998b. Spatial and temporal characteristics of the urban CO₂ dome over Phoenix, Arizona. *Preprint volume of the 23rd Conference on Agricultural & Forest Meteorology, 13th Conference on Biometeorology and Aerobiology, and 2nd Urban Environment Symposium*, pp. 46–48. American Meteorological Society, Boston, MA.

Kasting, J.F. 1993. Earth's early atmosphere. *Science* **259**: 920–926.

Pagani, M., Authur, M.A., and Freeman, K.H. 1999. Miocene evolution of atmospheric carbon dioxide. *Paleoceanography* **14**: 273–292.

Pearson, P.N. and Palmer, M.R. 1999. Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* **284**: 1824–1826.

Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M. 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**: 429–436.

2.1.1 Correlation with Temperature

According to the IPCC, the global warming of the mid- to late twentieth century and early twenty-first century was caused primarily by the rise in atmospheric CO₂ concentration. This assertion is controversial (see Smagorinsky *et al.* (1982) and Idso (1982) for early pro/con positions on the issue), and with the retrieval and preliminary analysis of the first long ice core from Vostok, Antarctica—which provided a 150,000-year history of both surface air temperature and atmospheric CO₂ concentration—the debate became even more intense. The close associations of the ups and downs of atmospheric CO₂ and temperature evident during glacial terminations and inceptions in that record, as well as in subsequent records of even greater length, led many supporters of

the CO₂-induced global warming theory to assert those observations proved anthropogenic CO₂ emissions were responsible for twentieth century global warming.

This contention was challenged by Idso (1989), who wrote, “changes in atmospheric CO₂ content never precede changes in air temperature, when going from glacial to interglacial conditions; and when going from interglacial to glacial conditions, the change in CO₂ concentration actually lags the change in air temperature (Genthon *et al.*, 1987).” He thus concludes, “changes in CO₂ concentration cannot be claimed to be the cause of changes in air temperature, for the appropriate sequence of events (temperature change following CO₂ change) is not only never present, it is actually violated in [at least] half of the record (Idso, 1988).”

The following subsections expand on such research. Our understanding of the relationship between atmospheric CO₂ and temperature has improved in the years since, clearly demonstrating the lack of a causal link.

References

Genthon, C., Barnola, J.M., Raynaud, D., Lorius, C., Jouzel, J., Barkov, N.I., Korotkevich, Y.S., and Kotlyakov, V.M. 1987. Vostok ice core: Climatic response to CO₂ and orbital forcing changes over the last climatic cycle. *Nature* **329**: 414–418.

Idso, S.B. 1982. *Carbon Dioxide: Friend or Foe?* IBR Press, Tempe, AZ.

Idso, S.B. 1988. Carbon dioxide and climate in the Vostok ice core. *Atmospheric Environment* **22**: 2341–2342.

Idso, S.B. 1989. *Carbon Dioxide and Global Change: Earth in Transition*. IBR Press, Tempe, AZ.

Smagorinsky, J., Bryan, K., Manabe, S., Armi, L., Bretherton, F.P., Cess, R.D., Gates, W.L., Hansen, J., and Kutzbach, J.E. (Eds.). 1982. *Carbon Dioxide and Climate: A Second Assessment*. National Academy Press, Washington, DC.

2.1.1.1 Geologic Epochs

Rothman (2002) derived a 500-million-year history of the air's CO₂ content based on considerations related to the chemical weathering of rocks, volcanic and metamorphic degassing, and the burial of organic carbon, along with considerations of the isotopic content of organic carbon and strontium in marine

sedimentary rocks. This analysis suggests over the majority of the half-billion-year record, Earth's atmospheric CO₂ concentration fluctuated between values two to four times greater than those of today at a dominant period on the order of 100 million years (see Figure 2.1.1.1.1). Over the past 175 million years, however, the data depict a long-term decline in the air's CO₂ content.

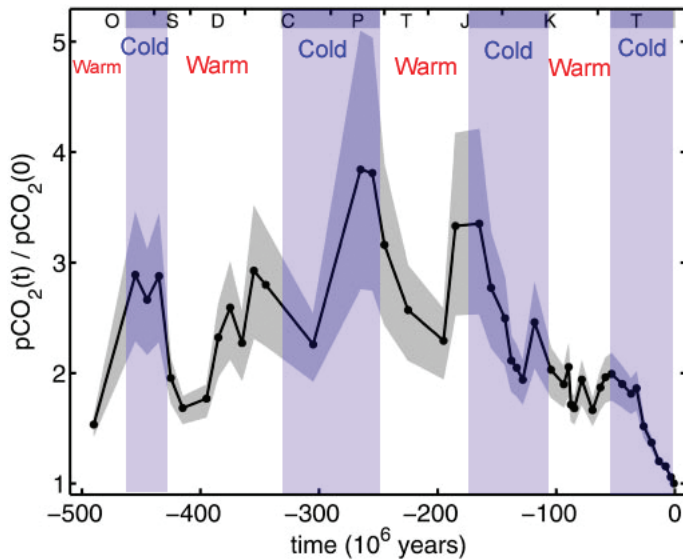


Figure 2.1.1.1.1. A 500-million-year record of the atmosphere's CO₂ concentration (relative to that of the present = 1) together with indications of periods of relative cold and warmth. Adapted from Rothman, D.H. 2002. Atmospheric carbon dioxide levels for the last 500 million years. *Proceedings of the National Academy of Sciences USA* **99**: 4167–4171.

With respect to the question of what correspondence might exist between ancient climates and atmospheric CO₂ concentrations, Rothman states the CO₂ history of Figure 2.1.1.1.1 “exhibits no systematic correspondence with the geologic record of climatic variations at tectonic time scales.” A visual examination of Rothman's plot of CO₂ and concomitant major cold and warm periods clearly indicates the three most striking peaks in the air's CO₂ concentration occur either totally or partially within periods of time when Earth's climate was relatively cool. Not only is there no support in these data for the claim that high atmospheric CO₂ concentrations tend to warm the planet, the data suggest there are times in Earth's history when just the opposite was the case.

Focusing on the middle Eocene climate of 43 million years ago, Pearson and Palmer (1999) report the planet then may have been as much as 5°C warmer than today, yet the mean CO₂ concentration of the atmosphere, as determined by pH data inferred from boron isotope composition in planktonic foraminifera, was only about 385 ppm.

Much the same was found by these authors one year later in an analysis of atmospheric CO₂ and temperature over the past 60 million years (Pearson and Palmer, 2000). Sixty million years before present (BP), the authors note, the atmosphere's CO₂ concentration, shown at the left in Figure 2.1.1.1.2, was approximately 3,600 ppm and the oxygen isotope ratio (at the right in the figure) was about 0.3 per mil (Figure 2.1.1.1.2, orange highlight). Thirteen million years later, the air's CO₂ concentration had dropped to 500 ppm, yet the oxygen isotope ratio dropped (implying a rise in temperature) to zero. That is just the opposite of what one would expect were CO₂ the driver of climate change.

Next comes a large spike in the air's CO₂ content, all the way up to a value of 2,400 ppm (Figure 2.1.1.1.2, blue). What does the oxygen isotope ratio do at that time? It rises slightly (implying the temperature falls slightly) to about 0.4 per mil, again just the opposite of what one would expect under the CO₂-induced global warming hypothesis.

After the spike in CO₂, the air's CO₂ concentration drops dramatically, declining to a minimum value of close to what it is today (Figure 2.1.1.1.2, purple). The oxygen isotope ratio barely changes at all, defying once again the assumption of the CO₂-induced global warming hypothesis.

Between this point and the break in the record at 40 million years BP, the air's CO₂ concentration rises again to approximately 1,000 ppm, and the oxygen isotope ratio rises slightly (implying a slight cooling) to 0.6 per mil (Figure 2.1.1.1.2, blue). Again, the common assumption of the CO₂-induced global warming hypothesis—that changes in atmospheric CO₂ drive changes in air temperature—fails.

Picking up the record at 24 million years BP, there are relatively tiny variations in atmospheric CO₂ concentration up to the present but large variations in oxygen isotope values, both up and down, again in clear contradiction of the CO₂-induced global warming hypothesis (Figure 2.1.1.1.2, yellow). The most interesting of these oxygen isotope changes is the dramatic increase (implying a dramatic cooling) over the most recent two million years, when the air's

Climate Change Reconsidered II

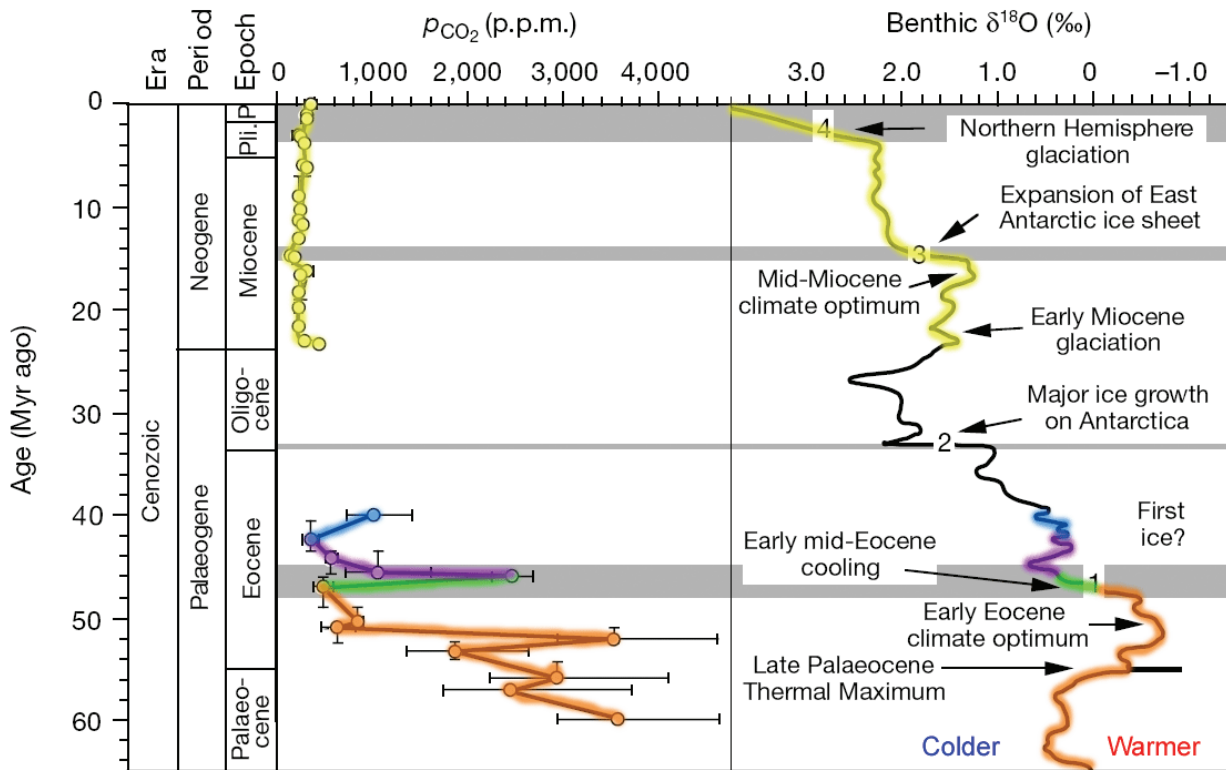


Figure 2.1.1.2. Atmospheric CO₂ concentration and proxy temperature over the past 60 million years. Adapted from Pearson, P.N. and Palmer, M.R. 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* 406: 695–699.

CO₂ concentration has risen slightly.

In another detailed review of Earth's thermal and CO₂ history, Pagani *et al.* (2005) examined these parameters over the most recent 50 million years. Their examination revealed essentially the same findings as the study of Pearson and Palmer (2000). As demonstrated in Figure 2.1.1.3, about 43 million years ago the atmosphere's CO₂ concentration was approximately 1,400 ppm and the oxygen isotope ratio (a proxy for temperature) was about 1.0 per mil. Then, over the next ten million years, the air's CO₂ concentration underwent three huge oscillations on the order of 1,000 ppm from peak to valley (Figure 2.1.1.3, red). In the first two oscillations, temperature appeared not to respond at all, exhibiting an uninterrupted slow decline represented by the steady upward trend in δ¹⁸O. Following the third rise in CO₂, however, temperatures seemed to respond, but in the opposite direction to what is expected according to the CO₂-induced global warming hypothesis—the rise in CO₂ was followed by the sharpest drop in temperature (rise in δ¹⁸O) of the entire record.

Following this large drop in temperature between 34 and 33 million years before present (Ma BP), the oxygen isotope ratio hovered around a value of 2.7 per mil from about 33 to 26 Ma BP, indicating little change in temperature over that period. The corresponding CO₂ concentration (Figure 2.1.1.3, green) was anything but constant, experiencing about a 500 ppm increase around 32 Ma BP, after which it dropped a full 1,000 ppm over the next two million years, only to rise again by a few hundred ppm, repeatedly defying the common causal assumption of the CO₂-induced global warming hypothesis.

Around 26 Ma BP, the oxygen isotope ratio dropped to about 1.4 per mil (implying a significant rise in temperature), during which time the air's CO₂ content (Figure 2.1.1.3, yellow) declined, once again the opposite of what one would expect were CO₂ driving climate change. Then, from 24 Ma BP to the end of the record at 5 Ma BP, there were relatively tiny variations in the atmosphere's CO₂ content (Figure 2.1.1.3, blue) but large variations in oxygen isotope values, both up and down.

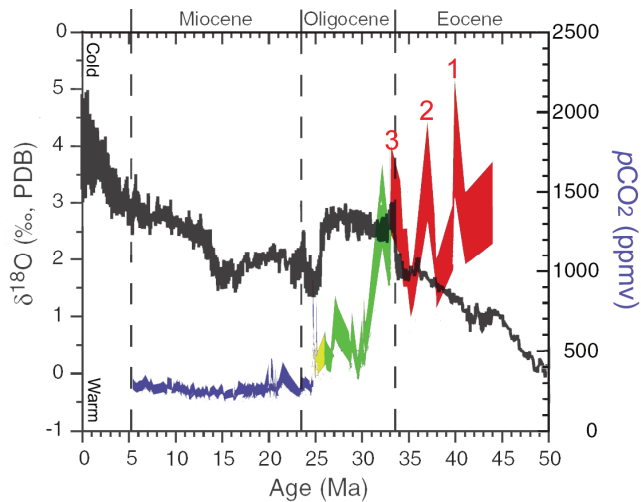


Figure 2.1.1.1.3. Atmospheric CO₂ concentration (multicolored line) and proxy temperature (black line) over the past 50 million years. Adapted from Pagani, M., Zachos, J.C., Freeman, K.H., Tipple, B., and Bohaty, S. 2005. Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Science* **309**: 600–603.

These observations, according to Pagani *et al.* (2005), “argue for a decoupling between global climate and CO₂” and stand in clear contradiction of the CO₂-induced global warming hypothesis.

Pagani *et al.* (1999), working with sediment cores from three deep-sea drilling sites, also found the air’s CO₂ concentration to be uniformly low (180 to 290 ppm) throughout the early to late Miocene (25 to 9 million years ago), at a time when deep-water and high-latitude surface water temperatures were as much as 6°C warmer than today. They stated their finding “appears in conflict with greenhouse theories of climate change.” In addition, they noted the air’s CO₂ concentration seemed to rise after the expansion of the East Antarctic Ice Sheet, also in conflict with greenhouse theories of climate change.

Considered in their entirety, the results of these studies present a truly chaotic picture with respect to any possible effect variations in atmospheric CO₂ concentration may have on global temperature. The IPCC has neglected to adequately address the inconsistency between these real-world observations and the model-based projections in their reports.

References

- Pagani, M., Authur, M.A., and Freeman, K.H. 1999. Miocene evolution of atmospheric carbon dioxide. *Paleoceanography* **14**: 273–292.
- Pagani, M., Zachos, J.C., Freeman, K.H., Tipple, B., and Bohaty, S. 2005. Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Science* **309**: 600–603.
- Pearson, P.N. and Palmer, M.R. 1999. Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* **284**: 1824–1826.
- Pearson, P.N. and Palmer, M.R. 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* **406**: 695–699.
- Rothman, D.H. 2002. Atmospheric carbon dioxide levels for the last 500 million years. *Proceedings of the National Academy of Sciences USA* **99**: 4167–4171.

2.1.1.2 Pleistocene Glacial/Interglacial Cycles

Several studies have shed additional light on the relationship between CO₂ and temperature as manifested throughout the past 800,000 years of dramatic glacial-interglacial climate cycles.

Fischer *et al.* (1999), for example, examined trends of atmospheric CO₂ and air temperature derived from Antarctic ice core data extending back 250,000 years. Over this period, the three most dramatic warming events experienced on Earth were the terminations of the last three ice ages; for each of these climatic transitions, Earth’s air temperature always rose well in advance of the increase in atmospheric CO₂. In each transition, the air’s CO₂ content did not begin to rise until 400 to 1,000 years after the planet began to warm.

Another team to study the CO₂-temperature relationship was that of Petit *et al.* (1999), who discovered during all glacial inception of the past half-million years, temperature always dropped well before the decline in the air’s CO₂ concentration. They conclude their data indicate “the CO₂ decrease lags the temperature decrease by several thousand years.” Likewise, Mudelsee (2001) determined variations in atmospheric CO₂ concentration lagged behind variations in air temperature by 1,300 to 5,000 years over the past 420,000 years. In addition, during certain climatic transitions characterized by rapid warmings of several degrees, which were followed by slower coolings that returned the climate to

essentially full glacial conditions, Stauffer *et al.* (1998) observe the atmospheric CO₂ concentration derived from ice core records typically varied by less than 10 ppm. They, too, consider the CO₂ perturbations to have been caused by the changes in climate, rather than vice versa.

Many other studies have demonstrated this reverse coupling of atmospheric CO₂ and temperature (Cheddadi *et al.*, 1998; Gagan *et al.*, 1998; Raymo *et al.*, 1998), where temperature is the independent variable that appears to induce changes in CO₂. In addition, Steig (1999) noted cases of the inverse coupling of the two parameters, showing between 7,000 and 5,000 years ago, atmospheric CO₂ concentrations increased by just over 10 ppm at a time when temperatures in both hemispheres cooled.

Caillon *et al.* (2003) measured the isotopic composition of argon—specifically, $\delta^{40}\text{Ar}$, which they argued “can be taken as a climate proxy, thus providing constraints about the timing of CO₂ and climate change”—in air bubbles in the Vostok ice core over the period that comprises what is called Glacial Termination III, about 240,000 years ago. The results of their meticulous analysis led them to conclude “the CO₂ increase lagged Antarctic deglacial warming by 800 ± 200 years” (see Figure 2.1.1.2.1)

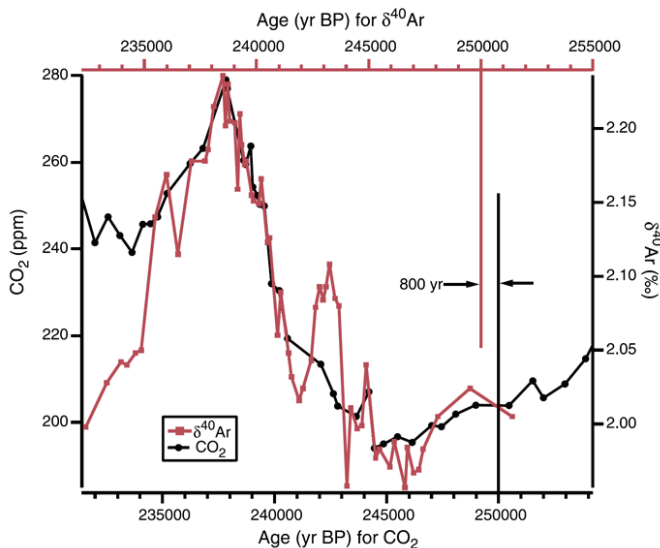


Figure 2.1.1.2.1. Isotopic argon and CO₂ values from Vostok Ice core air bubbles. Note the 800 year offset between the top ($\delta^{40}\text{Ar}$) and bottom (CO₂) axes for Age (yr BP). Reprinted with permission from Caillon, N., Severinghaus, J.P., Jouzel, J., Barnola, J.-M., Kang, J., and Lipenkov, V.Y. 2003. Timing of atmospheric CO₂ and Antarctic temperature changes across Termination III. *Science* **299**: 1728–1731.

This finding, in the words of Caillon *et al.*, “confirms that CO₂ is not the forcing that initially drives the climatic system during a deglaciation.” Nevertheless, they and others continue to hold the view that the subsequent increase in atmospheric CO₂—believed to be due to warming-induced CO₂ outgassing from the world’s oceans—serves to amplify the warming caused by whatever prompts the temperature to rise in the first place. This supposition is founded on unproven assumptions about the strength of CO₂-induced warming and is applied without any regard for biologically induced negative climate feedbacks that may occur in response to atmospheric CO₂ enrichment, as discussed later in this chapter. Moreover, there is no way to objectively determine the strength of the proposed amplification from the ice core data.

In light of these observations, the role of CO₂ as a primary driver of climate change on Earth would appear to be disproved; the CO₂ warming amplification hypothesis appears unlikely as well.

Another departure from standard greenhouse effect theory occurred over the 17,000-year period following the penultimate deglaciation, when the air’s CO₂ content was essentially constant but air temperature declined to values characteristic of glacial times (see Figure 2.1.1.2.2). An even greater contradiction of IPCC-based thinking occurred immediately thereafter, when CO₂ finally began to fall but temperature began to rise.

Also discovering an inverse greenhouse gas/temperature relationship were Indermuhle *et al.* (1999), who determined after the termination of the last great ice age the CO₂ content of the air gradually rose by approximately 25 ppm in almost linear fashion between 8,200 and 1,200 years ago, over a period of slow but steady decline in global air temperature. A year later, working with a high-resolution temperature and atmospheric CO₂ record spanning the period 60 to 20 thousand years ago, Indermuhle *et al.* (2000) discovered four distinct periods when temperatures rose by approximately 2°C and CO₂ rose by about 20 ppm. One of the statistical tests they performed on the data suggests the shifts in the air’s CO₂ content during these intervals *followed* the shifts in air temperature by approximately 900 years, and a second statistical test yielded a mean CO₂ lag time of 1,200 years.

Another pertinent study comes from Siegenthaler *et al.* (2005), who analyzed CO₂ and temperature proxy (δD , the ratio of deuterium to hydrogen) data derived from an ice core in Antarctica. Results of

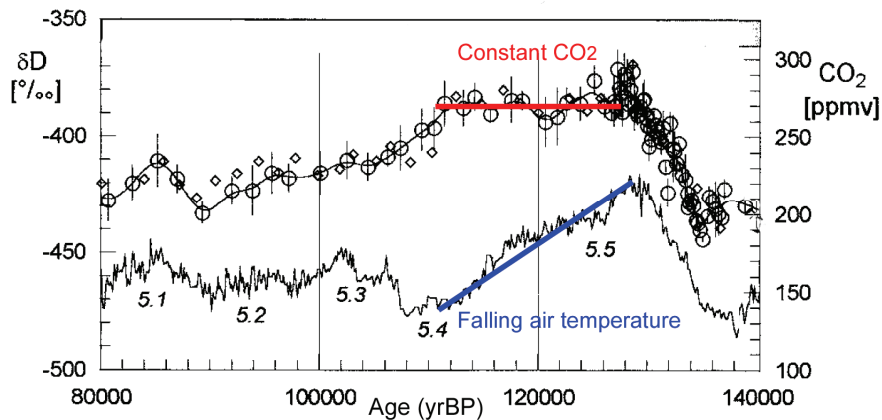


Figure 2.1.1.2.2. Atmospheric CO₂ and proxy temperature. Adapted from Fischer, H., Wahlen, M., Smith, J., Mastroianni, D., and Deck, B. 1999. Ice core records of atmospheric CO₂ around the last three glacial terminations. *Science* **283**: 1712–1714.

their analysis revealed a coupling of Antarctic temperature and CO₂ in which they obtained the best correlation between CO₂ and temperature “for a lag of CO₂ of 1900 years.” Over the course of glacial terminations V to VII, they observe “the highest correlation of CO₂ and deuterium, with use of a 20-ky window for each termination, yields a lag of CO₂ to deuterium of 800, 1600, and 2800 years, respectively.” In addition, they note “this value is consistent with estimates based on data from the past four glacial cycles,” citing the work of Fischer *et al.* (1999), Monnin *et al.* (2001), and Caillon *et al.* (2003). This too confirms temperature leads this tightly coupled relationship, while CO₂ lags, possibly providing only a fraction (which could well be miniscule) of the total glacial-to-interglacial temperature change.

Such observations do little to inspire confidence in projections that the CO₂ produced by the burning of fossil fuels will lead to significant global warming, where predicted warmings in some scenarios rival those experienced in glacial-to-interglacial transitions. Nevertheless, Siegenthaler *et al.* maintained the new findings “do not cast doubt ... on the importance of CO₂ as a key amplification factor of the large observed temperature variations of glacial cycles.” However, it should be noted that when temperature leads CO₂ by thousands of years, during both glacial terminations and inception (Genthon *et al.*, 1987; Fischer *et al.*, 1999; Petit *et al.*, 1999; Indermuhle *et al.*, 2000; Monnin *et al.*, 2001; Mudelsee, 2001; Caillon *et al.*, 2003), there is ample reason to conclude CO₂ plays but a minor role in enhancing

temperature changes that are clearly induced by something else.

Thomas Stocker (the second and corresponding author of the Siegenthaler *et al.* paper) was quoted by the BBC’s Richard Black (BBC News, 24 Nov 2005) as saying the relationship they observed between δD and CO₂ is “a very strong indication of the important role of CO₂ in climate regulation.” A more plausible statement, however, would be that the relationship is “a very strong indication of the important role of climate in CO₂ regulation.” As evidenced by 650,000 years of real-world data, wherever temperature went over this period, CO₂ (mostly)

followed.

Still other papers have chipped away at the IPCC-led hypothesis that atmospheric CO₂ is and will be the dominant driver of climate change both now and in the future.

Kirchner (2002) present a pair of interesting graphs, the first of which is a plot of temperature vs. atmospheric CO₂ concentration he derived from 400,000 years of Vostok ice core data, adapted as Figure 2.1.1.2.3. The plot in this graphic displays a fair amount of scatter but seems to suggest the existence of a crude linear relationship between the two variables, which is what Kirchner implied by drawing a best-fit linear regression line through the data (the solid dark red line).

However, the data may be equally well characterized as a two-dimensional distribution, such as that shown in Figure 2.1.1.2.4. The apex is anchored at the point defined by the coldest temperature and lowest CO₂ concentration of the data set. Rather than a crude linear relationship between temperature and CO₂, this “slice of pie” characterization may be preferred, for when the current temperature–CO₂ state of the world is plotted, it falls far below the linear relationship derived by Kirchner but right on the lower side of the piece of pie we would place over the data.

With respect to the meaning of the plotted relationship, Kirchner notes “despite greenhouse gas concentrations that are unprecedented in recent Earth

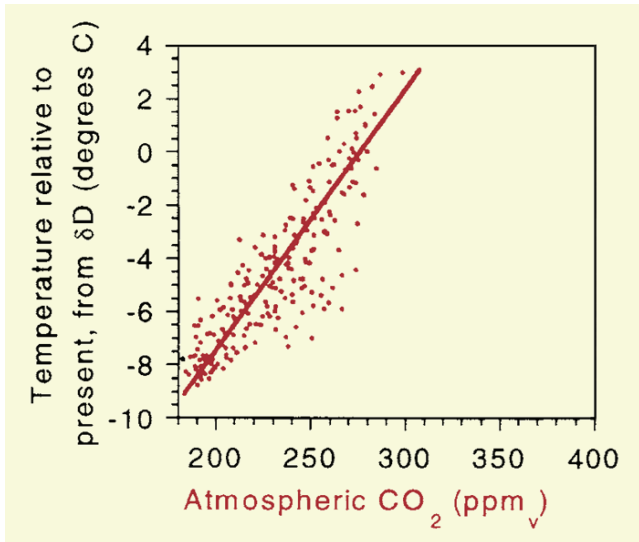


Figure 2.1.1.2.3. Scatter-plot of Vostok ice core-derived atmospheric CO₂ and proxy temperature data over the last 400,000 years. Adapted from Kirchner, J.W. 2002. *The Gaia Hypothesis: fact, theory, and wishful thinking. Climatic Change 52: 391–408.*

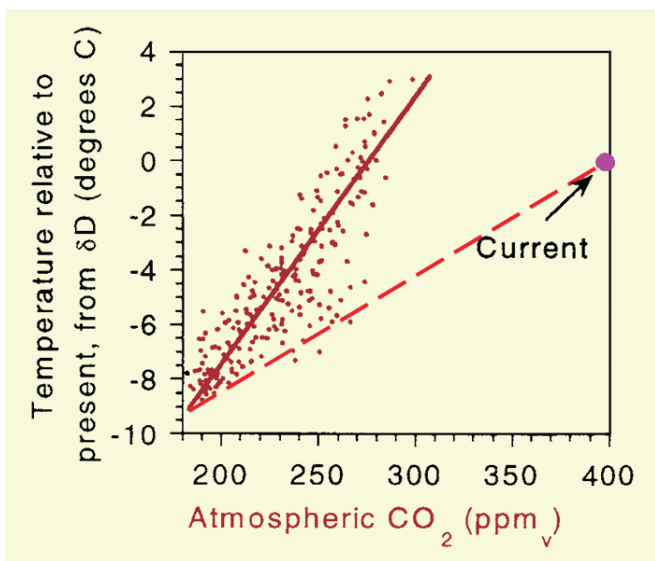


Figure 2.1.1.2.4. Adapted from Kirchner 2002, same as Figure 2.1.1.2.3, but with the current CO₂ concentration of the atmosphere and the dashed red line added.

history, global temperatures have not (yet) risen nearly as much as the correlations in the ice core records would indicate that they could.” He pointed out, for example, that his representation of the ice core data suggests “for the current composition of the atmosphere, current temperatures are anomalously cool by many degrees.” Kirchner’s work suggests the

anomaly is approximately 10°C, significantly more than the maximum warming currently predicted by the Intergovernmental Panel on Climate Change to accompany a doubling of the air’s CO₂ content. One might also say the data as depicted in Figure 2.1.1.2.4 suggests Earth’s current temperature is not “anomalous” at all.

Kirchner’s second graph (not shown), a plot of temperature vs. atmospheric methane concentration, is also of interest. The relationship described by the data is absolutely and unquestionably linear and exhibits very little scatter. When used to compute what the temperature of today’s Earth “should be,” on the basis of the current atmospheric methane concentration, the result is fully 40°C more than the planet’s current temperature. This graphic too provides no basis for characterizing Earth’s current temperature as anomalous. Instead, in both the case of methane and of CO₂, it is the atmospheric greenhouse gas concentration that is anomalous.

Since Kirchner’s temperature vs. atmospheric methane concentration plot reveals such a tight coupling of temperature and methane, but the relationship between the two is such that methane cannot be the determinant of temperature, it must be concluded that temperature is the determinant of atmospheric methane concentration ... as long as humanity is not a part of the picture.

For nearly all of the past 400,000 years, this restriction has applied. As humanity’s population and impact on the biosphere have grown over the past few centuries, however, this relationship has been outgrown, causing the atmosphere’s methane concentration to rise to levels far above anything experienced throughout the history of the Vostok ice core. But Earth’s temperature has not responded to the anthropogenic-induced methane increase and is currently about 3°C cooler than it was during the peak warmth of the prior 400,000 years (Figure 2.1.1.2.5), when the air’s methane concentration was only 40 percent of what it is today.

A similar conclusion can be reached about temperature and atmospheric CO₂ concentration: It is temperature change that elicits changes in the air’s CO₂ content and not vice versa, although the scatter in Kirchner’s temperature vs. atmospheric CO₂ concentration plot is sufficient to allow for significant independent movement by both of these parameters. The conclusion that atmospheric CO₂ concentration is not a major determinant of Earth’s temperature is supported by the fact that Earth is currently about 3°C cooler than it was during the peak warmth of the prior

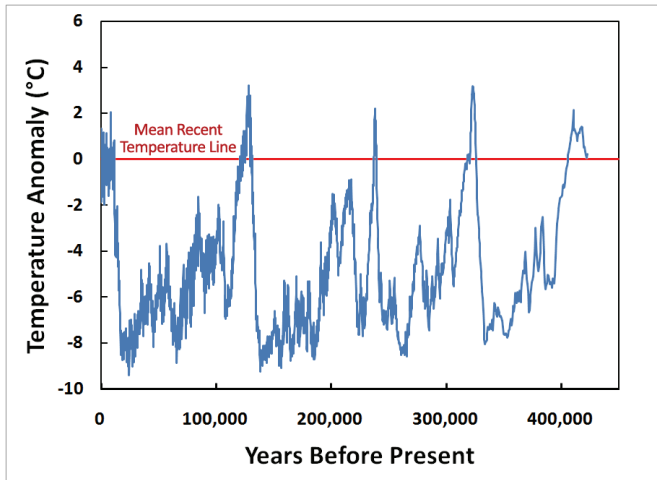


Figure 2.1.1.2.5. Proxy temperatures going back 420,000 years, based on tabular data presented in Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M. 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**: 429–436.

four interglacials, when the air’s CO₂ content was only about 75 percent of what it is today.

When considering the above observations together, the findings are remarkable. Since the occurrence of the peak temperature of the past 400,000 years, the concentrations of the two most powerful greenhouse gases in the atmosphere (exclusive of water vapor)—CO₂ and methane—have increased by approximately a third and 2.5-fold, respectively, yet Earth’s temperature has fallen by 3°C. Clearly, CO₂ and methane are not the important drivers of climate change the IPCC and others consider them to be.

References

Caillon, N., Severinghaus, J.P., Jouzel, J., Barnola, J.-M., Kang, J., and Lipenkov, V.Y. 2003. Timing of atmospheric CO₂ and Antarctic temperature changes across Termination III. *Science* **299**: 1728–1731.

Cheddadi, R., Lamb, H.F., Guiot, J., and van der Kaars, S. 1998. Holocene climatic change in Morocco: a quantitative reconstruction from pollen data. *Climate Dynamics* **14**: 883–890.

Fischer, H., Wahlen, M., Smith, J., Mastroianni, D., and Deck, B. 1999. Ice core records of atmospheric CO₂ around

the last three glacial terminations. *Science* **283**: 1712–1714.

Gagan, M.K., Ayliffe, L.K., Hopley, D., Cali, J.A., Mortimer, G.E., Chappell, J., McCulloch, M.T., and Head, M.J. 1998. Temperature and surface-ocean water balance of the mid-Holocene tropical western Pacific. *Science* **279**: 1014–1017.

Genthon, C., Barnola, J.M., Raynaud, D., Lorius, C., Jouzel, J., Barkov, N.I., Korotkevich, Y.S., and Kotlyakov, V.M. 1987. Vostok ice core: Climatic response to CO₂ and orbital forcing changes over the last climatic cycle. *Nature* **329**: 414–418.

Indermuhle, A., Monnin, E., Stauffer, B., and Stocker, T.F. 2000. Atmospheric CO₂ concentration from 60 to 20 kyr BP from the Taylor Dome ice core, Antarctica. *Geophysical Research Letters* **27**: 735–738.

Indermuhle, A., Stocker, T.F., Joos, F., Fischer, H., Smith, H.J., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R., and Stauffer, B. 1999. Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature* **398**: 121–126.

Kirchner, J.W. 2002. The Gaia Hypothesis: fact, theory, and wishful thinking. *Climatic Change* **52**: 391–408.

Monnin, E., Indermuhle, A., Dällenbach, A., Flückiger, J., Stauffer, B., Stocker, T.F., Raynaud, D., and Barnola, J.-M. 2001. Atmospheric CO₂ concentrations over the last glacial termination. *Nature* **291**: 112–114.

Mudelsee, M. 2001. The phase relations among atmospheric CO₂ content, temperature and global ice volume over the past 420 ka. *Quaternary Science Reviews* **20**: 583–589.

Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M. 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**: 429–436.

Raymo, M.E., Ganley, K., Carter, S., Oppo, D.W., and McManus, J. 1998. Millennial-scale climate instability during the early Pleistocene epoch. *Nature* **392**: 699–702.

Siegenthaler, U., Stocker, T., Monnin, E., Luthi, D., Schwander, J., Stauffer, B., Raynaud, D., Barnola, J.-M., Fischer, H., Masson-Delmotte, V., and Jouzel, J. 2005. Stable carbon cycle-climate relationship during the late Pleistocene. *Science* **310**: 1313–1317.

Stauffer, B., Blunier, T., Dällenbach, A., Indermuhle, A., Schwander, J., Stocker, T.F., Tschumi, J., Chappellaz, J., Raynaud, D., Hammer, C.U., and Clausen, H.B. 1998.

Atmospheric CO₂ concentration and millennial-scale climate change during the last glacial period. *Nature* **392**: 59–62.

Steig, E.J. 1999. Mid-Holocene climate change. *Science* **286**: 1485–1487.

2.1.1.3 Holocene

Several researchers have examined the relationship between atmospheric CO₂ and temperature during the transition from the glacial conditions of the last ice age to the interglacial conditions of the present Holocene. As in the studies examined in the preceding two sections, their data reveal a number of problems with the IPCC-based hypothesis that rising CO₂ will cause unprecedented warming of the planet.

Focusing on the period between 22,000 and 9,000 years ago, Monnin *et al.* (2001) found the start of the CO₂ increase lagged the start of the temperature increase by 800 years. An analysis of this most recent glacial/interglacial transition by Yokoyama *et al.* (2000), which also has been discussed by Clark and Mix (2000), revealed a rapid rise in sea level, caused by the melting of land-based ice that began approximately 19,000 years ago, preceded the post-glacial rise in atmospheric CO₂ concentration by about 3,000 years. Only after a couple thousand years did CO₂ concentration catch up with the sea level rise.

Stott *et al.* (2007) state establishing “the exact phasing of events during glacial terminations” is “a necessary step in understanding the physical relation between CO₂ forcing and climate change.” Working with a marine sediment core from the western tropical Pacific Ocean, Stott *et al.* set out to determine “the chronology of high- and low-latitude climate change at the last glacial termination by radiocarbon dating benthic and planktonic foraminiferal stable isotope and magnesium/calcium records.” This provided a temporal resolution of 25 to 50 years for each sample over the period stretching from 10 thousand to 22 thousand years before the present. The research team found “deep-sea temperatures warmed by ~2°C between 19 and 17 thousand years before the present, leading the rise in atmospheric CO₂ and tropical-surface-ocean warming by ~1000 years.”

Stott *et al.* conclude the cause of the deglacial deep-water warming “does not lie within the tropics, nor can its early onset between 19 and 17 thousand years before the present be attributed to CO₂ forcing.” And since the rate of deep-water warming did not increase after the start of the increase in the atmosphere’s CO₂ concentration (if anything, it

declined), there is no compelling reason to infer the deglacial increase in the air’s CO₂ content had anything to do with the warming that led to the ultimate development of the current interglacial.

Working in Africa, Tierney *et al.* (2008) report the initiation of the deglacial warming in southeast Africa “is consistent with rising temperatures at ~20,000 years B.P. in Antarctica,” but they add the deglacial warming “leads the deglacial CO₂ rise recorded in Antarctic ice cores by about 3,000 years.” They describe this as “a difference that is outside the chronological errors of the ice core and the lake surface temperature records.” Tierney *et al.* conclude “increasing greenhouse gas concentrations are therefore not responsible for the initial transmission of warming from the high latitudes to the southeast African tropics.”

McElwain *et al.* (2002) derived high-resolution (approximately 20- to 37-year accuracy) atmospheric CO₂ histories from stomatal frequencies measured on subfossil leaves of *Dryas integrifolia*, *Picea mariana*, *P. glauca*, and *Larix laricina* obtained from sediment cores extracted from two sites in New Brunswick, Canada that contained material spanning the period from approximately 13,000 to 10,500 years ago. Their data reveal an abrupt drop in atmospheric CO₂ concentration of approximately 75 ppm at the onset of the Younger Dryas cold event. This drop in CO₂ lagged the event-defining temperature drop by approximately 130 years. Then, at the end of the Younger Dryas, there was a rapid rise in atmospheric CO₂ concentration that was (within the time-resolution error bounds of the data) essentially coeval with the increase in temperature that brought an end to the Younger Dryas and initiated the Holocene. In absolute terms, the pre-Younger Dryas CO₂ concentration was approximately 300 to 320 ppm, the concentration during the Younger Dryas interval approximately 235 ppm, and the concentration immediately afterwards in the range of 285 to 300 ppm.

Comparing their results with atmospheric CO₂ concentrations derived from polar ice core data, the authors note the best such data available had time resolutions of approximately 200 to 550 years. Degrading (averaging) their data accordingly, they were able to closely match the ice core results, a steady increase in atmospheric CO₂ concentration from the beginning to the end of the Younger Dryas interval. But the ice core data could not mimic the much-finer-scale story told by their data, including the dramatic decline in atmospheric CO₂

concentration at the inception of the Younger Dryas and the dramatic increase in the air's CO₂ content at the conclusion of the cold event.

That the decline in atmospheric CO₂ concentration at the onset of the Younger Dryas lagged the decline in temperature by some 130 years clearly demonstrates the change in the air's CO₂ content did not cause the change in temperature, but that the temperature drop—or whatever caused it—was responsible for the decline in CO₂ concentration. There is little reason to believe the same was not true at the end of the Younger Dryas, although the authors' data resolution was not good enough to explicitly demonstrate that fact.

Other studies have demonstrated a complete uncoupling of CO₂ and temperature (Cheddadi *et al.*, 1998; Gagan *et al.*, 1998; Raymo *et al.*, 1998). Indermuhle *et al.* (1999) demonstrated after the termination of the last great ice age, the CO₂ content of the air gradually rose by approximately 25 ppm in almost linear fashion between 8,200 and 1,200 years ago, during a period of time that manifested a slow but steady decline in mean global air temperature. Steig (1999) found between 7,000 and 5,000 years ago, atmospheric CO₂ concentrations increased by just over 10 ppm while temperatures in both hemispheres cooled. These results are just the opposite of what would be expected if changes in

atmospheric CO₂ drove climate change as claimed by the CO₂ greenhouse effect theory.

The case for an uncoupling of CO₂ and temperature is driven home further by an examination of the long-term temperature record produced by the Greenland Ice Sheet Project (GISP2), depicted in Figure 2.1.1.3.1 as plotted by Drake (2012) and based on data reported by Alley (2004).

It is most interesting to note that over its first 4,800 years (fully 96 percent of the record), when temperature varied widely, the atmosphere's CO₂ concentration was extremely stable, between about 275 and 285 ppm, whereas over the past 200 years (the remaining 4 percent of the record), when the temperature shows but a fraction of a degree warming, the air's CO₂ concentration rose by more than an extra 100 ppm.

Although almost any long-term temperature history could be used to make this point, it is clear from this simple example that the air's CO₂ content is not a major driver of Earth's temperature. It may not even be a minor driver, and it may have even less of an effect on climate in the not-so-distant future as the population of the world reaches a peak.

Consider, for example, the work of Idso (1989), who derived a predictive relationship based on world population and atmospheric CO₂ concentration data, updated and presented here as Figure 2.1.1.3.2. The

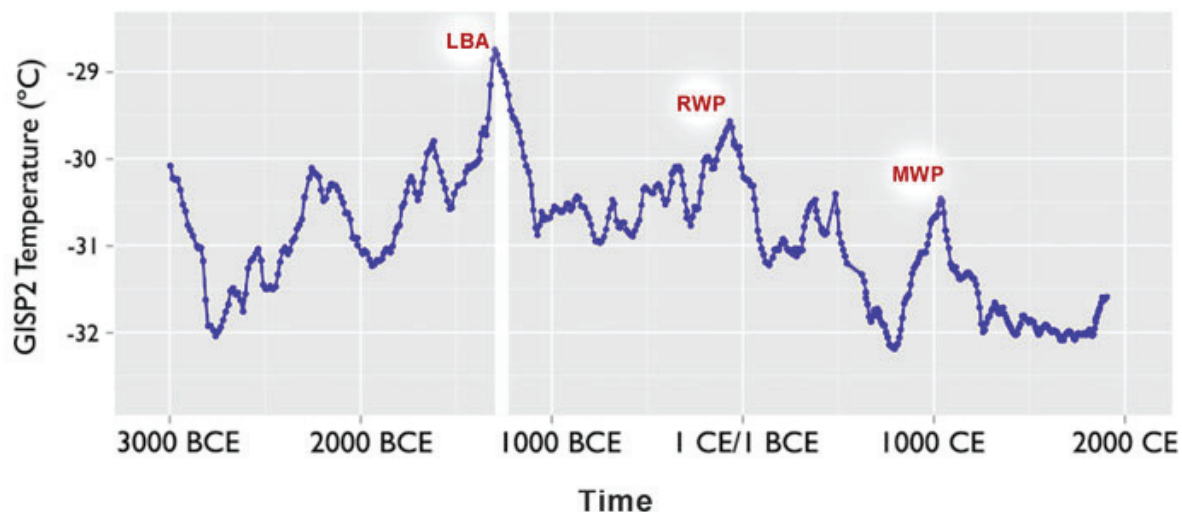


Figure 2.1.1.3.1. The past 5,000 years of the GISP2 temperature history of the Greenland Ice Sheet with general locations of the Late Bronze Age (LBA), the Roman Warm Period (RWP), and the Medieval Warm Period (MWP) indicated. Adapted from Drake, B.L. 2012. The influence of climatic change on the Late Bronze Age Collapse and the Greek Dark Ages. *Journal of Archaeological Science* 39: 1862–1870.

figure depicts a linear relationship between global population (an alternative representation of CO₂ emissions) and atmospheric CO₂ concentration, a relationship that has endured over time in spite of ongoing and sometimes rapid changes in energy sources and the energy mix as society has industrialized and modernized. That this relationship has remained steady over time is remarkable.

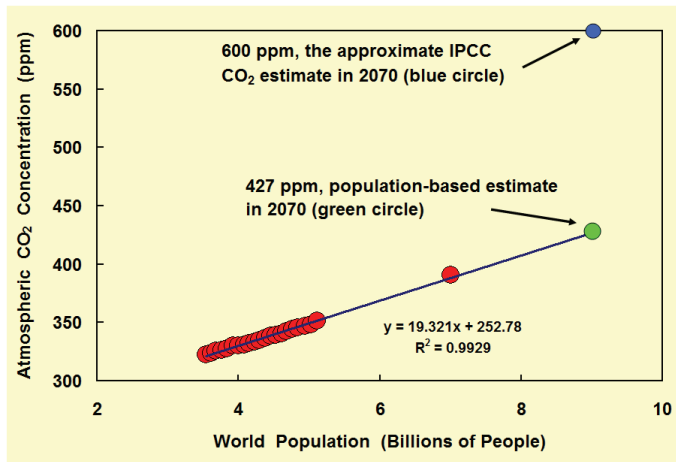


Figure 2.1.1.3.2. Atmospheric CO₂ concentration vs. world population based on data presented by Idso (1989), updated to 2011, the year Earth's population reached the seven billion mark. The linear regression line has been extrapolated to a population of nine billion persons. The IPCC-based projected CO₂ concentration in 2050 is also presented (blue circle). See Idso, S.B. 1989. *Carbon Dioxide and Global Change: Earth in Transition*. Tempe AZ: IBR Press.

The original linear relationship has been extended here to a world population of nine billion people, which is where Lutz *et al.* (2001) calculate the population of the planet will peak in the year 2070, according to the median result of their several projections. At this population, using the linear regression relationship depicted, an atmospheric CO₂ concentration of 427 ppm is calculated. Beyond this point in time, the peak in global population, the relationship suggests atmospheric CO₂ levels may level off and begin to drop as the planet's population stabilizes and/or begins to decline.

Such a conclusion is dramatically at odds with the IPCC projections, which predict far greater CO₂ concentrations for far greater times to come, but is likely far more robust. The equation derived in the above figure, for example, is based on data since

1650. For the past three-and-a-half centuries it has performed marvelously, including over the period of dramatic global population growth, during large changes in both the global source and mix of energy, and over the period of rapid growth in anthropogenic CO₂ emissions that occurred after World War II, suggesting this relationship will not suddenly cease to apply over the next six decades when the planet's population peaks. Although there may be slight variations ahead, they likely will be so small as to be essentially insignificant.

References

Alley, R.B. 2004. *GISP2 Ice Core Temperature and Accumulation Data*. In: Data Contribution Series #2004-013. NOAA/NGDC Paleoclimatology Program. IGBP PAGES World Data Center for Paleoclimatology, Boulder, Colorado, USA.

Cheddadi, R., Lamb, H.F., Guiot, J., and van der Kaars, S. 1998. Holocene climatic change in Morocco: a quantitative reconstruction from pollen data. *Climate Dynamics* **14**: 883–890.

Clark, P.U. and Mix, A.C. 2000. Ice sheets by volume. *Nature* **406**: 689–690.

Drake, B.L. 2012. The influence of climatic change on the Late Bronze Age Collapse and the Greek Dark Ages. *Journal of Archaeological Science* **39**: 1862–1870.

Gagan, M.K., Ayliffe, L.K., Hopley, D., Cali, J.A., Mortimer, G.E., Chappell, J., McCulloch, M.T., and Head, M.J. 1998. Temperature and surface-ocean water balance of the mid-Holocene tropical western Pacific. *Science* **279**: 1014–1017.

Idso, S.B. 1989. *Carbon Dioxide and Global Change: Earth in Transition*. Tempe AZ: IBR Press.

Indermuhle, A., Stocker, T.F., Joos, F., Fischer, H., Smith, H.J., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R., and Stauffer, B. 1999. Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature* **398**: 121–126.

Lutz, W., Sanderson, W., and Scherbov, S. 2001. The end of world population growth. *Nature* **412**: 543–545.

McElwain, J.C., Mayle, F.E., and Beerling, D.J. 2002. Stomatal evidence for a decline in atmospheric CO₂ concentration during the Younger Dryas stadial: a comparison with Antarctic ice core records. *Journal of Quaternary Science* **17**: 21–29.

Monnin, E., Indermühle, A., Dällenbach, A., Flückiger, J., Stauffer, B., Stocker, T.F., Raynaud, D., and Barnola, J.-M.

2001. Atmospheric CO₂ concentrations over the last glacial termination. *Nature* **291**: 112–114.

Raymo, M.E., Ganley, K., Carter, S., Oppo, D.W., and McManus, J. 1998. Millennial-scale climate instability during the early Pleistocene epoch. *Nature* **392**: 699–702.

Steig, E.J. 1999. Mid-Holocene climate change. *Science* **286**: 1485–1487.

Stott, L., Timmermann, A., and Thunell, R. 2007. Southern Hemisphere and deep-sea warming led deglacial atmospheric CO₂ rise and tropical warming. *Science* **318**: 435–438.

Tierney, J.E., Russell, J.M., Huang, Y., Sinninghe, J.S., Hopmans, E.C., and Cohen, A.S. 2008. Northern Hemisphere controls on tropical southeast African climate during the past 60,000 years. *Science* **322**: 252–255.

Yokoyama, Y., Lambeck, K., Deckker, P.D., Johnston, P., and Fifield, L.K. 2000. Timing of the Last Glacial Maximum from observed sea-level minima. *Nature* **406**: 713–716.

2.1.2 Atmospheric Residence Time of CO₂

In a paper published in the international peer-reviewed journal *Energy & Fuels*, Dr. Robert H. Essenhigh, professor of energy conversion at The Ohio State University, addressed the residence time (RT) of anthropogenic CO₂ in the air. Essenhigh (2009) notes the IPCC in its first report (Houghton *et al.*, 1990) gave an atmospheric CO₂ residence time (lifetime) of 50 to 200 years as a “rough estimate.” That estimate is confusingly presented as an adjustment time for a scenario with a given anthropogenic CO₂ input, and it ignores natural (sea and vegetation) CO₂ flux rates. Such estimates are analytically invalid and in conflict with the more correct explanation given elsewhere in the same IPCC report: “This means that on average it takes only a few years before a CO₂ molecule in the atmosphere is taken up by plants or dissolved in the ocean.”

Some 99 percent of the atmospheric CO₂ molecules are ¹²CO₂ molecules containing the stable isotope ¹²C (Segalstad, 1982). To calculate the RT of ¹²CO₂, Essenhigh used the 1990 IPCC data with 750 gigatons total mass atmospheric carbon and a natural input/output exchange rate of 150 gigatons of carbon per year (Houghton *et al.*, 1990). The characteristic decay time (denoted by the Greek letter tau) is the former value divided by the latter value: 750 / 150 = five years. This is similar to the ~5 years found from mass balance calculations of measured atmospheric

CO₂ ¹³C/¹²C carbon isotope data by Segalstad (1992), the ~5 years obtained from CO₂ solubility data by Murray (1992), and the ~5 years derived from CO₂ chemical kinetic data by Stumm and Morgan (1970).

Revelle and Suess (1957) calculated from data for the trace atmospheric molecule ¹⁴CO₂, containing the radioactive isotope ¹⁴C, that the amount of atmospheric “CO₂ derived from industrial fuel combustion” would be only 1.2% for an atmospheric CO₂ lifetime of five years, and 1.73% for a CO₂ lifetime of seven years (Segalstad, 1998). Essenhigh (2009) reviewed measurements of ¹⁴C from 1963 through 1995 and found the RT of atmospheric ¹⁴CO₂ is ~16 (16.3) years. He also used the ¹⁴C data to determine the time value (exchange time) for variation of the concentration difference between the northern and southern hemispheres is 2.2 years for atmospheric ¹⁴CO₂. This result compares well with the observed hemispheric transport of volcanic debris leading to “the year without a summer” in 1816 in the northern hemisphere after the Tambora volcano cataclysmic eruption in Indonesia in 1815.

Sundquist (1985) compiled a large number of measured RTs of CO₂ found by different methods. The list, containing RTs for both ¹²CO₂ and ¹⁴CO₂, was expanded by Segalstad (1998), showing a total range for all reported RTs from one to 15 years, with most RT values ranging from five to 15 years. Essenhigh (2009) emphasizes this list of measured values of RT compares well with his calculated RT of five years for atmospheric bulk ¹²CO₂ and ~16 years for atmospheric trace ¹⁴CO₂. In addition, he notes the annual oscillations in the measured atmospheric CO₂ levels would be impossible without a short atmospheric residence time for the CO₂ molecules. Essenhigh further suggests the difference in atmospheric CO₂ residence times between the gaseous molecules ¹²CO₂ and ¹⁴CO₂ may be due to differences in the kinetic absorption and/or dissolution rates of the two different gas molecules.

Essenhigh also discusses alternative ways of expressing residence time, such as fill time, decay time, e-fold time, turnover time, and lifetime, and whether the Earth system carbon cycle is in dynamic equilibrium or nonequilibrium status. He concludes (like Segalstad, 1998) residence time is a robust parameter independent of the status of equilibrium, and that alternative expressions of the residence time give corresponding values.

It is important to compare Essenhigh’s results with a paper on the same topic by Solomon *et al.*

(2009), the first author of which (Susan Solomon) co-chaired the IPCC's Working Group I addressing physical climate science. The Solomon team's paper was published after Essenhigh had submitted his manuscript to *Energy & Fuels*.

Solomon *et al.* (2009) say there is an irreversible climate change in progress due to the assimilation of CO₂ in the atmosphere, caused solely by rising anthropogenic CO₂ emissions. Their vision of the future is one in which the CO₂ level flattens out asymptotically toward infinity, giving a residence time of more than 1,000 years, without offering a definition or discussion of residence time or isotopic differences: "a quasi-equilibrium amount of CO₂ is expected to be retained in the atmosphere by the end of the millennium that is surprisingly large: typically ~40% of the peak concentration enhancement over preindustrial values (~280 ppmv)." Figure 1 of that paper shows a peak level at 1,200 ppmv atmospheric CO₂ in the year 2100, leveling off to an almost steady level of ~800 ppmv in the year 3000. It is not known how the 40% estimate was derived.

Solomon *et al.* say "this can be easily understood on the basis of the observed instantaneous airborne fraction (AF^{peak}) of ~50% of anthropogenic carbon emissions retained during their build-up in the atmosphere, together with well-established ocean chemistry and physics that require ~20% of the emitted carbon to remain in the atmosphere on thousand-year timescales [quasi-equilibrium airborne fraction (AF^{equil}), determined largely by the Revelle factor governing the long-term partitioning of carbon between the ocean and atmosphere/biosphere system]."

Solomon *et al.* (2009) neglect to consider other alternatives, however, such as that offered by Segalstad (1998), who addressed the 50 percent "missing sink" error of the IPCC, showing the Revelle evasion "buffer" factor is ideologically defined from an assumed model (atmospheric anthropogenic CO₂ increase) and an assumed preindustrial value for the CO₂ level, in conflict with the chemical Henry's Law governing the fast ~1:50 equilibrium partitioning of CO₂ between gas (air) and fluid (ocean) at Earth's average surface temperature. This CO₂ partitioning factor is strongly dependent on temperature because of the temperature-dependent retrograde aqueous solubility of CO₂, which facilitates fast degassing of dissolved CO₂ from a heated fluid phase (ocean), similar to what is experienced by heating a carbonated drink.

The correct estimate of the atmospheric residence

time of CO₂ is important. The IPCC has constructed a model claiming the natural CO₂ input/output is in static balance and all CO₂ added to the atmosphere from anthropogenic carbon combustion will stay there almost indefinitely. With an anthropogenic atmospheric CO₂ residence time of 50 to 200 years (Houghton, 1990) or near-infinite (Solomon *et al.*, 2009), there remains a 50 percent error (nicknamed the "missing sink") in the IPCC's model: The measured rise in the atmospheric CO₂ level is just half of that expected from the amount of anthropogenic CO₂ supplied to the atmosphere, and carbon isotope measurements invalidate the IPCC's model (Segalstad, 1992; Segalstad, 1998).

The alternative evaluation of the CO₂ residence time—giving values of about five years for the bulk of the atmospheric CO₂ molecules, as per Essenhigh's (2009) reasoning and numerous measurements with different methods—indicates CO₂ is part of a dynamic, not static, system, where about one-fifth of the atmospheric CO₂ pool is exchanged every year between different sources and sinks due to relatively fast equilibria and temperature-dependent CO₂ partitioning governed by the chemical Henry's Law (Segalstad 1992; Segalstad, 1996; Segalstad, 1998).

Starr (1993) also found the atmospheric lifetime of CO₂ is about five years, consistent with the seasonal photosynthesis swing of atmospheric CO₂ and the bomb ¹⁴C decay history. The short residence time suggests anthropogenic emissions contribute only a fraction of the observed atmospheric rise and other sources, such as ocean and volcanic degassing of CO₂, need to be sought.

References

- Essenhigh, R.E. 2009. Potential dependence of global warming on the residence time (RT) in the atmosphere of anthropogenically sourced carbon dioxide. *Energy & Fuels* **23**: 2773–2784.
- Houghton, J.T., Jenkins, G.J., and Ephraums, J.J. (Eds.) 1990. *Climate Change. The IPCC Scientific Assessment*. Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge.
- Murray, J.W. 1992. The oceans. In: Butcher, S.S., Charlson, R.J., Orians, G.H., and Wolfe, G.V. (Eds.). *Global biogeochemical cycles*, Academic Press, pp. 175–211.
- Revelle, R. and Suess, H. 1957. Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO₂ during past decades. *Tellus* **9**: 18–27.

Segalstad, T.V. 1982. Stable Isotope Analysis. In: *Stable Isotopes in Hydrocarbon Exploration*, Norwegian Petroleum Society 6904, Stavanger. Available at: <http://www.co2web.info/STABIS-ANAL.pdf>.

Segalstad, T.V. 1992. The amount of non-fossil-fuel CO₂ in the atmosphere. *AGU Chapman Conference on Climate, Volcanism, and Global Change*. March 23-27, 1992. Hilo, Hawaii. Available at: <http://www.co2web.info/hawaii.pdf>.

Segalstad, T.V. 1996. The distribution of CO₂ between atmosphere, hydrosphere, and lithosphere; minimal influence from anthropogenic CO₂ on the global “Greenhouse Effect.” In Emsley, J. (Ed.). *The Global Warming Debate. The Report of the European Science and Environment Forum*. Bourne Press Ltd., Bournemouth, Dorset, U.K. [ISBN 0952773406]: 41–50. Available at: <http://www.co2web.info/ESEFVO1.pdf>.

Segalstad, T.V. 1998. Carbon cycle modelling and the residence time of natural and anthropogenic atmospheric CO₂: on the construction of the “Greenhouse Effect Global Warming” dogma. In: Bate, R. (Ed.). *Global Warming: The Continuing Debate*. ESEF, Cambridge, U.K. [ISBN 0952773422]: 184–219. Available at: <http://www.co2web.info/ESEF3VO2.pdf>.

Solomon, S., Plattner, G.-K., Knutti, R., and Friedlingstein, P. 2009. Irreversible climate change due to carbon dioxide emissions. *Proceedings of the National Academy of Sciences of the USA [PNAS]* **106**, 6: 1704–1709.

Starr, C. 1993. Atmospheric residence time and the carbon cycle. *Energy* **18**: 1297–1310.

Stumm, W. and Morgan, J.J. 1970. Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. Wiley-Interscience.

Sundquist, E.T. 1985. Geological perspectives on carbon dioxide and the carbon cycle. In: Sundquist, E.T. and Broecker, W.S. (Eds.). *The carbon cycle and atmospheric CO₂: natural variations Archean to present*. *American Geophysical Union, Geophysical Monograph* **32**: 5–59.

2.2 Methane

What impact do global warming, the ongoing rise in the air’s carbon dioxide (CO₂) content, and other contemporary environmental trends have on the atmosphere’s methane (CH₄) concentration? Methane is a more powerful greenhouse gas, molecule for molecule, than is carbon dioxide. As discussed in the subsections below, there are significant forces at play that will likely produce a large negative feedback toward the future warming potential of this powerful

greenhouse gas, nearly all of which are ignored or downplayed by the IPCC.

2.2.1 Atmospheric Concentrations

Atmospheric methane’s contribution to anthropogenic climate forcing is estimated to be about half that of CO₂ when both direct and indirect components to its forcing are summed (see Figure 2.2.1.1). Nearly all models project atmospheric methane (CH₄) concentrations will increase for at least the next three decades, with many of the scenarios assuming a much larger increase throughout the twenty-first century. However, atmospheric methane concentrations currently lie far below the model projections in each of the four prior *Assessment Reports* of the IPCC (see Figure 2.2.1.2).

Shortly after release of the first IPCC *Assessment Report*, some researchers recognized the past two centuries’ dramatic increase in atmospheric methane concentrations, sparked by the Industrial Revolution, was abruptly slowing (Dlugokencky *et al.*, 1998; Francey *et al.*, 1999; Lassey *et al.*, 2000). Based on measurements from 43 globally distributed remote boundary-layer sites, Dlugokencky *et al.* (2003), for example, calculated global CH₄ concentration averages for the years 1984 to 2002. The results have been replotted in Figure 2.2.1.3, where the measurements are shown to fall into three groupings: initial and latter stages, to which have been fit linear regressions, and an intervening middle stage, to which has been fit a second-order polynomial.

Dlugokencky *et al.* noted the globally averaged atmospheric methane concentration “was constant at ~1751 ppb from 1999 through 2002,” which suggested, in their words, that “during this 4-year period the global methane budget has been at steady state.” They cautioned, “our understanding is still not sufficient to tell if the prolonged pause in CH₄ increase is temporary or permanent.”

Although initially contending in 2002 (Simpson *et al.*, 2002) it was “premature to believe that the CH₄ burden is ceasing to increase,” four years later Simpson *et al.* (2006) acknowledged the anomalous CH₄ growth spikes to which their earlier paper had referred were indeed “superimposed on an overall slowdown of the CH₄ growth rate.” The slowdown documented by Simpson *et al.* (2006) was so significant they reported “the global growth rate of atmospheric CH₄ has been near-zero for the past seven years, averaging 0.7 ± 2.6 ppbv year⁻¹.” They also state “opportunities exist for still further reduc-

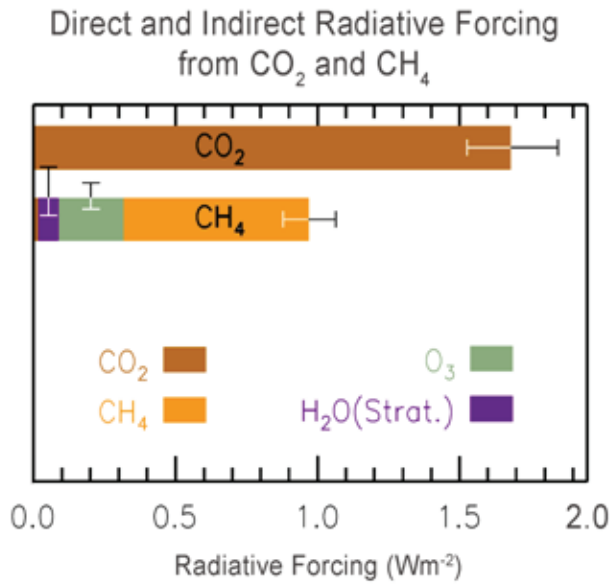


Figure 2.2.1.1. Direct and indirect radiative forcing from CO₂ and CH₄, as estimated by the IPCC. Adapted from IPCC, *Climate Change 2007: The Physical Science Basis*, p. 136, FAQ 2.1, Figure 2.

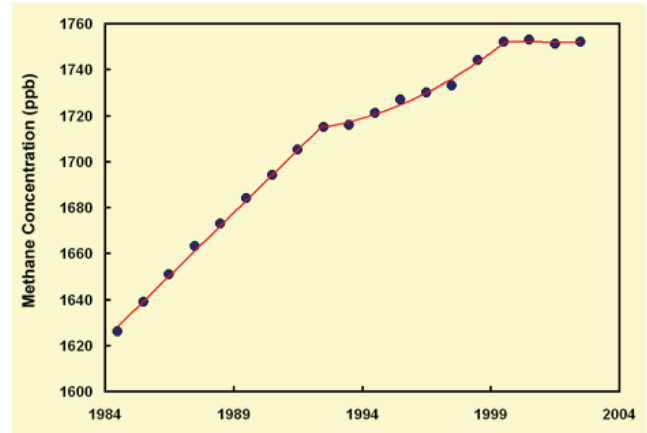


Figure 2.2.1.3. Global tropospheric methane (CH₄) concentration vs. time. Plotted from data tabulation in Dlugokencky, E.J., Houweling, S., Bruhwiler, L., Masarie, K.A., Lang, P.M., Miller, J.B., and Tans, P.P. 2003. Atmospheric methane levels off: Temporary pause or a new steady-state? *Geophysical Research Letters* **30**: 10.1029/2003GL018126.

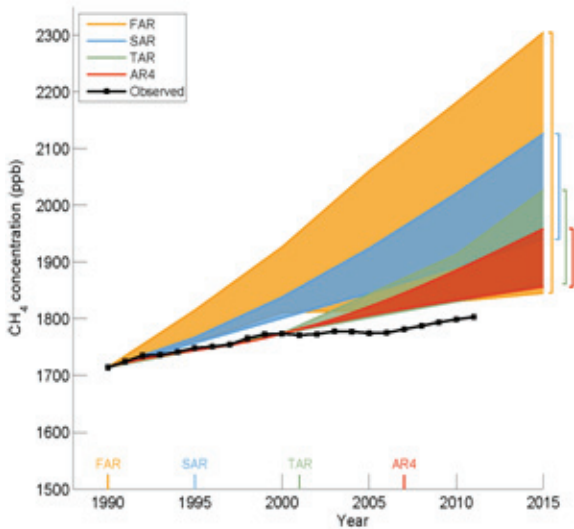


Figure 2.2.1.2. Atmospheric CH₄ projections vs observations for the first four IPCC Assessment Reports. Second Order Draft of AR5, dated October 5, 2012

tions,” noting “CH₄ levels may decrease if various CH₄ emission mitigation strategies are implemented.” They further note “the reduction of fossil fuel leakage has promise” and “because the leaking fossil fuels

have high value in the market, these mitigation steps can in some cases even be economically favorable.”

Simpson *et al.* (2006) point out “methane has been second only to carbon dioxide in enhanced climatic forcing from 1750 to the present.” Thus if atmospheric CH₄ levels continue to fall, rising atmospheric CO₂ levels might result in no net increase in the radiative forcing of climate. At the same time, the aerial fertilization and anti-transpirant effects of atmospheric CO₂ enrichment would grow, enhancing the efficiency of water and nutrient use by both natural and managed ecosystems. In addition, because methane is “an important source of tropospheric ozone,” as related by Simpson *et al.* (2006), the declining CH₄ concentration would alleviate much of the damage to Earth’s vegetation routinely caused by this most debilitating of air pollutants.

One year later, Khalil *et al.* (2007) combined two large atmospheric data sets to produce the unified set of data depicted in Figure 2.2.1.4, from which it is clear the rate of methane increase in the atmosphere has dropped dramatically over time. Khalil *et al.* report, “the trend has been decreasing for the last two decades until the present when it has reached near zero,” adding, “it is questionable whether human activities can cause methane concentrations to increase greatly in the future.”

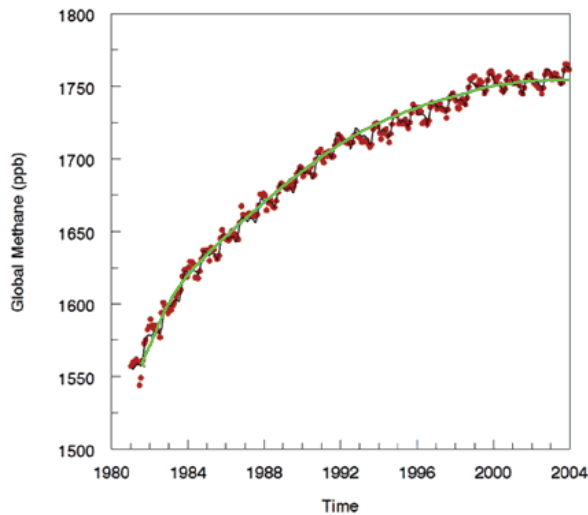


Figure 2.2.1.4. Global methane (CH_4) concentration. Adapted from Khalil, M.A.K., Butenhoff, C.L., and Rasmussen, R.A. 2007. Atmospheric methane: Trends and cycles of sources and sinks. *Environmental Science & Technology* 10.1021/es061791t.

Similar findings were reported in 2008 by Schnell and Dlugokencky, who presented an update through 2007 of atmospheric methane concentrations as determined from weekly discrete samples collected on a regular basis since 1983 at the NOAA/ESRL Mauna Loa Observatory (see Figure 2.2.1.5). Schnell and Dlugokencky note “atmospheric CH_4 has remained nearly constant since the late 1990s,” the exact cause(s) of which decline “are still unclear.”

In a contemporaneous study, Rigby *et al.* (2008) analyzed CH_4 data obtained from the Advanced Global Atmospheric Gases Experiment (AGAGE)—a network of five stations located in coastal regions at latitudes from 53°N to 41°S —and the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO), a network of eight locations around the globe that “provides an independent and complementary data set, and a wider latitudinal site distribution.” The sixteen scientists report their methane measurements, which run from January 1997 to April 2008, “show renewed growth from the end of 2006 or beginning of 2007 until the most recent measurements,” with the record-long range of methane growth rates hovering about zero but sometimes dropping five parts per billion (ppb) per year into the negative range, while rising near the end of the record to mean positive values of eight and 12

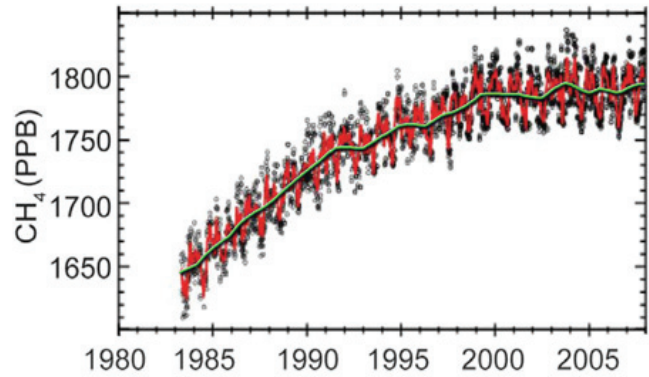


Figure 2.2.1.5. Trace gas mole fractions of methane (CH_4) as measured at Mauna Loa, Hawaii. Adapted from Schnell, R.C. and Dlugokencky, E. 2008. Methane. In: Levinson, D.H. and Lawrimore, J.H. (Eds.) *State of the Climate in 2007*. Special Supplement to the *Bulletin of the American Meteorological Society* **89**: S27.

ppb per year for the two measurement networks.

Does this recent increase provide renewed support for the IPCC’s projected increase in methane used in their model calculations of future global temperature? In a word, no—or at least not yet—for much larger increases in the methane growth rate have occurred over the past two to three decades. The most recent data from NOAA scientist Dr. Ed Dlugokencky, shown in Figure 2.2.1.6, show the global growth rate of atmospheric methane fell for nearly two decades and underwent a brief rise in 2004. That increase peaked in 2007, and since then the methane growth rate has been declining.

Only the passing of time will test the validity of atmospheric methane growth rate scenarios used by the IPCC in its projections of future climate. But if the past has taught us anything at all, it is that we do not know all we need to know about the factors that contribute to (the sources) and extract from (the sinks) methane in the atmosphere. That fact should be strikingly evident to the IPCC, whose methane projections have consistently outstretched the reality of observations in each of the prior four Assessment Reports, as illustrated earlier in Figure 2.2.1.2. The IPCC’s temperature projections, which incorporate the influence of methane, are likely overinflated as well.

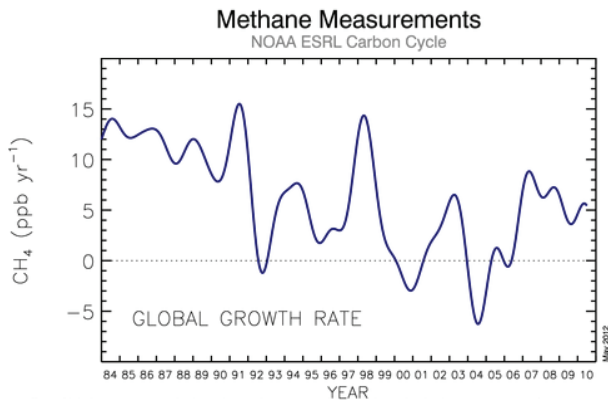


Figure 2.2.1.6. Global average growth rate of methane from the Carbon Cycle cooperative air sampling network, published by Ed Dlugokencky on the NOAA website <http://www.esrl.noaa.gov/gmd/ccgg/>.

References

- Dlugokencky, E.J., Houweling, S., Bruhwiler, L., Masarie, K.A., Lang, P.M., Miller, J.B., and Tans, P.P. 2003. Atmospheric methane levels off: Temporary pause or a new steady-state? *Geophysical Research Letters* **30**: 10.1029/2003GL018126.
- Dlugokencky, E.J., Masarie, K.A., Lang, P.M., and Tans, P.P. 1998. Continuing decline in the growth rate of the atmospheric methane burden. *Nature* **393**: 447–450.
- Francey, R.J., Manning, M.R., Allison, C.E., Coram, S.A., Etheridge, D.M., Langenfelds, R.L., Lowe, D.C., and Steele, L.P. 1999. A history of $\delta^{13}\text{C}$ in atmospheric CH_4 from the Cape Grim Air Archive and Antarctic firn air. *Journal of Geophysical Research* **104**: 23,631–23,643.
- Khalil, M.A.K., Butenhoff, C.L., and Rasmussen, R.A. 2007. Atmospheric methane: Trends and cycles of sources and sinks. *Environmental Science & Technology* 10.1021/es061791t.
- Lassey, K.R., Lowe, D.C., and Manning, M.R. 2000. The trend in atmospheric methane $\delta^{13}\text{C}$ and implications for constraints on the global methane budget. *Global Biogeochemical Cycles* **14**: 41–49.
- Rigby, M., Prinn, R.G., Fraser, P.J., Simmonds, P.G., Langenfelds, R.L., Huang, J., Cunnold, D.M., Steele, L.P., Krummel, P.B., Weiss, R.F., O'Doherty, S., Salameh, P.K., Wang, H.J., Harth, C.M., Muhle, J., and Porter, L.W. 2008. Renewed growth of atmospheric methane. *Geophysical Research Letters* **35**: 10.1029/2008GL036037.
- Schnell, R.C. and Dlugokencky, E. 2008. Methane. In: Levinson, D.H. and Lawrimore, J.H. (Eds.) *State of the*

Climate in 2007. Special Supplement to the *Bulletin of the American Meteorological Society* **89**: S27.

Simpson, I.J., Blake, D.R., and Rowland, F.S. 2002. Implications of the recent fluctuations in the growth rate of tropospheric methane. *Geophysical Research Letters* **29**: 10.1029/2001GL014521.

Simpson, I.J., Rowland, F.S., Meinardi, S., and Blake, D.R. 2006. Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane. *Geophysical Research Letters* **33**: 10.1029/2006GL027330.

2.2.2 Emissions to the Atmosphere

2.2.2.1 Agriculture

What effect, if any, does the rise in atmospheric carbon dioxide levels have on atmospheric methane concentrations? As noted earlier, this question has important implications because, molecule for molecule, methane is a more powerful greenhouse gas than carbon dioxide. This question is considered here as it applies to methane emissions associated with agricultural operations.

Schrope *et al.* (1999) found atmospheric CO_2 enrichment might significantly reduce methane emissions associated with the production of rice. They studied rice growing in large vats filled with topsoil and placed in greenhouse tunnels maintained at atmospheric CO_2 concentrations of 350 and 700 ppm. Each of the tunnels was subdivided into four sections that provided temperature treatments ranging from ambient to as much as 5°C above ambient.

The researchers found doubling the air's CO_2 content enhanced rice biomass production by up to 35 percent above-ground and up to 83 percent below-ground. And in an unanticipated development, methane emissions from the rice grown at 700 ppm CO_2 were found to be 10 to 45 times lower than emissions from the plants grown at 350 ppm. As Schrope *et al.* describe it, “the results of this study did not support our hypothesis that an effect of both increased carbon dioxide and temperature would be an increase in methane emissions.” On the contrary, they note “both increased carbon dioxide and increased temperatures were observed to produce decreased methane emissions,” except for the first 2°C increase above ambient, which produced a slight increase in methane evolution from the plant-soil system.

Schrope *et al.* stated their results “unequivocally support the conclusion that, during this study,

methane emissions from *Oryza sativa* [rice] plants grown under conditions of elevated CO₂ were dramatically reduced relative to plants grown in comparable conditions under ambient levels of CO₂.” They replicated their experiment in a second year of sampling and obtained essentially the same results.

Four years later, a study of the same phenomenon by a different set of scientists yielded a far different result under a different set of circumstances. Inubushi *et al.* (2003) grew a different cultivar of rice in 1999 and 2000 in paddy culture at Shizukuishi, Iwate, Japan in a free-air carbon dioxide enrichment (FACE) study where the air’s CO₂ concentration was increased 200 ppm above ambient. They found the extra CO₂ “significantly increased the CH₄ emissions by 38% in 1999 and 51% in 2000,” which they attributed to “accelerated CH₄ production as a result of increased root exudates and root autolysis products and to the increased plant-mediated CH₄ emission because of the higher rice tiller numbers under FACE conditions.” With such a dramatically different result from that of Schroppe *et al.*, many more studies likely will be required to clarify this relationship and determine which of these contrasting results is the more typical.

A related study was conducted by Kruger and Frenzel (2003), who note “rice paddies contribute approximately 10–13% to the global CH₄ emission (Neue, 1997; Crutzen and Lelieveld, 2001),” and “during the next 30 years rice production has to be increased by at least 60% to meet the demands of the growing human population (Cassman *et al.*, 1998).” They further note “increasing amounts of fertilizer will have to be applied to maximize yields [and] there is ongoing discussion on the possible effects of fertilization on CH₄ emissions.”

Kruger and Frenzel investigated the effects of N-fertilizer (urea) on CH₄ emission, production, and oxidation in rice culture in laboratory, microcosm, and field experiments conducted at the Italian Rice Research Institute in northern Italy. They report in some prior studies “N-fertilization stimulated CH₄ emissions (Cicerone and Shetter, 1981; Banik *et al.*, 1996; Singh *et al.*, 1996),” whereas “methanogenesis and CH₄ emission was found to be inhibited in others (Cai *et al.*, 1997; Schutz *et al.*, 1989; Lindau *et al.*, 1990).” That is similar to the polarized findings of Schroppe *et al.* and Inubushi *et al.* with respect to the effects of elevated CO₂ on methane emissions. In the mean, therefore, there may be little or no change in overall CH₄ emissions from rice fields in response to

elevated CO₂ and increased N-fertilization. With respect to their own study, for example, Kruger and Frenzel report “combining our field, microcosm and laboratory experiments we conclude that any agricultural praxis improving the N-supply to the rice plants will also be favorable for the CH₄ oxidizing bacteria,” noting “N-fertilization had only a transient influence and was counter-balanced in the field by an elevated CH₄ production.” The implication of these findings is noted in the concluding sentence of their paper: “Neither positive nor negative consequences for the overall global warming potential could be found.”

Additional understanding of CO₂-induced impacts on methane emissions from rice was gained by Cheng *et al.* (2008), who examined well-watered (flooded) and fertilized rice (*Oryza sativa* L.) plants. Plants were fumigated with air containing either 380 or 680 ppm CO₂ from the panicle formation stage at 59 days after transplanting (DAT) from seedling trays into pots within controlled-environment chambers maintained at either high (32°C) or low (22°C) night temperatures, with day temperature held constant at 32°C, until either 107 or 114 DAT. They measured the flux of methane between the pots and the atmosphere each day at 10:00 and 22:00 hours. At the conclusion of the experiment they determined the dry weight of each organ of all of the plants employed in the study.

The researchers found the extra 300 ppm of CO₂ increased CH₄ emissions by 32.2 percent in the low night temperature treatment, but by only 3.5 percent in the high night temperature treatment. They also found the elevated CO₂ increased the dry weight gained by the plants in the low night temperature treatment by 38.4 percent, but by a smaller 12.7 percent in the high night temperature treatment.

An interesting metric can be derived from these data: the ratio of the percent increase in CO₂-induced biomass production (a positive effect) to the percent increase in CO₂-induced CH₄ emissions (a negative effect) as the air’s CO₂ concentration rose from 380 to 680 ppm. This benefit/cost ratio was 1.19 in Cheng *et al.*’s low-night-temperature treatment and 3.63 in their high-night-temperature treatment. Thus, from the low-night-temperature to the high-night-temperature environment, as the air’s CO₂ concentration rose by 300 ppm, the benefit/cost ratio rose by a little more than 200 percent.

Because night temperatures rose significantly faster than day temperatures throughout most of the

world over the past several decades, this phenomenon may have had a net two-pronged *positive* effect on the biosphere, and it could have a similar positive effect in the future, increasing the aerial fertilization effect of atmospheric CO₂ enrichment at a considerably faster relative rate than the relative rate of CO₂-induced methane emissions to the atmosphere.

Introducing their study of the subject, Qaderi and Reid (2011) write the release of aerobic methane by vegetation has been indirectly confirmed by the field studies of Braga do Carmo *et al.* (2006), Crutzen *et al.* (2006), and Sanhueza and Donoso (2006), as well as by the satellite studies of Frankenberg *et al.* (2005, 2008). In addition, they note CH₄ emissions from plants can be stimulated by higher air temperatures (Vigano *et al.*, 2008; Qaderi and Reid, 2009) and water stress (Qaderi and Reid, 2009). And since “methane is the second most important long-lived greenhouse gas after carbon dioxide and is thought to be ~25 times more potent than CO₂ in its ability to act as a greenhouse gas,” as they describe it, they decided to see what effect the ongoing rise in the air’s CO₂ content might have on this phenomenon.

Qaderi and Reid “examined the combined effects of temperature, carbon dioxide and watering regime on CH₄ emissions from six commonly cultivated crop species: faba bean, sunflower, pea, canola, barley and wheat” in an experiment where “plants were grown from seeds in controlled-environment growth chambers under two temperature regimes (24°C day/20°C night and 30°C day/26°C night), two CO₂ concentrations (380 and 760 ppm) and two watering regimes (well watered and water stressed),” where the “plants were first grown under 24/20°C for one week from sowing, and then placed under experimental conditions for a further week,” after which “plant growth, gas exchange and CH₄ emission rates were determined.”

The researchers found “no detectable CH₄ from [a] control treatment (without plant tissue), indicating that CH₄ from the experimental treatments was emitted only from plant tissues.” Second, they found the plants grown under higher temperature and water stress emitted more CH₄ than those grown under lower temperature and no water stress. And third, they found “elevated CO₂ had the opposite effect,” “partially revers[ing]” the effects of the other two factors.

Qaderi and Reid comment, “although rising atmospheric CO₂ reduces plant CH₄ emissions, it may not fully reverse the effects of temperature and drought,” which they assumed would increase in

tandem with the ongoing rise in the air’s CO₂ content.

Another agricultural source of methane is the fermentation of feed in the rumen of cattle and sheep. Boadi *et al.* (2004) reviewed methods for reducing CH₄ emissions from dairy cows. At the time of their review, existing mitigation strategies for reducing emissions from dairy cows included the addition of ionophores and fats to their food and the use of high-quality forages and grains in their diet, while newer mitigation strategies included “the addition of probiotics, acetogens, bacteriocins, archaeal viruses, organic acids, [and] plant extracts (e.g., essential oils) to the diet, as well as immunization, and genetic selection of cows.” The researchers provide a table of 20 such strategies, where the average maximum potential CH₄ reduction that may result from the implementation of each strategy is 30 percent or more.

Fievez *et al.* (2003) studied the effects of various types and levels of fish-oil feed additives on this process by means of both *in vitro* and *in vivo* experiments with sheep, observing a maximal 80 percent decline in the ruminants’ production of methane when using fish-oil additives containing n-3-eicosapentanoic acid. The presence of condensed tannins found in certain pasture plants also can reduce methane emissions from sheep and cattle, which account for approximately 90 percent of New Zealand’s methane emissions. Enriching the air with CO₂ can increase the tannin concentrations of many forage plants.

It is thus possible increasing condensed tannin concentrations in pasture crops by genetic engineering and allowing the air’s CO₂ content to continue to rise could result in significant decreases in methane emissions from cattle and sheep. The outlook is also good for accomplishing this feat by including fish-oil feed additives in their diets. In addition, it is possible elevated CO₂ concentrations may lead directly to reduced methane emissions from rice culture, although more work must be done to test this hypothesis. Nevertheless, the balance of evidence suggests we can be cautiously optimistic about our agricultural intervention capabilities and their capacity to help stem the tide of Earth’s historically rising atmospheric methane concentration.

References

Banik, A., Sen, M., and Sen, S.P. 1996. Effects of inorganic fertilizers and micronutrients on methane production from wetland rice (*Oryza sativa* L.). *Biology*

and Fertility of Soils **21**: 319–322.

Boadi, D., Benchaar, C., Chiquette, J., and Masse, D. 2004. Mitigation strategies to reduce enteric methane emissions from dairy cows: Update review. *Canadian Journal of Animal Science* **84**: 319–335.

Braga do Carmo, J., Keller, M., Dezincourt Dias, J., Barbosa de Camargo, P., and Crill, P. 2006. A source of methane from upland forests in the Brazilian Amazon. *Geophysical Research Letters* **33**: 10.1029/2005GL025436.

Cai, Z., Xing, G., Yan, X., Xu, H., Tsuruta, H., Yogi, K., and Minami, K. 1997. Methane and nitrous oxide emissions from rice paddy fields as affected by nitrogen fertilizers and water management. *Plant and Soil* **196**: 7–14.

Cassman, K.G., Peng, S., Olk, D.C., Ladha, J.K., Reichardt, W., Doberman, A., and Singh, U. 1998. Opportunities for increased nitrogen-use efficiency from improved resource management in irrigated rice systems. *Field Crops Research* **56**: 7–39.

Cheng, W., Sakai, H., Hartley, A., Yagi, K., and Hasegawa, T. 2008. Increased night temperature reduces the stimulatory effect of elevated carbon dioxide concentration on methane emission from rice paddy soil. *Global Change Biology* **14**: 644–656.

Cicerone, R.J. and Shetter, J.D. 1981. Sources of atmospheric methane. Measurements in rice paddies and a discussion. *Journal of Geophysical Research* **86**: 7203–7209.

Crutzen, P.J. and Lelieveld, J. 2001. Human impacts on atmospheric chemistry. *Annual Review of Earth and Planetary Sciences* **29**: 17–45.

Crutzen, P.J., Sanhueza, E., and Brenninkmeijer, C.A.M. 2006. Methane production from mixed tropical savanna and forest vegetation in Venezuela. *Atmospheric Chemistry and Physics Discussions* **6**: 3093–3097.

Fievez, V., Dohme, F., Danneels, M., Raes, K., and Demeyer, D. 2003. Fish oils as potent rumen methane inhibitors and associated effects on rumen fermentation in vitro and in vivo. *Animal Feed Science and Technology* **104**: 41–58.

Frankenberg, C., Bergamaschi, P., Butz, A., Houweling, S., Meirink, J.F., Notholt, J., Petersen, A.K., Schrijver, H., Warneke, T., and Aben, I. 2008. Tropical methane emissions: A revised view from SCIAMACHY onboard ENVISAT. *Geophysical Research Letters* **35**: 10.1029/goo8GL034300.

Frankenberg, C., Meirink, J.F., van Weele, M., Platt, U., and Wagner, T. 2005. Assessing methane emissions from global space-borne observations. *Science* **308**: 1010–1014.

Inubushi, K., Cheng, W., Aonuma, S., Hoque, M.M., Kobayashi, K., Miura, S., Kim, H.Y., and Okada, M. 2003. Effects of free-air CO₂ enrichment (FACE) on CH₄ emission from a rice paddy field. *Global Change Biology* **9**: 1458–1464.

Kruger, M. and Frenzel, P. 2003. Effects of N-fertilisation on CH₄ oxidation and production, and consequences for CH₄ emissions from microcosms and rice fields. *Global Change Biology* **9**: 773–784.

Lindau, C.W., DeLaune, R.D., and Patrick Jr., W.H. *et al.* 1990. Fertilizer effects on dinitrogen, nitrous oxide, and methane emission from lowland rice. *Soil Science Society of America Journal* **54**: 1789–1794.

Neue, H.U. 1997. Fluxes of methane from rice fields and potential for mitigation. *Soil Use and Management* **13**: 258–267.

Qaderi, M.M. and Reid, D.M. 2009. Methane emissions from six crop species exposed to three components of global climate change: temperature, ultraviolet-B radiation and water stress. *Physiologia Plantarum* **137**: 139–147.

Qaderi, M.M. and Reid, D.M. 2011. Stressed crops emit more methane despite the mitigating effects of elevated carbon dioxide. *Functional Plant Biology* **38**: 97–105.

Sanhueza, E. and Donoso, L. 2006. Methane emission from tropical savanna *Trachypogon* sp. grasses. *Atmospheric Chemistry and Physics* **6**: 5315–5319.

Schrope, M.K., Chanton, J.P., Allen, L.H., and Baker, J.T. 1999. Effect of CO₂ enrichment and elevated temperature on methane emissions from rice, *Oryza sativa*. *Global Change Biology* **5**: 587–599.

Schutz, H., Holzapfel-Pschorn, A., and Conrad, R. *et al.* 1989. A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy. *Journal of Geophysical Research* **94**: 16405–16416.

Singh, J.S., Singh, S., and Raghubanshi, A.S. *et al.* 1996. Methane flux from rice/wheat agroecosystem as affected by crop phenology, fertilization and water level. *Plant and Soil* **183**: 323–327.

Vigano, I., van Weelden, H., Holzinger, R., Keppler, F., and Rockmann, T. 2008. Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components. *Biogeosciences Discussions* **5**: 243–270.

2.2.2.2 Natural Vegetation

Continuing our investigation of the effect of rising temperature, rising atmospheric carbon dioxide (CO₂)

concentrations, and other environmental trends on the atmosphere's methane (CH₄) concentration, in this section we consider methane emissions associated with natural vegetation.

Frolking and Roulet (2007) point out “throughout the Holocene, northern peatlands have both accumulated carbon and emitted methane,” and “their impact on climate radiative forcing has been the net of cooling (persistent CO₂ uptake) and warming (persistent CH₄ emission).” They developed Holocene peatland carbon flux trajectories based on estimates of contemporary CH₄ flux, total accumulated peat C, and peatland initiation dates, which they used as inputs to a simple atmospheric perturbation model to calculate the net radiative impetus for surface air temperature change.

Frolking and Roulet note early in the Holocene the capture of CO₂ and emission of CH₄ by Earth's northern peatlands was likely to have produced a net warming impetus of up to +0.1 W m⁻². Over the following 8,000 to 11,000 years, however, they say Earth's peatlands have been doing the opposite, such that the current radiative forcing due to these atmospheric CO₂ and CH₄ perturbations represents a net cooling force on the order of -0.22 to -0.56 W m⁻². The impetus for global cooling due to carbon sequestration by Earth's peatlands historically has been—and currently is—significantly greater than the global warming potential produced by peatlands' emissions of methane.

Toet *et al.* (2001) point out, “only three previous published studies have assessed the impacts of O₃ on CH₄ and CO₂ fluxes in peatlands.” Niemi *et al.* (2002), as they describe it, “reported that CH₄ emissions more than doubled when peatland microcosms were exposed to 100 ppb O₃ over 4–7 weeks during summer in controlled-environment chambers.” In contrast, they note, “Rinnan *et al.* (2003) reported no significant effect on CH₄ emissions of a 7-week exposure of peat microcosms to 100 or 200 ppb O₃.” Finally, they note “Morsky *et al.* (2008) reported that open-field exposure of boreal peatland microcosms in central Finland to a doubling of ambient O₃ concentrations caused a decrease in CH₄ emission at the end of the first growing season,” but they note the decrease “was lost in the three subsequent growing seasons.” Prior work on the subject thus has not provided a definitive answer to the core question of whether rising O₃ concentrations have a significant effect on methane emissions from peatlands.

In a study more reflective of reality in terms of

scale, Toet *et al.* moved up in size from microcosms to mesocosms, collected from a lowland raised bog on the northern shore of Morecambe Bay, Cumbria, UK (54°13'N, 3°1'W) and subsequently placed into open-top chambers situated on a level gravel base at Newcastle University's field station (54°59'N, 1°48'W). For the next two years they observed what happened in four ambient and four O₃-enriched chambers, the latter of which had their atmospheric O₃ concentrations raised by 50 ppb for eight hours of each day during the summer period (April-early October) and by 10 ppb for eight hours of each day throughout the winter.

The researchers found “methane emissions were significantly reduced, by about 25%, by elevated ozone during midsummer periods of both years,” but “no significant effect of ozone was found during the winter periods.” After a lengthy discussion of their findings and those of other researchers they cite, Toet *et al.* conclude, in the final sentence of their paper, “increased O₃ could be a significant brake on the increased flux of CH₄ that is expected as these northern peatlands warm.”

Davidson *et al.* (2004) report the climate of the Amazon Basin may become gradually drier due to the intensification of a number of different phenomena, including (1) less recirculation of water between the increasingly deforested region and the atmosphere, (2) more rainfall inhibition by smoke caused by increased biomass burning, and (3) a warming-induced increase in the frequency and/or intensity of El Niño events that have historically brought severe drought to the eastern Amazon Basin (Nepstad *et al.*, 1999; see Timmermann *et al.*, 1999 as well). They devised an experiment to determine the consequences of the drying of the soil of an Amazonian moist tropical forest for the net surface-to-air fluxes of two important greenhouse gases: nitrous oxide (N₂O) and methane (CH₄).

In the Tapajos National Forest near Santarem, Brazil, the researchers modified a one-hectare plot of land covered by mature evergreen trees so as to dramatically reduce the amount of rain that reached the forest floor (throughfall) while maintaining an otherwise-similar one-hectare plot of land as a control for comparison. Prior to making this modification, they measured the gas exchange characteristics of the two plots for a period of 18 months. After initiating the throughfall-exclusion treatment, they continued their measurements for an additional three years. This protocol revealed, in their words, that the “drier soil conditions caused by throughfall exclusion inhibited

N₂O and CH₄ production and promoted CH₄ consumption.” They state “the exclusion manipulation lowered annual N₂O emissions by >40% and increased rates of consumption of atmospheric CH₄ by a factor of >4,” which they attribute to the “direct effect of soil aeration on denitrification, methanogenesis, and methanotrophy.”

If global warming did indeed increase the frequency and/or intensity of El Niño events—which real-world data suggest is highly debatable (see Chapter 4)—the work of Davidson *et al.* (2004) suggests the anticipated drying of the Amazon Basin would initiate a strong negative feedback to warming via drying-induced reductions in the evolution of N₂O and CH₄ from its soils and a drying-induced increase in the consumption of CH₄ by its soils. Although Davidson *et al.* envisaged a more extreme second phase response, “in which drought-induced plant mortality is followed by increased mineralization of C and N substrates from dead fine roots and by increased foraging of termites on dead coarse roots” (a response that would be expected to increase N₂O and CH₄ emissions), it should be noted the projected rise in the air’s CO₂ content likely would prohibit such extreme events from occurring, in light of the tendency for elevated levels of atmospheric CO₂ to increase the water use efficiency of plants, which would enable the Amazon Basin’s vegetation to continue to flourish under significantly drier conditions than those of the present.

Strack *et al.* (2004) also note climate models predict increases in evapotranspiration that could lead to drying in a warming world and a subsequent lowering of water tables in high northern latitudes. This prediction stresses the importance of determining how lowered water tables will affect peatland emissions of CH₄. In a theoretical study of the subject, Roulet *et al.* (1992) calculated that for a decline of 14 cm in the water tables of northern Canadian peatlands, due to climate-model-derived increases in temperature (3°C) and precipitation (1mm/day) predicted for a doubling of the air’s CO₂ content, CH₄ emissions would decline by 74 to 81 percent. In an attempt to obtain some experimental data on the subject, over the period 2001–2003 Strack *et al.* measured CH₄ fluxes to the atmosphere at different locations that varied in depth-to-water table within natural portions of a poor fen in central Quebec, Canada as well as within control portions of the fen that had been drained eight years earlier.

The Canadian scientists report, “methane

emissions and storage were lower in the drained fen.” The greatest reductions (up to 97 percent) were measured at the higher locations, whereas at the lower locations there was little change in CH₄ flux. Averaging the results over all locations, the researchers determined the “growing season CH₄ emissions at the drained site were 55% lower than the control site,” indicating the biosphere appears to be able to resist warming influences.

In one final study of anaerobic conditions, Garnet *et al.* (2005) grew seedlings of three emergent aquatic macrophytes (*Orontium aquaticum* L., *Peltandra virginica* L., and *Juncus effusus* L.) and one coniferous tree (*Taxodium distichum* L.), all of which are native to eastern North America, in a five-to-one mixture of well-fertilized mineral soil and peat moss in pots submerged in water in tubs located within controlled environment chambers for a period of eight weeks. Concomitantly, they measured the amount of CH₄ emitted by the plant foliage, along with net CO₂ assimilation rate and stomatal conductance, which were made to vary by changing the CO₂ concentration of the air surrounding the plants and the density of the photosynthetic photon flux impinging on them.

The researchers found methane emissions from the four wetland species increased linearly with increases in both stomatal conductance and net CO₂ assimilation rate, but changes in stomatal conductance affected foliage methane flux “three times more than equivalent changes in net CO₂ assimilation,” making stomatal conductance the more significant of the two CH₄ emission-controllers. They note evidence of stomatal control of CH₄ emission also has been reported for *Typha latifolia* (Knapp and Yavitt, 1995) and *Carex* (Morrissey *et al.*, 1993), two other wetland plants. Since atmospheric CO₂ enrichment leads to approximately equivalent but oppositely directed changes in foliar net CO₂ assimilation (which is increased) and stomatal conductance (which is reduced) in most herbaceous plants (the type that comprise most wetlands), it can be appreciated that the ongoing rise in the air’s CO₂ content should be acting to reduce methane emissions from Earth’s wetland vegetation.

Shifting to studies examining aerobic conditions, Dueck *et al.* (2007) point out recent findings suggest terrestrial plants may “emit methane under aerobic conditions by an as yet unknown physiological process (Keppler *et al.*, 2006), and in this way may substantially contribute to the annual global methane budget (Bousquet *et al.*, 2006),” resulting in

“estimated values for methane emission by terrestrial plants varying between 10 and 260 Tg yr⁻¹ (Houweling *et al.*, 2006; Keppler *et al.*, 2006; Kirschbaum *et al.*, 2006).” The 15 Dutch researchers conducted two experiments involving six plant species—*Ocimum basilicum* L. (basil), *Triticum aestivum* L. (wheat), *Zea mays* L. (maize), *Salvia officinalis* L. (sage), *Lycopersicon esculentum* Miller (tomato), and *Oenothera biennis* L. (common evening primrose)—the first three of which also were used by Keppler *et al.* (2006).

The experiments were performed in “a unique hermetically sealed plant growth chamber with a volume of 3500 liters, specifically designed for atmospheric isotope labeling,” where “plants were grown hydroponically to exclude any methane production derived from anaerobic soil pockets.” Dueck *et al.* reported there was no evidence for substantial aerobic methane emission by the terrestrial plants they studied, stating, “maximally,” it was only “0.3% of the previously published studies.” They indicate methane concentrations in continuous-flow gas cuvettes with plants “were not significantly higher than those of control cuvettes without plants,” stating for both short and long terms, they “did not find any evidence of a substantial emission of methane.”

Keppler *et al.*'s findings have been further challenged by other researchers. Beerling *et al.* (2008), for example, raised the C₄ plant *Zea mays* and the C₃ plant *Nicotiana tabacum* from seed for six weeks at an ambient CO₂ concentration of 400 ppm and an ambient methane concentration of 1,800 ppb, after which their leaves were studied in “a custom-built flowthrough cuvette with a sufficiently large area to allow the detection of methane emissions” via “a process gas chromatograph linked to a high-precision, high-accuracy flame ionization detector” in a controlled-environment room. The team of five U.K. researchers report “well-illuminated actively photosynthesizing *Z. mays* leaves did not, in our experimental system, emit substantial quantities of methane during repeated three-hour high irradiance episodes,” and “neither did we detect methane emissions from actively respiring leaves during repeated three-hour dark periods.” They additionally state “measurements with leaves of the C₃ species *N. tabacum* also failed to detect substantial aerobic methane emissions in the light when photosynthesizing with regular stomatal conductances, and in the dark when respiring.”

Nisbet *et al.* (2009) “conducted further experiments on plants grown in controlled

conditions” and “re-analyzed the previously published data” on the topic. The 14 researchers (13 from the U.K. and one from Sweden) demonstrated “plants do not contain a biochemical mechanism for methanogenesis” and “cannot produce methane as an end-product or by-product of their metabolism.” The researchers determined “when plants transpire, any methane that is already dissolved in the water derived from the soil will be released into the atmosphere” and “under high stress conditions, such as high UV radiation, methane is released as part of the cellular breakdown process.” In light of such findings, plus “a new analysis of global methane levels from satellite retrievals,” Nisbet *et al.* conclude “plants are not a major source of the global methane production.” They do, however, acknowledge “the role of plants in moving methane about”—that is, their importance in the global cycling of methane, but not its production.

Wang *et al.* (2009) conclude after their review of the scientific literature that “aerobic CH₄ [methane] emissions from plants may be affected by O₂ stress or any other stress leading to ROS [reactive oxygen species] production,” leading the team of researchers to examine whether physical injury also would affect CH₄ emissions from plants. Their work revealed “physical injury (cutting) stimulated CH₄ emissions from fresh twigs of *Artemisia* species under aerobic conditions” and “more cutting resulted in more CH₄ emissions,” as did hypoxia in both cut and uncut *Artemisia frigida* twigs.

In discussing their findings and those of previous studies that suggest, in their words, “that a variety of environmental stresses stimulate CH₄ emission from a wide variety of plant species,” Wang *et al.* conclude “global change processes, including climate change, depletion of stratospheric ozone, increasing ground-level ozone, spread of plant pests, and land-use changes, could cause more stress in plants on a global scale, potentially stimulating more CH₄ emission globally,” while further concluding “the role of stress in plant CH₄ production in the global CH₄ cycle could be important in a changing world.”

While many factors “could” be important in stimulating methane emissions, the ongoing rise in the air's CO₂ content is countering stress-induced CH₄ emissions from plants. Although environmental stresses of all types generate highly reactive oxygenated compounds that damage plants, atmospheric CO₂ enrichment typically boosts the production of antioxidant enzymes that scavenge and detoxify those oxygenated compounds. The rise in the air's CO₂ content should have been alleviating the

level of stress experienced by Earth's plants, and this phenomenon should have been reducing the rate at which the planet's vegetation releases CH₄ to the atmosphere. Perhaps that is why the rate-of-rise of the atmosphere's methane concentration has changed little in recent decades.

References

- Beerling, D.J., Gardiner, T., Leggett, G., McLeod, A., and Quick, W.P. 2008. Missing methane emissions from leaves of terrestrial plants. *Global Change Biology* **14**: 1821–1826.
- Bousquet, P., Ciais, P., Miller, J.B., Dlugokencky, E.J., Hauglustaine, D.A., Prigent, C., van der Werf, G.R., Peylin, P., Brunke, E.-G., Carouge, C., Langenfelds, R.L., Lathiere, J., Papa, F., Ramonet, M., Schmidt, M., Steele, L.P., Tyler, S.C., and White, J. 2006. Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature* **443**: 439–443.
- Davidson, E.A., Ishida, F.Y., and Nepstad, D.C. 2004. Effects of an experimental drought on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest. *Global Change Biology* **10**: 718–730.
- Dueck, T.A., de Visser, R., Poorter, H., Persijn, S., Gorissen, A., de Visser, W., Schapendonk, A., Verhagen, J., Snel, J., Harren, F.J.M., Ngai, A.K.Y., Verstappen, F., Bouwmeester, H., Voesenek, L.A.C., and van der Werf, A. 2007. No evidence for substantial aerobic methane emission by terrestrial plants: a ¹³C-labelling approach. *New Phytologist* **175**: 29–35.
- Frolking, S. and Roulet, N.T. 2007. Holocene radiative forcing impact of northern peatland carbon accumulation and methane emissions. *Global Change Biology* **13**: 1079–1088.
- Garnet, K.N., Megonigal, J.P., Litchfield, C., and Taylor Jr., G.E. 2005. Physiological control of leaf methane emission from wetland plants. *Aquatic Botany* **81**: 141–155.
- Houweling, S., Rockmann, T., Aben, I., Keppler, F., Krol, M., Meirink, J.F., Dlugokencky, E.J., and Frankenberg, C. 2006. Atmospheric constraints on global emissions of methane from plants. *Geophysical Research Letters* **33**: L15821.
- Keppler, F., Hamilton, J.T.G., Brass, M., and Rockmann, T. 2006. Methane emissions from terrestrial plants under aerobic conditions. *Nature* **439**: 187–191.
- Kirshbaum, M.U.F., Bruhn, D., Etheridge, D.M., Evans, J.R., Farquhar, G.D., Gifford, R.M., Ki, P., and Winters, A.J. 2006. Comment on the quantitative significance of aerobic methane release by plants. *Functional Plant Biology* **33**: 521–530.
- Knapp, A.K. and Yavitt, J.B. 1995. Gas exchange characteristics of *Typha latifolia* L. from nine sites across North America. *Aquatic Botany* **49**: 203–215.
- Morrissey, L.A., Zobel, D., and Livingston, G.P. 1993. Significance of stomatal control of methane release from *Carex*-dominated wetlands. *Chemosphere* **26**: 339–356.
- Morsky, S.K., Haapala, J.K., Rinnan, R., Tiiva, P., Saarnio, S., Silvola, J., Holopainen, T., and Martikainen, P.J. 2008. Long-term ozone effects on vegetation, microbial community and methane dynamics of boreal peatland microcosms in open-field studies. *Global Change Biology* **14**: 1891–1903.
- Nepstad, D.C., Verissimo, A., Alencar, A., Nobre, C., Lima, E., Lefebvre, P., Schlesinger, P., Potter, C., Moutinho, P., Mendoza, E., Cochrane, M., and Brooks, V. 1999. Large-scale impoverishment of Amazonian forests by logging and fire. *Nature* **398**: 505–508.
- Niemi, R., Martikainen, P.J., Silvola, J., and Holopainen, T. 2002. Ozone effects on Sphagnum mosses, carbon dioxide exchange and methane emission in boreal peatland microcosms. *Science of the Total Environment* **289**: 1–12.
- Nisbet, R.E.R., Fisher, R., Nimmo, R.H., Bendall, D.S., Crill, P.M., Gallego-Sala, A.V., Hornibrook, E.R.C., Lopez-Juez, E., Lowry, D., Nisbet, P.B.R., Shuckburgh, E.F., Sriskantharajah, S., Howe, C.J., and Nisbet, E.G. 2009. Emission of methane from plants. *Proceedings of the Royal Society B*: 10.1098/rspb.2008.1731.
- Rinnan, R., Impio, M., Silvola, J., Holopainen, T., and Martikainen, P.J. 2003. Carbon dioxide and methane fluxes in boreal peatlands with different vegetation cover—effects of ozone or ultraviolet-B exposure. *Oecologia* **137**: 475–483.
- Roulet, N., Moore, T., Bubier, J., and Lafleur, P. 1992. Northern fens: Methane flux and climatic change. *Tellus Series B* **44**: 100–105.
- Strack, M., Waddington, J.M., and Tuittila, E.-S. 2004. Effect of water table drawdown on northern peatland methane dynamics: Implications for climate change. *Global Biogeochemical Cycles* **18**: 10.1029/2003GB002209.
- Timmermann, A., Oberhuber, J., Bacher, A., Esch, M., Latif, M., and Roeckner, E. 1999. Increased El Niño frequency in a climate model forced by future greenhouse warming. *Nature* **398**: 694–696.

Toet, S., Ineson, P., Peacock, S., and Ashmore, M. 2011. Elevated ozone reduces methane emissions from peatland mesocosms. *Global Change Biology* 17: 288–296.

Wang, Z.-P., Gullledge, J., Zheng, J.-Q., Liu, W., Li, L.-H., and Han, X.-G. 2009. Physical injury stimulates aerobic methane emissions from terrestrial plants. *Biogeosciences* 6: 615–621.

2.2.3 Extraction from the Atmosphere

Methane is an important greenhouse gas, contributing roughly 20 percent of total non-H₂O radiative forcing (Menyailo and Hungate, 2003). Its atmospheric concentration is determined by the difference between how much CH₄ goes into the air (emissions) and how much comes out of it (extractions) over any particular time period. In this section we examine factors that act to extract methane from the atmosphere.

According to Prinn *et al.* (1992), one of the major means by which methane is removed from the atmosphere is via oxidation by methanotrophic bacteria in the aerobic zones of soils; the magnitude of this phenomenon is believed to be equivalent to the annual input of methane to the atmosphere (Watson *et al.*, 1992). This soil sink for methane appears to be ubiquitous, as methane uptake has been observed in soils of tundra (Whalen and Reeburgh, 1990), boreal forests (Whalen *et al.*, 1992), temperate forests (Stuedler *et al.*, 1989; Yavitt *et al.*, 1990), grasslands (Mosier *et al.*, 1997), arable lands (Jensen and Olsen, 1998), tropical forests (Keller, 1986; Singh *et al.*, 1997), and deserts (Striegl *et al.*, 1992). Forest soils—especially boreal and temperate forest upland soils (Whalen and Reeburgh, 1996)—appear to be the most efficient (Le Mer and Roger, 2001).

Tamai *et al.* (2003) studied methane uptake rates by the soils of three Japanese cypress plantations composed of 30- to 40-year-old trees. Through all seasons of the year, they found methane was absorbed by the soils of all three sites, being positively correlated with temperature, as has been observed in several other studies (Peterjohn *et al.*, 1994; Dobbie and Smith, 1996; Prieme and Christensen, 1997; Saari *et al.*, 1998). Methane absorption was even more strongly positively correlated with the C/N ratio of the cypress plantations' soil organic matter.

Based on these results, it can be surmised that CO₂-induced global warming is capable of producing two biologically mediated negative feedbacks to counter the increase in temperature: a warming-induced increase in methane uptake from the atmosphere that is experienced by essentially all soils,

and an increase in soil methane uptake from the atmosphere produced by the increase in plant-litter C/N ratio that typically results from atmospheric CO₂ enrichment.

Menyailo and Hungate (2003) assessed the influence of six boreal forest species—spruce, birch, Scots pine, aspen, larch, and Arolla pine—on soil CH₄ consumption in a Siberian artificial afforestation experiment, in which the six common boreal tree species had been grown under common garden conditions for the past 30 years under the watchful eye of the staff of the Laboratory of Soil Science of the Institute of Forest, Siberian Branch of the Russian Academy of Sciences (Menyailo *et al.*, 2002). The authors determined “soils under hardwood species (aspen and birch) consumed CH₄ at higher rates than soils under coniferous species and grassland.” Under low soil moisture conditions, for example, the soils under the two hardwood species consumed 35 percent more CH₄ than the soils under the four conifers, while under high soil moisture conditions they consumed 65 percent more. As for the implications of these findings, Pastor and Post (1988) suggested, in the words of Menyailo and Hungate, that “changes in temperature and precipitation resulting from increasing atmospheric CO₂ concentrations will cause a northward migration of the hardwood-conifer forest border in North America.” If such a shifting of species occurs, it likely will lead to an increase in methane consumption by soils and a reduction in methane-induced global warming potential—a biologically mediated negative feedback factor that is not reflected in models of global climate change.

More recently, Livesley *et al.* (2009) wrote, “soils provide the largest terrestrial carbon store, the largest atmospheric CO₂ source, the largest terrestrial N₂O [nitrous oxide] source and the largest terrestrial CH₄ sink, as mediated through root and soil microbial processes” and “a change in land use or management can alter these soil processes such that net greenhouse gas exchange may increase or decrease.” As Mutuo *et al.* (2005) have noted, “intensified agricultural practices lead to a reduction in ecosystem carbon stocks, mainly due to removal of aboveground biomass as harvest and loss of carbon as CO₂ through burning and/or decomposition,” such as occurs in response to tillage operations. Mutuo *et al.* further report upland forests typically consume methane, and “conversion of tropical forest soils to agriculture in general has been shown to reduce the sink strength for methane (Keller *et al.*, 1990; Keller and Reiners, 1994; Stuedler *et al.*, 1996; Verchot *et al.*, 2000)” by

50 percent or more.

Seeking to learn more about how greenhouse gas emission and absorption differ between forests and pastures, Livesley *et al.* (2009) “measured soil-atmosphere exchange of CO₂, N₂O and CH₄ in four adjacent land-use systems (native eucalypt woodland, clover-grass pasture, *Pinus radiata* and *Eucalyptus globulus* plantation) for short, but continuous, periods between October 2005 and June 2006 using an automated trace gas measurement system near Albany in southwest Western Australia.” The six scientists discovered soil N₂O emissions were more than an order of magnitude greater in the pasture than in the natural and managed forests, while soil CH₄ uptake was greatest in the native woodland, even though the measured rates of uptake there were, as they describe it, “still small when compared with many other studies on native forest soils worldwide.” They determined the pasture soil had the least soil CH₄ uptake (a mean of 17 percent of that in the native woodland) and that it was an occasional CH₄ source, “possibly related to its greater soil water status, greater soil nitrogen status and possible differences in soil microbial community structure.” In between these two extremes, they found “afforestation with pines or eucalypts increased CH₄ uptake to 32% and 43% of that in the native woodland, respectively.” With respect to CO₂, they noted “it is widely accepted that afforestation leads to an increase in carbon sequestration through tree biomass growth.”

Livesley *et al.* reported their study confirmed “there is a triple greenhouse-gas benefit from afforestation of pasture systems,” noting in addition to carbon sequestration via tree biomass, “there is a decrease in N₂O emissions because of lower nitrogen inputs and a tighter nutrient cycling, and an increase in CH₄ uptake by forest soils.”

Guckland *et al.* (2009) conducted a two-year study of a deciduous mixed forest in the Hainich National Park, Thuringia, Germany, where they established 18 sub-plots spread throughout three types of forest and, using dark closed chambers from September 2005 to September 2007, they measured net fluxes of CH₄ every two weeks. Stand A, as they describe it, “was a single-species stand covered with European beech as the predominant tree species,” while stand B “was a three-species stand with beech, ash and lime as predominant species, and stand C was covered with beech, ash, lime, hornbeam and maple as predominant species.”

Guckland *et al.* report “the variation of CH₄

uptake over time could be explained to a large extent by changes in soil moisture in the upper five centimeters of the mineral soil,” such that “the CH₄ uptake during the main growing period (May-September) increased considerably with decreasing precipitation rate.” This finding, they write, is “in accordance with the general observation that soil moisture is the primary environmental control on CH₄ uptake in soils because it regulates methane flux into the soil through diffusion (Smith *et al.*, 2000; Butterbach-Bahl and Papen, 2002; Boroken *et al.*, 2006).” They also report the methane flux response to soil moisture content was linear, as has been found to be the case in other studies (Dobbie and Smith, 1996; Bradford *et al.*, 2001; Price *et al.*, 2003). In addition, they observed “low CH₄ uptake activity during winter was further reduced by periods with soil frost and snow cover.” Such findings, in the words of the three researchers, “suggest that climate change [in this case, global warming] will result in increasing CH₄ uptake rates in this region because of the trend to drier summers and warmer winters.”

Carter *et al.* (2011) introduce their study of the subject by stating, “in temperate regions, climate change is predicted to increase annual mean temperature and intensify the duration and frequency of summer droughts, which together with elevated atmospheric carbon dioxide concentrations, may affect the exchange of nitrous oxide and methane between terrestrial ecosystems and the atmosphere.” Working in a dry temperate heathland with a nutrient-poor sandy soil located about 50 km northwest of Copenhagen, Denmark—the vegetation of which was dominated by Scotch Heather (*Calluna vulgaris*), Wavy Hairgrass (*Deschampsia flexuosa*), and various mosses—Carter *et al.* investigated “the effects of future climatic and atmospheric conditions on the biosphere-atmosphere exchange of N₂O and CH₄.”

The eight Danish researchers report warming by itself increased CH₄ uptake by about 20 percent, whereas “elevated concentrations of atmospheric CO₂ had no overall effect on the CH₄ flux, but reduced the CH₄ uptake during one measuring campaign in the winter season.” They add, “in combination, the stimulating effect of warming and the episodic reducing effect of CO₂ on the CH₄ uptake resulted in a modest, but insignificant, increase in the CH₄ uptake when comparing the multifactor treatment including elevated CO₂, warming and summer drought with the ambient treatment.” Carter *et al.* conclude their study “highlights the importance of evaluating climate

change parameters in multifactor treatments as the response of CH₄ and N₂O flux rates to different two- and three-factor combinations may not be predicted from the responses to the individual treatments.” They further state “overall, our study suggests that in the future, CH₄ uptake may increase slightly, while N₂O emission will remain unchanged in temperate ecosystems on well-aerated soils.”

Zheng *et al.* (2012) reiterate that “methane is the second most important greenhouse gas contributing roughly 20% to observed global warming (IPCC, 2007),” while adding “oxidation of CH₄ in soil by methane-oxidizing bacteria (methanotrophs) currently removes 30 Tg annually from the atmosphere, which equals 5.4% of the global CH₄ sink (IPCC, 2007).” They note CH₄-eating bacteria “play a critical role in the mitigation of global warming.” Exploring this potential role further, Zheng *et al.* studied the effects of a 1.2°C higher daylight temperature together with a 1.7°C higher nighttime temperature, with and without continuous concomitant grazing by adult Tibetan sheep, on methanotrophic abundance, community composition, and activity. The work was conducted at the Haibei Alpine Meadow Ecosystem Research Station of the Chinese Academy of Sciences in Qinghai Province in the northeastern corner of the Tibetan Plateau, while utilizing the infrared heating system and free-air temperature enhancement protocol developed by Kimball *et al.* (2008).

In the non-grazed treatments, Zheng *et al.* (2012) found the experimental warming increased methanotrophic abundance by approximately 93 percent, while in the grazed treatments, warming boosted methanotrophic abundance by more than twice that amount (183 percent) (see Figure 2.2.3.1).

Zheng *et al.* conclude the Tibetan Plateau “may remove more CH₄ [from the atmosphere] under future climate conditions.” By inference, that will likely be the case almost everywhere, as they note “methanotrophs are widely distributed in various environments (e.g., McDonald *et al.*, 2008; Op den Camp *et al.*, 2009; Semrau *et al.*, 2010), such as in paddy soils (Bodelier *et al.*, 2000; Zheng *et al.*, 2008), forest soils (Mohanty *et al.*, 2007; Kolb, 2009), landfill soils (Chen *et al.*, 2007; Einola *et al.*, 2007; Semrau, 2011), grassland soils (Zhou *et al.*, 2008; Abell *et al.*, 2009), oil field soil (Zhang *et al.*, 2010), and extreme thermoacidophilic environments (Dunfield *et al.*, 2007; Pol *et al.*, 2007; Islam *et al.*, 2008).” This terrestrial effect of global warming constitutes a significant biologically induced negative feedback, independent of the additional feedbacks

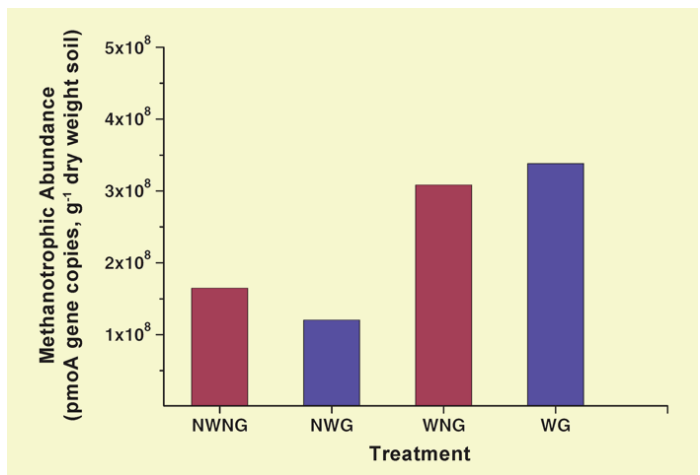


Figure 2.2.3.1. Methanotrophic abundance, expressed as the number of pmoA gene copies of methanotrophs in the soils of the four different treatments (NWNG no warming with no grazing, NWG no warming with grazing, WNG warming with no grazing, WG warming with grazing). Adapted from Zheng, Y., Yang, W., Sun, X., Wang, S.-P., Rui, Y.-C., Luo, C.-Y., and Guo, L.-D. 2012. Methanotrophic community structure and activity under warming and grazing of alpine meadow on the Tibetan Plateau. *Applied Microbiology and Biotechnology* **93**: 2193–2203.

described above that are brought about by mere increases in the air’s CO₂ concentration.

References

- Abell, G.C.J., Stralis-Pavese, N., Sessitsch, A., and Bodrossy, L. 2009. Grazing affects methanotroph activity and diversity in an alpine meadow soil. *Environmental Microbiology Reports* **1**: 457–465.
- Bodelier, P.L.E., Roslev, P., Henckel, T., and Frenzel, P. 2000. Stimulation by ammonium-based fertilizers of methane oxidation in soil around rice roots. *Nature* **403**: 421–424.
- Borken, W., Davidson, E.A., Savage, K., Sundquist, E.T., and Steudler, P. 2006. Effect of summer throughfall exclusion, summer drought, and winter snow cover on methane fluxes in a temperate forest soil. *Soil Biology & Biochemistry* **38**: 1388–1395.
- Bradford, M.A., Ineson, P., Wookey, P.A., and Lappin-Scott, H.M. 2001. Role of CH₄ oxidation, production and transport in forest soil CH₄ flux. *Soil Biology & Biochemistry* **33**: 1625–1631.
- Butterbach-Bahl, K. and Papen, H. 2002. Four years continuous record of CH₄-exchange between the atmosphere and untreated and limed soil of an N-saturated

- spruce and beech forest ecosystem in Germany. *Plant and Soil* **240**: 77–90.
- Carter, M.S., Ambus, P., Albert, K.R., Larsen, K.S., Andersson, M., Prieme, A. van der Linden, L., and Beier, C. 2011. Effects of elevated atmospheric CO₂, prolonged summer drought and temperature increase on N₂O and CH₄ fluxes in a temperate heathland. *Soil Biology & Biochemistry* **43**: 1660–1670.
- Chen, Y., Dumont, M.G., Cebon, A., and Murrell, J.C. 2007. Identification of active methanotrophs in a landfill cover soil through detection of expression of 16S rRNA and functional genes. *Environmental Microbiology* **9**: 2855–2869.
- Dobbie, K.E. and Smith, K.A. 1996. Comparison of CH₄ oxidation rates in woodland, arable and set aside soils. *Soil Biology & Biochemistry* **28**: 1357–1365.
- Dunfield, P.F., Yuryev, A., Senin, P., Smirnova, A.V., Stott, M.B., Hou, S.B., Ly, B., Saw, J.H., Zhou, Z.M., Ren, Y., Wang, J.M., Mountain, B.W., Crowe, M.A., Weatherby, T.M., Bodelier, P.L.E., Liesack, W., Feng, L., Wang, L., and Alam, M. 2007. Methane oxidation by an extremely acidophilic bacterium of the phylum Verrucomicrobia. *Nature* **450**: 879–882.
- Einola, J.K.M., Kettunen, R.H., and Rintala, J.A. 2007. Responses of methane oxidation to temperature and water content in cover soil of a boreal landfill. *Soil Biology and Biochemistry* **39**: 1156–1164.
- Guckland, A., Flessa, H., and Prenzel, J. 2009. Controls of temporal and spatial variability of methane uptake in soils of a temperate deciduous forest with different abundance of European beech (*Fagus sylvatica* L.). *Soil Biology & Biochemistry* **41**: 1659–1667.
- IPCC. 2007. *Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., and Miller, H.L. (Eds.) Cambridge University Press, Cambridge, United Kingdom, pp. 539–543.
- Islam, T., Jensen, S., Reigstad, L.J., Larsen, O., and Birkeland, N.K. 2008. Methane oxidation at 55°C and pH 2 by a thermoacidophilic bacterium belonging to the Verrucomicrobia phylum. *Proceedings of the National Academy of Sciences, USA* **105**: 300–304.
- Jensen, S. and Olsen, R.A. 1998. Atmospheric methane consumption in adjacent arable and forest soil systems. *Soil Biology & Biochemistry* **30**: 1187–1193.
- Keller, M. 1986. Emissions of N₂O, CH₄, and CO₂ from tropical forest soils. *Journal of Geophysical Research* **91**: 11,791–11,802.
- Keller, M., Mitre, M.E., and Stallard, R.F. 1990. Consumption of atmospheric methane in soils of Central Panama: Effects of agricultural development. *Global Biogeochemical Cycles* **4**: 21–27.
- Keller, M. and Reiners, W.A. 1994. Soil-atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. *Global Biogeochemical Cycles* **8**: 399–409.
- Kimball, B.A., Conley, M.M., Wang, S.P., Lin, X.W., Luo, C.Y., Morgan, J., and Smith, D. 2008. Infrared heater arrays for warming ecosystem field plots. *Global Change Biology* **14**: 309–320.
- Kolb, S. 2009. The quest for atmospheric methane oxidizers in forest soils. *Environmental Microbiology Reports* **1**: 336–346.
- Le Mer, J. and Roger, P. 2001. Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology* **37**: 25–50.
- Livesley, S.J., Kiese, R., Miehle, P., Weston, C.J., Butterbach-Bahl, K., and Arndt, S.K. 2009. Soil-atmosphere exchange of greenhouse gases in a *Eucalyptus marginata* woodland, a clover-grass pasture and *Pinus radiata* and *Eucalyptus globulus* plantations. *Global Change Biology* **15**: 425–440.
- McDonald, I.R., Bodrossy, L., Chen, Y., and Murrell, J.C. 2008. Molecular ecology techniques for the study of aerobic methanotrophs. *Applied Environmental Microbiology* **74**: 1305–1315.
- Menyailo, O.V. and Hungate, B.A. 2003. Interactive effects of tree species and soil moisture on methane consumption. *Soil Biology & Biochemistry* **35**: 625–628.
- Menyailo, O.V., Hungate, B.A., and Zech, W. 2002. Tree species mediated soil chemical changes in a Siberian artificial afforestation experiment. *Plant and Soil* **242**: 171–182.
- Mohanty, S.R., Bodelier, P.L.E., and Conrad, R. 2007. Effect of temperature on composition of the methanotrophic community in rice field and forest soil. *FEMS Microbiology Ecology* **62**: 24–31.
- Mosier, A.R., Parton, W.J., Valentine, D.W., Ojima, D.S., Schimel, D.S., and Heinemeyer, O. 1997. CH₄ and N₂O fluxes in the Colorado shortgrass steppe. 2. Long-term impact of land use change. *Global Biogeochemical Cycles* **11**: 29–42.
- Mutuo, P.K., Cadisch, G., Albrecht, A., Palm, C.A., and Verchot, L. 2005. Potential of agroforestry for carbon sequestration and mitigation of greenhouse gas emissions

- from soils in the tropics. *Nutrient Cycling in Agroecosystems* **71**: 45–54.
- Op den Camp, H.J.M., Islam, T., Stott, M.B., Harhangi, H.R., Hynes, A., Schouten, S., Jetten, M.S.M., Birkeland, N.K., Pol, A., and Dunfield, P.F. 2009. Environmental, genomic and taxonomic perspectives on methanotrophic *Verrucomicrobia*. *Environmental Microbiology Reports* **1**: 293–306.
- Pastor, J. and Post, W.M. 1988. Response of northern forests to CO₂-induced climate change. *Nature* **334**: 55–58.
- Peterjohn, W.T., Melillo, J.M., Steudler, P.A., and Newkirk, K.M. 1994. Responses of trace gas fluxes and N availability to experimentally elevated soil temperatures. *Ecological Applications* **4**: 617–625.
- Pol, A., Heijmans, K., Harhangi, H.R., Tedesco, D., Jetten, M.S.M., and Op den Camp, H.J.M. 2007. Methanotrophy below pH 1 by a new *Verrucomicrobia* species. *Nature* **450**: 874–878.
- Price, S.J., Sherlock, R.R., Kelliher, F.M., McSeveny, T.M., Tate, K.R., and Condron, L.M. 2003. Pristine New Zealand forest soil is a strong methane sink. *Global Change Biology* **10**: 16–26.
- Prieme, A. and Christensen, S. 1997. Seasonal and spatial variation of methane oxidation in a Danish spruce forest. *Soil Biology & Biochemistry* **29**: 1165–1172.
- Prinn, R., Cunnold, D., Simmonds, P., Alyea, F., Boldi, R., Crawford, A., Fraser, P., Gutzler, D., Hartley, D., Rosen, R., and Rasmussen, R. 1992. Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978–1990. *Journal of Geophysical Research* **97**: 2445–2461.
- Saari, A., Heiskanen, J., and Martikainen, P.J. 1998. Effect of the organic horizon on methane oxidation and uptake in soil of a boreal Scots pine forest. *FEMS Microbiology Ecology* **26**: 245–255.
- Semrau, J.D. 2011. Current knowledge of microbial community structures in landfills and its cover soils. *Applied Microbiology and Biotechnology* **89**: 961–969.
- Semrau, J.D., DiSpirito, A.A., and Yoon, S. 2010. Methanotrophs and copper. *FEMS Microbiology Reviews* **34**: 496–531.
- Singh, J.S., Singh, S., Raghubanshi, A.S., Singh, S., Kashyap, A.K., and Reddy, V.S. 1997. Effect of soil nitrogen, carbon and moisture on methane uptake by dry tropical forest soils. *Plant and Soil* **196**: 115–121.
- Smith, K.A., Dobbie, K.E., Ball, B.C., Bakken, L.R., Sitaula, B.K., Hansen, S., Brumme, R., Borken, W., Christensen, S., Prieme, A., Fowler, D., MacDonald, J.A., Skiba, U., Klemedtsson, L., Kasimir-Klemedtsson, A., Degorrska, A., and Orlanski, P. 2000. Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink. *Global Change Biology* **6**: 791–803.
- Steudler, P.A., Bowden, R.D., Meillo, J.M., and Aber, J.D. 1989. Influence of nitrogen fertilization on CH₄ uptake in temperate forest soils. *Nature* **341**: 314–316.
- Steudler, P.A., Melillo, J.M., Feigl, B.J., Neill, C., Piccolo, M.C., and Cerri, C. 1996. Consequences of forest-to-pasture conversion on CH₄ fluxes in the Brazilian Amazon Basin. *Journal of Geophysical Research* **101**: 547–554.
- Striegl, R.G., McConnaughey, T.A., Thorstensen, D.C., Weeks, E.P., and Woodward, J.C. 1992. Consumption of atmospheric methane by desert soils. *Nature* **357**: 145–147.
- Tamai, N., Takenaka, C., Ishizuka, S., and Tezuka, T. 2003. Methane flux and regulatory variables in soils of three equal-aged Japanese cypress (*Chamaecyparis obtusa*) forests in central Japan. *Soil Biology & Biochemistry* **35**: 633–641.
- Verchot, L.V., Davidson, E.A., Cattanio, J.H., and Ackerman, I.L. 2000. Land-use change and biogeochemical controls on methane fluxes in soils of eastern Amazon. *Ecosystems* **3**: 41–56.
- Watson, R.T., Meira Filho, L.G., Sanhueza, E., and Janetos, A. 1992. Sources and sinks. In: Houghton, J.T., Callander, B.A., and Varney, S.K. (Eds.) *Climate Change 1992: The Supplementary Report to The IPCC Scientific Assessment*, Cambridge University Press, Cambridge, UK, pp. 25–46.
- Whalen, S.C. and Reeburgh, W.S. 1990. Consumption of atmospheric methane by tundra soils. *Nature* **346**: 160–162.
- Whalen, S.C. and Reeburgh, W.S. 1996. Moisture and temperature sensitivity of CH₄ oxidation in boreal soils. *Soil Biology & Biochemistry* **28**: 1271–1281.
- Whalen, S.C., Reeburgh, W.S., and Barber, V.A. 1992. Oxidation of methane in boreal forest soils: a comparison of seven measures. *Biogeochemistry* **16**: 181–211.
- Yavitt, J.B., Downey, D.M., Lang, D.E., and Sextone, A.J. 1990. CH₄ consumption in two temperate forest soils. *Biogeochemistry* **9**: 39–52.
- Zhang, F., She, Y.H., Zheng, Y., Zhou, Z.F., Kong, S.Q., and Hou, D.J. 2010. Molecular biologic techniques applied to the microbial prospecting of oil and gas in the Ban 876 gas and oil field in China. *Applied Microbiology and Biotechnology* **86**: 1183–1194.
- Zheng, Y., Yang, W., Sun, X., Wang, S.-P., Rui, Y.-C., Luo, C.-Y., and Guo, L.-D. 2012. Methanotrophic community structure and activity under warming and

grazing of alpine meadow on the Tibetan Plateau. *Applied Microbiology and Biotechnology* **93**: 2193–2203.

Zheng, Y., Zhang, L.M., Zheng, Y.M., Di, H.J., and He, J.Z. 2008. Abundance and community composition of methanotrophs in a Chinese paddy soil under long-term fertilization practices. *Journal of Soils and Sediments* **8**: 406–414.

Zhou, X.Q., Wang, Y.F., Huang, X.Z., Tian, J.Q., and Hao, Y.B. 2008. Effect of grazing intensities on the activity and community structure of methane-oxidizing bacteria of grassland soil in Inner Mongolia. *Nutrient Cycling in Agroecosystems* **80**: 145–152.

2.3 Nitrous Oxide

Nitrous oxide (N₂O) is an influential greenhouse gas, with a global warming potential approximately 300 times that of CO₂ on a per-molecule basis (IPCC, 2001). According to Cantarel *et al.* (2011), nitrous oxide “has shown linear increases of 0.2–0.3% per year over the last few decades, largely as a result of changes in agricultural practices and direct emissions from agricultural soils (IPCC, 2007).”

Consequently, understanding the factors that control the concentration of N₂O in the atmosphere and how the sources and sinks of N₂O vary with changes in climate and other factors is an important concern among the scientific community. This section reviews research that has been conducted on this topic, beginning with a discussion of studies examining how increases in atmospheric CO₂ might modify the release of N₂O into the atmosphere.

One of the main sources of nitrous oxide is agriculture, which accounts for almost half of N₂O emissions in some countries (Pipatti, 1997). And with N₂O originating from microbial N cycling in soil—mostly from aerobic nitrification or from anaerobic denitrification (Firestone and Davidson, 1989)—there is a concern that CO₂-induced increases in carbon input to soil, together with increasing N input from other sources, will increase substrate availability for denitrifying bacteria and may result in higher N₂O emissions from agricultural soils as the air’s CO₂ content continues to rise.

In a study designed to investigate this possibility, Kettunen *et al.* (2007a) grew mixed stands of timothy (*Phleum pratense*) and red clover (*Trifolium pratense*) in sandy-loam-filled mesocosms at low and moderate soil nitrogen levels within greenhouses maintained at either 360 or 720 ppm CO₂, while measuring harvestable biomass production and N₂O

evolution from the mesocosm soils over the course of three crop cuttings. This work revealed the total harvestable biomass production of *P. pratense* was enhanced by the experimental doubling of the air’s CO₂ concentration by 21 percent and 26 percent, respectively, in the low and moderate soil N treatments, while corresponding biomass enhancements for *T. pratense* were 22 percent and 18 percent. In addition, the researchers found after emergence of the mixed stand and during vegetative growth before the first harvest and N fertilization, N₂O fluxes were higher under ambient CO₂ in both the low and moderate soil N treatments. It was not until the water table had been raised and extra fertilization given after the first harvest that the elevated CO₂ seemed to increase N₂O fluxes.

The four Finnish researchers conclude the mixed stand of *P. pratense* and *T. pratense* was “able to utilize the increased supply of atmospheric CO₂ for enhanced biomass production without a simultaneous increase in the N₂O fluxes,” thereby raising “the possibility of maintaining N₂O emissions at their current level, while still enhancing the yield production [via the aerial fertilization effect of elevated CO₂] even under low N fertilizer additions.”

Kettunen *et al.* (2007b) also grew timothy (*Phleum pratense*) in monoculture within sandy-soil-filled mesocosms located within greenhouses maintained at atmospheric CO₂ concentrations of either 360 or 720 ppm for a period of 3.5 months at moderate (standard), low (half-standard), and high (1.5 times standard) soil N supply, while they measured the evolution of N₂O from the mesocosms, vegetative net CO₂ exchange, and final above- and below-ground biomass production over the course of three harvests. The elevated CO₂ concentration increased the net CO₂ exchange of the ecosystems (which phenomenon was primarily driven by CO₂-induced increases in photosynthesis) by about 30 percent, 46 percent, and 34 percent at the low, moderate, and high soil N levels, respectively. The elevated CO₂ increased the above-ground biomass of the crop by about 8 percent, 14 percent, and 8 percent at the low, moderate, and high soil N levels, and its below-ground biomass by 28 percent, 27 percent, and 41 percent at the same respective soil N levels. Kettunen *et al.* report once again, “an explicit increase in N₂O fluxes due to the elevated atmospheric CO₂ concentration was not found.”

While working at the Nevada Desert FACE facility northwest of Las Vegas, Nevada (USA),

McCalley *et al.* (2011) measured soil fluxes of reactive N gases (NO, NO_y, NH₃) and N₂O in plots receiving long-term fumigation with ambient (380 ppm) and elevated (550 ppm) CO₂. These treatments were begun in April 1997; reactive N gas flux measurements were made under these conditions several years later in April 2005, July 2005, July 2006, January 2007, and March 2007, as well as after the termination of CO₂ fumigation in July 2007, October 2007, January 2008, and April 2008.

The five researchers report “long-term exposure to elevated CO₂ decreased reactive N gas emissions from Mojave Desert soils” primarily “in islands of fertility created by the dominant shrub *Larrea tridentata*,” especially “in the spring and fall when recent precipitation, either natural or artificial, created soil conditions that are optimal for biological activity.” Emissions of N₂O, on the other hand, were “a very small component” of gaseous N loss and were “largely insensitive to elevated CO₂.” In addition, the five researchers state the greater-than-60 percent reductions in reactive N gas fluxes during periods of peak N demand imply elevated CO₂ is “increasing the retention of biologically available N during critical growth periods,” a major benefit for desert ecosystems.

As reported earlier in our discussion of methane extraction from the atmosphere, Livesley *et al.* (2009) point out “soils provide the largest terrestrial carbon store, the largest atmospheric CO₂ source, the largest terrestrial N₂O source and the largest terrestrial CH₄ sink, as mediated through root and soil microbial process” and “a change in land use or management can alter these soil processes such that net greenhouse gas exchange may increase or decrease.” Seeking to determine how the emission and absorption of these three greenhouse gases differ between forests and pastures, they “measured soil-atmosphere exchange of CO₂, N₂O and CH₄ in four adjacent land-use systems (native eucalypt woodland, clover-grass pasture, *Pinus radiata* and *Eucalyptus globulus* plantation) for short, but continuous, periods between October 2005 and June 2006 using an automated trace gas measurement system near Albany in southwest Western Australia.”

With respect to nitrous oxide, the six scientists discovered soil N₂O emissions were more than an order of magnitude greater in the pasture than in the natural and managed forests. Given the authors’ findings with respect to CO₂ and CH₄, they conclude “there is a triple greenhouse-gas benefit from afforestation of pasture systems,” where in addition to

carbon sequestration via tree biomass, “there is a decrease in N₂O emissions because of lower nitrogen inputs and a tighter nutrient cycling, and an increase in CH₄ uptake by forest soils.”

In a different type of study, driven by the possibility that the climate of the Amazon Basin may gradually become drier due to a warming-induced increase in the frequency and/or intensity of El Niño events that have historically brought severe drought to the region, Davidson *et al.* (2004) devised an experiment to determine the consequences of the drying of the soil of an Amazonian moist tropical forest for the net surface-to-air fluxes of both N₂O and methane (CH₄).

As we reported earlier in our discussion of this study with respect to methane, the researchers modified a one-hectare plot of land covered by mature evergreen trees so as to dramatically reduce the amount of rain that reached the forest floor (throughfall), while maintaining an otherwise similar one-hectare plot of land as a control for comparison. Prior to making this modification, the three researchers measured the gas exchange characteristics of the two plots for a period of 18 months, and after initiating the throughfall-exclusion treatment, they continued their measurements for an additional three years. This work revealed the “drier soil conditions caused by throughfall exclusion inhibited N₂O and CH₄ production and promoted CH₄ consumption.” They note “the exclusion manipulation lowered annual N₂O emissions by >40 percent and increased rates of consumption of atmospheric CH₄ by a factor of >4,” which they attributed to the “direct effect of soil aeration on denitrification, methanogenesis, and methanotrophy.”

Other researchers also have examined the relationship between nitrous oxide emissions and soil water status. Goldberg and Gebauer (2009), for example, investigated the influence of drying and rewetting events on N₂O emissions from the soil of a mature Norway spruce forest in Northeast Bavaria, Germany. They point out “the only sink for N₂O considered in global models is the destruction of atmospheric N₂O in the stratosphere through photolysis and photooxidation (IPCC, 2007).” Citing the 2007 IPCC report, they note “soils have been identified as the main sources for atmospheric N₂O.”

To learn more about the emission of N₂O from wet vs. dry soils, Goldberg and Gebauer induced an artificial summer drought of 46 days duration (which was accompanied by a natural drought) via throughfall exclusion (TE) that was provided by

special roof installations, which they followed with an experimental rewetting of 66 mm over two days, during which periods (and before and after them) they closely monitored N₂O fluxes from the soils of the TE and unaltered control (C) plots that were exposed to the elements.

The two researchers write, “before the drought, both the C and TE plots showed slightly positive N₂O fluxes from the soil to the atmosphere,” in harmony with the sentiment of the IPCC. During the drought, on the other hand, “the soil of both the throughfall exclusion and control plots served as an N₂O sink,” contrary to what might have been expected in light of IPCC statements. They state, “the sink strength of the throughfall exclusion plots was doubled compared with the control plots.” Rewetting “turned the soil into a source for atmospheric N₂O again,” but “it took almost four months to turn the cumulative soil N₂O fluxes from negative (sink) to positive (source) values.” Goldberg and Gebauer conclude, “long drought periods can lead to drastic decreases of N₂O fluxes from soils to the atmosphere or may even turn forest soils temporarily to N₂O sinks,” which may in some places persist for years at a time. It is also possible that over the entire terrestrial surface of the planet, the net result is that “soils are the main sources for atmospheric N₂O,” as stated by the IPCC. Nevertheless, the two scientists conclude that what they call an unbalanced global N₂O budget “underlines the likelihood of a hitherto unconsidered sink function of soils.”

In combining the effects of soil water status and atmospheric CO₂ on N₂O emissions, Welzmler *et al.* (2008) measured N₂O and denitrification emission rates in a C₄ sorghum [*Sorghum bicolor* (L.) Moench] production system with ample and limited flood irrigation rates under free-air CO₂ enrichment (seasonal mean = 579 ppm) and control (seasonal mean = 396 ppm) conditions during the 1998 and 1999 summer growing seasons at the experimental FACE site near Maricopa, Arizona (USA). They found “elevated CO₂ did not result in increased N₂O or N-gas emissions with either ample or limited irrigation,” which they describe as being “consistent with findings for unirrigated western U.S. ecosystems reported by Billings *et al.* (2002) for Mojave Desert soils and by Mosier *et al.* (2002) for Colorado shortgrass steppe.” Welzmler *et al.* say their results suggest “as CO₂ concentrations increase, there will not be major increases in denitrification in C₄ cropping environments such as irrigated sorghum in

the desert southwestern United States,” which further suggests there will not be an increased impetus for global warming due to this phenomenon.

Adding temperature to the mix, Cantarel *et al.* (2011) monitored N₂O fluxes in an *in situ* ecosystem manipulation experiment simulating the climate predicted for the study area (an upland temperate grassland in the French Massif Central region), making use of the Clermont Climate Change Experiment facility, where Bloor *et al.* (2010) were conducting “a long-term grassland study of multiple climate changes applied in an additive experimental design.” Over a two-year period, they monitored N₂O fluxes under conditions “simulating the climate predicted for the study area in 2080 (3.5°C temperature increase, 20% reduction in summer rainfall and atmospheric CO₂ levels of 600 ppm).”

“Overall,” as the four researchers describe the results of their study, “experimental warming had a positive effect on the annual N₂O emissions.” However, and “contrary to expectations,” as they put it, “combined summer drought and warming had no significant effect on mean N₂O fluxes recorded at any time,” nor did “elevated CO₂ in combination with warming and drought.”

Also writing in 2011, Carter *et al.* (2011) note “in temperate regions, climate change is predicted to increase annual mean temperature and intensify the duration and frequency of summer droughts, which together with elevated atmospheric carbon dioxide concentrations, may affect the exchange of nitrous oxide (N₂O) and methane (CH₄) between terrestrial ecosystems and the atmosphere.” Working in a dry, temperate heathland with a nutrient-poor sandy soil located about 50 km northwest of Copenhagen, Denmark—the vegetation of which was dominated by Scotch Heather (*Calluna vulgaris*), Wavy Hairgrass (*Deschampsia flexuosa*), and various mosses—Carter *et al.* set out to investigate “the effects of future climatic and atmospheric conditions on the biosphere-atmosphere exchange of N₂O and CH₄.”

With respect to N₂O emissions (we reported their results with respect to methane earlier), the researchers found “as single experimental factors, elevated CO₂, temperature and summer drought had no major effect on the N₂O fluxes, but the combination of CO₂ and warming stimulated N₂O emission, whereas the N₂O emission ceased when CO₂ was combined with drought.” Carter *et al.* conclude their study “highlights the importance of evaluating climate change parameters in multifactor

treatments as the response of CH₄ and N₂O flux rates to different two- and three-factor combinations may not be predicted from the responses to the individual treatments.” They add, “overall, our study suggests that in the future, CH₄ uptake may increase slightly, while N₂O emission will remain unchanged in temperate ecosystems on well-aerated soils.”

The research reviewed here thus suggests concerns about additional global warming arising from enhanced N₂O emissions from agricultural soils in a CO₂-enriched atmosphere of the future are not well founded.

References

- Billings, S.A., Schaeffer, S.M., and Evans, R.D. 2002. Trace N gas losses and mineralization in Mojave Desert soils exposed to elevated CO₂. *Soil Biology and Biochemistry* **34**: 1777–1784.
- Bloor, J.M.G., Pichon, P., Falcimagne, R., Leadley, P., and Soussana, J.F. 2010. Effects of warming, summer drought and CO₂ enrichment on aboveground biomass production, flowering phenology and community structure in an upland grassland ecosystem. *Ecosystems* **13**: 888–900.
- Cantarel, A.A.M., Bloor, J.M.G., Deltroy, N., and Soussana, J.-F. 2011. Effects of climate change drivers on nitrous oxide fluxes in an upland temperate grassland. *Ecosystems* **14**: 223–233.
- Carter, M.S., Ambus, P., Albert, K.R., Larsen, K.S., Andersson, M., Prieme, A. van der Linden, L., and Beier, C. 2011. Effects of elevated atmospheric CO₂, prolonged summer drought and temperature increase on N₂O and CH₄ fluxes in a temperate heathland. *Soil Biology & Biochemistry* **43**: 1660–1670.
- Davidson, E.A., Ishida, F.Y., and Nepstad, D.C. 2004. Effects of an experimental drought on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest. *Global Change Biology* **10**: 718–730.
- Firestone, M.K. and Davidson, E.A. 1989. Microbiological basis of NO and N₂O production and consumption in soil. In: Andreae, M.O. and Schimel, D.S. (Eds.) *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. Wiley, Chichester, pp. 7–21.
- Goldberg, S.D. and Gebauer, G. 2009. Drought turns a Central European Norway spruce forest soil from an N₂O source to a transient N₂O sink. *Global Change Biology* **15**: 850–860.
- IPCC. 2001. *Climate Change 2001: Contribution of the Working Group II to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. McCarthy, J.J., Canzani, O.F., Leary, N.A., Dokken, D.J. and White, K.S. (Eds.) Cambridge University Press, Cambridge, UK.
- IPCC. 2007. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Solomon, S., Qin, D., Manning, M., Marquis, M., Avery, K., Tignor, M.M.B., Le Roy Miller Jr., H. and Chen, Z. (Eds.) Cambridge University Press, Cambridge, UK.
- Kettunen, R., Saarnio, S., Martikainen, P.J., and Silvola, J. 2007a. Can a mixed stand of N₂-fixing and non-fixing plants restrict N₂O emissions with increasing CO₂ concentration? *Soil Biology & Biochemistry* **39**: 2538–2546.
- Kettunen, R., Saarnio, S., and Silvola, J. 2007b. N₂O fluxes and CO₂ exchange at different N doses under elevated CO₂ concentration in boreal agricultural mineral soil under *Phleum pratense*. *Nutrient Cycling in Agroecosystems* **78**: 197–209.
- Livesley, S.J., Kiese, R., Miehle, P., Weston, C.J., Butterbach-Bahl, K., and Arndt, S.K. 2009. Soil-atmosphere exchange of greenhouse gases in a *Eucalyptus marginata* woodland, a clover-grass pasture and *Pinus radiata* and *Eucalyptus globulus* plantations. *Global Change Biology* **15**: 425–440.
- McCalley, C.K., Strahm, B.D., Sparks, K.L., Eller, A.S.D., and Sparks, J.P. 2011. The effect of long-term exposure to elevated CO₂ on nitrogen gas emissions from Mojave Desert soils. *Journal of Geophysical Research* **116**: 10.1029/2011JG001667.
- Mosier, A.R., Morgan, J.A., King, J.Y., LeCain, D., and Milchunas, D.G. 2002. Soil-atmosphere exchange of CH₄, CO₂, NO_x, and N₂O in the Colorado shortgrass steppe under elevated CO₂. *Plant and Soil* **240**: 201–211.
- Pipatti, R. 1997. Suomen metaani- ja dityppioksidipaastojen rajoittamisen mahdollisuudet ja kustannustehokkuus. VTT tiedotteita. 1835, Espoo.
- Welzmler, J.T., Matthias, A.D., White, S., and Thompson, T.L. 2008. Elevated carbon dioxide and irrigation effects on soil nitrogen gas exchange in irrigated sorghum. *Soil Science Society of America Journal* **72**: 393–401.

2.4 Clouds

Understanding how Earth’s clouds respond to anthropogenic-induced perturbations of the atmosphere is of paramount importance in determining the impact of the ongoing rise in the air’s CO₂ content on global climate. Both naturally occurring and manmade aerosols have a strong influence on cloud albedo (solar reflectance) and

cloud cover, with a global mean thermal forcing estimated to be of approximately the same magnitude as that of mankind's production of greenhouse gases, but of opposite sign.

The following subsections present brief reviews of a number of scientific papers that address these important subjects. Additional information can be found in related subjects treated in this volume, including the inadequacies of climate models in dealing with clouds and the climatic influence of aerosols (see Chapter 1).

2.4.1 Albedo

Perhaps the best-known imputed impact of mankind on climate is the enhancement of the atmosphere's greenhouse effect said to be produced by the carbon dioxide released into the atmosphere by the burning of fossil fuels such as coal, gas, and oil. There are, however, several other ways in which human activities are believed to influence Earth's climate, and many of these phenomena tend to *cool* the globe, primarily by enhancing its albedo, or reflectance of incoming solar radiation.

Ferek *et al.* (1998), for example, observed an increase in the reflectance of solar radiation from clouds exposed to the airborne effluents of ships, while Capaldo *et al.* (1999) determined this phenomenon creates a significant cooling influence over water surfaces in the Northern and Southern Hemispheres. Facchini *et al.* (1999) report organic solutes evolving from agricultural/industrial regions tend to enhance cloud reflectance over land.

Charlson *et al.* (2001) note clouds droplets "are the most important factor controlling the albedo (reflectivity) and hence the temperature of our planet," and manmade aerosols "have a strong influence on cloud albedo, with a global mean forcing estimated to be of the same order (but opposite in sign) as that of greenhouse gases." Even a small change in cloud properties could determine whether the combined influence of anthropogenic activities results in a net warming or cooling of the planet.

The results of several empirical studies led Charlson *et al.* to conclude the anthropogenic impetus for cooling "may be even larger than anticipated." He and his colleagues point out the early IPCC assessments of the situation "do not include the combined influences of some recently identified chemical factors, each of which leads to additional negative forcing (cooling) on top of that currently estimated." They write, "It has recently become clear

that soluble gases, slightly soluble solutes [aerosols], and surface tension depression by organic substances also influence the formation of cloud droplets." The ways in which mankind's activities influence these processes tend to produce extra cloud cooling power that is nowhere to be found in early IPCC analyses of cloud effects on climate.

Consider, for example, the original hypothesis developed by Charlson *et al.* (1987), which has inspired literally hundreds of subsequent confirmatory studies, wherein biology plays an integral role in mitigating global warming. This scenario begins with an initial impetus for warming that stimulates primary production in marine phytoplankton, which results in the production of more copious quantities of dimethylsulphoniopropionate (DMSP), which leads to the evolution of greater amounts of dimethyl sulphide (DMS) in the surface waters of the world's oceans. The DMS diffuses into the atmosphere, where it is oxidized, which leads to the creation of acidic aerosols that function as cloud condensation nuclei. Those nuclei create more and brighter clouds of higher albedo, which reflect more incoming solar radiation back to space, which cools the planet and thereby counters the initial impetus for warming.

Simo and Pedros-Alio (1999) added even more complexity to this scenario by describing a number of short-term photo-induced (and, therefore, mixing-depth mediated) influences on several complex physiological phenomena manifest in marine phytoplankton, as well as longer-term variations in vertical mixing that influence planktonic succession and food-web structure. Ayers and Gillett (2000) summarized empirical evidence in support of Charlson *et al.*'s hypothesis obtained from data collected at Cape Grim, Tasmania since 1988, as well as from what has been reported in prior studies of the subject. They too conclude there is "compelling observational evidence to suggest that DMS and its atmospheric products participate significantly in processes of climate regulation and reactive atmospheric chemistry in the remote marine boundary layer."

Sciare *et al.* (2000) made continuous measurements of atmospheric DMS concentration and a number of environmental parameters from 1990 to 1999 at Amsterdam Island in the southern Indian Ocean, finding a clear seasonal variation with a factor of 20 difference in amplitude between the maximum atmospheric DMS concentration in austral summer and the minimum in austral winter. The DMS

anomalies were found to be “closely related to sea surface temperature anomalies, clearly indicating a link between DMS and climate changes.” They found a sea surface temperature increase of only 1°C was sufficient to increase the atmospheric DMS concentration by as much as 50 percent on a monthly basis, providing what they called a “very important” albedo-moderated negative feedback on the original impetus for warming. (DMS will be discussed more thoroughly later in this chapter.)

In addition to DMS, there is COS, carbonyl sulfide, which operates in a somewhat similar albedo-enhancing fashion over land. COS is the most stable and abundant reduced sulfur gas in the atmosphere and a major player in determining Earth’s radiation balance. After making its way into the stratosphere, it can be photo-dissociated, as well as oxidized, to form SO₂, which is typically converted to sulfate aerosol particles that are highly reflective of incoming solar radiation and, therefore, have the capacity to significantly cool Earth. Like DMS, COS is heavily influenced by planetary biology.

In a study of COS uptake by a lichen species found in an open-oak woodland in central California, Kuhn and Kesselmeier (2000) observed the rate of absorption of COS from the atmosphere by this species declined dramatically once air temperature rose above 25°C. Thus, when temperatures begin to become uncomfortably warm for this and many other species of plants (and animals), more COS remains in the air, which increases the potential for more of it to make its way into the stratosphere, where it can be converted into sulfate aerosol particles that can reflect more incoming solar radiation back to space and thereby cool Earth. Since the consumption of COS by lichens is under the physiological control of carbonic anhydrase—the key enzyme for COS uptake in all higher plants, algae, and soil organisms—one could expect this phenomenon to be generally operative over much of the planet, which it is. This biological “thermostat” may be powerful enough to define an upper limit above which the surface air temperature of Earth may be restricted from rising, even when changes in other forcing factors, such as greenhouse gases, produce a substantial impetus for warming. (COS will be discussed more completely later in this chapter.)

That several of the above-described phenomena, as well as others yet to be elucidated, may be occurring at the present time is suggested by the study of Herman *et al.* (2001), who used satellite data to determine changes in radiation reflected back to space

over the period 1979 to 1992. Their data indicate “there have been increases in reflectivity (cloudiness) poleward of 40°N and 30°S, with some smaller but significant changes occurring in the equatorial and lower middle latitudes.” And they state the overall long-term effect is for an increase in radiation reflected back to space of 2.8 W m⁻² per decade, from which they conclude, “there is a likely cooling effect” provided “by changes in the amount of snow/ice, cloudiness, and aerosols.”

One year later, Chou *et al.* (2002) analyzed aerosol optical properties retrieved from the satellite-mounted Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and used them in conjunction with a radiative transfer model of the planet’s atmosphere to calculate the climatic effects of aerosols over Earth’s oceans. They found “aerosols reduce the annual-mean net downward solar flux by 5.4 W m⁻² at the top of the atmosphere, and by 5.9 W m⁻² at the surface.” During the large Indonesian fires of September–December 1997, however, the radiative impetus for cooling at the top of the atmosphere was more than 10 W m⁻², and it was more than 25 W m⁻² at the surface of the sea in the vicinity of Indonesia.

The magnitude of the radiative warming impetus predicted at the start of the global warming controversy to occur in response to a nominal doubling of the air’s CO₂ content is about 4 W m⁻², less than what researchers have found to be the radiative cooling effect of atmospheric aerosols. Thus over the majority of the planet’s surface, the radiative cooling influence of atmospheric aerosols (many of which are produced by anthropogenic activities) likely prevails, suggesting a probable net anthropogenic-induced climatic signal that must be very close to zero and nowhere near capable of producing what the IPCC refers to as the unprecedented warming of the twentieth century.

Breon *et al.* (2002) assessed the effects of atmospheric aerosols around the globe on cloud microphysics via data on aerosol concentration and cloud droplet radii obtained from the polarization and directionality of the Earth reflectances (POLDER) instrument on the Advanced Earth-Observing Satellite (ADEOS), which began operation on 30 October 1996 and ended on 30 June 1997. In their words, the study’s results “clearly demonstrate a significant impact of aerosols on cloud microphysics.” As aerosol concentrations increased, cloud droplet radii decreased, which should produce a cooling influence due to the greater albedo generally associated with smaller cloud droplets. The researchers also

determined “the bulk of the aerosol load originates from slash-and-burn agriculture practices and from highly polluted areas,” such that “a large fraction of the observed aerosol effect on clouds is probably of anthropogenic origin.”

Although Breon *et al.* were unable to quantify the degree of cooling provided by the presence of the aerosols they studied, they nevertheless concluded this anthropogenic counterforce to the warming impetus provided by the ongoing rise in the air’s CO₂ content is “significant and occurs on a global scale.”

Several natural and anthropogenic-induced negative feedbacks clearly are capable of maintaining the climate of the globe within a temperature range conducive to the continued well-being of all forms of life on Earth. Many of these feedbacks have yet to receive the attention they merit from the IPCC.

References

- Ayers, G.P. and Gillett, R.W. 2000. DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry. *Journal of Sea Research* **43**: 275–286.
- Breon, F.-M., Tanre, D., and Generoso, S. 2002. Aerosol effect on cloud droplet size monitored from satellite. *Science* **295**: 834–838.
- Capaldo, K., Corbett, J.J., Kasibhatla, P., Fischbeck, P., and Pandis, S.N. 1999. Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean. *Nature* **400**: 743–746.
- Charlson, R.J., Lovelock, J.E., Andrea, M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- Charlson, R.J., Seinfeld, J.H., Nenes, A., Kulmala, M., Laaksonen, A., and Facchini, M.C. 2001. Reshaping the theory of cloud formation. *Science* **292**: 2025–2026.
- Chou, M.-D., Chan, P.-K., and Wang, M. 2002. Aerosol radiative forcing derived from SeaWiFS-retrieved aerosol optical properties. *Journal of the Atmospheric Sciences* **59**: 748–757.
- Facchini, M.C., Mircea, M., Fuzzi, S., and Charlson, R.J. 1999. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **401**: 257–259.
- Ferek, R.J., Hegg, D.A., Hobbs, P.V., Durkee, P., and Nielsen, K. 1998. Measurements of ship-induced tracks in clouds off the Washington coast. *Journal of Geophysical Research* **103**: 23,199–23,206.
- Herman, J.R., Larko, D., Celarier, E., and Ziemke, J. 2001. Changes in the Earth’s UV reflectivity from the surface, clouds, and aerosols. *Journal of Geophysical Research* **106**: 5353–5368.
- Kuhn, U. and Kesselmeier, J. 2000. Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research* **105**: 26,783–26,792.
- Loflund, M., Kasper-Giebl, A., Schuster, B., Giebl, H., Hitzenberger, R., and Puxbaum, H. 2002. Formic, acetic, oxalic, malonic and succinic acid concentrations and their contribution to organic carbon in cloud water. *Atmospheric Environment* **36**: 1553–1558.
- Sciare, J., Mihalopoulos, N., and Dentener, F.J. 2000. Interannual variability of atmospheric dimethylsulfide in the southern Indian Ocean. *Journal of Geophysical Research* **105**: 26,369–26,377.
- Simo, R. and Pedros-Alio, C. 1999. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature* **402**: 396–399.

2.4.2 Cloud Cover

In addition to cloud albedo, the reaction of cloud cover to anthropogenic-induced changes in the atmosphere is an important part of the discussion over how climate will be affected by an ongoing rise in the air’s carbon dioxide content. Here we review scientific papers that address this topic.

Ferek *et al.* (1998) determined cloud condensation nuclei in the airborne effluents of ships off the west coast of the United States were responsible for producing ship tracks—brighter and more persistent streaks in the overlying layer of natural and less-reflective cloud, both of which exert a cooling influence during daylight hours. Similarly, based on what is known about the properties of the aerosols responsible for jet aircraft contrails, Meerkotter *et al.* (1999) suggest the presence of such contrails tends to cool Earth’s surface during daylight hours but warm it at night. They also note aircraft emissions may cause additional indirect climate forcing by changing the particle size of natural cirrus clouds, concluding “this indirect forcing may be comparable to the direct forcing due to additional contrail cloud cover.”

Boucher (1999) and Nakanishi *et al.* (2001) both find aircraft-induced increases in high-cloud amount may also have a warming effect, although Charlson *et al.* (2001) contend the net effect of all anthropogenic-

produced aerosols averaged over the globe is a cooling.

Facchini *et al.* (1999) studied the effects of atmospheric solutes collected from cloud water in the Po Valley of Italy. They found water vapor was more likely to form on its organic-solute-affected aerosols of lower surface tension—as opposed to the less-organic-solute-affected aerosols of the natural environment with their higher surface tension—creating more, smaller, and therefore more highly reflective cloud droplets, which tend to cool the local environment. They also observed the organic fractions and concentrations of the aerosols they studied were similar to those found in air downwind of other large agricultural/industrial regions, hinting at the likely widespread occurrence of this human-induced cooling influence.

Studying this phenomenon several years earlier, Kulmala *et al.* (1993) noted “it is likely that the smaller droplet size will decrease precipitation so that the clouds will have a longer lifetime.” In addition, they observed “cloud formation can take place at smaller saturation ratios of water vapor” in the presence of organic-solute-affected aerosols, suggesting clouds will be able to form earlier and in places where they would not otherwise form. In response to this particular type of anthropogenic effluent, therefore, cloud lifetimes expand at both ends—they are born earlier and die later, so to speak.

How significant are these phenomena? Leitch *et al.* (1992) conclude the increased radiative cooling power due only to the increase in cloud albedo that results from pollution-induced increases in cloud droplet concentration averages about 2 W m^{-2} over North America, about half the radiative warming power typically predicted to accompany a nominal doubling of the air’s CO_2 content. Adding the impact of increased cloud cover likely would make the overall effect considerably greater.

Satheesh and Ramanathan (2000) measured the clear-sky radiative consequences of the December-to-April northeastern low-level monsoonal flow of air that transports sulphates, nitrates, organics, soot, and fly ash (among other anthropogenically produced substances) from the Indian subcontinent and southern Asia thousands of kilometers over the north Indian Ocean and as far south as 10°S latitude. They found the “mean clear-sky solar radiative heating for the winters of 1998 and 1999 decreased at the ocean surface by 12 to 30 W m^{-2} ,” which Schwartz and Buseck (2000) point out is “three to seven times as great as global average longwave (infrared) radiative

forcing by increases in greenhouse gases over the industrial period ... but opposite in sign.”

This finding was somewhat tempered by the study of Ackerman *et al.* (2000), who suggest the large cooling effect likely was counterbalanced by a simultaneous reduction in cloud cover. But in an analysis of a long-term study of real-world data, Norris (2001) proved that suggestion to be wrong, reaffirming the overall implications of the Satheesh and Ramanathan study.

Norris reasoned that if the conclusion of Ackerman *et al.* was correct, the great increase in anthropogenic aerosol emissions from southern and southeast Asia over the past half-century should have significantly decreased the low-level cloud cover over the northern Indian Ocean during this period. A test of this idea with data from the Extended Edited Cloud Report Archive, however, revealed daytime low-level cloud cover over this part of the world in fact increased, and it did so in both the Northern and Southern Hemispheric regions of the study area and at essentially all hours of the day.

Croke *et al.* (1999) determined the mean cloud cover of three regions of the United States (coastal southwest, coastal northeast, and southern plains) rose from 35 percent to 47 percent from 1900 to 1987, while global mean air temperature rose by approximately 0.5°C . Similarly, Chernykh *et al.* (2001) determined global cloud cover rose by nearly 6 percent between 1964 and 1998. These observations suggest Earth’s hydrologic cycle does indeed tend to moderate the thermal effects of any impetus for warming and, as noted by the latter authors, is “consistent with the decrease in diurnal temperature range evident over most of the globe.”

Another way by which clouds tend to stabilize Earth’s climate was suggested by Sud *et al.* (1999). Based on data from the Tropical Ocean Global Atmosphere Coupled Ocean-Atmosphere Response Experiment, these investigators found deep convection in the tropics acts as a thermostat to keep vacillation of sea surface temperature (SST) within a rather narrow range. Starting at the low end of the range, the tropical ocean acts as a net receiver of energy and warms. Soon thereafter, however, the cloud-base airmass is charged with the moist static energy needed for clouds to reach the upper troposphere, and the cloud cover thus formed reduces the amount of solar radiation received at the sea surface, while its cool and dry downdrafts also tend to promote surface cooling. This “thermostat-like control,” as Sud *et al.* put it, tends to “ventilate the

tropical ocean efficiently and help contain the SST between 28–30°C.”

Lindzen *et al.* (2001) described another mechanism through which tropical ocean temperatures may be constrained by cloud-mediated phenomena. Based on upper-level cloudiness data obtained from the Japanese Geostationary Meteorological Satellite and SST data obtained from the National Centers for Environmental Protection, these researchers determined the cloudy moist region of the eastern part of the tropical western Pacific “appears to act as an infrared adaptive iris that opens up and closes down the regions free of upper-level clouds, which more effectively permit infrared cooling, in such a manner as to resist changes in tropical surface temperature.” The strong inverse relationship they found between upper-level cloud area and mean SST was determined to be sufficient to “more than cancel all the positive feedbacks in the more sensitive current climate models.”

Plant life also plays an important role in stabilizing climate. The pioneering paper of Charlson *et al.* (1987), for example, describes how an initial SST increase leads to increased phytoplanktonic productivity in Earth’s oceans, which leads to a greater sea-to-air flux of dimethyl sulfide (DMS), which undergoes a gas-to-particle conversion that leads to greater numbers of cloud condensation nuclei that create more and brighter clouds that reflect more incoming solar radiation back to space, thereby countering the initial impetus for warming. Subsequently, Ayers and Gillett (2000) reviewed what had been learned in the following years, concluding “major links in the feedback chain proposed by Charlson *et al.* (1987) have a sound physical basis,” additionally noting there is “compelling observational evidence to suggest that DMS and its atmospheric products participate significantly in processes of climate regulation and reactive atmospheric chemistry in the remote marine boundary layer of the Southern Hemisphere.”

Further support for the powerful negative feedback loop is provided by Simo and Pedros-Alio (1999), who studied the effect of the depth of the surface mixing-layer on DMS production. (For a more complete discussion of DMS, see the section on Dimethylsulfide, this chapter.)

Although studies of real-world phenomena continue to clarify the workings of the planet’s climate system and improve our understanding of it, computer models have a difficult time capturing the

system’s complexities. Groisman *et al.* (2000), for example, evaluated the ability of several climate models to reproduce mean daily cloud-temperature relations at different times of year. Although most models did a good job in the cold part of the year, “large discrepancies between empirical data and some models are found for summer conditions.” The overall cloud effect on summer near-surface air temperature computed by one of the models was of the wrong sign.

In another study, Gordon *et al.* (2000) examined the response of a coupled general circulation model of the atmosphere to quasi-realistic specified marine stratocumulus clouds and compared the results to what they obtained from their model when operating in its normal mode, which fails to adequately express the presence of the clouds and their effects. When they removed the low clouds, as occurs in the model’s normal application, the sea surface temperature warmed by fully 5.5°C.

Two years later, two data-based studies published in *Science*—Chen *et al.* (2002) and Wielicki *et al.* (2002)—revealed what Hartmann (2002) called a pair of “tropical surprises.” The first of the seminal discoveries was the finding of both Chen *et al.* and Wielicki *et al.* that the amount of thermal radiation emitted to space at the top of the tropical atmosphere increased by about 4 W m⁻² between the 1980s and the 1990s; the second was that the amount of reflected sunlight decreased by 1 to 2 W m⁻² over the same period, with the net result that more total radiant energy exited the tropics in the latter decade.

These changes were significant. The measured thermal radiative energy loss at the top of the tropical atmosphere, for example, was of the same magnitude as the thermal radiative energy gain generally predicted for a doubling of the air’s CO₂ content. Yet as Hartman noted, “only very small changes in average tropical surface temperature were observed during this time.” So what went wrong—or more correctly, what went right?

For one, the competing change in solar radiation reception driven by changes in cloud cover allowed more solar radiation to reach the surface of Earth’s tropical region and warm it. These changes were produced by what Chen *et al.* determined to be “a decadal-time-scale strengthening of the tropical Hadley and Walker circulations.” Moreover, the past quarter-century’s slowdown in the meridional overturning circulation of the upper 100 to 400 meters of the tropical Pacific Ocean, recently reported by

McPhaden and Zhang (2002), would have promoted tropical sea surface warming by reducing the rate of supply of relatively colder water to the region of equatorial upwelling.

These observations provide several new phenomena for the models to replicate as a test of their ability to properly represent the real world. McPhaden and Zhang note, for example, the meridional overturning circulation of the upper Pacific Ocean provides “an important dynamical constraint for model studies that attempt to simulate recent observed decadal changes in the Pacific.” If the climate models cannot reconstruct this simple wind-driven circulation, it is difficult to be confident in their projections.

In an application of this principle, Wielicki *et al.* (2002) tested the ability of four state-of-the-art climate models and one weather assimilation model to reproduce the observed decadal changes in top-of-the-atmosphere thermal and solar radiative energy fluxes that occurred over the past two decades. No significant decadal variability was exhibited by any of the models, and all were unable to reproduce even the cyclical seasonal change in tropical albedo. The administrators of the test conclude “the missing variability in the models highlights the critical need to improve cloud modeling in the tropics so that prediction of tropical climate on interannual and decadal time scales can be improved.” Hartmann is more candid in his scoring of the test, saying it indicates “the models are deficient.” He notes, “if the energy budget can vary substantially in the absence of obvious forcing,” as it did over the prior two decades, “then the climate of Earth has modes of variability that are not yet fully understood and cannot yet be accurately represented in climate models.” (Additional discussion of climate models’ treatment of clouds can be found in Chapter 1.)

Fu *et al.* (2002) and Hartmann and Michelsen (2002) continued to chip away at the adaptive infrared iris concept of Lindzen *et al.* (2001). Fu *et al.* argue “the contribution of tropical high clouds to the feedback process would be small since the radiative forcing over the tropical high cloud region is near zero and not strongly positive,” while also claiming to show water vapor and low cloud effects are overestimated by Lindzen *et al.* by at least 60 percent and 33 percent, respectively. Fu and his colleagues obtained a feedback factor in the range of -0.15 to -0.51, compared to Lindzen *et al.*’s larger negative feedback factor of -0.45 to -1.03.

Chou *et al.* (2002) responded, suggesting Fu *et*

al.’s approach of specifying longwave emission and cloud albedos “appears to be inappropriate for studying the iris effect.” They note, “thin cirrus are widespread in the tropics and ... low boundary clouds are optically thick,” and “the cloud albedo calculated by [Fu *et al.*] is too large for cirrus clouds and too small for boundary layer clouds,” so that “the near-zero contrast in cloud albedos derived by [Fu *et al.*] has the effect of underestimating the iris effect.” Chou *et al.* ultimately agreed Lindzen *et al.* “may indeed have overestimated the iris effect somewhat, though hardly by as much as that suggested by [Fu *et al.*].”

Two years later, Minnis *et al.* (2004) analyzed surface-based measurements of cirrus coverage (CC) for different parts of the world for the period 1971–1995 while employing similar measurements obtained from the International Satellite Cloud Climatology Project (ISCCP) for 1984–1996 as a consistency check. The linear trends they derived from the data were input to a relationship between changes in cirrus amount and surface temperature (derived from a general circulation model of the atmosphere) in order to calculate their climatic impact over the United States.

Minnis *et al.* report “values of CC increased over the United States, the North Atlantic and Pacific, and Japan, but dropped over most of Asia, Europe, Africa, and South America,” noting “the largest concentrated increases occurred over the northern Pacific and Atlantic and roughly correspond to the major air traffic routes.” Their U.S. temperature assessment additionally indicates “the cirrus trends over the United States are estimated to cause a tropospheric warming of 0.2°–0.3°C per decade, a range that includes the observed tropospheric temperature trend of 0.27°C per decade between 1975 and 1994.” Those results suggest nearly all of the surface warming observed over the United States between 1975 and 1994, which they reported to be 0.54°C, may have been due to aircraft-induced increases in cirrus cloud cover and not the increase in the air’s CO₂ content over that period.

Harrison and Stephenson (2005) reasoned that because the net global effect of clouds is cooling (Hartmann, 1993), any widespread increase in the amount of overcast days could reduce air temperature globally, just as local overcast conditions can do so locally. They compared the ratio of diffuse to total solar radiation (the diffuse fraction, DF) measured daily at 0900 UT at Whiteknights, Reading (UK) in 1997–2004 with the traditional subjective determination of cloud amount made simultaneously

by a human observer as well as with daily average temperature. They then compared the DF measured at Jersey between 1968 and 1994 with corresponding daily mean neutron count rates measured at Climax, Colorado (USA), which provide a globally representative indicator of the galactic cosmic ray flux.

Their work revealed “across the UK, on days of high cosmic ray flux (above 3600×10^2 neutron counts per hour, which occur 87% of the time on average) compared with low cosmic ray flux, (i) the chance of an overcast day increases by $19\% \pm 4\%$, and (ii) the diffuse fraction increases by $2\% \pm 0.3\%$.” In addition, they found “during sudden transient reductions in cosmic rays (e.g. Forbush events), simultaneous decreases occur in the diffuse fraction,” and they note the latter of these observations indicates diffuse radiation changes are, indeed, “unambiguously due to cosmic rays.” They further report, “at Reading, the measured sensitivity of daily average temperatures to DF for overcast days is -0.2 K per 0.01 change in DR” and suggest the well-known inverse relationship between galactic cosmic rays and solar activity will lead to cooling at solar minima. They note, “this might amplify the effect of the small solar cycle variation in total solar irradiance, believed to be underestimated by climate models (Stott *et al.*, 2003) which neglect a cosmic ray effect.” In addition, although the effect they detect is small, they state it is “statistically robust” and the cosmic ray effect on clouds likely “will emerge on long time scales with less variability than the considerable variability of daily cloudiness.”

The following year, Palle *et al.* (2006) used the most up-to-date cloud cover data from the International Satellite Cloud Climatology Project and, following the protocols of Palle *et al.* (2004), derived globally averaged albedo anomalies and related solar radiative forcing anomalies experienced by Earth over the prior two decades. In addition, the four researchers explored the effects on total radiative forcing (solar plus thermal) of observed changes in the amounts of low-, high-, and mid-level clouds that occurred between 2000 and 2004.

Between 1985 and 2000, Palle *et al.* calculated, the flux of solar radiation absorbed by the Earth-atmosphere system rose by about 8 W m^{-2} in response to an observed decline in total cloud amount. Thereafter, total cloud amount began to rise, but because of a concomitant redistribution of cloud types (an increase in high- and mid-level clouds that tend to

warm the planet, and a decrease in low-level clouds that tend to cool the planet), they conclude the positive radiative forcing trend experienced between 1985 and 2000 may have continued to the time of the writing of their paper, even in the face of an increasing total cloud amount.

Palle *et al.* note the increase in radiative forcing produced by the increasing atmospheric concentrations of all greenhouse gases since 1850 was roughly 2.5 W m^{-2} . Compared to the increase in radiative forcing that may have been experienced between 1985 and 2005 as a result of observed changes in total cloud amount and the fractions of clouds located at different elevations ($\sim 11 \text{ W m}^{-2}$, according to the data and analyses of Palle *et al.*), the 20-year change in radiative forcing due to CO_2 alone would have been truly minuscule, suggesting the angst manifest over anthropogenic CO_2 emissions may be misplaced. And if a radiative forcing of $\sim 11 \text{ W m}^{-2}$ raised mean global air temperature by only a fraction of a degree, as occurred between 1985 and 2005, it would appear Earth’s climate is much less responsive to changes in radiative forcing than the IPCC and most climate modelers claim it to be.

One additional study merits discussion here. Based on approximately 185 million synoptic weather observations obtained from 5,400 stations worldwide, covering all continents and many islands, Warren *et al.* (2007) developed separate day and night histories of cloud amount for nine cloud types for the 26-year period 1971–1996. This work revealed, “there are large regional changes in cloud-type amounts, and significant changes in the global averages of some cloud types.” More specifically, they state “the time series of total-cloud-cover anomalies for individual continents show a large decrease for South America, small decreases for Eurasia and Africa, and no trend for North America.” They also observe “the zonal average trends of total cloud cover are positive in the Arctic winter and spring, 60° – 80°N , but negative in all seasons at most other latitudes.” In addition, they state “night trends agree with day trends for total cloud cover and for all cloud types except cumulus,” and “cirrus trends are generally negative over all continents.” They found these changes “compensate each other to result in only a small trend of global average land cloud cover, $-0.7\% \text{ decade}^{-1}$.” In addition, they note “this small negative trend is further compensated by a small positive trend over the ocean of $+0.4\% \text{ decade}^{-1}$ (Norris, 1999), resulting in almost no trend for global average cloud cover over

the past few decades.”

Although Warren *et al.* acknowledged the significance of changes in cloud type and amount for global and regional climate change and vice versa, they did not speculate on the climatic implications of their findings, noting “it will be important to prepare cloud datasets for the more recent years [post 1996], when changes may become more noticeable with increased global warming.”

The IPCC claims in AR5 that “the net radiative feedback due to all cloud types is likely positive” (p. 9 of the Summary for Policy Makers, Second Order Draft of AR5, dated October 5, 2012). Contrary to that assessment, as shown in this section and the preceding section of this chapter, substantial research indicates the net global effect of cloud feedbacks is one of cooling, the magnitude of which may equal or exceed the warming projected from increasing greenhouse gases.

References

- Ackerman, A.S., Toon, O.B., Stevens, D.E., Heymsfield, A.J., Ramanathan, V., and Welton, E.J. 2000. Reduction of tropical cloudiness by soot. *Science* **288**: 1042–1047.
- Ayers, G.P. and Gillett, R.W. 2000. DMS and its oxidation products in the remote marine atmosphere: Implications for climate and atmospheric chemistry. *Journal of Sea Research* **43**: 275–286.
- Boucher, O. 1999. Air traffic may increase cirrus cloudiness. *Nature* **397**: 30–31.
- Charlson, R.J., Lovelock, J.E., Andrea, M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- Charlson, R.J., Seinfeld, J.H., Nenes, A., Kulmala, M., Laaksonen, A., and Facchini, M.C. 2001. Reshaping the theory of cloud formation. *Science* **292**: 2025–2026.
- Chen, J., Carlson, B.E., and Del Genio, A.D. 2002. Evidence for strengthening of the tropical general circulation in the 1990s. *Science* **295**: 838–841.
- Chernykh, I.V., Alduchov, O.A., and Eskridge, R.E. 2001. Trends in low and high cloud boundaries and errors in height determination of cloud boundaries. *Bulletin of the American Meteorological Society* **82**: 1941–1947.
- Chou, M.-D., Lindzen, R.S., and Hou, A.Y. 2002. Reply to: “Tropical cirrus and water vapor: an effective Earth infrared iris feedback?” *Atmospheric Chemistry and Physics* **2**: 99–101.
- Croke, M.S., Cess, R.D., and Hameed, S. 1999. Regional cloud cover change associated with global climate change: Case studies for three regions of the United States. *Journal of Climate* **12**: 2128–2134.
- Facchini, M.C., Mircea, M., Fuzzi, S., and Charlson, R.J. 1999. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **401**: 257–259.
- Ferek, R.J., Hegg, D.A., Hobbs, P.V., Durkee, P., and Nielsen, K. 1998. Measurements of ship-induced tracks in clouds off the Washington coast. *Journal of Geophysical Research* **103**: 23,199–23,206.
- Fu, Q., Baker, M., and Hartmann, D.L. 2002. Tropical cirrus and water vapor: An effective Earth infrared iris feedback? *Atmospheric Chemistry and Physics* **2**: 31–37.
- Gordon, C.T., Rosati, A., and Gudgel, R. 2000. Tropical sensitivity of a coupled model to specified ISCCP low clouds. *Journal of Climate* **13**: 2239–2260.
- Groisman, P.Ya., Bradley, R.S., and Sun, B. 2000. The relationship of cloud cover to near-surface temperature and humidity: Comparison of GCM simulations with empirical data. *Journal of Climate* **13**: 1858–1878.
- Harrison, R.G. and Stephenson, D.B. 2005. Empirical evidence for a nonlinear effect of galactic cosmic rays on clouds. *Proceedings of the Royal Society A*: 10.1098/rspa.2005.1628.
- Hartmann, D.L. 1993. Radiative effects of clouds on Earth’s climate. In: Hobbs, P.V. (Ed.) *Aerosol-Cloud-Climate Interactions*. Academic Press, New York, NY, USA.
- Hartmann, D.L. 2002. Tropical surprises. *Science* **295**: 811–812.
- Hartmann, D.L. and Michelsen, M.L. 2002. No evidence for IRIS. *Bulletin of the American Meteorological Society* **83**: 249–254.
- Kulmala, M., Laaksonen, A., Korhonen, P., Vesala, T., and Ahonen, T. 1993. The effect of atmospheric nitric acid vapor on cloud condensation nucleus activation. *Journal of Geophysical Research* **98**: 22,949–22,958.
- Leitch, W.R., Isaac, G.A., Stapp, J.W., Banic, C.M., and Wiebe, H.A. 1992. The relationship between cloud droplet number concentrations and anthropogenic pollution: Observations and climatic implications. *Journal of Geophysical Research* **97**: 2463–2474.
- Lindzen, R.S., Chou, M.-D., and Hou, A.Y. 2001. Does the Earth have an adaptive infrared iris? *Bulletin of the American Meteorological Society* **82**: 417–432.
- McPhaden, M.J. and Zhang, D. 2002. Slowdown of the meridional overturning circulation in the upper Pacific Ocean. *Nature* **415**: 603–608.
- Meerkotter, R., Schumann, U., Doelling, D.R., Minnis, P.,

Nakajima, T., and Tsushima, Y. 1999. Radiative forcing by contrails. *Annales Geophysicae* **17**: 1080–1094.

Minnis, P., Ayers, J.K., Palikonda, R., and Phan, D. 2004. Contrails, cirrus trends, and climate. *Journal of Climate* **17**: 1671–1685.

Nakanishi, S., Curtis, J., and Wendler, G. 2001. The influence of increased jet airline traffic on the amount of high level cloudiness in Alaska. *Theoretical and Applied Climatology* **68**: 197–205.

Norris, J.R. 1999. On trends and possible artifacts in global ocean cloud cover between 1952 and 1995. *Journal of Climate* **12**: 1864–1870.

Norris, J.R. 2001. Has northern Indian Ocean cloud cover changed due to increasing anthropogenic aerosol? *Geophysical Research Letters* **28**: 3271–3274.

Palle, E., Goode, P.R., Montanes-Rodriguez, P., and Koonin, S.E. 2004. Changes in Earth's reflectance over the past two decades. *Science* **304**: 1299–1301.

Palle, E., Goode, P.R., Montanes-Rodriguez, P., and Koonin, S.E. 2006. Can Earth's albedo and surface temperatures increase together? *EOS, Transactions, American Geophysical Union* **87**: 37, 43.

Satheesh, S.K. and Ramanathan, V. 2000. Large differences in tropical aerosol forcing at the top of the atmosphere and Earth's surface. *Nature* **405**: 60–63.

Schwartz, S.E. and Buseck, P.R. 2000. Absorbing phenomena. *Science* **288**: 989–990.

Simo, R. and Pedros-Alio, C. 1999. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature* **402**: 396–399.

Stott, P.A., Jones, G.S., and Mitchell, J.F.B. 2003. Do models underestimate the solar contribution to recent climate change? *Journal of Climate* **16**: 4079–4093.

Sud, Y.C., Walker, G.K., and Lau, K.-M. 1999. Mechanisms regulating sea-surface temperatures and deep convection in the tropics. *Geophysical Research Letters* **26**: 1019–1022.

Warren, S.G., Eastman, R.M., and Hahn, C.J. 2007. A survey of changes in cloud cover and cloud types over land from surface observations, 1971–96. *Journal of Climate* **20**: 717–738.

Wielicki, B.A., Wong, T., Allan, R.P., Slingo, A., Kiehl, J.T., Soden, B.J., Gordon, C.T., Miller, A.J., Yang, S.-K., Randall, D.A., Robertson, F., Susskind, J., and Jacobowitz, H. 2002. Evidence for large decadal variability in the tropical mean radiative energy budget. *Science* **295**: 841–844.

2.5 Aerosols

Aerosols are an important factor in global temperature because they affect Earth's energy budget through their ability to reflect and scatter light and their propensity to absorb and radiate thermal radiation. In its *Fifth Assessment Report* (AR5), the IPCC concludes “the total aerosol effect is estimated as [a radiative forcing] of -0.7 and [an adjusted forcing] of -0.9 W m⁻²” (p. 8-4 of Chapter 8, Second Order Draft of AR5, dated October 5, 2012). Such estimates were revised downward (a less-negative feedback) from the IPCC's *Fourth Assessment Report*, but as demonstrated in this section, many studies indicate aerosols are capable of producing a much stronger cooling effect, thus calling into question the IPCC's decision to downgrade the strength of this negative feedback. Several studies suggest the radiative forcing of aerosols may be as large as, or larger than, the radiative forcing due to atmospheric CO₂.

Our review of aerosol studies begins with an analysis of the total aerosol effect on climate, followed by a separate discussion of four important aerosol categories: (1) Biological (Aquatic), (2) Biological (Terrestrial), (3) Non-Biological (Anthropogenic), and (4) Non-Biological (Natural).

2.5.1 Total Aerosol Effect

Ghan *et al.* (2001) studied the positive radiative forcings of greenhouse gases and the negative radiative forcings of anthropogenic aerosols, reporting current best estimates of “the total global mean present-day anthropogenic forcing range from 3 W m⁻² to -1 W m⁻²,” which represents everything from a modest warming to a slight cooling. After performing their own analysis, they reduced the range somewhat but found it still stretched from a small cooling influence to a modest impetus for warming. “Clearly,” they conclude, “the great uncertainty in the radiative forcing must be reduced if the observed climate record is to be reconciled with model predictions and if estimates of future climate change are to be useful in formulating emission policies.”

Vogelmann *et al.* (2003) point out “mineral aerosols have complex, highly varied optical properties that, for equal loadings, can cause differences in the surface IR [infrared] flux between 7 and 25 W m⁻² (Sokolik *et al.*, 1998).” They note “only a few large-scale climate models currently consider aerosol IR effects (e.g., Tegen *et al.*, 1996; Jacobson, 2001) despite their potentially large forcing.” The

researchers used high-resolution spectra to obtain the IR radiative forcing at Earth's surface for aerosols encountered in the outflow from northeastern Asia, based on measurements made by the Marine-Atmospheric Emitted Radiance Interferometer from the NOAA Ship *Ronald H. Brown* during the Aerosol Characterization Experiment-Asia. They determined "daytime surface IR forcings are often a few $W m^{-2}$ and can reach almost $10 W m^{-2}$ for large aerosol loadings." These values, in their words, "are comparable to or larger than the 1 to $2 W m^{-2}$ change in the globally averaged surface IR forcing caused by greenhouse gas increases since pre-industrial times" and "highlight the importance of aerosol IR forcing which should be included in climate model simulations."

Similar findings were reported by Chou *et al.* (2002), who analyzed aerosol optical properties retrieved from the satellite-mounted Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and used them in conjunction with a radiative transfer model of the planet's atmosphere to calculate the climatic effects of aerosols over Earth's major oceans. In general, this effort revealed "aerosols reduce the annual-mean net downward solar flux by $5.4 W m^{-2}$ at the top of the atmosphere, and by $5.9 W m^{-2}$ at the surface." During the large Indonesian fires of September-December 1997, however, the radiative impetus for cooling at the top of the atmosphere was more than $10 W m^{-2}$, while it was more than $25 W m^{-2}$ at the surface of the sea in the vicinity of Indonesia.

Wild (1999) used a comprehensive set of collocated surface and satellite observations to calculate the amount of solar radiation absorbed in the atmosphere over equatorial Africa and compared the results with the predictions of three general circulation models of the atmosphere. The climate models did not properly account for spatial and temporal variations in atmospheric aerosol concentrations, leading them to predict regional and seasonal values of solar radiation absorption in the atmosphere with underestimation biases of up to $30 W m^{-2}$. By way of comparison, as noted by Vogelmann *et al.*, the globally averaged surface IR forcing caused by greenhouse gas increases since pre-industrial times is 1 to $2 W m^{-2}$.

Aerosol uncertainties and the problems they generate figure prominently in a study by Anderson *et al.* (2003), who note there are two different ways by which the aerosol forcing of climate may be computed. The first is forward calculation, based, in their words, on "knowledge of the pertinent aerosol

physics and chemistry." The second approach is inverse calculation, based on "the total forcing required to match climate model simulations with observed temperature changes."

The first approach utilizes known physical and chemical laws and assumes nothing about the outcome of the calculation. The second approach, in considerable contrast, is based on matching residuals, where the aerosol forcing is computed from what is required to match the calculated change in temperature with the observed change over some period of time. Consequently, in the words of Anderson *et al.*, "to the extent that climate models rely on the results of inverse calculations, the possibility of circular reasoning arises."

Which approach do climate models typically employ? "Unfortunately," Anderson *et al.* write, "virtually all climate model studies that have included anthropogenic aerosol forcing as a driver of climate change have used only aerosol forcing values that are consistent with the inverse approach." Anderson *et al.* report the negative forcing of anthropogenic aerosols derived by forward calculation is "considerably greater" than that derived by inverse calculation; if forward calculation is employed, the results "differ greatly" and "even the sign of the total forcing is in question." This implies "natural variability (that is, variability not forced by anthropogenic emissions) is much larger than climate models currently indicate," they write. Anderson *et al.* conclude, "inferences about the causes of surface warming over the industrial period and about climate sensitivity may therefore be in error."

Schwartz (2004) also addressed the subject of uncertainty as it applies to the role of aerosols in climate models. Noting the National Research Council (1979) concluded "climate sensitivity [to CO_2 doubling] is likely to be in the range $1.5-4.5^\circ C$ " and "remarkably, despite some two decades of intervening work, neither the central value nor the uncertainty range has changed," Schwartz opines this continuing uncertainty "precludes meaningful model evaluation by comparison with observed global temperature change or empirical determination of climate sensitivity" and "raises questions regarding claims of having reproduced observed large-scale changes in surface temperature over the 20th century."

Schwartz thus contends climate model predictions of CO_2 -induced global warming "are limited at present by uncertainty in radiative forcing of climate change over the industrial period, which is dominated by uncertainty in forcing by aerosols," and if this

situation is not improved, “it is likely that in another 20 years it will still not be possible to specify the climate sensitivity with [an] uncertainty range appreciably narrower than it is at present.” He adds, “the need for reducing the uncertainty from its present estimated value by at least a factor of 3 and perhaps a factor of 10 or more seems inescapable if the uncertainty in climate sensitivity is to be reduced to an extent where it becomes useful for formulating policy to deal with global change.”

Lubin and Vogelmann (2006) employed five multisensor radiometric data sets from the North Slope of Alaska to study how enhanced concentrations of anthropogenic aerosols originating from industrial regions of lower latitudes alter the microphysical properties of Arctic clouds via a process known as the first indirect effect of aerosols. They determined this phenomenon operates in low optically thin single-layered Arctic clouds, producing an increase in the downwelling flux of longwave (thermal) radiation. Under frequently occurring cloud types, they found anthropogenic aerosols regularly advected into the Arctic lead to an average increase of 3.4 W m^{-2} in the downward-directed thermal radiation flux at Earth’s surface. The two researchers state “the observed longwave enhancement has climatological significance.”

The work of Charlson *et al.* (2005) supports that assessment. They report the longwave radiative forcing provided by all greenhouse gas increases since the beginning of the industrial era amounts to 2.4 W m^{-2} , citing the work of Anderson *et al.* (2003). Similarly, Palle *et al.* (2004) state “the latest IPCC report argues for a 2.4 W m^{-2} increase in CO_2 longwave forcing since 1850.” Consequently, if the calculations of Lubin and Vogelmann are correct, the longwave radiative forcing of the anthropogenic aerosols that are advected into the Arctic may be larger than the combined forcing of all greenhouse gas increases since the beginning of the industrial era, suggesting recent increases in anthropogenic aerosol emissions could be the primary source of whatever Arctic warming may have occurred in recent years.

Jaenicke *et al.* (2007) reviewed the status of research being conducted on biological materials in the atmosphere, which they denominate primary biological atmospheric particles or PBAPs. Originally, these particles were restricted to culture-forming units, including pollen, bacteria, mold, and viruses, but they also include fragments of living and dead organisms and plant debris, human and animal

epithelial cells, broken hair filaments, parts of insects, shed feather fractions, etc., which they lumped together under the category of “dead biological matter.”

With respect to the meteorological and climatic relevance of these particles, Jaenicke *et al.* note many PBAPs, including “decaying vegetation, marine plankton and bacteria are excellent ice nuclei,” and “one can easily imagine the [IR] influence on cloud cover, climate forcing and feedback and global precipitation distribution.”

In describing their own measurements and those of others, which they said “have now been carried out at several geographical locations covering all seasons of the year and many characteristic environments,” Jaenicke *et al.* report, “by number and volume, the PBAP fraction is ~20 percent of the total aerosol, and appears rather constant during the year.” In addition, they write “the impression prevails that the biological material, whether produced directly or shed during the seasons, sits on surfaces, ready to be lifted again in resuspension.”

In a brief summation of their findings, the German researchers state “the overall conclusion can only be that PBAPs are a major fraction of atmospheric aerosols, and are comparable to sea salt over the oceans and mineral particles over the continents.” Consequently, they note, “the biosphere must be a major source for directly injected biological particles, and those particles should be taken into account in understanding and modeling atmospheric processes.” They further note “the IPCC-Report of 2007 does not even mention these particles” and “this disregard of the biological particles requires a new attitude.”

Ramanathan *et al.* (2007) point out light-absorbing and light-scattering aerosols “contribute to atmospheric solar heating and surface cooling,” and “the sum of the two climate forcing terms—the net aerosol forcing effect—is thought to be negative and may have masked as much as half of the global warming attributed to the recent rapid rise in greenhouse gases.” They caution there is “at least a fourfold uncertainty in the aerosol forcing effect.”

Ramanathan *et al.* studied this phenomenon as it has never been studied before, using “three lightweight unmanned aerial vehicles that were vertically stacked between 0.5 and 3 km over the polluted Indian Ocean.” The unmanned vehicles “deployed miniaturized instruments measuring aerosol concentrations, soot amount and solar fluxes”

within the atmospheric brown clouds (ABCs) demonstrated to envelop “most of Asia and the adjacent oceans” during “the six-month-long tropical dry season,” when “convective coupling between the surface and the troposphere is weak [and] aerosol solar heating can amplify the effect of greenhouse gases in warming the atmosphere while simultaneously cooling the surface.” The seven scientists report finding “atmospheric brown clouds enhanced lower atmospheric solar heating by about 50 per cent” during the period of their study. Over the Indian Ocean and Asia during the long tropical dry season, they conclude, general circulation model simulations suggest “atmospheric brown clouds contribute as much as the recent increase in anthropogenic greenhouse gases to regional lower atmospheric warming trends.”

Vautard *et al.* (2009) analyzed the frequency of occurrence of low horizontal visibility conditions over the past three decades at 342 meteorological stations scattered throughout Europe at 0300, 0900, 1500, and 2100 Universal Time, comparing their results with concomitant changes in near-surface air temperature and with spatial and temporal variations in sulfur dioxide emissions. “By enabling less energy to be received at the surface during daytime,” they point out, “the low-visibility phenomenon inhibits surface heating, and therefore induces a lower local temperature.” Since low-visibility conditions were presumed to have declined over the three-decade period due to the implementation of more effective air pollution control measures, the researchers anticipated a warming trend would be evident in the temperature data.

The three researchers document “a massive decline (about 50% in 30 years) of low-visibility occurrence throughout Europe,” and they report this decline was “spatially and temporally correlated with trends in sulfur dioxide emissions, suggesting a significant contribution of air-quality improvements” to the improvement in visibility. By statistically linking local visibility changes with temperature variations, they found “the reduction in low-visibility conditions could have contributed on average to about 10–20% of Europe’s recent daytime warming and to about 50% of eastern European warming.”

The work of Vautard *et al.* (2009) strongly suggests the cleaning-up of European air pollution over the past three decades has been responsible for much of that region’s recent warming, and it is likely that effect has been seen elsewhere around the globe as well. Their findings also provide support for an

urban heat island effect other researchers suggest has inflated the global temperature record.

Mischenko *et al.* (2007) presented a plot of the global monthly average of the column aerosol optical thickness (AOT) of the atmosphere that stretches from August 1981 to June 2005, which they developed from “the longest uninterrupted record of global satellite estimates of the column AOT over the oceans, the Global Aerosol Climatology Project (GACP) record.” This record was derived from “the International Satellite Cloud Climatology Project (ISCCP) DX radiance data set,” which is “composed of calibrated and sampled Advanced Very High Resolution Radiometer radiances.”

As shown in Figure 2.5.1.1, “the green line reveals a long-term decreasing tendency in the tropospheric AOT,” such that “the resulting decrease in the tropospheric AOT during the 14-year period [1991–2005] comes out to be 0.03.” This trend, they note, “is significant at the 99% confidence level.” They explain “observations of downward solar radiation fluxes at Earth’s surface have shown a recovery from the previous decline known as global ‘dimming’, with the ‘brightening’ beginning around 1990.” Their AOT record harmonizes with these observations as well as with estimated trends in primary anthropogenic emissions of SO₂ and black carbon, which they said are known to “contribute substantially to the global AOT.”

These facts raise serious questions about attributions of late-twentieth-century global warming to the increase in the atmosphere’s CO₂ concentration. As noted by Stanhill (2007), changes in the flux of solar radiation received at the surface of Earth as a consequence of the global dimming and brightening phenomena far exceed the changes in longwave radiative forcing produced by historical changes in the air’s CO₂ content. These observations would appear to relegate anthropogenic CO₂ emissions to a much less important role in terms of their ability to elicit significant changes in Earth’s surface temperature.

The IPCC and others contend recent global brightening is merely allowing CO₂-induced warming to become more evident, which enables them to further contend the CO₂ greenhouse effect is actually much stronger than originally believed, having been masked for some time by the cooling power of the prior buildup of the great aerosol load of the atmosphere. Consequently, proponents of the theory of CO₂-induced global warming, such as *Science* magazine’s Richard Kerr, are found writing news

Forcings and Feedbacks

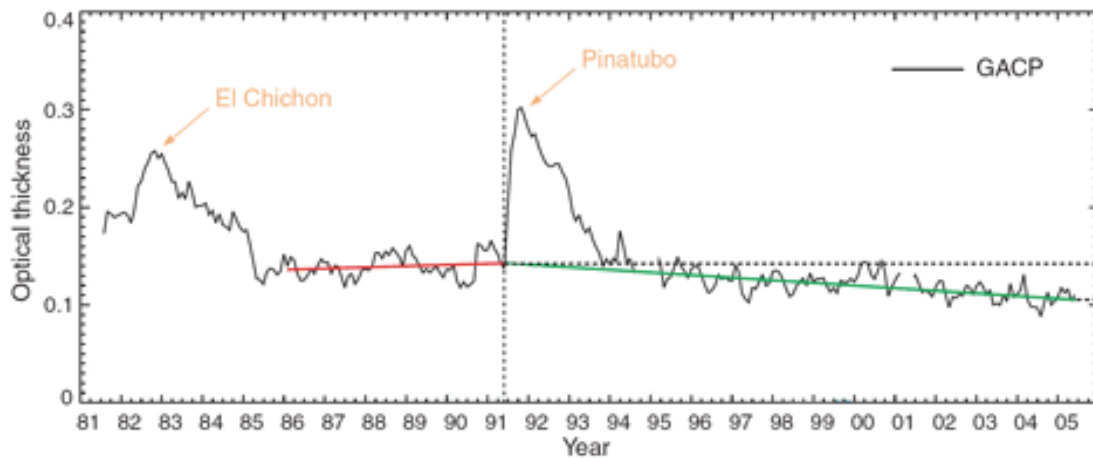


Figure 2.5.1.1. The GACP record of the globally averaged column AOT over the world's oceans. Adapted from Mishchenko, M.I., Geogdzhayev, I.V., Rossow, W.B., Cairns, B., Carlson, B.E., Laci, A.A., Liu, L., and Travis, L.D. 2007. Long-term satellite record reveals likely recent aerosol trend. *Science* **315**: 1543.

items with titles that ask, “Is a thinning haze unveiling the real global warming?” (Kerr, 2007), when a better question to ask (or at least a reasonable alternative) might have been, “Is a thinning haze revealing its own great power to warm Earth?” Such writers seem to have no trouble finding scientists willing to cast doubt on what they perceive to be the disturbing implications of the unfolding aerosol work. In the case of Kerr’s article, the doubter was Sarah Doherty of the University of Washington, who says there’s simply too much uncertainty in the aerosol data and the problem lies, in part, “in stringing together records from five different instruments flown on five different satellites over the years.”

As if anticipating such an attack, Mishchenko *et al.* clearly state “the successful validation of GACP retrievals using precise Sun photometer data taken from 1983 through 2004 indicates that the ISCCP radiance calibration is likely to be reliable,” and they further note “this conclusion is reinforced by the close correspondence of calculated and observed top of atmosphere solar fluxes.” What is more, they state, “the GACP AOT record appears to be self-consistent, with no drastic intra-satellite variations, and is consistent with the Stratospheric Aerosol and Gas Experiment record.”

Mishchenko *et al.* present ample reason to suspect a significant portion of the observed warming of the twentieth century may have been caused not by increasing atmospheric CO₂ concentrations, but by the increase in surface heating provided by the atmosphere’s declining aerosol optical thickness.

References

- Anderson, T.L., Charlson, R.J., Schwartz, S.E., Knutti, R., Boucher, O., Rodhe, H., and Heintzenberg, J. 2003. Climate forcing by aerosols—a hazy picture. *Science* **300**: 1103–1104.
- Charlson, R.J., Valero, F.P.J., and Seinfeld, J.H. 2005. In search of balance. *Science* **308**: 806–807.
- Chou, M-D., Chan, P-K., and Wang, M. 2002. Aerosol radiative forcing derived from SeaWiFS-retrieved aerosol optical properties. *Journal of the Atmospheric Sciences* **59**: 748–757.
- Ghan, S.J., Easter, R.C., Chapman, E.G., Abdul-Razzak, H., Zhang, Y., Leung, L.R., Laulainen, N.S., Saylor, R.D., and Zaveri, R.A. 2001. A physically based estimate of radiative forcing by anthropogenic sulfate aerosol. *Journal of Geophysical Research* **106**: 5279–5293.
- IPCC. 2007-I. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., and H.L. Miller (Eds.). Cambridge University Press, Cambridge, UK.
- Jacobson, M.Z. 2001. Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols. *Journal of Geophysical Research* **106**: 1551–1568.
- Jaenicke, R., Matthias-Maser, S., and Gruber, S. 2007. Omnipresence of biological material in the atmosphere. *Environmental Chemistry* **4**: 217–220.

Kerr, R.A. 2007. Is a thinning haze unveiling the real global warming? *Science* **315**: 1480.

Lubin, D. and Vogelmann, A.M. 2006. A climatologically significant aerosol longwave indirect effect in the Arctic. *Nature* **439**: 453–456.

Mishchenko, M.I., Geogdzhayev, I.V., Rossow, W.B., Cairns, B., Carlson, B.E., Lacis, A.A., Liu, L., and Travis, L.D. 2007. Long-term satellite record reveals likely recent aerosol trend. *Science* **315**: 1543.

National Research Council. 1979. *Carbon Dioxide and Climate: A Scientific Assessment*. National Academy of Sciences, Washington, DC, USA.

Palle, E., Goode, P.R., Montanes-Rodriguez, P., and Koonin, S.E. 2004. Changes in Earth's reflectance over the past two decades. *Science* **304**: 1299–1301.

Ramanathan, V., Ramana, M.V., Roberts, G., Kim, D., Corrigan, C., Chung, C., and Winker, D. 2007. Warming trends in Asia amplified by brown cloud solar absorption. *Nature* **448**: 575–578.

Schwartz, S.E. 2004. Uncertainty requirements in radiative forcing of climate. *Journal of the Air & Waste Management Association* **54**: 1351–1359.

Sokolik, I.N., Toon, O.B., and Bergstrom, R.W. 1998. Modeling the radiative characteristics of airborne mineral aerosols at infrared wavelengths. *Journal of Geophysical Research* **103**: 8813–8826.

Stanhill, G. 2007. A perspective on global warming, dimming, and brightening. *EOS, Transactions, American Geophysical Union* **88**: 58.

Tegen, I., Lacis, A.A., and Fung, I. 1996. The influence on climate forcing of mineral aerosols from disturbed soils. *Nature* **380**: 419–422.

Vogelmann, A.M., Flatau, P.J., Szczodrak, M., Markowicz, K.M., and Minnett, P.J. 2003. Observations of large aerosol infrared forcing at the surface. *Geophysical Research Letters* **30**: 10.1029/2002GL016829.

Wild, M. 1999. Discrepancies between model-calculated and observed shortwave atmospheric absorption in areas with high aerosol loadings. *Journal of Geophysical Research* **104**: 27,361–27,371.

2.5.2 Biological

In a Research Front article in *Environmental Chemistry*, Jaenicke *et al.* (2007) reviewed the status of research being conducted on biological materials in the atmosphere, which they denominated primary biological atmospheric particles or PBAPs. Originally, these particles were restricted to culture

forming units, including pollen, bacteria, mold, and viruses, but they also include fragments of living and dead organisms and plant debris, human and animal epithelial cells, broken hair filaments, parts of insects, shed feather fractions, etc., which Jaenicke *et al.* (2007) categorized as dead biological matter.

With respect to the meteorological and climatic relevance of these particles, they note many PBAPs, including “decaying vegetation, marine plankton and bacteria are excellent ice nuclei”; “one can easily imagine [their] influence on cloud cover, climate forcing and feedback and global precipitation distribution,” they write.

In describing their own measurements and those of others, which they said “have now been carried out at several geographical locations covering all seasons of the year and many characteristic environments,” Jaenicke *et al.* report “by number and volume, the PBAP fraction is ~20% of the total aerosol, and appears rather constant during the year.” The German researchers added, “the impression prevails that the biological material, whether produced directly or shed during the seasons, sits on surfaces, ready to be lifted again in resuspension.” They conclude “PBAPs are a major fraction of atmospheric aerosols, and are comparable to sea salt over the oceans and mineral particles over the continents”; consequently, “the biosphere must be a major source for directly injected biological particles, and those particles should be taken into account in understanding and modeling atmospheric processes.” They note “the IPCC-Report of 2007 does not even mention these particles” and “this disregard of the biological particles requires a new attitude.”

As research summarized in the following two subsections demonstrates, biologically induced aerosols act as very real and significant feedbacks to global warming. The IPCC's “new attitude” must include a willingness to acknowledge that current climate models fail to capture many important forcings and feedbacks. When that which is missing is factored in and properly modeled, conclusions radically different from those currently offered by the IPCC are likely.

Others have come to this conclusion. The international team of scientists of Fuzzi *et al.* (2006)—researchers from Finland, Germany, Greece, Italy, Japan, Switzerland, and the United States—found “in spite of impressive advances in recent years ... our understanding of organic aerosol composition, physical and chemical properties, sources, transformation and removal characteristics is very limited,

and estimates of their actual environmental effects are highly uncertain.” They conclude, “a comprehensive characterization and mechanistic understanding of particle sources, properties, and transformation is required for quantitative assessment, reliable prediction, and efficient control of natural and anthropogenic aerosol effects on climate,” and they identify a host of related “outstanding issues for future research.”

References

Fuzzi, S., Andreae, M.O., Huebert, B.J., Kulmala, M., Bond, T.C., Boy, M., Doherty, S.J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Russell, L.M., and Poschl, U. 2006. Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. *Atmospheric Chemistry and Physics* **6**: 2017–2038.

Jaenicke, R., Matthias-Maser, S., and Gruber, S. 2007. Omnipresence of biological material in the atmosphere. *Environmental Chemistry* **4**: 217–220.

2.5.2.1 Aquatic

Perhaps the most researched aquatic aerosol feedback loop is the multistage negative feedback phenomenon involving dimethylsulfide, described many years ago by Charlson *et al.* (1987). In the ensuing years, much research has been conducted supporting various stages of this phenomenon, the topic of discussion in subsection 2.5.2.1.1 below.

But other biological aerosols of aquatic origin also have been shown by scientists to have the ability to significantly influence climate. The work of O’Dowd *et al.* (2002) describes one such feedback that by itself may have the capacity to thwart the CO₂ greenhouse effect.

Writing about the O’Dowd *et al.* research in a companion “news and views” article in *Nature*, Kolb (2002) noted the researchers had discovered “a previously unrecognized source of aerosol particles” by unraveling “a photochemical phenomenon that occurs in sea air and produces aerosol particles composed largely of iodine oxides.”

O’Dowd *et al.* used a smog chamber operated under coastal atmospheric conditions to demonstrate “new particles can form from condensable iodine-containing vapors, which are the photolysis products of biogenic iodocarbons emitted from marine algae.” With the help of aerosol formation models, they also

demonstrated concentrations of condensable iodine-containing vapors over the open ocean “are sufficient to influence marine particle formation.”

The aerosol particles O’Dowd *et al.* discovered can function as cloud condensation nuclei (CCN), helping to create new clouds that reflect more incoming solar radiation back to space and thereby cool the planet. With respect to the negative feedback nature of this phenomenon, O’Dowd *et al.* cite the work of Latus *et al.* (2000), who demonstrated emissions of iodocarbons from marine biota “can increase by up to 5 times as a result of changes in environmental conditions associated with global change.” As O’Dowd *et al.* note, “increasing the source rate of condensable iodine vapors will result in an increase in marine aerosol and CCN concentrations of the order of 20–60%” and “changes in cloud albedo resulting from changes in CCN concentrations of this magnitude can lead to an increase in global radiative forcing similar in magnitude, but opposite in sign, to the forcing induced by greenhouse gases.”

Two years later and working with a different set of coauthors (O’Dowd *et al.*, 2004), O’Dowd measured size-resolved physical and chemical properties of aerosols found in northeast Atlantic marine air arriving at the Mace Head Atmospheric Research station on the west coast of Ireland during phytoplanktonic blooms. In the winter, when biological activity was at its lowest, the research team found the organic fraction of the submicrometer aerosol mass was about 15 percent. In spring through autumn, when biological activity was high, they found “the organic fraction dominates and contributes 63% to the submicrometer aerosol mass (about 45% is water-insoluble and about 18% water-soluble).” O’Dowd *et al.* then performed model simulations indicating the marine-derived organic matter “can enhance the cloud droplet concentration by 15% to more than 100% and is therefore an important component of the aerosol-cloud-climate feedback system involving marine biota.”

Such findings, the researchers state, “completely change the picture of what influences marine cloud condensation nuclei given that water-soluble organic carbon, water-insoluble organic carbon and surface-active properties, all of which influence the cloud condensation nuclei activation potential, are typically not parameterized in current climate models.” They add, “an important source of organic matter from the ocean is omitted from current climate-modelling predictions and should be taken into account.”

References

- Charlson, R.J., Lovelock, J.E., Andrea, M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- Kolb, C.E. 2002. Iodine’s air of importance. *Nature* **417**: 597–598.
- Laternus, F., Giese, B., Wiencke, C., and Adams, F.C. 2000. Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae—The influence of abiotic factors. *Fresenius’ Journal of Analytical Chemistry* **368**: 297–302.
- O’Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J., and Putaud, J.-P. 2004. Biogenically driven organic contribution to marine aerosol. *Nature* **431**: 676–680.
- O’Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G., and Hoffmann, T. 2002. Marine aerosol formation from biogenic iodine emissions. *Nature* **417**: 632–636.

2.5.2.1.1 Dimethylsulfide

According to the latest IPCC report, “there is *medium confidence* for a weak feedback involving dimethyl sulfide (DMS), cloud condensation nuclei (CCN), and cloud albedo due to a weak sensitivity of CCN population to changes in DMS emissions” (p. 21 of the Technical Summary, Second Order Draft of AR5, dated October 5, 2012). A review of the scientific literature, however, reveals the strength of this negative feedback is likely much larger than the IPCC asserts, perhaps even strong enough to counter the threat of greenhouse gas-induced global warming.

Dimethylsulfide, or DMS, is an organosulfur compound with the formula $(\text{CH}_3)_2\text{S}$. It is the most abundant biologically produced sulfur compound in the atmosphere, emitted to the air primarily by marine phytoplankton.

Charlson *et al.* (1987) discussed the plausibility of a multistage negative feedback process whereby warming-induced increases in the emission of DMS from the world’s oceans tend to counteract the effects of the initial impetus for warming. They hypothesized the global radiation balance is significantly influenced by the albedo of marine stratus clouds: the greater the cloud albedo, the less the input of solar radiation to Earth’s surface. The albedo of these clouds, in turn, is known to be a function of cloud droplet concentration—the more and smaller the cloud

droplets, the greater the cloud albedo and the reflection of solar radiation—which is dependent upon the availability of cloud condensation nuclei upon which the droplets form: the more cloud condensation nuclei, the more and smaller the cloud droplets. In completing the negative feedback loop, Charlson *et al.* note the concentration of cloud condensation nuclei often depends upon the flux of biologically produced DMS from the world’s oceans: the higher the sea surface temperature, the greater the sea-to-air flux of DMS.

Since the publication of Charlson *et al.*’s initial work, much empirical evidence has been gathered in support of their hypothesis. The review of Ayers and Gillett (2000), for example, concludes “major links in the feedback chain proposed by Charlson *et al.* (1987) have a sound physical basis” and there is “compelling observational evidence to suggest that DMS and its atmospheric products participate significantly in processes of climate regulation and reactive atmospheric chemistry in the remote marine boundary layer of the Southern Hemisphere.”

Simo and Pedros-Alio (1999) used satellite imagery and *in situ* experiments to study the production of DMS by enzymatic cleavage of dimethylsulphonioacetate in the North Atlantic Ocean about 400 km south of Iceland. They found the depth of the surface mixing-layer has a substantial influence on DMS yield in the short term, as do seasonal variations in vertical mixing in the longer term, which led them to conclude “climate-controlled mixing controls DMS production over vast regions of the ocean.”

Hopke *et al.* (1999) analyzed weekly concentrations of 24 different airborne particulates measured at the northernmost manned site in the world—Alert, Northwest Territories, Canada—from 1980 to 1991. They found concentrations of biogenic sulfur, including sulfate and methane sulfonate, were low in winter but high in summer, and the year-to-year variability in the strength of the biogenic sulfur signal was strongly correlated with the mean temperature of the Northern Hemisphere. “This result,” the authors state, “suggests that as the temperature rises, there is increased biogenic production of the reduced sulfur precursor compounds that are oxidized in the atmosphere to sulfate and methane sulfonate and could be evidence of a negative feedback mechanism in the global climate system.”

Is that negative feedback phenomenon powerful enough to counter the threat of greenhouse gas-

induced global warming? Sciare *et al.* (2000) examined ten years of DMS data from Amsterdam Island in the southern Indian Ocean, finding a sea surface temperature increase of only 1°C was sufficient to increase the atmospheric DMS concentration by as much as 50 percent. This finding suggests the degree of warming typically predicted to accompany a doubling of the air's CO₂ content would increase the atmosphere's DMS concentration by a factor of three or more, providing what they call a "very important" negative feedback that could potentially offset the original impetus for warming.

Kouvarakis and Mihalopoulos (2002) conducted research even more directly supportive of Charlson *et al.*'s hypothesis, measuring seasonal variations of gaseous DMS and its oxidation products—non-sea-salt sulfate (nss-SO₄²⁻) and methanesulfonic acid (MSA)—at a remote coastal location in the Eastern Mediterranean Sea from May 1997 through October 1999, as well as the diurnal variation of DMS during two intensive measurement campaigns conducted in September 1997. In the seasonal investigation, measured DMS concentrations tracked sea surface temperature (SST) almost perfectly, going from a low of 0.87 nmol m⁻³ in the winter to a high of 3.74 nmol m⁻³ in the summer. The diurnal studies reached a similar conclusion: DMS concentrations were lowest when it was coldest (just before sunrise), rose rapidly as it warmed thereafter to about 1,100, after which they dipped slightly and then experienced a further rise to the time of maximum temperature at 2,000, whereupon a decline in both temperature and DMS concentration set in that continued until just before sunrise. Because concentrations of DMS and its oxidation products rise dramatically in response to both diurnal and seasonal increases in SST, there is every reason to believe the same negative feedback phenomenon would operate in the case of the long-term warming that could arise from increasing greenhouse gas concentrations, substantially muting the climatic effects of those gases.

Baboukas *et al.* (2002) report the results of nine years of measurements of methanesulfonate (MS-), an exclusive oxidation product of DMS, in rainwater at Amsterdam Island. Their data, too, revealed "a well distinguished seasonal variation with higher values in summer, in line with the seasonal variation of its gaseous precursor (DMS)," which "further confirms the findings of Sciare *et al.* (2000)." The MS-anomalies in the rainwater were found to be closely related to SST anomalies; Baboukas *et al.* say this

observation provides even more support for "the existence of a positive ocean-atmosphere feedback on the biogenic sulfur cycle above the Austral Ocean," which water body they describe as "one of the most important DMS sources of the world."

Toole and Siegel (2004) note the DMS negative feedback process has been shown to operate in the 15 percent of the world's oceans "consisting primarily of high latitude, continental shelf, and equatorial upwelling regions," where DMS may be accurately predicted as a function of the ratio of the amount of surface chlorophyll derived from satellite observations to the depth of the climatological mixed layer, which they refer to as the "bloom-forced regime." For the other 85 percent of the world's marine waters, they demonstrate modeled surface DMS concentrations are independent of chlorophyll and are a function of the mixed layer depth alone, which they called the "stress-forced regime." Their study revealed how the warming-induced DMS negative feedback cycle operates in these waters.

For oligotrophic regimes, Toole and Siegel found "DMS biological production rates are negatively or insignificantly correlated with phytoplankton and bacterial indices for abundance and productivity while more than 82% of the variability is explained by UVR(325) [ultraviolet radiation at 325 nm]." This relationship, in their words, is "consistent with recent laboratory results (e.g., Sunda *et al.*, 2002)," which demonstrated intracellular DMS concentration and its biological precursors (particulate and dissolved dimethylsulfoniopropionate) "dramatically increase under conditions of acute oxidative stress such as exposure to high levels of UVR," which "are a function of mixed layer depth."

These results—which Toole and Siegel confirmed via an analysis of the Dacey *et al.* (1998) 1992–1994 organic sulfur time-series sampled in concert with the U.S. JGOFS Bermuda Atlantic Time-Series Study (Steinberg *et al.*, 2001)—suggest, in their words, "the potential of a global change-DMS-climate feedback." Specifically, they state "UVR doses will increase as a result of observed decreases in stratospheric ozone and the shoaling of ocean mixed layers as a result of global warming (e.g., Boyd and Doney, 2002)," and "in response, open-ocean phytoplankton communities should increase their DMS production and ventilation to the atmosphere, increasing cloud condensing nuclei, and potentially playing out a coupled global change-DMS-climate feedback."

This second DMS-induced negative feedback

cycle, which operates over 85 percent of the world's marine waters and complements the first DMS-induced negative feedback cycle, which operates over the other 15 percent, is another manifestation of the capacity of Earth's biosphere to regulate its affairs in such a way as to maintain climatic conditions over the vast majority of the planet's surface.

A DMS-induced negative climate feedback phenomenon may also operate over the terrestrial surface of the globe, where the volatilization of reduced sulfur gases from soils may be just as important as marine DMS emissions in enhancing cloud albedo (Idso, 1990). On the basis of experiments that showed soil DMS emissions to be positively correlated with soil organic matter content, for example, and noting additions of organic matter to a soil tend to increase the amount of sulfur gases emitted from it, Idso (1990) hypothesized that because atmospheric CO₂ is an effective aerial fertilizer, augmenting its atmospheric concentration and thereby increasing vegetative inputs of organic matter to Earth's soils should produce an impetus for cooling, even in the absence of surface warming.

About the same time Charlson *et al.* (1987) developed their hypothesis, Martin and Fitzwater (1988) and Martin *et al.* (1988) developed what has come to be known as the Iron Hypothesis (Martin, 1990), which posits that iron-rich dust swept up from exposed continental shelves during glacial maxima by the greatly enhanced winds of those periods fertilized the world's oceans to the point where their phytoplanktonic productivity rose so high it drew the air's CO₂ concentration down from typical interglacial values (280 ppm) to the much lower values characteristic of glacials (180 ppm). The IronEx studies of Martin *et al.* (1994) and Coale *et al.* (1996) confirmed the fundamental premise of this hypothesis. After fertilizing patches of seawater in high-nitrate low-chlorophyll (HNLC) regions of the equatorial Pacific with bio-available iron, they found, in the words of Turner *et al.* (2004), that this procedure "benefited all the major groups of the algal community, including those which produce significant amounts of intracellular dimethylsulfoniopropionate (DMSPp)," the precursor of DMS, which also increased in concentration as a result of the experimental iron treatment (Turner *et al.*, 1996).

In the aftermath of these demonstrations, large-scale ocean fertilization with bio-available iron came to be viewed as a viable potential strategy for the mitigation of global warming. Not only could its

implementation result in the quick removal of CO₂ from the atmosphere in response to heightened phytoplanktonic productivity, it could also lead to the reflection of more incoming solar radiation back to space as a result of greater DMSPp production.

But the studies supporting the second of these two pathways to planetary cooling had been conducted in the equatorial Pacific; it was not known whether the findings could be extrapolated to other HNLC ecosystems, such as those of the Southern Ocean. Thus, Turner *et al.* (2004) conducted two additional iron-release experiments: the Southern Ocean Iron Release Experiment (SOIREE), which took place south of Australia in February 1999, and EisenEx, which took place south of Africa in November 2000.

In both of these studies, Turner *et al.* reported "the experimental patches (~50 km²) were created by pumping dissolved iron sulfate into the mixed layer, as the ships sailed on a spiral track out from, and relative to, a buoy." The initial levels of dissolved iron in these patches rapidly decreased and additional injections were made during the experiments. "In SOIREE," the scientists note, "the major increase in DMS occurred several days after the maximum in DMSPp and by the end of the study DMS levels at 30 m depth were 6.5-fold higher in treated waters than outside," while "in EisenEx, highest observed DMS concentrations [occurred] on days 5 and 12, about 2-fold higher than initial levels." They also report a series of ocean color images from SeaWiFS revealed a feature with enhanced chlorophyll levels close to the SOIREE site (Boyd *et al.*, 2000), noting "Abraham *et al.* (2000) argue that this was our patch which had spread to cover 1100 km²."

Turner *et al.* report "recent coupled ocean-atmosphere modeling studies show that even a relatively small change in marine DMS emissions may have a significant impact on global temperatures: ± ~1°C for a halving or doubling of DMS emissions, respectively." In addition, they note "evidence from ice cores suggests that changes in DMS emission at least as large as this have occurred in the past (Legrand *et al.*, 1991) and so it is easily conceivable that significant changes in DMS emissions would occur in future climate scenarios."

Operating in tandem, it is clear the marine-productivity-mediated increase in reflected solar radiation to space (via the Charlson *et al.* mechanism) and the more direct marine-productivity-mediated increase in the removal of CO₂ from the atmosphere possess the capacity to substantially counter whatever warming of the planet might occur in response to

future anthropogenic CO₂ emissions.

In another study of the Charlson *et al.* (1987) hypothesis, Broadbent and Jones (2004) explored the possibility that coral reefs may be major participants in the biostabilization of Earth's climate. Working in waters off the coast of Australia, they note "Jones *et al.* (1994) and Broadbent *et al.* (2002) report that corals in the Great Barrier Reef (GBR) contain significant amounts of DMSP in their zooxanthellae, suggesting that coral reefs are potentially significant sources of DMS to the water column of reef areas and that coral reefs themselves may be significant sources of atmospheric DMS to the marine boundary layer (Jones and Trevena, 2005)." The two researchers measured concentrations of DMS and DMSP within mucus ropes, coral mucus, surface films, and sediment pore waters collected from Kelso Reef, One Tree Reef, and Nelly Bay Reef in Australia's GBR. Broadbent and Jones found "the concentrations of DMS and DMSP measured in mucus ropes and surface-water samples at One Tree Reef and Kelso Reef are the highest yet reported in the marine environment," exceeding those measured in "highly productive polar waters (Fogelqvist, 1991; Trevena *et al.*, 2000, 2003), and sea ice algal communities (Kirst *et al.*, 1991; Levasseur *et al.*, 1994; Trevena *et al.*, 2003)." They state, "concentrations of DMS ranged from 61 to 18,665 nM and for DMSP, from 1,978 to 54,381 nM, representing concentration factors (CF = concentration in the mucus ropes divided by the concentration in seawater from 0.5 m depth) ranging from 59 to 12,342 for DMS and 190 to 6,926 for DMSP." In addition, they report "concentrations of DMSP in coral mucus were also exceptionally high, with mucus from *Acropora formosa* containing the highest levels of DMSP." Finally, they observe DMS and DMSP concentrations were substantially higher than water-column concentrations in both surface microlayer samples and coral-reef sediment pore waters. Broadbent and Jones conclude "the elevated concentrations of DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters strongly suggest that coral reefs in the GBR are significant sources of these two sulphur substances," which in turn suggests coral reefs may figure prominently in the Charlson *et al.* phenomenon that helps to keep Earth's temperature from rising too high.

Jones and Trevena (2005) measured dissolved DMS, DMSP, the water-to-air flux of DMS, and atmospheric DMS concentration during a winter

voyage through the northern GBR, Coral Sea, Gulf of Papua (GOP), and Solomon and Bismarck Seas. This work revealed the "highest levels of most of these constituents occurred in the northern GBR, NW Coral Sea and GOP, with highest levels of atmospheric DMS often occurring in south-easterly to southerly trade winds sampled in the region where the highest biomass of coral reefs occur." They also found the increase in atmospheric DMS "was mainly a result of a combination of high winds and the extremely low tides in July, when a high biomass of coral reefs in this region was aerielly exposed." These findings helped solidify the link between coral zooxanthellae activity and the atmospheric concentration of DMS, which Broadbent and Jones (2004) called "a negative greenhouse gas"; i.e., one that tends to cool the planet. Thus, it broadens the base of the CLAW hypothesis (named for the four scientists of Charlson *et al.* (1987) who formulated it—Charlson, Lovelock, Andreae, and Warren) and makes it more likely the hypothesis represents a viable mechanism for tempering, and possibly even capping, global warming.

Several additional studies have probed the robustness of the CLAW hypothesis. Gunson *et al.* (2006), for example, performed a number of climate simulations using a coupled ocean-atmosphere general circulation model that included an atmospheric sulfur cycle and a marine ecosystem model. They determined "the modeled global climate is sensitive to ocean DMS production in the manner hypothesized by CLAW" and "perturbations to ocean DMS production cause significant impacts on global climate." For a halving of oceanic DMS emissions, for example, they found the modeled net cloud radiative forcing increased by 3 W/m² and, through a readjustment of the global radiative energy balance, the surface air temperature rose by 1.6°C. For a doubling of oceanic DMS emissions, they found net cloud radiative forcing declined by just under 2 W/m² and the surface air temperature decreased by just under 1°C. These findings suggest Earth's climate system is indeed capable of successfully buffering itself against the propensity for warming created by rising atmospheric CO₂ concentrations.

Wong *et al.* (2006) recorded DMS concentrations and physical oceanographic data at ocean stations P20 and P26 in the Gulf of Alaska in the Northeast Pacific Ocean. As the sea surface temperature of a region rises, they found, "the stratification of the upper water column intensifies and oceanic upwelling weakens,"

such that “in the nutrient-rich waters of the sub-Arctic Pacific, higher stratification and shallower mixed layer favor the growth of small-sized phytoplankton such as flagellates, dinoflagellates and coccolithophorids.” Noting “most prolific DMSP producers are members of these phytoplankton groups,” they state, “consequently, the local ecosystem is shifted towards one with structure and function adapted to production of DMSP and DMS.”

The four researchers point out, “globally, a larger part of the warming oceans may have highly stratified water for a longer part of the year,” adding “these conditions could enhance the shift in the marine ecosystem described herein, and might induce more rapid turnover of DMSP and higher production of DMS,” such that “in a warming global climate, we might anticipate an increasing emission of biogenic DMS from the ocean surface,” which would tend to counteract whatever impetus for warming was causing sea surface temperatures to rise.

Also in 2006, Meskhidze and Nenes explored the effects of ocean biological productivity on the microphysical and radiative properties of marine clouds over a large and seasonally recurring phytoplankton bloom in the Southern Ocean in the vicinity of South Georgia Island, where upwelling nutrient-rich waters “can support massive phytoplankton blooms, with chlorophyll *a* concentrations more than an order of magnitude higher than the background.” They used the Sea-viewing Wide Field-of-view Sensor to obtain the needed chlorophyll data and the Moderate Resolution Imaging Spectroradiometer to determine the effective radii of cloud condensation nuclei.

The researchers discovered “cloud droplet number concentration over the bloom was twice what it was away from the bloom, and cloud effective radius was reduced by 30%,” such that “the resulting change in the short-wave radiative flux at the top of the atmosphere was -15 watts per square meter, comparable to the aerosol indirect effect over highly polluted regions.” Meskhidze and Nenes conclude secondary organic aerosol formation in remote marine air may need to be included in global climate models, as it may play, as they describe it, “a considerable role in climate transition.”

In another experiment, part of the Third Pelagic Ecosystem CO₂ Enrichment Study, Wingenter *et al.* (2007) investigated the effects of atmospheric CO₂ enrichment on marine microorganisms within nine marine mesocosms maintained within 2-m-diameter polyethylene bags submerged to a depth of 10 m in a

fjord at the Large-Scale Facilities of the Biological Station of the University of Bergen in Espesgrend, Norway. Three of these mesocosms were maintained at ambient levels of CO₂ (~375 ppm or base CO₂), three were maintained at levels expected to prevail at the end of the current century (760 ppm or 2xCO₂), and three were maintained at levels predicted for the middle of the next century (1150 ppm or 3xCO₂). During the 25 days of their experiment, the 12 researchers followed the development and subsequent decline of induced blooms of the coccolithophorid *Emiliania huxleyi* in the three CO₂ environments, carefully measuring several physical, chemical, and biological parameters along the way.

Wingenter *et al.*'s measurements and analyses indicated “dimethylsulfide production followed the development and decline of the phytoplankton bloom” and “maximum DMS concentrations coincided with the peak in chlorophyll-*a* concentrations in the present day CO₂ treatment, but were delayed by 1–3 days relative to chlorophyll-*a* in the double and triple CO₂ treatments.” In addition, they found “DMS was 26% and 18% higher in the 2x and 3xCO₂ mesocosms, respectively (days 0–17).” The iodocarbon chloriodomethane (CH₂CII) had its peak concentration about 6 to 10 days after the chlorophyll-*a* maximum, but its estimated abundance was 46 percent higher in the 2xCO₂ mesocosms and 131 percent higher in the 3xCO₂ mesocosms.

The international team of scientists concludes “the differences in DMS and CH₂CII concentrations may be viewed as a result of changes to the ecosystems as a whole brought on by the CO₂ perturbations.” Because emissions of both DMS (Bates *et al.*, 1992) and various iodocarbons (O'Dowd *et al.*, 2002; Jimenez *et al.*, 2003) typically lead to an enhancement of cloud condensation nuclei in the marine atmosphere, the CO₂-induced stimulations of the marine emissions of these two substances provide a natural brake on the tendency for global warming to occur, as they lead to the creation of more highly reflective clouds over greater areas of the world's oceans. Consequently, as Wingenter *et al.* note, “these processes may help contribute to the homeostasis of the planet.”

Vogt *et al.* (2008) also analyzed the effects of atmospheric CO₂ enrichment on marine microorganisms and DMS production under the same three CO₂ concentrations as those employed by Wingenter *et al.* (2007)—375, 760, and 1150 ppm—for a period of 24 days. They found no significant phytoplankton species shifts among treatments and

noted “ecosystem composition, bacterial and phytoplankton abundances and productivity, grazing rates and total grazer abundance and reproduction were not significantly affected by CO₂-induced effects,” citing in support of this statement the work of Riebesell *et al.* (2007), Riebesell *et al.* (2008), Egge *et al.* (2007), Paulino *et al.* (2007), Larsen *et al.* (2007), Suffrian *et al.* (2008), and Carotenuto *et al.* (2007). In addition, they note “while DMS stayed elevated in the treatments with elevated CO₂, we observed a steep decline in DMS concentration in the treatment with low CO₂” i.e., the ambient CO₂ treatment.

The eight researchers conclude “the system under study was surprisingly resilient to abrupt and large pH changes,” contrary to what the IPCC characteristically predicts about CO₂-induced “ocean acidification.” That may be why Vogt *et al.* describe the marine ecosystem they studied as “surprisingly” resilient.

Working in the coastal waters of Korea from November 21 to December 11, 2008, Kim *et al.* (2010) also conducted a CO₂ enrichment experiment, utilizing 2,400-liter mesocosm enclosures to simulate three sets of environmental conditions—an ambient control (~400 ppm CO₂ and ambient temperature), an acidification treatment (~900 ppm CO₂ and ambient temperature), and a greenhouse treatment (~900 ppm CO₂ and ~3°C warmer-than-ambient temperature). Within these mesocosms they initiated phytoplankton blooms by adding equal quantities of nutrients to each mesocosm on day 0, while for 20 days thereafter they measured numerous pertinent parameters within each mesocosm. They found “the total accumulated DMS concentrations (integrated over the experimental period) in the acidification and greenhouse mesocosms were approximately 80% and 60% higher than the values measured in the control mesocosms, respectively.”

“Autotrophic nanoflagellates (which are known to be significant DMSP producers) showed increased growth in response to elevated CO₂,” they note, and “grazing rates [of microzooplankton] were significantly higher in the treatment mesocosms than in the control mesocosms.” Kim *et al.* conclude, “in the context of global environmental change, the key implication of our results is that DMS production resulting from CO₂-induced grazing activity may increase under future high CO₂ conditions” and, therefore, “DMS production in the ocean may act to counter the effects of global warming in the future.”

Watanabe *et al.* (2007) utilized sea surface DMS

data and other hydrographic parameters measured in the North Pacific Ocean between latitudes 25 and 55°N to develop and validate an empirical equation for sea surface DMS concentration that uses sea surface temperature, sea surface nitrate concentration, and latitude as input data. By applying the algorithm they developed to hydrographic time series data sets pertaining to the western North Pacific that span the period 1971 to 2000, the seven researchers found the annual flux of DMS from sea to air in that region increased by 1.9–4.8 μmol m⁻² year⁻¹. This increase, they write, “was equal to the annual rate of increase of about 1% of the climatological annual averaged flux of DMS in the western North Pacific in the last three decades.” These observations suggest the negative climate feedback phenomenon driven by increasing oceanic DMS concentrations is “alive and well.”

Working with climate and DMS production data from the region of the Barents Sea (70–80°N, 30–35°E) obtained over the period 1998 to 2002, Qu and Gabric (2010) employed a genetic algorithm to calibrate chlorophyll-*a* measurements (obtained from SeaWiFS satellite data) for use in a regional DMS production model. Then, using GCM temperature outputs for the periods of 1960–1970 (pre-industry CO₂ level) and 2078–2086 (triple the pre-industry CO₂ level), they calculated the warming-induced enhancement of the DMS flux from the Barents Sea region. The two researchers report “significantly decreasing ice coverage, increasing sea surface temperature and decreasing mixed-layer depth could lead to annual DMS flux increases of more than 100% by the time of equivalent CO₂ tripling (the year 2080).” They state “such a large change would have a great impact on the Arctic energy budget and may offset the effects of anthropogenic warming that are amplified at polar latitudes” and add “many of these physical changes will also promote similar perturbations for other biogenic species (Leck *et al.*, 2004), some of which are now thought to be equally influential to the aerosol climate of the Arctic Ocean.”

One year later, working with *Phaeocystis antarctica*—a polar prymnesiophyte or haptophyte (marine microalga or phytoplankton)—Orellana *et al.* (2011) measured the concentrations of DMS and DMSP in whole cells and isolated secretory vesicles of the species as well as in samples of broken cells, because, as they elucidated, “in addition to autolysis (Hill *et al.*, 1998), viral lysis (Malin *et al.*, 1998), and zooplankton grazing (Dacey and Wakeham, 1986;

Wolfe and Steinke, 1996), it is believed that DMSP passively diffuses into seawater.” They note “understanding the regulation of this mechanism is necessary in order to obtain a correct partitioning of the cellular and extracellular DMSP and DMS pools in seawater and allow predictions of global budgets.” The four U.S. researchers demonstrate “DMSP and DMS were stored in the secretory vesicles of *Phaeocystis antarctica*,” where “they were trapped within a polyanionic gel matrix, which prevented an accurate measurement of their concentration in the absence of a chelating agent.” They conclude, “the pool of total DMSP in the presence of *Phaeocystis* may be underestimated by as much as half.”

Noting “models for the distribution of marine DMS have lately been increasing in number and complexity, such that a regional portrait of their evolving climate response is constructible,” Cameron-Smith *et al.* (2011) employed the most recent version of the Community Climate System Model (CCSM), described by Collins *et al.* (2006), to produce the first marine sulfur simulations performed with what they refer to as “the most sophisticated ocean sulfur cycle model yet reported.”

In one of their simulations, the atmospheric CO₂ concentration was held steady at 355 ppm, while in another it was set at 970 ppm in order to simulate the climate near the end of the twenty-first century as projected by the IPCC (2001) SRES A1F1 emissions scenario. The latter CO₂ concentration and its modeled climatic consequences resulted in the simulation of “rings of high DMS near Antarctica due to the inclusion of a *Phaeocystis* parameterization.” This unicellular, photosynthetic, eukaryotic alga generates, in the words of the five U.S. scientists, “several times the typical DMSP level (dimethyl sulfoniopropionate, a major DMS precursor) and favors cold water habitat (Matrai and Vernet, 1997).”

Consequently, the modeled global warming produced by the specified increase in the atmosphere’s CO₂ concentration resulted in a migration of *Phaeocystis* species toward the cooler waters of higher latitudes. Under these conditions the model employed by Cameron-Smith *et al.* simulated increases in the “zonal averaged DMS flux to the atmosphere of over 150% in the Southern Ocean,” which they report was “due to concurrent sea ice changes and ocean ecosystem composition shifts caused by changes in temperature, mixing, nutrient, and light regimes.” Based on other modeling exercises they conducted, they state the shift in the location of maximum DMS emissions towards colder

regions “is usually reinforced with even more sophisticated models.”

Cameron-Smith and colleagues conclude, “in global estimates involving constant upward or downward DMS flux changes, average planetary surface temperatures separate by three or more degrees Celsius,” citing the work of Charlson *et al.* (1987) and Gunson *et al.* (2006). This strong biological response to a CO₂-induced impetus for warming can result in a greatly strengthened negative regional feedback that results in more incoming solar radiation being reflected back to space with enhanced regional cooling. The resulting DMS-enhanced “thermal insulating” of Antarctica from the rest of the world by this mechanism could significantly reduce the propensity for that continent’s ice sheets to lose mass and contribute to sea level rise, even in a world that is experiencing a net warming.

References

- Abraham, E.R., Law, C.S., Boyd, P.W., Lavender, S.J., Maldonado, M.T., and Bowie, A.R. 2000. Importance of stirring in the development of an iron-fertilized phytoplankton bloom. *Nature* **407**: 727–730.
- Ayers, G.P. and Gillett, R.W. 2000. DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry. *Journal of Sea Research* **43**: 275–286.
- Baboukas, E., Sciare, J., and Mihalopoulos, N. 2002. Interannual variability of methanesulfonate in rainwater at Amsterdam Island (Southern Indian Ocean). *Atmospheric Environment* **36**: 5131–5139.
- Bates, T.S., Lamb, B.K., Guenther, A., Dignon, J., and Stoiber, R.E. 1992. Sulfur emissions to the atmosphere from natural sources. *Journal of Atmospheric Chemistry* **14**: 315–337.
- Boyd, P.W. and Doney, S.C. 2002. Modeling regional responses by marine pelagic ecosystems to global climate change. *Geophysical Research Letters* **29**: 10.1029/2001GL014130.
- Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzpek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J. 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* **407**: 695–702.

Forcings and Feedbacks

- Broadbent, A.D., Jones, G.B., and Jones, R.J. 2002. DMSP in corals and benthic algae from the Great Barrier Reef. *Estuarine, Coastal and Shelf Science* **55**: 547–555.
- Cameron-Smith, P., Elliott, S., Maltrud, M., Erickson, D., and Wingenter, O. 2011. Changes in dimethyl sulfide oceanic distribution due to climate change. *Geophysical Research Letters* **38**: 10.1029/2011GL047069.
- Carotenuto, Y., Putzeys, S., Simonelli, P., Paulino, A., Meyerhofer, M., Suffrian, K., Antia, A., and Nejtgaard, J.C. 2007. Copepod feeding and reproduction in relation to phytoplankton development during the PeECE III mesocosm experiment. *Biogeosciences Discussions* **4**: 3913–3936.
- Charlson, R.J., Lovelock, J.E., Andrea, M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- Collins, W.D., Bitz, C.M., Blackmon, M.L., Bonan, G.B., Bretherton, C.S., Carton, J.A., Chang, P., Doney, S.C., Hack, J.J., Henderson, T.B., Kiehl, J.T., Large, W.G., McKenna, D.S., Santer, B.D., and Smith, R.D. 2006. The Community Climate System Model Version 3 (CCSM3). *Journal of Climate* **19**: 2122–2143.
- Dacey, J.W.H., Howse, F.A., Michaels, A.F., and Wakeham, S.G. 1998. Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea. *Deep Sea Research* **45**: 2085–2104.
- Dacey, J.W.H. and Wakeham, S.G. 1986. Oceanic dimethylsulfide: production during zooplankton grazing. *Science* **233**: 1314–1316.
- Egge, J., Thingstad, F., Engel, A., Bellerby, R.G.J., and Riebesell, U. 2007. Primary production at elevated nutrient and pCO₂ levels. *Biogeosciences Discussions* **4**: 4385–4410.
- Fogelqvist, E. 1991. Dimethylsulphide (DMS) in the Weddell Sea surface and bottom water. *Marine Chemistry* **35**: 169–177.
- Gunson, J.R., Spall, S.A., Anderson, T.R., Jones, A., Totterdell, I.J., and Woodage, M.J. 2006. Climate sensitivity to ocean dimethylsulphide emissions. *Geophysical Research Letters* **33**: 10.1029/2005GL024982.
- Hill, R.W., White, B.A., Cottrell, M.T., and Dacey, J.W.H. 1998. Virus-mediated total release of dimethylsulfoniopropionate from marine phytoplankton: a potential climate process. *Aquatic and Microbial Ecology* **14**: 1–6.
- Hopke, P.K., Xie, Y., and Paatero, P. 1999. Mixed multiway analysis of airborne particle composition data. *Journal of Chemometrics* **13**: 343–352.
- Idso, S.B. 1990. A role for soil microbes in moderating the carbon dioxide greenhouse effect? *Soil Science* **149**: 179–180.
- Jimenez, J.L., Bahreini, R., Cocker III, D.R., Zhuang, H., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., O'Dowd, C.D., and Hoffmann, T. 2003. New particle formation from photooxidation of diiodomethane (CH₂I₂). *Journal of Geophysical Research* **108**: 10.1029/2002JD002452.
- Jones, G.B. and Trevena, A.J. 2005. The influence of coral reefs on atmospheric dimethylsulphide over the Great Barrier Reef, Coral Sea, Gulf of Papua and Solomon and Bismarck Seas. *Marine and Freshwater Research* **56**: 85–93.
- Kim, J.-M., Lee, K., Yang, E.J., Shin, K., Noh, J.H., Park, K.-T., Hyun, B., Jeong, H.-J., Kim, J.-H., Kim, K.Y., Kim, M., Kim, H.-C., Jang, P.-G., and Jang, M.-C. 2010. Enhanced production of oceanic dimethylsulfide resulting from CO₂-induced grazing activity in a high CO₂ world. *Environmental Science & Technology*: 10.1021/es102028k.
- Kirst, G.O., Thiel, C., Wolff, H., Nothnagel, J., Wanzek, M., and Ulmke, R. 1991. DMSP in ice algae and its possible role. *Marine Chemistry* **35**: 381–388.
- Kouvarakis, G. and Mihalopoulos, N. 2002. Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere. *Atmospheric Environment* **36**: 929–938.
- Larsen, J.B., Larsen, A., Thyraug, R., Bratbak, G., and Sandaa R.-A. 2007. Marine viral populations detected during a nutrient induced phytoplankton bloom at elevated pCO₂ levels. *Biogeosciences Discussions* **4**: 3961–3985.
- Leck, C., Tjernstrom, M., Matrai, P., Swietlicki, E., and Bigg, E.K. 2004. Can marine micro-organisms influence melting of the Arctic pack ice? *EOS, Transactions, American Geophysical Union* **85**: 25–36.
- Legrand, M., Feniet-Saigne, C., Sattzman, E.S., Germain, C., Barkov, N.I., and Petrov, V.N. 1991. Ice-core record of oceanic emissions of dimethylsulfide during the last climate cycle. *Nature* **350**: 144–146.
- Levasseur, M., Gosselin, M., and Michaud, S. 1994. A new source of dimethylsulphide (DMS) for the Arctic atmosphere: ice diatoms. *Marine Biology* **121**: 381–387.
- Malin, G., Wilson, W.H., Bratbak, G., Liss, P.S., and Mann, N.H. 1998. Elevated production of dimethylsulfide resulting from viral infection of cultures of *Phaeocystis pouchetii*. *Limnology and Oceanography* **43**: 1389–1393.
- Martin, J.H. 1990. Glacial-interglacial CO₂ change: The iron hypothesis. *Paleoceanography* **5**: 1–13.

- Martin, J.H. and Fitzwater, S.E. 1988. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature* **331**: 341–343.
- Martin, J.H., Gordon, M., and Fitzwater, S. 1988. Oceanic iron distributions in relation to phytoplanktonic productivity. *EOS: Transactions of the American Geophysical Union* **69**: 1045.
- Matrai, P. and Vernet, M. 1997. Dynamics of the vernal bloom in the marginal ice zone of the Barents Sea: Dimethyl sulfide and dimethylsulfoniopropionate budgets. *Journal of Geophysical Research* **102**: 22,965–22,979.
- Meskhidze, N. and Nenes, A. 2006. Phytoplankton and cloudiness in the Southern Ocean. *Science* **314**: 1419–1423.
- O’Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G., and Hoffmann, T. 2002. Marine aerosol formation from biogenic iodine emissions. *Nature* **417**: 632–636.
- Orellana, M.V., Matrai, P.A., Janer, M., and Rauschenberg, C.D. 2011. Dimethylsulfoniopropionate storage in *Phaeocystis* (Prymnesiophyceae) secretory vesicles. *Journal of Phycology* **47**: 112–117.
- Paulino, A.I., Egge, J.K., and Larsen, A. 2007. Effects of increased atmospheric CO₂ on small and intermediate sized osmotrophs during a nutrient induced phytoplankton bloom. *Biogeosciences Discussions* **4**: 4173–4195.
- Qu, B. and Gabric, A.J. 2010. Using genetic algorithms to calibrate a dimethylsulfide production model in the Arctic Ocean. *Chinese Journal of Oceanology and Limnology* **28**: 573–582.
- Riebesell, U., Bellerby, R.G.J., Grossart, H.-P., and Thingstad, F. 2008. Mesocosm CO₂ perturbation studies: from organism to community level. *Biogeosciences Discussions* **5**: 641–659.
- Riebesell, U., Schulz, K., Bellerby, R., Botros, M., Fritsche, P., Meyerhofer, M., Neill, C., Nondal, G., Oschlies, A., Wohlers, J., and Zollner, E. 2007. Enhanced biological carbon consumption in a high CO₂ ocean. *Nature* **450**: 10.1038/nature06267.
- Sciare, J., Mihalopoulos, N., and Dentener, F.J. 2000. Interannual variability of atmospheric dimethylsulfide in the southern Indian Ocean. *Journal of Geophysical Research* **105**: 26,369–26,377.
- Simo, R. and Pedros-Alio, C. 1999. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature* **402**: 396–399.
- Steinberg, D.K., Carlson, C.A., Bates, N.R., Johnson, R.J., Michaels, A.F., and Knap, A.H. 2001. Overview of the US JGOFS Bermuda Atlantic Time-series Study (BATS): a decade-scale look at ocean biology and biogeochemistry. *Deep Sea Research Part II: Topical Studies in Oceanography* **48**: 1405–1447.
- Suffrian, K., Simonelli, P., Nejtgaard, J.C., Putzeys, S., Carotenuto, Y., and Antia, A.N. 2008. Microzooplankton grazing and phytoplankton growth in marine mesocosms with increased CO₂ levels. *Biogeosciences Discussions* **5**: 411–433.
- Sunda, W., Kieber, D.J., Kiene, R.P., and Huntsman, S. 2002. An antioxidant function for DMSP and DMS in marine algae. *Nature* **418**: 317–320.
- Toole, D.A. and Siegel, D.A. 2004. Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: Closing the loop. *Geophysical Research Letters* **31**: 10.1029/2004GL019581.
- Trevena, A.J., Jones, G.B., Wright, S.W., and Van den Enden, R.L. 2000. Profiles of DMSP, algal pigments, nutrients and salinity in pack ice from eastern Antarctica. *Journal of Sea Research* **43**: 265–273.
- Trevena, A.J., Jones, G.B., Wright, S.W., and Van den Enden, R.L. 2003. Profiles of dimethylsulphoniopropionate (DMSP), algal pigments, nutrients, and salinity in the fast ice of Prydz Bay, Antarctica. *Journal of Geophysical Research* **108**: 3145–3156.
- Turner, S.M., Harvey, M.J., Law, C.S., Nightingale, P.D., and Liss, P.S. 2004. Iron-induced changes in oceanic sulfur biogeochemistry. *Geophysical Research Letters* **31**: 10.1029/2004GL020296.
- Turner, S.M., Nightingale, P.D., Spokes, L.J., Liddicoat, M.I., and Liss, P.S. 1996. Increased dimethyl sulphide concentrations in sea water from in situ iron enrichment. *Nature* **383**: 513–517.
- Vogt, M., Steinke, M., Turner, S., Paulino, A., Meyerhofer, M., Riebesell, U., LeQuere, C., and Liss, P. 2008. Dynamics of dimethylsulphoniopropionate and dimethylsulphide under different CO₂ concentrations during a mesocosm experiment. *Biogeosciences* **5**: 407–419.
- Watanabe, Y.W., Yoshinari, H., Sakamoto, A., Nakano, Y., Kasamatsu, N., Midorikawa, T., and Ono, T. 2007. Reconstruction of sea surface dimethylsulfide in the North Pacific during 1970s to 2000s. *Marine Chemistry* **103**: 347–358.
- Wingenter, O.W., Haase, K.B., Zeigler, M., Blake, D.R., Rowland, F.S., Sive, B.C., Paulino, A., Thyrraug, R., Larsen A., Schulz, K., Meyerhofer, M., and Riebesell, U. 2007. Unexpected consequences of increasing CO₂ and ocean acidity on marine production of DMS and CH₂ClI: Potential climate impacts. *Geophysical Research Letters* **34**: 10.1029/2006GL028139.

Wolfe, G.V. and Steinke, M. 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. *Limnology and Oceanography* **41**: 1151–1160.

Wong, C.-S., Wong, S.-K. E., Pena, A., and Levasseur, M. 2006. Climatic effect on DMS producers in the NE sub-Arctic Pacific: ENSO on the upper ocean. *Tellus* **58B**: 319–326.

2.5.2.2 Terrestrial

Just as marine phytoplankton respond to rising temperatures by emitting gases that ultimately lead to less global warming, so too do terrestrial plants. What is more, Earth's terrestrial plants have a tendency to operate in this manner more effectively as the air's CO₂ content rises.

A good introduction to this subject is provided by the review paper of Peñuelas and Llusia (2003), who point out biogenic volatile organic compounds (BVOCs) constitute “one of nature's biodiversity treasures.” Comprised of isoprene, terpenes, alkanes, alkenes, alcohols, esters, carbonyls, and acids, this diverse group of substances is produced by a variety of processes occurring in many plant tissues. Some of the functions of these substances, according to the two scientists, include acting as “deterrents against pathogens and herbivores, or to aid wound sealing after damage (Pichersky and Gershenzon, 2002).” They also state BVOCs provide a means “to attract pollinators and herbivore predators, and to communicate with other plants and organisms (Peñuelas *et al.*, 1995; Shulaev *et al.*, 1997).”

Of particular importance within the context of global climate change, in the opinion of Peñuelas and Llusia, is the growing realization that “isoprene and monoterpenes, which constitute a major fraction of BVOCs, might confer protection against high temperatures” by acting “as scavengers of reactive oxygen species produced [within plants] under high temperatures.” The claimed ill effects of CO₂-induced global warming on Earth's vegetation thus may be countered by two ameliorative phenomena: the aerial fertilization effect of atmospheric CO₂ enrichment, which is typically more strongly expressed at higher temperatures, and the tendency for rising air temperatures and CO₂ concentrations to spur the production of higher concentrations of heat-stress-reducing BVOCs. With respect to temperature, Peñuelas and Llusia calculate “global warming over the past 30 years could have increased the BVOC global emissions by approximately 10 percent, and a

further 2–3°C rise in the mean global temperature ... could increase BVOC global emissions by an additional 30–45 percent.”

Other phenomena may similarly favor plants. Peñuelas and Llusia note “the increased release of nitrogen into the biosphere by man probably also enhances BVOC emissions by increasing the level of carbon fixation and the activity of the responsible enzymes (Litvak *et al.*, 1996).” The conversion of abandoned agricultural lands to forests and the implementation of planned reforestation projects should help the rest of the biosphere too; Peñuelas and Llusia report additional numbers of “*Populus*, *Eucalyptus* or *Pinus*, which are major emitters, might greatly increase BVOC emissions.”

With respect to how increased BVOC emissions might affect climate change itself, Peñuelas and Llusia point out “BVOCs generate large quantities of organic aerosols that could affect climate significantly by forming cloud condensation nuclei.” They conclude, “there should be a net cooling of the Earth's surface during the day because of radiation interception,” noting Shallcross and Monks (2000) “have suggested that one of the reasons plants emit the aerosol isoprene might be to cool the surroundings in addition to any physiological or evaporative effects that might cool the plant directly.”

Not all experiments have reported increases in plant BVOC emissions with increasing atmospheric CO₂ concentrations. Rapparini *et al.* (2004) found long-term exposure to high levels of atmospheric CO₂ did not significantly affect BVOC emissions from mature downy and holly oak trees growing close to a natural CO₂ spring in central Italy. Similarly, Constable *et al.* (1999) reported no effect of elevated CO₂ on monoterpene emissions from Ponderosa pine and Douglas fir trees. And some studies have reported decreases in BVOC emissions, such as those of Vuorinen *et al.* (2004), who worked with cabbage plants, and Loreto *et al.* (2001), who studied monoterpene emissions from oak seedlings. But Staudt *et al.* (2001) observed CO₂-induced increases in BVOC emissions in the identical species of oak studied by Vuorinen *et al.* (2004).

An explanation for this wide range of results comes from Baraldi *et al.* (2004), who—after exposing sections of a southern California chaparral ecosystem to atmospheric CO₂ concentrations ranging from 250 to 750 ppm in 100-ppm increments for a period of four years—concluded “BVOC emission can remain nearly constant as rising CO₂ reduces

emission per unit leaf area while stimulating biomass growth and leaf area per unit ground area.” In most of the cases investigated, however, BVOC emissions tended to increase with atmospheric CO₂ enrichment, and the increases were often large.

Jasoni *et al.* (2003), for example, grew onions from seed for 30 days in individual cylindrical flow-through growth chambers under controlled environmental conditions at atmospheric CO₂ concentrations of either 400 or 1,000 ppm. At the end of the study, the plants in the CO₂-enriched chambers had 40 percent more biomass than the plants grown in ambient air, and their photosynthetic rates were 22 percent greater. In addition, the CO₂-enriched plants exhibited 17-fold and 38-fold increases in emissions of the BVOC hydrocarbons 2-undecanone and 2-tridecanone, respectively, which Jasoni *et al.* note “confer insect resistance against a major agricultural pest, spider mites.” They conclude “plants grown under elevated CO₂ will accumulate excess carbon and at least a portion of this excess carbon is funneled into an increased production of BVOCs.”

Focusing on actively wet-spore-discharging Ascomycota (AAM) and actively wet-spore-discharging Basidiomycota (ABM), Elbert *et al.* (2007) “address the active (forcible) discharge of fungal spores, which is accompanied by the emission of aqueous droplets containing carbohydrates and inorganic ions, ... summarize the information on the atmospheric abundance of wet and dry discharged fungal spores that is available from earlier scientific studies made at various locations around the world, ... and present new measurement results and budget calculations for aerosol samples from tropical rainforests in Amazonia.” The four researchers confirmed AAM and ABM are major sources of primary biogenic aerosols, finding from their own work that “in pristine tropical rainforest air, fungal spores indeed account for a major fraction of coarse particulate matter (up to ~45%).” They also calculated the emission rate of total fungal spores (~50 Tg yr⁻¹) “is of similar magnitude as current estimates of the rates of emission and formation of other types of continental air particulate matter (primary and secondary organic aerosols).”

Of particular interest in the context of rising near-surface air temperatures and atmospheric CO₂ concentrations, Elbert *et al.* write, “global warming and increasing CO₂ concentrations may enhance the spread of fungi and emission of fungal spores,” citing the works of Klironomos *et al.* (1997), Hoyer *et al.* (2007), and Raupach *et al.* (2007), while further

concluding “an increase of fungal spores acting as cloud condensation and ice nuclei may influence the hydrological cycle and provide either positive or negative feedbacks to climate change.”

Raisanen *et al.* (2008) sought to determine to what extent a doubling of the air’s CO₂ content and a 2°–6°C increase in air temperature might affect the emission of monoterpenes from 20-year-old Scots pine (*Pinus sylvestris* L.) seedlings. They studied the two phenomena and their interaction within closed-top chambers built on a naturally seeded stand of the trees in eastern Finland that had been exposed to the four treatments—ambient CO₂ and ambient temperature, ambient temperature and elevated CO₂, ambient CO₂ and elevated temperature, elevated temperature and elevated CO₂—for the prior five years.

Over the five-month growing season of May–September, the three Finnish researchers found total monoterpene emissions in the elevated-CO₂-only treatment were 5 percent greater than those in the ambient CO₂, ambient temperature treatment. Emissions in the elevated-temperature-only treatment were 9 percent less than those in ambient air. In the presence of both elevated CO₂ and elevated temperature, there was an increase of fully 126 percent in the total amount of monoterpenes emitted over the growing season, which led the authors to conclude, “the amount of monoterpenes released by Scots pines into the atmosphere during a growing season will increase substantially in the predicted future climate.”

Kavouras *et al.* (1998) measured a number of atmospheric gases and particles in a eucalyptus forest in Portugal and analyzed their observations for evidence of biologically produced gases being converted to particles that could function as cloud condensation nuclei. They found certain hydrocarbons emitted by vegetation (isoprene and terpenes, in particular) do indeed experience gas-to-particle transformations. Aerosols (or *biosols*) produced from two of these organic acids (cis- and trans-pinonic acid) comprised as much as 40 percent of the fine particle atmospheric mass during daytime hours.

A similar study was conducted by O’Dowd *et al.* (2002), who measured aerosol electrical-mobility size-distributions before and during the initial stage of an atmospheric nucleation event over a boreal forest in Finland. Simultaneously, organic vapor growth rate measurements were made of particles that nucleated into organic cloud-droplets in the flow-tube cloud

chamber of a modified condensation-particle counter. They determined newly formed aerosol particles over forested areas “are composed primarily of organic species, such as cis-pinonic acid and pinonic acid, produced by oxidation of terpenes in organic vapors released from the canopy.” They point out “aerosol particles produced over forested areas may affect climate by acting as nuclei for cloud condensation,” adding there remain numerous uncertainties involving complex feedback processes “that must be determined if we are to predict future changes in global climate.”

Also working in Finland, Tunved *et al.* (2006) analyzed a five-year (1999–2004) April–September database of aerosol number-size distribution obtained from three monitoring stations in the Finnish boreal zone of Europe—Varrio (67°46'N, 29°35'E), Pallas (68°01'N, 24°10'E), and Hyytiala (61°51'N, 24°17'E)—in an investigation of “the characteristic changes of the aerosol population in air masses undergoing marine to continental transition over forested areas in northern Norway, Sweden and Finland” that are “substantially lacking in anthropogenic aerosol sources.” According to the ten European researchers authoring this study, their results “clearly show that a substantial gas-to-particle [trans]formation of biogenic volatile organic carbon [BVOC] to secondary organic aerosol [SOA] takes place over the boreal forest in northern Europe” and “these BVOCs are most likely emitted from the forest itself and, based on previous findings, are most likely constituted of terpenes.”

Their analysis further “suggests an apparent mass yield in the range of 5 to 10%” and that “the boreal forest typically sustains 1000 to 2000 particles cm^{-3} in a climatic relevant size range (~40 to 100 nm).” Because they “provided a similar mechanistic and quantitative behavior for two widely separate locations (more than 700 km apart),” they report, “the derived relations suggest that similar mechanisms control the aerosol number and mass evolution over large areas in the boreal regions of the Northern Hemisphere.” Tunved *et al.* conclude their findings have “important implications for radiation budget estimates and relevancy for the evaluation of feedback loops believed to determine our future climate,” noting their study establishes that boreal forest “is a major source of climate-relevant aerosol particles” “capable of competing with the anthropogenic CCN [cloud condensation nuclei] loadings transported over forested areas.”

Shifting from trees to a much smaller plant, Kuhn

and Kesselmeier (2000) collected lichens from an open oak woodland in central California, USA and studied their uptake of carbonyl sulfide (COS) in a dynamic cuvette system under controlled conditions in the laboratory. When the lichens were optimally hydrated, COS was absorbed from the atmosphere by the lichens at a rate that gradually doubled as air temperature rose from approximately 3° to 25°C, whereupon the rate of COS absorption dropped precipitously, reaching a value of zero at 35°C.

COS is the most stable and abundant reduced sulfur gas in the atmosphere and a major player in determining Earth’s radiation budget. After making its way into the stratosphere, it can be photo-dissociated, as well as oxidized, to form SO_2 , which is typically converted to sulfate aerosol particles that are highly reflective of incoming solar radiation and, therefore, have the capacity to significantly cool Earth as more and more of them collect above the tropopause. Biologically modulated COS concentrations may play a role in regulating Earth’s surface air temperature.

Once air temperature rises above 25°C, the rate of removal of COS from the air by this species of lichen declines dramatically. More COS thus remains in the air and is likely to make its way into the stratosphere, where it can be converted into sulfate aerosol particles that can reflect more incoming solar radiation back to space and thereby cool Earth. Since the consumption of COS by lichens is under the physiological control of carbonic anhydrase, which is the key enzyme for COS uptake in all higher plants, algae, and soil organisms, this phenomenon is likely to be generally operative throughout much of the plant kingdom. This biological “thermostat” may be powerful enough to define an upper limit above which the surface air temperature of the planet may be restricted from rising, even when changes in other forcing factors, such as greenhouse gases, produce an impetus for it to do so. (For more about COS, see Section 2.6.2 below.)

Although BVOCs emitted from terrestrial plants both small and large are important to Earth’s climate, trees tend to dominate. Recent research suggests another way in which their response to atmospheric CO_2 enrichment may provide an effective counterbalance to the greenhouse properties of CO_2 .

The phenomenon begins with the propensity for CO_2 -induced increases in BVOCs, together with the cloud particles they spawn, to enhance the amount of diffuse solar radiation reaching Earth’s surface

(Suraqui *et al.*, 1974; Abakumova *et al.*, 1996). That is followed by the ability of enhanced diffuse lighting to reduce the volume of shade within vegetative canopies (Roderick *et al.*, 2001), followed by the tendency for less internal canopy shading to enhance whole-canopy photosynthesis (Healey *et al.*, 1998). The end result is a greater photosynthetic extraction of CO₂ from the air and subsequent reduction of the strength of the atmosphere's greenhouse effect.

The significance of this process is described and documented at some length in Section 2.6.3 of this report. For example, Roderick *et al.* conclude the Mt. Pinatubo eruption—a unique natural experiment to evaluate the overall climatic sensitivity of the planet—may have resulted in the removal of an extra 2.5 Gt of carbon from the atmosphere due to its diffuse-light-enhancing stimulation of terrestrial photosynthesis in the year following the eruption. Additional real-world evidence for the existence of this phenomenon was provided by Gu *et al.* (2003), Law *et al.* (2002), Farquhar and Roderick (2003), Reichenau and Esser (2003), and Niyogi *et al.* (2004).

One final beneficial effect of CO₂-induced increases in BVOC emissions is the propensity of BVOCs to destroy tropospheric ozone, as documented by Goldstein *et al.* (2004). Earth's vegetation is responsible for the production of vast amounts of ozone (O₃) (Chameides *et al.*, 1988; Harley *et al.*, 1999), but it is also responsible for destroying much of it. Goldstein *et al.* mention three major routes by which O₃ exits the air near Earth's surface: leaf stomatal uptake, surface deposition, and within-canopy gas-phase chemical reactions with BVOCs.

The first of these exit routes, according to Goldstein *et al.*, accounts for 30 to 90 percent of total ecosystem O₃ uptake from the atmosphere (that is, O₃ destruction), and the remainder typically has been attributed to deposition on non-stomatal surfaces. However, they note “Kurpius and Goldstein (2003) recently showed that the non-stomatal flux increased exponentially as a function of temperature at a coniferous forest site,” and “the exponential increase with temperature was consistent with the temperature dependence of monoterpene emissions from the same ecosystem, suggesting O₃ was lost via gas phase reactions with biogenically emitted terpenes before they could escape the forest canopy.”

Schade and Goldstein (2003) had demonstrated forest thinning dramatically enhances monoterpene emissions. Goldstein *et al.* (2004) took another important step toward clarifying the issue by measuring the effect of forest thinning on O₃

destruction in an attempt to see if it is enhanced along with the thinning-induced increase in monoterpene emissions.

In a ponderosa pine plantation in the Sierra Nevada Mountains of California, USA, a management procedure to improve forest health and optimize tree growth was initiated on May 11, 2000 and continued through June 15, 2000. This procedure involved the use of a masticator to mechanically “chew up” smaller unwanted trees and leave their debris on site, which reduced plantation green leaf biomass by just over half. Monoterpene mixing ratios and fluxes were measured hourly within the plantation canopy, while total ecosystem O₃ destruction was “partitioned to differentiate loss due to gas-phase chemistry from stomatal uptake and deposition.”

Goldstein *et al.* report both the destruction of ozone due to gas-phase chemistry and emissions of monoterpenes increased dramatically with the onset of thinning, and these phenomena continued in phase with each other thereafter. They “infer that the massive increase of O₃ flux during and following mastication is driven by loss of O₃ through chemical reactions with unmeasured terpenes or closely related BVOCs whose emissions were enhanced due to wounding [by the masticator].” They write, “considered together, these observations provide a conclusive picture that the chemical loss of O₃ is due to reactions with BVOCs emitted in a similar manner as terpenes” and “we can conceive no other possible explanation for this behavior other than chemical O₃ destruction in and above the forest canopy by reactions with BVOCs.”

Goldstein *et al.* conclude their results “suggest that total reactive terpene emissions might be roughly a factor of 10 higher than the typically measured and modeled monoterpene emissions, making them larger than isoprene emissions on a global scale.” This would mean vegetative emissions of terpenes, which lead to the destruction of ozone, are significantly greater than vegetative emissions of isoprene, which lead to the creation of ozone (Poisson *et al.*, 2000). In addition, there is substantial evidence to suggest the ongoing rise in the air's CO₂ content may lead to an overall reduction in vegetative isoprene emissions while enhancing vegetative productivity, which may lead to an overall increase in vegetative terpene emissions. There is thus reason to believe the ongoing rise in the air's CO₂ content will help reduce the ongoing rise in the air's O₃ concentration.

There is growing evidence that rising air

temperatures and atmospheric CO₂ concentrations significantly increase desirable vegetative BVOC emissions, particularly from trees—the most prominent photosynthetic force on the planet—and that this phenomenon has important and highly beneficial biospheric consequences. These findings further demonstrate that the biology of Earth influences the climate of Earth. They reveal a direct connection between the metabolic activity of trees and the propensity for the atmosphere to produce clouds; the metabolic activity of lichens and the presence of sulfate aerosol particles in the atmosphere that reflect incoming solar radiation; and the increased presence of BVOCs caused by rising CO₂ and an increase in diffuse solar radiation, which leads to increased photosynthetic extraction of CO₂ from the air. In each case, the relationship is self-protecting of the biosphere, and in each case the feedbacks are either ignored or downplayed by the IPCC.

References

- Abakumova, G.M., Feigelson, E.M., Russak, V., and Stadnik, V.V. 1996. Evaluation of long-term changes in radiation, cloudiness, and surface temperature on the territory of the former Soviet Union. *Journal of Climatology* **9**: 1319–1327.
- Baldocchi, D., Falge, E., Gu, L.H., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., Evans, R., Fuentes, J., Goldstein, A., Katul, G., Law, B., Lee, X.H., Malhi, Y., Meyers, T., Munger, W., Oechel, W., Paw U, K.T., Pilegaard, K., Schmid, H.P., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. 2001. FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities. *Bulletin of the American Meteorological Society* **82**: 2415–2434.
- Baraldi, R., Rapparini, F., Oechel, W.C., Hastings, S.J., Bryant, P., Cheng, Y., and Miglietta, F. 2004. Monoterpene emission responses to elevated CO₂ in a Mediterranean-type ecosystem. *New Phytologist* **161**: 17–21.
- Chameides, W.L., Lindsay, R.W., Richardson, J., and Kiang, C.S. 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* **241**: 1473–1475.
- Constable, J.V.H., Litvak, M.E., Greenberg, J.P., and Monson, R.K. 1999. Monoterpene emission from coniferous trees in response to elevated CO₂ concentration and climate warming. *Global Change Biology* **5**: 255–267.
- Elbert, W., Taylor, P.E., Andreae, M.O., and Pöschl, U. 2007. Contribution of fungi to primary biogenic aerosols in the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions. *Atmospheric Chemistry and Physics* **7**: 4569–4588.
- Farquhar, G.D. and Roderick, M.L. 2003. Pinatubo, diffuse light, and the carbon cycle. *Science* **299**: 1997–1998.
- Goldstein, A.H., McKay, M., Kurpius, M.R., Schade, G.W., Lee, A., Holzinger, R., and Rasmussen, R.A. 2004. Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs. *Geophysical Research Letters* **31**: 10.1029/2004GL021259.
- Gu, L., Baldocchi, D.D., Wofsy, S.C., Munger, J.W., Michalsky, J.J., Urbanski, S.P., and Boden, T.A. 2003. Response of a deciduous forest to the Mount Pinatubo eruption: Enhanced photosynthesis. *Science* **299**: 2035–2038.
- Harley, P.C., Monson, R.K., and Lerdau, M.T. 1999. Ecological and evolutionary aspects of isoprene emission from plants. *Oecologia* **118**: 109–123.
- Healey, K.D., Rickert, K.G., Hammer, G.L., and Bange, M.P. 1998. Radiation use efficiency increases when the diffuse component of incident radiation is enhanced under shade. *Australian Journal of Agricultural Research* **49**: 665–672.
- Holben, B.N., Tanré, D., Smirnov, A., Eck, T.F., Slutsker, I., Abuhassan, N., Newcomb, W.W., Schafer, J.S., Chatenet, B., Lavenue, F., Kaufman, Y.J., Castle, J.V., Setzer, A., Markham, B., Clark, D., Frouin, R., Halthore, R., Karneli, A., O'Neill, N.T., Pietras, C., Pinker, R.T., Voss, K., and Zibordi, G. 2001. An emerging ground-based aerosol climatology: Aerosol Optical Depth from AERONET. *Journal of Geophysical Research* **106**: 12,067–12,097.
- Hoye, T.T., Post, E., Meltofte, H., Schmidt, N.M., and Forchhammer, M.C. 2007. Rapid advancement of spring in the High Arctic. *Current Biology* **17**: R449–R451.
- Idso, S.B. 1998. CO₂-induced global warming: a skeptic's view of potential climate change. *Climate Research* **10**: 69–82.
- Jasoni, R., Kane, C., Green, C., Peffley, E., Tissue, D., Thompson, L., Payton, P., and Pare, P.W. 2003. Altered leaf and root emissions from onion (*Allium cepa* L.) grown under elevated CO₂ conditions. *Environmental and Experimental Botany* **51**: 273–280.
- Kavouras, I.G., Mihalopoulos, N., and Stephanou, E.G. 1998. Formation of atmospheric particles from organic acids produced by forests. *Nature* **395**: 683–686.
- Klironomos, J.N., Rillig, M.C., Allen, M.F., Zak, D.R.,

- Pregitzer, K.S., and Kubiske, M.E. 1997. Increased levels of airborne fungal spores in response to *Populus tremuloides* grown under elevated atmospheric CO₂. *Canadian Journal of Botany* **75**: 1670–1673.
- Kuhn, U. and Kesselmeier, J. 2000. Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research* **105**: 26,783–26,792.
- Kurpius, M.R. and Goldstein, A.H. 2003. Gas-phase chemistry dominates O₃ loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere. *Geophysical Research Letters* **30**: 10.1029/2002GL016785.
- Law, B.E., Falge, E., Gu, L., Baldocchi, D.D., Bakwin, P., Berbigier, P., Davis, K., Dolman, A.J., Falk, M., Fuentes, J.D., Goldstein, A., Granier, A., Grelle, A., Hollinger, D., Janssens, I.A., Jarvis, P., Jensen, N.O., Katul, G., Mahli, Y., Matteucci, G., Meyers, T., Monson, R., Munger, W., Oechel, W., Olson, R., Pilegaard, K., Paw U, K.T., Thorgeirsson, H., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. 2002. Environmental controls over carbon dioxide and water vapor exchange of terrestrial vegetation. *Agricultural and Forest Meteorology* **113**: 97–120.
- Litvak, M.E., Loreto, F., Harley, P.C., Sharkey, T.D., and Monson, R.K. 1996. The response of isoprene emission rate and photosynthetic rate to photon flux and nitrogen supply in aspen and white oak trees. *Plant, Cell and Environment* **19**: 549–559.
- Loreto, F., Fischbach, R.J., Schnitzler, J.P., Ciccioli, P., Brancaleoni, E., Calfapietra, C., and Seufert, G. 2001. Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak *Quercus ilex* L. grown at elevated CO₂ concentrations. *Global Change Biology* **7**: 709–717.
- Niyogi, D., Chang, H.-I., Saxena, V.K., Holt, T., Alapaty, K., Booker, F., Chen, F., Davis, K.J., Holben, B., Matsui, T., Meyers, T., Oechel, W.C., Pielke Sr., R.A., Wells, R., Wilson, K., and Xue, Y. 2004. Direct observations of the effects of aerosol loading on net ecosystem CO₂ exchanges over different landscapes. *Geophysical Research Letters* **31**: 10.1029/2004GL020915.
- O'Dowd, C.D., Aalto, P., Hameri, K., Kulmala, M., and Hoffmann, T. 2002. Atmospheric particles from organic vapors. *Nature* **416**: 497–498.
- Peñuelas, J. and Llusia, J. 2003. BVOCs: plant defense against climate warming? *Trends in Plant Science* **8**: 105–109.
- Peñuelas, J., Llusia, J., and Estiarte, M. 1995. Terpenoids: a plant language. *Trends in Ecology and Evolution* **10**: 289.
- Pichersky, E. and Gershenzon, J. 2002. The formation and function of plant volatiles: perfumes for pollinator attraction and defense. *Current Opinion in Plant Biology* **5**: 237–243.
- Poisson, N., Kanakidou, M., and Crutzen, P.J. 2000. Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modeling results. *Journal of Atmospheric Chemistry* **36**: 157–230.
- Raisanen, T., Ryyppo, A., and Kellomaki, S. 2008. Effects of elevated CO₂ and temperature on monoterpene emission of Scots pine (*Pinus sylvestris* L.). *Atmospheric Environment* **42**: 4160–4171.
- Rapparini, F., Baraldi, R., Miglietta, F., and Loreto, F. 2004. Isoprenoid emission in trees of *Quercus pubescens* and *Quercus ilex* with lifetime exposure to naturally high CO₂ environment. *Plant, Cell and Environment* **27**: 381–391.
- Raupach, M.R., Marland, G., Ciais, P., Le Quere, C., Canadell, J.G., Klepper, G., and Field, C.B. 2007. Global and regional drivers of accelerating CO₂ emissions. *Proceedings of the National Academy of Sciences, USA* **104**: 10,288–10,293.
- Reichenau, T.G. and Esser, G. 2003. Is interannual fluctuation of atmospheric CO₂ dominated by combined effects of ENSO and volcanic aerosols? *Global Biogeochemical Cycles* **17**: 10.1029/2002GB002025.
- Roderick, M.L., Farquhar, G.D., Berry, S.L., and Noble, I.R. 2001. On the direct effect of clouds and atmospheric particles on the productivity and structure of vegetation. *Oecologia* **129**: 21–30.
- Sarmiento, J.L. 1993. Atmospheric CO₂ stalled. *Nature* **365**: 697–698.
- Schade, G.W. and Goldstein, A.H. 2003. Increase of monoterpene emissions from a pine plantation as a result of mechanical disturbances. *Geophysical Research Letters* **30**: 10.1029/2002GL016138.
- Shallcross, D.E. and Monks, P.S. 2000. A role for isoprene in biosphere-climate-chemistry feedbacks. *Atmospheric Environment* **34**: 1659–1660.
- Shulaev, V., Silverman, P., and Raskin, I. 1997. Airborne signaling by methyl salicylate in plant pathogen resistance. *Nature* **385**: 718–721.
- Stanhill, G. and Cohen, S. 2001. Global dimming: a review of the evidence for a widespread and significant reduction in global radiation with discussion of its probable causes and possible agricultural consequences. *Agricultural and Forest Meteorology* **107**: 255–278.
- Staudt, M., Joffre, R., Rambal, S., and Kesselmeier, J. 2001. Effect of elevated CO₂ on monoterpene emission of young *Quercus ilex* trees and its relation to structural and

ecophysiological parameters. *Tree Physiology* **21**: 437–445.

Suraqui, S., Tabor, H., Klein, W.H., and Goldberg, B. 1974. Solar radiation changes at Mt. St. Katherine after forty years. *Solar Energy* **16**: 155–158.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P.P., Komppula, M., and Kulmala, M. 2006. High natural aerosol loading over boreal forests. *Science* **312**: 261–263.

Vuorinen, T., Reddy, G.V.P., Nerg, A.-M., and Holopainen, J.K. 2004. Monoterpene and herbivore-induced emissions from cabbage plants grown at elevated atmospheric CO₂ concentration. *Atmospheric Environment* **38**: 675–682.

2.5.2.2.1 Isoprene

Isoprene (C₅H₈ or 2-methyl-1,3-butadiene) is a highly reactive non-methane hydrocarbon (NMHC) emitted by vegetation; it is responsible for the production of tropospheric ozone (Chameides *et al.*, 1988; Harley *et al.*, 1999), a debilitating scourge of plant and animal life alike. Poisson *et al.* (2000) calculated current levels of NMHC emissions—the vast majority of which are isoprene, accounting for more than twice as much as all other NMHCs combined—may increase surface ozone concentrations by up to 40 percent in the marine boundary-layer and 50 to 60 percent over land. They further estimated the current tropospheric ozone content extends the atmospheric lifetime of methane, one of the world’s most powerful greenhouse gases, by approximately 14 percent.

A few experiments have suggested elevated concentrations of atmospheric carbon dioxide have little or no effect on the emission of isoprene by certain plant species (Buckley, 2001; Baraldi *et al.*, 2004; Rapparini *et al.*, 2004). But a much larger number of experiments suggest substantial CO₂-induced reductions in isoprene emissions, as demonstrated by the work of Monson and Fall (1989), Loreto and Sharkey (1990), Sharkey *et al.* (1991), and Loreto *et al.* (2001). We here provide short synopses of several other such studies along with some of the implications of their more robust findings.

Rosentiel *et al.* (2003) studied three 50-tree cottonwood plantations growing in separate mesocosms within the forestry section of the Biosphere 2 facility near Oracle, Arizona, USA. One of these mesocosms was maintained at an

atmospheric CO₂ concentration of 430 ppm, while the other two were enriched to concentrations of 800 and 1,200 ppm for an entire growing season. Integrated over that period, the total above-ground biomass of the trees in the latter two mesocosms was increased by 60 percent and 82 percent, respectively, while their production of isoprene was decreased by 21 percent and 41 percent, respectively.

Scholefield *et al.* (2004) measured isoprene emissions from *Phragmites australis* (a grass) growing at different distances from a natural CO₂ spring in central Italy. Atmospheric CO₂ concentrations of approximately 350, 400, 550, and 800 ppm had likely prevailed at the locations they measured for the entire lifetimes of the plants. Across this CO₂ gradient, plant isoprene emissions fell as the air’s CO₂ concentration rose. Over the first 50 ppm CO₂ increase, isoprene emissions were reduced to approximately 65 percent of what they were at ambient CO₂; for CO₂ increases of 200 and 450 ppm, isoprene emissions were reduced to about 30 percent and 7 percent of what they were in the 350-ppm-CO₂ air. The researchers note these reductions were likely caused by reductions in leaf isoprene synthase, which was observed to be highly correlated with isoprene emissions. This led them to conclude, “elevated CO₂ generally inhibits the expression of isoprenoid synthesis genes and isoprene synthase activity which may, in turn, limit formation of every chloroplast-derived isoprenoid.” They thus state the “basal emission rate of isoprene is likely to be reduced under future elevated CO₂ levels.”

Centritto *et al.* (2004) grew hybrid poplar saplings for one full growing season in a forced-air CO₂ enrichment (FACE) facility located at Rapolano, Italy, where the air’s CO₂ concentration was increased by approximately 200 ppm. They found “isoprene emission is reduced in elevated CO₂, in terms of both maximum values of isoprene emission rate and isoprene emission per unit of leaf area averaged across the total number of leaves per plant,” a reduction of approximately 34 percent. When isoprene emission was summed over the entire plant profile, the reduction was not nearly so great (only 6 percent), because of the greater number of leaves on the CO₂-enriched saplings. “However,” they point out, “Centritto *et al.* (1999), in a study with potted cherry seedlings grown in open-top chambers, and Gielen *et al.* (2001), in a study with poplar saplings exposed to FACE, showed that the stimulation of total leaf area in response to elevated CO₂ was a transient

effect, because it occurred only during the first year of growth.” Thus, they conclude, “it may be expected that with similar levels of leaf area, the integrated emission of isoprene would have been much lower in elevated CO₂.” They say their work, “as well as that reported by Scholefield *et al.* (2004), in a companion experiment on *Phragmites* growing in a nearby CO₂ spring, mostly confirm that isoprene emission is inversely dependent on CO₂ [concentration] when this is above ambient, and suggests that a lower fraction of C will be re-emitted in the atmosphere as isoprene by single leaves in the future.”

Working at the Aspen FACE facility near Rhinelander, Wisconsin, USA, Calfapietra *et al.* (2008) measured emissions of isoprene from sun-exposed upper-canopy leaves of an O₃-tolerant clone and an O₃-sensitive clone of trembling aspen (*Populus tremuloides* Michx.) trees growing in either normal ambient air, air enriched with an extra 190–200 ppm CO₂, air with 1.5 times the normal ozone concentration, or air simultaneously enriched with the identical concentrations of both gases.

For trees growing in air of ambient ozone concentration, the extra 190 ppm of CO₂ decreased the mean isoprene emission rate by 11.7 percent in the O₃-tolerant aspen clone and by 22.7 percent in the O₃-sensitive clone. For trees growing in air with 1.5 times the ambient ozone concentration, the extra CO₂ decreased the mean isoprene emission rate by 10.4 percent in the O₃-tolerant clone and by 32.7 percent in the O₃-sensitive clone. At the same time, and in the same order, net photosynthesis rates were increased by 34.9 percent, 47.4 percent, 31.6 percent, and 18.9 percent.

Possell *et al.* (2004) grew seedlings of English oak (*Quercus robur*), one to a mesocosm (16 cm diameter, 60 cm deep), in either fertilized or unfertilized soil in solardomes maintained at atmospheric CO₂ concentrations of either ambient or ambient plus 300 ppm for one full year, at the conclusion of which period they measured rates of isoprene emissions from the trees’ foliage together with their rates of photosynthesis. In the unfertilized trees, the 300 ppm increase in the air’s CO₂ concentration reduced isoprene emissions by 63 percent on a leaf area basis and 64 percent on a biomass basis, while in the fertilized trees the extra CO₂ reduced isoprene emissions by 70 percent on a leaf area basis and 74 percent on a biomass basis. In addition, the extra CO₂ boosted leaf photosynthesis rates by 17 percent in the unfertilized trees and 13 percent in the fertilized trees.

Possell *et al.* (2005) performed multiple three-week-long experiments with two known isoprene-emitting herbaceous species (*Mucuna pruriens* and *Arundo donax*), which they grew in controlled environment chambers maintained at two different sets of day/night temperatures (29/24°C and 24/18°C) and atmospheric CO₂ concentrations characteristic of glacial (180 ppm), preindustrial (280 ppm), and current (366 ppm) conditions, where canopy isoprene emission rates were measured on the final day of each experiment. They obtained what they describe as “the first empirical evidence for the enhancement of isoprene production, on a unit leaf area basis, by plants that grew and developed in [a] CO₂-depleted atmosphere.” These results, in their words, “support earlier findings from short-term studies with woody species (Monson and Fall, 1989; Loreto and Sharkey, 1990).”

Then, combining their emission rate data with those of Rosenstiel *et al.* (2003) for *Populus deltoides*, Centritto *et al.* (2004) for *Populus x euroamericana*, and Scholefield *et al.* (2004) for *Phragmites australis*, Possell *et al.* developed a single downward-trending isoprene emissions curve that stretches from 180 to 1,200 ppm CO₂, where it asymptotically approaches a value that is an order of magnitude less than what it is at 180 ppm.

Working at the Biosphere 2 facility near Oracle, Arizona, USA in enclosed ultraviolet light-depleted mesocosms (to minimize isoprene depletion by atmospheric oxidative reactions such as those involving OH), Pegoraro *et al.* (2005) studied the effects of atmospheric CO₂ enrichment (1,200 ppm compared to an ambient concentration of 430 ppm) and drought on the emission of isoprene from cottonwood (*Populus deltoides* Bartr.) foliage and its absorption by the underlying soil for both well-watered and drought conditions. They found “under well-watered conditions in the agriforest stands, gross isoprene production (i.e., the total production flux minus the soil uptake) was inhibited by elevated CO₂ and the highest emission fluxes of isoprene were attained in the lowest CO₂ treatment.” The elevated CO₂ treatment resulted in a 46 percent reduction in gross isoprene production. In addition, the researchers found drought suppressed the isoprene sink capacity of the soil beneath the trees, but “the full sink capacity of dry soil was recovered within a few hours upon rewetting.”

Putting a slightly negative slant on their findings, Pegoraro *et al.* suggest “in future, potentially hotter, drier environments, higher CO₂ may not mitigate

isoprene emission as much as previously suggested.” But it should be noted that climate models generally predict an intensification of the hydrologic cycle in response to rising atmospheric CO₂ concentrations, and that the anti-transpirant effect of atmospheric CO₂ enrichment typically leads to increases in the moisture contents of soils beneath vegetation. Over the latter decades of the twentieth century, when the IPCC claims Earth warmed at a rate and to a level unprecedented over the past two millennia, soil moisture data from around the world tended to display upward trends. Robock *et al.* (2000), for example, collected soil moisture data from more than 600 stations across a variety of climatic regimes, determining, “In contrast to predictions of summer desiccation with increasing temperatures, for the stations with the longest records, summer soil moisture in the top 1 m has increased while temperatures have risen.” In a subsequent study of “45 years of gravimetrically observed plant available soil moisture for the top 1 m of soil, observed every 10 days for April–October for 141 stations from fields with either winter or spring cereals from the Ukraine for 1958–2002,” Robock *et al.* (2005) found “a positive soil moisture trend for the entire period of observation,” noting “even though for the entire period there is a small upward trend in temperature and a downward trend in summer precipitation, the soil moisture still has an upward trend for both winter and summer cereals.” A CO₂-enriched world of the future will likely present the best of both aspects of isoprene activity: less production by vegetation and more consumption by soils.

In addressing how well climate models predict the response of isoprene emission to future global change, Monson *et al.* (2007) note such predictions “probably contain large errors” because “the fundamental logic of such models is that changes in NPP [net primary production] will produce more or less biomass capable of emitting isoprene, and changes in climate will stimulate or inhibit emissions per unit of biomass.” The 12 researchers continue, “these models tend to ignore the discovery that there are direct effects of changes in the atmospheric CO₂ concentration on isoprene emission that tend to work in the opposite direction to that of stimulated NPP.” Their results show, in their words, “that growth in an atmosphere of elevated CO₂ inhibited the emission of isoprene at levels that completely compensate for possible increases in emission due to increases in aboveground NPP.” Monson *et al.* state, “to a large

extent, the modeling has ‘raced ahead’ of our mechanistic understanding of how isoprene emissions will respond to the fundamental drivers of global change.” They conclude, “without inclusion of these effects in the current array of models being used to predict changes in atmospheric chemistry due to global change, one has to question the relevance of the predictions.”

Arnth *et al.* (2008) used a mechanistic isoprene-dynamic vegetation model of European woody vegetation to “investigate the interactive effects of climate and CO₂ concentration on forest productivity, species composition, and isoprene emissions for the periods 1981–2000 and 2081–2100,” which included a parameterization of the now-well-established direct CO₂-isoprene inhibition phenomenon described in the studies discussed above. They found “across the model domain,” the CO₂-isoprene inhibition effect “has the potential to offset the stimulation of [isoprene] emissions that could be expected from warmer temperatures and from the increased productivity and leaf area of emitting vegetation.”

In something of a challenge to this thesis, Kiendler-Scharr *et al.* (2009) “present evidence from simulation experiments conducted in a plant chamber that isoprene can significantly inhibit new particle formation.” The significance of this finding, they write, derives from the fact that “the most abundant volatile organic compounds emitted by terrestrial vegetation are isoprene and its derivatives, such as monoterpenes and sesquiterpenes” and that (as described in the “This Issue” abstract section of *Nature* (p. 311)) “these compounds are involved in the formation of organic aerosols [the “new particles” mentioned by them], which act as ‘seeds’ for cloud formation and hence as cooling agents via an effect on radiative forcing.” Moreover, as Ziemann (2009) explained in a “News & Views” article that discusses the Kiendler-Scharr *et al.* paper, “clouds formed at higher CCN [cloud condensation nuclei] concentrations have more and smaller drops than those formed at lower concentrations, and so reflect more sunlight and are longer-lived—effects that, at the global scale, enhance the planetary cooling that counteracts some of the warming caused by greenhouse gases.” Thus, if vegetative isoprene emissions were to increase, driven directly by rising temperatures and/or indirectly by warming-induced changes in the species composition of boreal forests (as further suggested by Ziemann), the resulting decrease in CCN concentrations “could lead to

increased global-warming trends,” as suggested by Kiendler-Sharr in a “Making the Paper” article in the same issue of *Nature* (p. 313).

The story propounded by these facts may seem to deliver a devastating blow to the negative CO₂-induced isoprene feedback, yet, and almost as an afterthought, Ziemann writes consideration also should be given to what he calls “the potential suppression of terpene emissions by elevated carbon dioxide concentrations.” When this is done, as demonstrated by the multiple sets of observational data of Young *et al.* (2009) and plotted in Figure 2.5.2.2.1.1, it becomes clear that rising atmospheric CO₂ concentrations will significantly decrease isoprene emissions from plants and thereby increase cloud condensation nuclei concentrations and lead to a cooling of the planet.

Wilkinson *et al.* (2009) grew three-year-old cottonwood trees and two-year-old aspen trees in controlled-environment chambers maintained for several weeks at atmospheric CO₂ concentrations of 400 and 800 ppm, with the aspen trees also exposed to CO₂ concentrations of 600 and 1,200 ppm. In addition, they grew two-year-old sweetgum and eucalyptus trees in another controlled-environment facility maintained at CO₂ concentrations of 240 and 380 ppm. They measured the isoprene emission rate (IS) of the trees’ leaves, finding “IS was approximately 30% and 18% lower, respectively, for eucalyptus and sweetgum trees grown at 520 ppm CO₂, compared with trees grown at 240 ppm CO₂.” The nine researchers also found the cottonwood and aspen trees “exhibited a 30–40% reduction in isoprene emission rate when grown at 800 ppm CO₂, compared with 400 ppm CO₂,” and the aspen trees “exhibited a 33% reduction when grown at 1200 ppm CO₂, compared with 600 ppm CO₂.”

Wilkinson *et al.* then “used current models of leaf isoprene emission to demonstrate that significant errors occur if the CO₂ inhibition of isoprene is not taken into account,” developing in the process “a quantitative algorithm that can be used to scale IS at the leaf level to changes in atmospheric and intercellular CO₂” that can be “incorporated into larger-scale models that aim to predict regional or global patterns in IS,” which can further be used to address “important questions concerning atmospheric chemistry in the face of future global change projections.”

In a related paper published in the same issue of *Global Change Biology*, Heald *et al.* (2009) incorporated an empirical model of observed isoprene

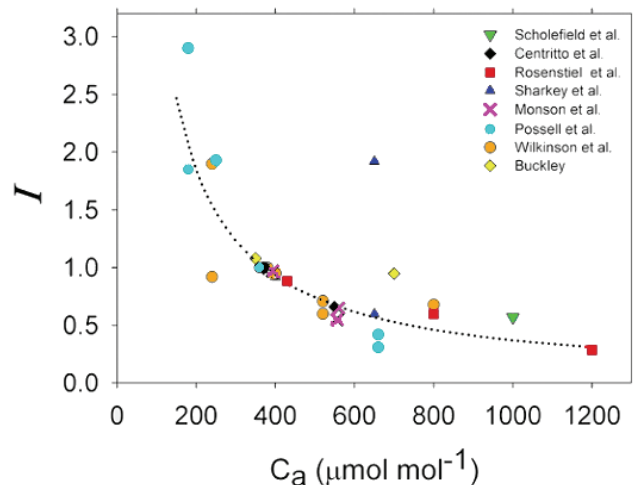


Figure 2.5.2.2.1.1. Field and laboratory observations of leaf isoprene emissions (I) from plants grown in a variety of atmospheric CO₂ concentrations (Ca), normalized to a value of unity at Ca = 370 μmol mol⁻¹ (= 370 ppm). Reprinted with permission from Young, P.J., Arneth, A., Schurgers, G., Zeng, G., and Pyle, J.A. 2009. The CO₂ inhibition of terrestrial isoprene emission significantly affects future ozone projections. *Atmospheric Chemistry and Physics* 9: 2793–2803.

emissions response to changes in atmospheric CO₂ concentration in the long-term growth environment and short-term changes in intercellular CO₂ concentrations into a biogenic emission model embedded within the Community Land Model of the global NCAR Community Climate System Model. They found “the large increases in future isoprene emissions typically predicted in models, which are due to a projected warmer climate, are entirely offset by including the CO₂ effects.”

Lathiere *et al.* (2010) utilized the Model of Emissions of Gases and Aerosols from Nature (MEGAN), developed by Guenther *et al.* (2006), to calculate changes in isoprene emissions from the terrestrial biosphere in response to climate change, atmospheric CO₂ increase, and land use change throughout the twentieth century. They found between 1901 and 2002, climate change at the global scale “was responsible for a 7% increase in isoprene emissions,” but “rising atmospheric CO₂ caused a 21% reduction,” and “by the end of the 20th century, anthropogenic cropland expansion had the largest impact, reducing isoprene emissions by 15%.” As a result, “overall, these factors combined to cause a 24% decrease in global isoprene emissions during the 20th century.” The three scientists also warned “the possible rapid expansion of biofuel production with

high isoprene-emitting plant species (e.g., oil palm, willow and poplar) may reverse the trend by which conversion of land to food crops leads to lower isoprene emissions.”

The research reviewed here strongly suggests the ongoing rise in atmospheric CO₂ concentrations will reduce atmospheric isoprene concentrations, which will lead to increases in cloud condensation nuclei concentrations, ultimately leading to a cooling of the planet—a negative feedback ignored by most proponents of the CO₂-induced global warming theory.

References

- Arnth, A., Schurgers, G., Hickler, T., and Miller, P.A. 2008. Effects of species composition, land surface cover, CO₂ concentration and climate on isoprene emissions from European forests. *Plant Biology* **10**: 150–162.
- Baraldi, R., Rapparini, F., Oechel, W.C., Hastings, S.J., Bryant, P., Cheng, Y., and Miglietta, F. 2004. Monoterpene emission responses to elevated CO₂ in a Mediterranean-type ecosystem. *New Phytologist* **161**: 17–21.
- Buckley, P.T. 2001. Isoprene emissions from a Florida scrub oak species grown in ambient and elevated carbon dioxide. *Atmospheric Environment* **35**: 631–634.
- Calfapietra, C., Scarascia-Mugnozza, G., Karnosky, D.F., Loreto, F., and Sharkey, T.D. 2008. Isoprene emission rates under elevated CO₂ and O₃ in two field-grown aspen clones differing in their sensitivity to O₃. *New Phytologist* **179**: 55–61.
- Centritto, M., Lee, H., and Jarvis, P. 1999. Interactive effects of elevated [CO₂] and water stress on cherry (*Prunus avium*) seedlings. I. Growth, total plant water use efficiency and uptake. *New Phytologist* **141**: 129–140.
- Centritto, M., Nascetti, P., Petrilli, L., Raschi, A., and Loreto, F. 2004. Profiles of isoprene emission and photosynthetic parameters in hybrid poplars exposed to free-air CO₂ enrichment. *Plant, Cell and Environment* **27**: 403–412.
- Chameides, W.L., Lindsay, R.W., Richardson, J., and Kiang, C.S. 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* **241**: 1473–1475.
- Gielen, B., Calfapietra, C., Sabatti, M., and Ceulemans, R. 2001. Leaf area dynamics in a poplar plantation under free-air carbon dioxide enrichment. *Tree Physiology* **21**: 1245–1255.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., and Geron, C. 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics* **6**: 3181–3210.
- Harley, P.C., Monson, R.K., and Lerdau, M.T. 1999. Ecological and evolutionary aspects of isoprene emission from plants. *Oecologia* **118**: 109–123.
- Heald, C.L., Wilkinson, M.J., Monson, R.K., Alo, C.A., Wang, G., and Guenther, A. 2009. Response of isoprene emission to ambient CO₂ changes and implications for global budgets. *Global Change Biology* **15**: 1127–1140.
- Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, T.F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A. 2009. New particle formation in forests inhibited by isoprene emissions. *Nature* **461**: 381–384.
- Lathiere, J., Hewitt, C.N., and Beerling, D.J. 2010. Sensitivity of isoprene emissions from the terrestrial biosphere to 20th century changes in atmospheric CO₂ concentration, climate, and land use. *Global Biogeochemical Cycles* **24**: 10.1029/2009GB003548.
- Loreto, F., Fischbach, R.J., Schnitzler, J.-P., Ciccioli, P., Brancaleoni, E., Calfapietra, C., and Seufert, G. 2001. Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak *Quercus ilex* L. grown at elevated CO₂ concentrations. *Global Change Biology* **7**: 709–717.
- Loreto F. and Sharkey, T.D. 1990. A gas exchange study of photosynthesis and isoprene emission in red oak (*Quercus rubra* L.). *Planta* **182**: 523–531.
- Monson, R.K. and Fall, R. 1989. Isoprene emission from aspen leaves. *Plant Physiology* **90**: 267–274.
- Monson, R.K., Trahan, N., Rosenstiel, T.N., Veres, P., Moore, D., Wilkinson, M., Norby, R.J., Volder, A., Tjoelker, M.G., Briske, D.D., Karnosky, D.F., and Fall, R. 2007. Isoprene emission from terrestrial ecosystems in response to global change: minding the gap between models and observations. *Philosophical Transactions of the Royal Society A* **365**: 1677–1695.
- Pegoraro, E., Abrell, L., van Haren, J., Barron-Gafford, G., Grieve, K.A., Malhi, Y., Murthy, R., and Lin, G. 2005. The effect of elevated atmospheric CO₂ and drought on sources and sinks of isoprene in a temperate and tropical rainforest mesocosm. *Global Change Biology* **11**: 1234–1246.
- Poisson, N., Kanakidou, M., and Crutzen, P.J. 2000. Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modeling results. *Journal of Atmospheric Chemistry* **36**: 157–230.
- Possell, M., Heath, J., Hewitt, C.N., Ayres, E., and

Kerstiens, G. 2004. Interactive effects of elevated CO₂ and soil fertility on isoprene emissions from *Quercus robur*. *Global Change Biology* **10**: 1835–1843.

Possell, M., Hewitt, C.N., and Beerling, D.J. 2005. The effects of glacial atmospheric CO₂ concentrations and climate on isoprene emissions by vascular plants. *Global Change Biology* **11**: 60–69.

Rapparini, F., Baraldi, R., Miglietta, F., and Loreto, F. 2004. Isoprenoid emission in trees of *Quercus pubescens* and *Quercus ilex* with lifetime exposure to naturally high CO₂ environment. *Plant, Cell and Environment* **27**: 381–391.

Robock, A., Mu, M., Vinnikov, K., Trofimova, I.V., and Adamenko, T.I. 2005. Forty-five years of observed soil moisture in the Ukraine: No summer desiccation (yet). *Geophysical Research Letters* **32**: 10.1029/2004GL021914.

Robock, A., Vinnikov, K.Y., Srinivasan, G., Entin, J.K., Hollinger, S.E., Speranskaya, N.A., Liu, S., and Namkhai, A. 2000. The global soil moisture data bank. *Bulletin of the American Meteorological Society* **81**: 1281–1299.

Rosentiel, T.N., Potosnak, M.J., Griffin, K.L., Fall, R., and Monson, R.K. 2003. Increased CO₂ uncouples growth from isoprene emission in an agriforest ecosystem. *Nature* advance online publication, 5 January 2003 (doi:10.1038/nature 01312).

Scholefield, P.A., Doick, K.J., Herbert, B.M.J., Hewitt, C.N.S., Schnitzler, J.-P., Pinelli, P., and Loreto, F. 2004. Impact of rising CO₂ on emissions of volatile organic compounds: isoprene emission from *Phragmites australis* growing at elevated CO₂ in a natural carbon dioxide spring. *Plant, Cell and Environment* **27**: 393–401.

Sharkey, T.D., Loreto, F., and Delwiche, C.F. 1991. High carbon dioxide and sun/shade effect on isoprene emissions from oak and aspen tree leaves. *Plant, Cell and Environment* **14**: 333–338.

Wilkinson, M.J., Monson, R.K., Trahan, N., Lee, S., Brown E., Jackson, R.B., Polley, H.W., Fay, P.A., and Fall, R. 2009. Leaf isoprene emission rate as a function of atmospheric CO₂ concentration. *Global Change Biology* **15**: 1189–1200.

Young, P.J., Arneth, A., Schurgers, G., Zeng, G., and Pyle, J.A. 2009. The CO₂ inhibition of terrestrial isoprene emission significantly affects future ozone projections. *Atmospheric Chemistry and Physics* **9**: 2793–2803.

Ziemann, P.J. 2009. Thwarting the seeds of clouds. *Nature* **461**: 353–354.

2.5.3 Non-Biological

2.5.3.1 Anthropogenic

There are several ways the activities of humanity lead to the creation of aerosols that have the potential to alter Earth's radiation balance and affect its climate. Contrails created in the wake of emissions from jet aircraft are one example. Minnis *et al.* (2004) have calculated nearly all of the surface warming observed over the United States between 1975 and 1994 (0.54°C) may be explained by aircraft-induced increases in cirrus cloud coverage over that period. If true, this would imply little or none of the observed U.S. warming during that period could be attributed to the increase in the air's CO₂ content.

Ship tracks—bright streaks that form in layers of marine stratus clouds—are another example. Created by emissions from ocean-going vessels, these persistent and highly reflective linear patches of low-level clouds tend to cool the planet (Ferek *et al.*, 1998; Schreier *et al.*, 2006).

Schreier *et al.* (2006) developed an algorithm “to determine ship tracks from satellite data in an automated way,” after which “a scene on 10 February 2003 was chosen to extract the optical and microphysical cloud modifications from ship emissions using Terra-MODIS satellite data,” in which “a combination of the semi-analytical approach SACURA [Kokhanovsky *et al.*, 2003] with a look-up-table for optically thin clouds [Mayer and Kylling, 2005] was used to calculate cloud properties.” The analysis revealed, on average, cloud “optical thickness was increased from 20.7 up to 34.6 and the effective [droplet] radius was decreased from 13.2 μm to 10.1 μm,” while “the calculated average droplet number concentration increased from 79 up to 210 cm⁻³.”

Using these numbers to calculate changes in the radiative energy budget above and below the marine stratus clouds influenced by the ship emissions, Schreier *et al.* (2006) reported “a decrease of 43.2 W m⁻² for the surface radiation below the ship tracks and an increase of 40.8 W m⁻² for the increased reflectivity at the top of the atmosphere.” They note, “if the whole low-cloud area with 6.7% ship-track-pixels is taken into account, a decrease in the radiation at the surface of 2.1 W m⁻² and an increase of 2.0 W m⁻² in backscattered solar radiation [is] found.” The eight German researchers thus conclude, “modifications of clouds by international shipping can be an important contributor to climate on a local scale.”

As for the global scale, averaged over the surface of Earth both day and night and over the year, Capaldo *et al.* (1999) calculated this phenomenon creates a mean negative radiative forcing of -0.16 W m^{-2} in the Northern Hemisphere and -0.06 W m^{-2} in the Southern Hemisphere. Compare these values to a much smaller estimate from the IPCC (compare the W m^{-2} with the mW m^{-2} unit), which concluded in its most recent assessment, “the global radiative forcing of visible ship tracks has been estimated from satellite and found to be insignificant at about -0.5 mW m^{-2} ” (p. 7-39 of Chapter 7, Second Order Draft of AR5, dated October 5, 2012). For additional context, the IPCC calculates a positive radiative forcing of approximately 4 W m^{-2} due to a 300 ppm increase in the atmosphere’s CO_2 concentration.

In some cases, the atmosphere over the sea also carries a considerable burden of anthropogenically produced aerosols from terrestrial sites. In recent years, attention to this topic has centered on highly polluted air from south and southeast Asia that makes its way over the northern Indian Ocean during the dry monsoon season. There has been much discussion about the impact of this phenomenon on regional climates. Norris (2001) looked at cloud cover as the ultimate arbiter of the competing hypotheses, finding daytime low-level oceanic cloud cover increased substantially over the last half of the past century in both the Northern and Southern Hemispheres at essentially all hours of the day. This finding is indicative of a pervasive net cooling effect.

Aerosol-generating human activities also have a significant impact on local, as well as more wide-ranging, climatic phenomena over land. Sahai (1998) pointed out although suburban areas of Nagpur, India had warmed over recent decades, the central part of the city had cooled, especially during the day, because of “increasing concentrations of suspended particulate matter.” Similarly, outside but adjacent to industrial complexes in the Po Valley of Italy, Facchini *et al.* (1999) found water vapor was more likely to form on aerosols altered by human-produced organic solutes, and this phenomenon led to the creation of more numerous and more highly reflective cloud droplets that had a tendency to cool the surface below them.

Rosenfeld (2000) studied pollution tracks downwind of urban/industrial complexes in Turkey, Canada, and Australia. His findings indicate the clouds comprising these pollution tracks were composed of small droplets that suppressed

precipitation by inhibiting further coalescence and ice precipitation formation. In commenting on this research, Toon (2000) notes when clouds are composed of smaller droplets, they will not “rain out” as quickly and therefore will last longer and cover more of Earth, both of which effects tend to cool the globe.

In reviewing these and other advances in the field of anthropogenic aerosol impacts on clouds, Charlson *et al.* (2001) note droplet clouds “are the most important factor controlling the albedo (reflectivity) and hence the temperature of our planet.” They also note manmade aerosols “have a strong influence on cloud albedo, with a global mean forcing estimated to be of the same order (but opposite in sign) as that of greenhouse gases” and “both the forcing [of this impetus for cooling] and its magnitude may be even larger than anticipated.” Failure to include these important phenomena in climate change deliberations “poses additional uncertainty beyond that already recognized by the Intergovernmental Panel on Climate Change, making the largest uncertainty in estimating climate forcing even larger.”

Devasthale *et al.* (2005) examine the possible influence of aerosols on cloud-top temperature (CTT) using long-term satellite brightness temperatures from the Advanced Very High Resolution Radiometer onboard the NOAA satellite series over eastern and central Europe. In order to identify and quantify possible aerosol-induced changes, CTTs were compared for two four-year periods of distinctively higher (1985–1998) and lower (1997–2000) anthropogenic pollution loads.

Devasthale *et al.* report the results of the analysis were “astonishing.” For all types and levels of clouds analyzed, over both land and sea, lower CTTs were observed during the higher pollution levels of the late 1980s, such that the tops of low- and medium-level clouds were more than 2°C colder during that period, and about 4°C colder if convective clouds were included. Regions of greater CTT variability coincided with metropolitan areas and industrial centers that contained higher concentrations of particulate matter and black carbon inventories.

One implication of these findings, the researchers noted, is the “observed indirect aerosol effect in the thermal infrared on regional scale could be equally important if not dominant over the solar radiation changes and thus needs to be further investigated for other regions.” This effect may be large enough to have had a significant influence on the near-surface

and tropospheric temperature histories of the past few decades.

Another pertinent observation comes from Stanhill and Cohen (2001), who reviewed numerous solar radiation measurement programs around the world to see if there had been any trend in the mean amount of solar radiation falling on the surface of Earth over the past half-century. They determined there was a significant 50-year downward trend in this parameter that “has globally averaged $0.51 \pm 0.05 \text{ W m}^{-2}$ per year, equivalent to a reduction of 2.7 percent per decade, [which] now totals 20 W m^{-2} .” They conclude the most probable explanation for this observation “is that increases in man-made aerosols and other air pollutants have changed the optical properties of the atmosphere, in particular those of clouds.”

This surface-cooling influence falls in the mid-range of a similar solar radiative perturbation documented by Satheesh and Ramanathan (2000) in their study of the effects of human-induced pollution over the tropical northern Indian Ocean, where they determined “mean clear-sky solar radiative heating for the winters of 1998 and 1999 decreased at the ocean surface by 12 to 30 W m^{-2} .” Hence, the decline in solar radiation reception discovered by Stanhill and Cohen could well be real, representing a strong counter-influence to the enhanced greenhouse effect produced by the increase in atmospheric CO_2 concentration.

Alpert *et al.* (2005) hypothesized the dimming of the 1950s through 1980s could be explained by the anthropogenic release of pollutants, such as sulfates, nitrates, and black carbon, which acted to reduce the amount of solar radiation received at Earth’s surface. To test this theory, for the 25-year period 1964–1989 the authors examined trends in the surface receipt of solar radiation at 144 urban sites (population greater than 100,000 persons) and 174 rural sites (population less than 100,000 persons) for various latitudinal bands as well as for the entire globe. For the globe as a whole, they found both urban and rural locations showed a decline in surface solar radiation over the period of study. The rate of decline at the urban locations was approximately 2.6 times larger than that observed at the rural locations ($-0.41 \text{ W m}^{-2}\text{yr}^{-1}$ vs. $-0.16 \text{ W m}^{-2}\text{yr}^{-1}$). In addition, a sharper decline in surface solar radiation receipt was found between 10°N and 40°N , the latitudinal zone nearly coincident with the zone of maximum fossil fuel emissions in the Northern Hemisphere reported by Stanhill and Cohen (2001) for the period 1960–1990. The latitude band

from 15°S to 15°N displayed the opposite trend: Instead of dimming, this region experienced a brightening of $0.58 \text{ W m}^{-2}\text{yr}^{-1}$, a finding consistent with those of Pinker *et al.* (2005), who reported a persistent increase in surface solar radiation over the latitudes 20°S to 20°N based on satellite data.

According to Alpert *et al.*, their findings suggest solar dimming is “significantly dominated by large cities’ contributions to the atmospheric pollution” and it is “essentially a local phenomenon, observed only in a limited part of the total land area.” The magnitudes of the original dimming and the more recent brightening are much greater than the magnitude of the increase in total greenhouse-gas-induced radiative forcing over this period, yet another good reason to suggest the global instrumental temperature record may be significantly “polluted” in a way that has heretofore not been adequately appreciated.

In a more recent study, Ruckstuhl *et al.* (2008) presented “observational evidence of a strong decline in aerosol optical depth over mainland Europe during the last two decades of rapid warming”—when air temperatures rose by about 1°C after 1980—via analyses of “aerosol optical depth measurements from six specific locations and surface irradiance measurements from a large number of radiation sites in Northern Germany and Switzerland.” They observed a decline in aerosol concentration of up to 60 percent and found “a statistically significant increase of solar irradiance under cloud-free skies since the 1980s.” The value of the direct aerosol effect of this radiative forcing was approximately 0.84 W m^{-2} ; when combined with the concomitant cloud-induced radiative forcing of about 0.16 W m^{-2} , it led to a total radiative surface climate forcing over mainland Europe of about 1 W m^{-2} that “most probably strongly contributed to the recent rapid warming in Europe.” Cleaning up significantly polluted skies, it seems, can provide an even greater impetus for climate warming than does the carbon dioxide concurrently emitted to them.

Mission *et al.* (2005) note “anthropogenic aerosols have more efficient optical extinction for light than natural aerosols (Carrico *et al.*, 2003; Seinfeld and Pandis, 1998) and are responsible for about half of the extinction and scattering of light by particles globally (Houghton *et al.*, 2001).” Increases in atmospheric aerosols, while reducing the total flux of solar radiation received at Earth’s surface, increase the flux of *diffuse* light received there, such that the volume of shade within forest canopies is so greatly

decreased it enhances whole-canopy photosynthesis to the point that more CO₂ is extracted from the atmosphere under high-aerosol-content conditions than under more pristine conditions (see, for example, the work of Roderick *et al.* (2001), Law *et al.* (2002), and Gu *et al.* (2003)).

Mission *et al.* determined the recurrent influx of air pollution from California's Central Valley to the Blodgett Forest site during summer afternoons decreased total irradiance there by 11 percent from what it was at comparable times relative to solar noon in the mornings. Diffuse radiation, on the other hand, was 24 percent higher in the afternoons; this effect predominated to the extent that "aerosol loading caused net uptake of CO₂ by the forest to increase by 8% in the afternoon." The presence of atmospheric aerosols not only reduces the receipt of solar radiation at Earth's surface, providing an impetus for cooling, it also enhances forest rates-of-removal of CO₂ from the atmosphere, which over the long term provides yet another cooling effect.

Su *et al.* (2011) describe and demonstrated how reactive nitrogen compounds, such as those found in synthetic fertilizers, may be acted upon by soil microbes to produce nitrites in both agricultural soils and the soils of forests and boreal regions; and they show how the photolysis of the nitrous acid (HONO) consequently found in these soils can produce up to ~30 percent of the atmosphere's total OH concentration. Their findings explain the origin, size, and diurnal variation of field observations that had previously suggested there was a large unknown source of HONO having the characteristics they identified.

The phenomenon described by the ten scientists plays an important role in the atmosphere's photochemistry, which in turn plays a key role in the planet's energy balance, because OH radicals act as precursors of aerosols that can contribute to climate change by reflecting a portion of the incoming solar radiation from the Sun back to space, thereby exerting a cooling influence on the planet. To quote the international team of researchers, "because of enhanced fertilizer use and soil acidification in developing countries (Guo *et al.*, 2010), the release of HONO from soil nitrite might strongly increase in the course of global change, resulting in elevated OH concentrations and amplified oxidizing capacity of the lower troposphere," which would tend to impede the warming that helped to initiate the phenomenon, illustrating yet another of the "checks and balances"

built into Earth's highly complex climatic system.

In further commentary on Su *et al.*'s findings, Kulmala and Petaja (2011) rhetorically asked: "What would happen if global HONO emissions from soil doubled within the next 25 years?" In answer, they said it "could increase the atmosphere's ability to cleanse itself of volatile compounds such as methane," a powerful greenhouse gas. Perhaps that is why atmospheric methane concentrations have risen at a much slower rate over the prior two decades than they had previously risen, as has been reported by Simpson *et al.* (2002), Dlugokencky *et al.* (2003), Khalil *et al.* (2007), Schnell and Dlugokencky (2008), and other researchers.

Anthropogenic aerosols clearly affect climate in ways that rival or even exceed the likely effect of rising atmospheric CO₂ levels. As great progress has been made in recent decades to reduce air pollution in developed countries, it is entirely possible the lion's share of warming has been produced by the removal from the atmosphere of true air pollutants.

References

- Alpert, P., Kishcha, P., Kaufman, Y.J., and Schwarzbard, R. 2005. Global dimming or local dimming?: Effect of urbanization on sunlight availability. *Geophysical Research Letters* **32**: L17802, doi:10.1029/2005GL023320.
- Capaldo, K., Corbett, J.J., Kasibhatla, P., Fischbeck, P., and Pandis, S.N. 1999. Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean. *Nature* **400**: 743–746.
- Carrico, C.M., Bergin, M.H., Xu, J., Baumann, K., and Maring, H. 2003. Urban aerosol radiative properties: measurements during the 1999 Atlanta supersite experiment. *Journal of Geophysical Research* **108**: 10.1029/2001JD001222.
- Charlson, R.J., Seinfeld, J.H., Nenes, A., Kulmala, M., Laaksonen, A., and Facchini, M.C. 2001. Reshaping the theory of cloud formation. *Science* **292**: 2025–2026.
- Devasthale, A., Krüger, O., and Grassl, H. 2005. Change in cloud-top temperatures over Europe. *IEEE Geoscience and Remote Sensing Letters* **2**: 333–336.
- Dlugokencky, E.J., Houweling, S., Bruhwiler, L., Masarie, K.A., Lang, P.M., Miller, J.B., and Tans, P.P. 2003. Atmospheric methane levels off: Temporary pause or a new steady-state? *Geophysical Research Letters* **30**: 10.1029/2003GL018126.
- Facchini, M.C., Mircea, M., Fuzzi, S., and Charlson, R.J.

1999. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **401**: 257–259.
- Ferek, R.J., Hegg, D.A., Hobbs, P.V., Durkee, P., and Nielsen, K. 1998. Measurements of ship-induced tracks in clouds off the Washington coast. *Journal of Geophysical Research* **103**: 23,199–23,206.
- Ghan, S.J., Easter, R.C., Chapman, E.G., Abdul-Razzak, H., Zhang, Y., Leung, L.R., Laulainen, N.S., Saylor, R.D., and Zaveri, R.A. 2001. A physically based estimate of radiative forcing by anthropogenic sulfate aerosol. *Journal of Geophysical Research* **106**: 5279–5293.
- Gu, L., Baldocchi, D.D., Wofsy, S.C., Munger, J.W., Michalsky, J.J., Urbanski, S.P., and Boden, T.A. 2003. Response of a deciduous forest to the Mount Pinatubo eruption: Enhanced photosynthesis. *Science* **299**: 2035–2038.
- Guo, J.H., Liu, X.J., Zhang, Y., Shen, J.L., Han, W.X., Zhang, W.F., Christie, P., Goulding, K.W.T., Vitousek, P.M., and Zhang, F.S. 2010. Significant acidification in Chinese croplands. *Science* **327**: 1008–1010.
- Houghton, J.T., Ding, Y., Griggs, D.J., Nogue, M., van der Linden, P.J., Dai, X., Maskell, K., and Johnson, C.A. (Eds.). *Climate Change 2001. Contribution of Working Group I to the Third Assessment Report of the IPCC*. Cambridge University Press, Cambridge, UK/New York, NY, USA, p. 881.
- Khalil, M.A.K., Butenhoff, C.L., and Rasmussen, R.A. 2007. Atmospheric methane: Trends and cycles of sources and sinks. *Environmental Science & Technology* 10.1021/es061791t.
- Kokhanovsky, A.A., Rozanov, V.V., Zege, E.P., Bovensmann, H., and Burrows, J.P. 2003. A semi-analytical cloud retrieval algorithm using backscattered radiation in 0.4–2.4 micrometers spectral range. *Journal of Geophysical Research* **108**: 10.1029/2001JD001543.
- Kulmala, M. and Petaja, T. 2011. Soil nitrites influence atmospheric chemistry. *Science* **333**: 1586–1587.
- Law, B.E., Falge, E., Gu, L., Baldocchi, D.D., Bakwin, P., Berbigier, P., Davis, K., Dolman, A.J., Falk, M., Fuentes, J.D., Goldstein, A., Granier, A., Grelle, A., Hollinger, D., Janssens, I.A., Jarvis, P., Jensen, N.O., Katul, G., Mahli, Y., Matteucci, G., Meyers, T., Monson, R., Munger, W., Oechel, W., Olson, R., Pilegaard, K., Paw U, K.T., Thorgeirsson, H., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. 2002. Environmental controls over carbon dioxide and water vapor exchange of terrestrial vegetation. *Agricultural and Forest Meteorology* **113**: 97–120.
- Mayer, B. and Kylling, A. 2005. The libRadtran software package for radiative transfer calculations, description and examples of use. *Atmospheric Chemistry and Physics* **5**: 1855–1877.
- Minnis, P., Ayers, J.K., Palikonda, R., and Phan, D. 2004. Contrails, cirrus trends, and climate. *Journal of Climate* **17**: 1671–1685.
- Misson, L., Lunden, M., McKay, M., and Goldstein, A.H. 2005. Atmospheric aerosol light scattering and surface wetness influence the diurnal pattern of net ecosystem exchange in a semi-arid ponderosa pine plantation. *Agricultural and Forest Meteorology* **129**: 69–83.
- Norris, J.R. 2001. Has northern Indian Ocean cloud cover changed due to increasing anthropogenic aerosol? *Geophysical Research Letters* **28**: 3271–3274.
- Pinker, R.T., Zhang, B., and Dutton, E.G. 2005. Do satellites detect trends in surface solar radiation? *Science* **308**: 850–854.
- Roderick, M.L., Farquhar, G.D., Berry, S.L., and Noble, I.R. 2001. On the direct effect of clouds and atmospheric particles on the productivity and structure of vegetation. *Oecologia* **129**: 21–30.
- Rosenfeld, D. 2000. Suppression of rain and snow by urban and industrial air pollution. *Science* **287**: 1793–1796.
- Ruckstuhl, C., Philipona, R., Behrens, K., Coen, M.C., Durr, B., Heimo, A., Matzler, C., Nyeki, S., Ohmura, A., Vuilleumier, L., Weller, M., Wehrl, C., and Zelenka, A. 2008. Aerosol and cloud effects on solar brightening and the recent rapid warming. *Geophysical Research Letters* **35**: 10.1029/2008GL034228.
- Sahai, A.K. 1998. Climate change: a case study over India. *Theoretical and Applied Climatology* **61**: 9–18.
- Satheesh, S.K. and Ramanathan, V. 2000. Large differences in tropical aerosol forcing at the top of the atmosphere and Earth's surface. *Nature* **405**: 60–63.
- Schnell, R.C. and Dlugokencky, E. 2008. Methane. In: Levinson, D.H. and Lawrimore, J.H. (Eds.) *State of the Climate in 2007*. Special Supplement to the *Bulletin of the American Meteorological Society* **89**: S27.
- Schreier, M., Kokhanovsky, A.A., Eyring, V., Bugliaro, L., Mannstein, H., Mayer, B., Bovensmann, H., and Burrows, J.P. 2006. Impact of ship emissions on the microphysical, optical and radiative properties of marine stratus: a case study. *Atmospheric Chemistry and Physics* **6**: 4925–4942.
- Seinfeld, J. and Pandis, S. 1998. *Atmospheric Chemistry and Physics*. John Wiley, New York, NY, USA, p. 1326.
- Simpson, I.J., Blake, D.R., and Rowland, F.S. 2002. Implications of the recent fluctuations in the growth rate of tropospheric methane. *Geophysical Research Letters* **29**: 10.1029/2001GL014521.

Stanhill, G. and Cohen, S. 2001. Global dimming: a review of the evidence for a widespread and significant reduction in global radiation with discussion of its probable causes and possible agricultural consequences. *Agricultural and Forest Meteorology* **107**: 255–278.

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F.X., Andreae, M.O., Cheng, P., Zhang, Y., and Poschl, U. 2011. Soil nitrite as a source of atmospheric HONO and OH radicals. *Science* **333**: 1616–1618.

Toon, O.W. 2000. How pollution suppresses rain. *Science* **287**: 1763–1765.

2.5.3.1.1 Black Carbon

Kaspari *et al.* (2011) point out “black carbon (BC, the absorbing component of soot) produced by the incomplete combustion of biomass, coal and diesel fuels can significantly contribute to climate change by altering the Earth’s radiative balance,” noting “BC is estimated to have 55% of the radiative forcing effect of CO₂ (Ramanathan and Carmichael, 2008),” in line with the approximately 1 W m⁻² radiative forcing of black carbon reported by Hansen (2002).

Kaspari *et al.* further note BC remains “one of the largest sources of uncertainty in analyses of climate change.” They developed a high-resolution BC record spanning the period AD 1860–2000 from a Mt. Everest ice core extracted from the East Rongbuk glacier located on the mountain’s northeast ridge on the north slope of the Himalaya, which record, in their words, “provides the first pre-industrial-to-present record of BC concentrations from the Himalayas.” The seven scientists determined “BC concentrations from 1975–2000 relative to 1860–1975 have increased approximately threefold, indicating that BC from anthropogenic sources is being transported to high elevation regions of the Himalaya.” In addition, “the increase in Everest BC during the 1970s is simultaneous with a rise in BC emissions as estimated from historical records of energy-related combustion in South Asia and the Middle East (Bond *et al.*, 2007).”

Kaspari *et al.* said their findings suggest “a reduction in BC emissions may be an effective means to reduce the effect of absorbing impurities on snow albedo and melt, which affects Himalayan glaciers and the availability of water resources in major Asian rivers.” Ramanathan and Carmichael (2008) note the majority of BC emissions (60 percent) arise from “cooking with biofuels such as wood, dung and crop

residue” and from “open biomass burning (associated with deforestation and crop residue burning),” while Venkataraman *et al.* (2005) note control of BC emissions through cleaner cooking technologies alone could help in “reducing health risks to several hundred million users.” It would seem reducing biofuel sources of BC emissions would be a prudent goal.

Also working in Asia, Kopacz *et al.* (2011) point out “the Himalayas and the Tibetan Plateau, also collectively known as the Third Pole, represent a large area of seasonal and permanent snow cover,” which is “surrounded by growing emissions of Asian air pollutants.” They note observations of black carbon (BC) content in snow “show a rapidly increasing trend,” citing the work of Xu *et al.* (2009). For their own study of the subject, Kopacz *et al.* used a global chemical transport model to identify the location from which the BC arriving at a variety of locations in the Himalayas and the Tibetan Plateau originates, after which they calculated its direct and snow-albedo radiative forcings.

According to the six U.S. scientists, the results indicated “emissions from northern India and central China contribute the majority of BC to the Himalayas,” and “the Tibetan Plateau receives most BC from western and central China, as well as from India, Nepal, the Middle East, Pakistan and other countries.” In addition, they report the radiative forcing due to the direct effect of BC at five glacier sites has “a global annual mean of +0.32 W/m², while “the local monthly mean radiative forcing due to changes in snow-albedo ranges from +3.78 to +15.6 W/m².”

Researching a much larger region of the globe, for the period 1875–2000, Novakov *et al.* (2003) presented “estimates of past fossil-fuel BC emissions from the United States, United Kingdom, Germany, Soviet Union, India and China,” which nations in 1990 accounted for “about 70% and 60%, respectively, of the world consumption of coal and diesel fuel, which are the principal BC-producing fossil-fuels.” The authors report a “rapid increase [in BC] in the latter part of the 1800s, ... leveling off in the first half of the 1900s, and ... re-acceleration in the past 50 years as China and India developed.” They estimate the climate forcing by BC aerosols to be “of the order of +0.5 W m⁻²,” two-thirds greater than the +0.3 W m⁻² forcing estimate of the IPCC (p. 18 of the Technical Summary, Second Order Draft of AR5, dated October 5, 2012). They also note

“estimates of the current anthropogenic BC climate forcing are of the order of 1/3 to 1/2 of the current CO₂ forcing.”

It is apparent that modern trends in BC have presented a significant radiative forcing across many parts of the globe meriting serious examination and future study, especially by the IPCC, in order to correctly interpret past, present, and future climate trends.

References

- Bond, T., Bhardwaj, E., Dong, R., Jogani, S., Jung, C., Roden, D., Streets, G., and Trautmann, N. 2007. Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850-2000. *Global Biogeochemical Cycles* **21**: 10.1029/2006GB002840.
- Hansen, J.E. 2002. A brighter future. *Climatic Change* **52**: 435–440.
- Kaspari, S.D., Schwikowski, M., Gysel, M., Flanner, M.G., Kang, S., Hou, S., and Mayewski, P.A. 2011. Recent increase in black carbon concentrations from a Mt. Everest ice core spanning 1860-2000 AD. *Geophysical Research Letters* **38**: 10.1029/2010GL046096.
- Kopacz, M., Mauzerall, D.L., Wang, J., Leibensperger, E.M., Henze, D.K., and Singh, K. 2011. Origin and radiative forcing of black carbon transported to the Himalayas and Tibetan Plateau. *Atmospheric Chemistry and Physics* **11**: 2837–2852.
- Novakov, T., Ramanathan, V., Hansen, J.E., Kirchstetter, T.W., Sato, M., Sinton, J.E., and Sathaye, J.A. 2003. Large historical changes of fossil-fuel black carbon aerosols. *Geophysical Research Letters* **30**: 10.1029/2002GL016345.
- Ramanathan, V. and Carmichael, G. 2008. Global and regional climate changes due to black carbon. *Nature Geoscience* **1**: 221–227.
- Venkataraman, C., Habib, G., Eiguren-Fernandez, A., Miguel, A.H., and Friedlander, S.K. 2005. Residential biofuels in South Asia: Carbonaceous aerosol emissions and climate impacts. *Science* **307**: 1454–1456.
- Xu, B.-Q., Wang, M., Joswiak, D.R., Cao, J.-J., Yao, T.-D., Wu, G.-J., Yang, W., and Zhao, H.-B. 2009. Deposition of anthropogenic aerosols in a southeastern Tibetan glacier. *Journal of Geophysical Research* **114**: 10.1029/2008JD011510.

2.5.3.2 Natural

We conclude this section with a brief discussion of a non-biological, naturally produced aerosol: dust.

Dust is about as natural and ubiquitous a substance as there is. One might expect scientists to have a pretty good handle on what it does to Earth’s climate, but that is not the case.

Sokolik (1999), with the help of nine colleagues, summarized the sentiments of a number of scientists who had devoted their lives to studying the subject. According to Sokolik, state-of-the-art climate models “rely heavily on oversimplified parameterizations” of many important dust-related phenomena, “while ignoring others.” As a result, Sokolik concludes “the magnitude and even the sign of dust net direct radiative forcing of climate remains unclear.”

Sokolik says there are a number of unanswered questions about airborne dust: How does one quantify dust emission rates from natural and anthropogenic sources with required levels of temporal and spatial resolution? How does one accurately determine the composition, size, and shape of dust particles from ground-based and aircraft measurements? How does one adequately measure and model light absorption by mineral particles? How does one link the ever-evolving optical, chemical, and physical properties of dust to its life cycle in the air? How does one model complex multi-layered aerosol stratification in the dust-laden atmosphere? And how does one quantify airborne dust properties from satellite observations?

In discussing these questions, Sokolik observed what is currently known, or believed to be known, about dust emissions “is largely from micro-scale experiments and theoretical studies.” He suggests new global data sets are needed to provide “missing information” on input parameters (such as soil type, surface roughness, and soil moisture) required to model dust emission rates, and improvements in methods used to determine some of these parameters are also “sorely needed.” How to adequately measure light absorption by mineral particles is an “outstanding problem,” he notes, and it “remains unknown how well these measurements represent the light absorption by aerosol particles suspended in the atmosphere.” It is easy to understand why Sokolik concludes “a challenge remains in relating dust climatology and the processes controlling the evolution of dust at all relevant spatial/temporal scales needed for chemistry and climate models.”

Vogelmann *et al.* (2003) reiterated that “mineral aerosols have complex, highly varied optical properties that, for equal loadings, can cause differences in the surface IR flux [of] between 7 and 25 W m⁻² (Sokolik *et al.*, 1998),” while at the same time acknowledging “only a few large-scale climate

models currently consider aerosol IR effects (e.g., Tegen *et al.*, 1996; Jacobson, 2001) despite their potentially large forcing.” Vogelmann *et al.* “use[d] high-resolution spectra to obtain the IR radiative forcing at the surface for aerosols encountered in the outflow from northeastern Asia,” based on measurements made by the Marine-Atmospheric Emitted Radiance Interferometer aboard the NOAA Ship *Ronald H. Brown* during the Aerosol Characterization Experiment-Asia. This work led them to conclude, “daytime surface IR forcings are often a few W m^{-2} and can reach almost 10 W m^{-2} for large aerosol loadings,” which values, in their words, “are comparable to or larger than the 1 to 2 W m^{-2} change in the globally averaged surface IR forcing caused by greenhouse gas increases since pre-industrial times.” Vogelmann *et al.* conclude their results “highlight the importance of aerosol IR forcing which should be included in climate model simulations.”

Another aspect of the dust-climate connection centers on the African Sahel, which has figured prominently in discussions of climate change since it began to experience extended drought conditions in the late 1960s and early ‘70s. Initial studies of the drought attributed it to anthropogenic factors such as overgrazing of the region’s fragile grasses, which tends to increase surface albedo, which was envisioned to reduce precipitation, resulting in a further reduction in the region’s vegetative cover (Otterman, 1974; Charney, 1975). That scenario was challenged by Jackson and Idso (1975) and Idso (1977) on the basis of empirical observations, while Lamb (1978) and Folland *et al.* (1986) attributed the drought to large-scale atmospheric circulation changes triggered by multidecadal variations in sea surface temperature.

Building on the insights provided by these latter investigations, Giannini *et al.* (2003) presented evidence based on an ensemble of integrations with a general circulation model of the atmosphere—forced only by the observed record of sea surface temperature—which suggests the “variability of rainfall in the Sahel results from the response of the African summer monsoon to oceanic forcing amplified by land-atmosphere interaction.” The success of this analysis led them to attribute “the recent drying trend in the semi-arid Sahel ... to warmer-than-average low-latitude waters around Africa, which, by favoring the establishment of deep convection over the ocean, weaken the continental

convergence associated with the monsoon and engender widespread drought from Senegal to Ethiopia.” They further conclude “the secular change in Sahel rainfall during the past century was not a direct consequence of regional environmental change, anthropogenic in nature or otherwise.”

In a companion article, Prospero and Lamb (2003) report measurements made from 1965 to 1998 in the Barbados trade winds show large interannual changes in the concentration of dust of African origin that are highly anticorrelated with the prior year’s rainfall in the Soudano-Sahel. They noted the 2001 IPCC report “assumes that natural dust sources have been effectively constant over the past several hundred years and that all variability is attributable to human land-use impacts.” But “there is little firm evidence to support either of these assumptions,” they write.

Huang *et al.* (2011) calculated bulk sediment fluxes and analyzed grain-size distributions of detrital sediments over the past two millennia from an 11.12 meter sediment core obtained from Asia’s Aral Sea, after which they compared their results with the temperature history of the Northern Hemisphere produced by Mann and Jones (2003), with an emphasis “placed on the variations at the transition from the Medieval Warm Period (MWP) to Little Ice Age (LIA) since this period is the most pronounced climatic transformation during the last millennium,” citing in this regard the studies of Yang *et al.* (2002), Trouet *et al.* (2009), and Chen *et al.* (2010).

The comparison revealed “a remarkably low deposition [of dust] during AD 1–350,” which would have been part of the Roman Warm Period; “a moderately high value from AD 350–720,” which corresponds to the Dark Ages Cold Period; “a return to a relatively low level between AD 720 and AD 1400,” which includes the Medieval Warm Period; “an exceptionally high deposition from AD 1400 to the 1940s,” which includes the Little Ice Age; and what they refer to as “an abnormally low value since the 1940s,” when the Current Warm Period may be considered to have begun.

The four researchers state the temporal variations in the dust deposition are consistent with changes in the “mean atmospheric temperature of the northern hemisphere during the past 2000 years, with low/high annual temperature anomalies corresponding to high/low dust supplies in the Aral Sea sediments, respectively,” reinforcing the reality of a non-CO₂-induced forcing of Earth’s surface air temperature.

Clearly, much remains to be learned about the climatic impacts of dust, whose radiative impacts, the IPCC has concluded, “are too uncertain” to include in their estimates of radiative forcing (p. 18 of the Technical Summary, Second Order Draft of AR5, dated October 5, 2012).

References

- Charney, J.G. 1975. Dynamics of desert and drought in the Sahel. *Quarterly Journal of the Royal Meteorological Society* **101**: 193–202.
- Chen, F.H., Chen, J.H., Holmes, J., Boomer, I., Austin, P., Gates, J.B., Wang, N.L., Brooks, S.J., and Zhang, J.W. 2010. Moisture changes over the last millennium in arid central Asia: a review, synthesis and comparison with monsoon region. *Quaternary Science Reviews* **29**: 1055–1068.
- Folland, C.K., Palmer, T.N., and Parker, D.E. 1986. Sahel rainfall and worldwide sea temperatures, 1901–85. *Nature* **320**: 602–607.
- Giannini, A., Saravanan, R., and Chang, P. 2003. Oceanic forcing of Sahel rainfall on interannual to interdecadal time scales. *Science* **302**: 1027–1030.
- Houghton, J.T., Ding, Y., Griggs, D.J., Noguera, M., van der Linden, P.J., Xiaosu, D., Maskell, K., and Johnson, C.A. (Eds.). 2001. *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK.
- Huang, X., Oberhansli, H., von Suchodoletz, H., and Sorrel, P. 2011. Dust deposition in the Aral Sea: implications for changes in atmospheric circulation in central Asia during the past 2000 years. *Quaternary Science Reviews* **30**: 3661–3674.
- Idso, S.B. 1977. A note on some recently proposed mechanisms of genesis of deserts. *Quarterly Journal of the Royal Meteorological Society* **103**: 369–370.
- Jackson, R.D. and Idso, S.B. 1975. Surface albedo and desertification. *Science* **189**: 1012–1013.
- Jacobson, M.Z. 2001. Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols. *Journal of Geophysical Research* **106**: 1551–1568.
- Lamb, P.J. 1978. Large-scale tropical Atlantic surface circulation patterns associated with sub-Saharan weather anomalies. *Tellus* **30**: 240–251.
- Mann, M.E. and Jones, P.D. 2003. Global surface temperatures over the past two millennia. *Geophysical Research Letters* **30**: 10.1029/2003GL017814.
- Otterman, J. 1974. Baring high-albedo soils by overgrazing: a hypothesized desertification mechanism. *Science* **186**: 531–533.
- Prospero, J.M. and Lamb, P.J. 2003. African droughts and dust transport to the Caribbean: climate change implications. *Science* **302**: 1024–1027.
- Sokolik, I.N. 1999. Challenges add up in quantifying radiative impact of mineral dust. *EOS: Transactions, American Geophysical Union* **80**: 578.
- Sokolik, I.N., Toon, O.B., and Bergstrom, R.W. 1998. Modeling the radiative characteristics of airborne mineral aerosols at infrared wavelengths. *Journal of Geophysical Research* **103**: 8813–8826.
- Tegen, I., Lacis, A.A., and Fung, I. 1996. The influence on climate forcing of mineral aerosols from disturbed soils. *Nature* **380**: 419–422.
- Trouet, V., Esper, J., Graham, N.E., Baker, A., Scourse, J.D., and Frank, D.C. 2009. Persistent positive north Atlantic oscillation mode dominated the medieval climate anomaly. *Science* **324**: 78–80.
- Vogelmann, A.M., Flatau, P.J., Szczodrak, M., Markowicz, K.M., and Minnett, P.J. 2003. Observations of large aerosol infrared forcing at the surface. *Geophysical Research Letters* **30**: 10.1029/2002GL016829.
- Yang, B., Brauning, A., Johnson, K.R., and Shi, Y.F. 2002. General characteristics of temperature variation in China during the last two millennia. *Geophysical Research Letters* **29**: 10.1029/2001GL014485.

2.6 Other Forcings and Feedbacks

Researchers have identified other forcings and feedbacks about which little is currently known, or acknowledged by the IPCC, but which may ultimately prove to be important drivers of climate change. Other variables, currently considered insignificant, may with changing conditions become important as thresholds change. This section explores some of those phenomena described in the peer-reviewed scientific literature.

2.6.1 Carbon Sequestration

As the carbon dioxide content of the air continues to rise, nearly all of Earth’s plants will respond by increasing their photosynthetic rates and producing more biomass. These increases in productivity will likely lead to greater amounts of carbon sequestration in both above- and below-ground plant parts as well as in soils. But how powerful is the carbon sequestering ability of Earth’s vegetation? Is it

powerful enough to slow the rise of atmospheric CO₂ to provide a natural brake on CO₂-induced global warming? How is it affected by an increase in air temperature? This section reviews the results of studies that have addressed these and other important questions pertaining to biospheric carbon sequestration.

Early investigation into this topic occurred more than two decades ago when many people were concerned the air's CO₂ content would rise in direct proportion to the magnitude of humanity's increasing emissions of carbon dioxide. Idso (1991a,b) felt otherwise and predicted the air's CO₂ content would rise at a rate that would be a declining percentage of anthropogenic CO₂ emissions, hypothesizing the productivity of Earth's plant life would rise in response to the ongoing increase in the air's CO₂ content—due to the well-known aerial fertilization effect of carbon dioxide—thereby resulting in ever more CO₂ being removed from the atmosphere each year. Vindication of Idso's thesis came via real-world data a decade later, with Wofsy (2001) reporting in a "Climate Change" article in *Science* that "emission rates of CO₂ from combustion of fossil fuel have increased almost 40 percent in the past 20 years, but the amount of CO₂ accumulating in the atmosphere has stayed the same or even declined slightly."

Other studies also have demonstrated this increased ability of the biosphere to sequester carbon from the atmosphere as the air's CO₂ concentration has gradually risen over the past few decades and throughout the Industrial Revolution. Working in the coterminous United States, for example, Pacala *et al.* (2001) found estimates of the country's 48-state carbon sequestering power have grown significantly over the past several years, from a range of 0.08–0.35 x 10¹⁵ grams of carbon per year (Pg C yr⁻¹) in the 1980s to a range of 0.37–0.71 Pg C yr⁻¹ by the turn of the century, with some evidence suggesting values as high as 0.81–0.84 Pg C yr⁻¹ (Fan *et al.*, 1998).

Similarly, Fang *et al.* (2001) reported increases in carbon sequestration in China. With a little help from the Chinese government via several "ecological restoration projects" aimed primarily at afforestation and reforestation, the world's most populous country has turned around what had been a losing proposition with respect to carbon capture by forests, where an average of 0.021 Pg C yr⁻¹ had been sequestered there for about the last two decades of their study.

Harrison *et al.* (2008) used the Joint UK Land Environment Simulator (JULES), a land surface and

carbon cycle model, to simulate the biospheric carbon balance of Europe and its sensitivity to rising CO₂ and changes in climate experienced over the period 1948–2005. Over the 57-year period of their study, Harrison *et al.* report "the impact of climate changes since 1948 has been to decrease the ability of Europe to store carbon by 97 TgC year⁻¹," but "the effect of rising atmospheric CO₂ has been to stimulate increased uptake and storage." This latter phenomenon apparently was so strong it led, in their words, to "a net increase in stored carbon of 114 TgC year⁻¹."

In addition to stimulating *terrestrial* carbon storage, the rising atmospheric CO₂ concentration also should enhance *oceanic* carbon sequestration. Wolf-Gladrow *et al.* (1999) reviewed the direct effects of atmospheric CO₂ enrichment on marine biota and oceanic "carbon pumps," concluding an increase in the air's CO₂ content should increase the capacity of Earth's oceans to take up and store more atmospheric CO₂.

Working on both fronts (land and ocean), Joos and Bruno (1998) utilized ice cores and direct observations of atmospheric CO₂ and ¹³C to reconstruct the histories of terrestrial and oceanic uptake of anthropogenic carbon over the past two centuries. During the initial portion of this period and persisting into the first decades of the past century, they determined the biosphere as a whole supplied carbon to the atmosphere. Thereafter, however, the biosphere became a carbon sink. In further scrutinizing their data, they note the current global carbon sink has been growing in magnitude for at least the past hundred years.

In reviewing the progress of research dealing with the global carbon cycle, Tans and White (1998) conclude "early estimates of huge losses of carbon from plants and soils due to biomass burning and deforestation have recently given way to the idea of a terrestrial biosphere nearly balanced (globally) with respect to carbon." After analyzing O₂/N₂ measurements of background air collected at Cape Grim, Tasmania from 1978 to 1997, Langenfelds *et al.* (1999) determined the surface fluxes of carbon over this 19-year period were "essentially in balance." In other words, essentially all of the carbon released to the air as a consequence of the activities of man was removed from the atmosphere by the biological activities of predominantly terrestrial vegetation.

Khatiwala *et al.* (2009) note the world's oceans play "a crucial role in mitigating the effects of [rising

Climate Change Reconsidered II

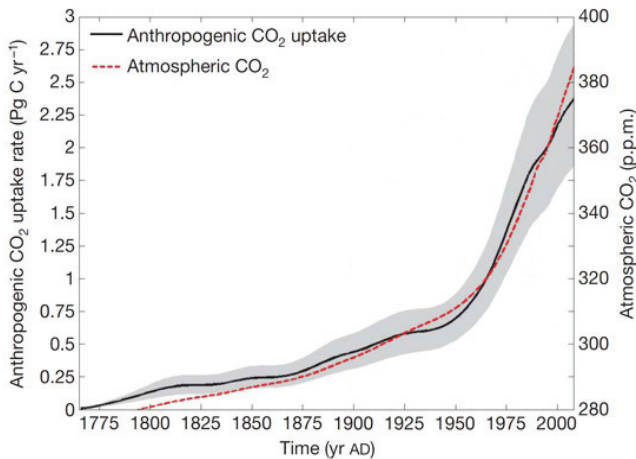


Figure 2.6.1.1. Atmospheric CO₂ concentration and oceanic uptake rate of anthropogenic carbon (with shaded error envelope) plotted against time. Adapted from Khatiwala, S. Primeau, F., and Hall, T. 2009. Reconstruction of the history of anthropogenic CO₂ concentrations in the ocean. *Nature* **462**: 346–349.

atmospheric CO₂] to the climate system.” They derived “an observationally based reconstruction of the spatially-resolved, time-dependent history of anthropogenic carbon in the ocean over the industrial era [AD 1765 to AD 2008],” based on the known history of the air’s CO₂ concentration and analyses of the oceanic transport of “a suite of well sampled oceanic tracers such as chlorofluorocarbons, natural ¹⁴C, temperature, and salinity from the GLODAP and World Ocean Atlas databases.” The three U.S. researchers determined the amount of anthropogenic CO₂ taken up by the world’s oceans has been increasing with the passage of time, pretty much in phase with the atmosphere’s ever-increasing CO₂ concentration, as shown in Figure 2.6.1.1.

In addition, Khatiwala *et al.* note after the sharp increase in the anthropogenic CO₂ uptake rate after the 1950s there has been “a small decline in the rate of increase in the last few decades.” This latest deviation of the oceanic CO₂ uptake rate (from its correlation with the atmosphere’s CO₂ concentration) is similar to those of prior such deviations, which have been of both a positive and negative nature. The size of the error envelope (the shaded area in Figure 2.6.1.1) associated with the anthropogenic CO₂ uptake rate allows for the possibility that its correlation with the atmosphere’s CO₂ concentration

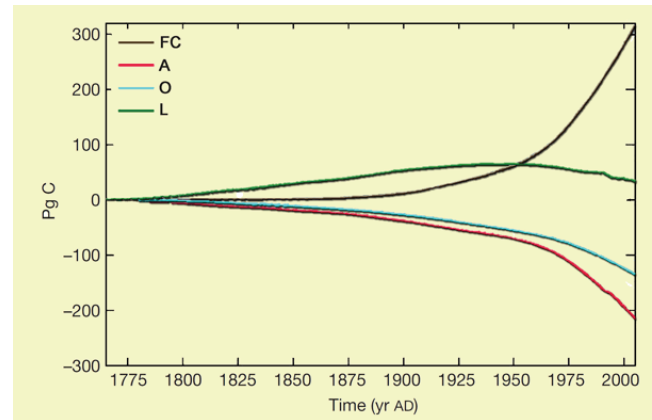


Figure 2.6.1.2. The evolution of anthropogenic-produced carbon originating from fossil fuel use and cement production (FC), together with the similar evolution of the three anthropogenic carbon sinks—atmosphere (A), ocean (O), and land (L)—between AD 1765 and 2005. Adapted from Khatiwala, S. Primeau, F., and Hall, T. 2009. Reconstruction of the history of anthropogenic CO₂ concentrations in the ocean. *Nature* **462**: 346–349.

could have been essentially perfect from about the 1860s through and including the present time.

Writing about Khatiwala *et al.*’s work in the November 19, 2009 issue of *The New York Times*, Sindya Bhanoo presented a distinctly pessimistic slant to the scientists’ findings, stating the growth in the ocean’s uptake rate of anthropogenic carbon “has slowed since the 1980s, and markedly so since 2000,” implying “the research suggests that the seas cannot indefinitely be considered a reliable ‘carbon sink’ as humans generate heat-trapping gases.” Bhanoo quotes Khatiwala himself as saying the recent trend to lower values of the ocean’s uptake rate of anthropogenic carbon “implies that more of the emissions will remain in the atmosphere.”

Quite to the contrary, however, the finely intertwined relationship of the two parameters of Figure 2.6.1.1 clearly demonstrates, well within the accuracy of the various measurements involved, that the global ocean is constantly adjusting its uptake rate of anthropogenic carbon on multi-decadal time scales to “keep up” with the rate at which the air’s CO₂ content rises in response to anthropogenic carbon inputs.

In light of their independent assessment of the absorption of anthropogenic CO₂ by the global ocean, and knowing the historical record of fossil fuel use

and cement production as well as the concomitant change in the atmosphere's CO₂ content, Khatiwala *et al.* also calculated, as a residual, the net absorption of anthropogenic CO₂ by Earth's land surface since the inception of the Industrial Revolution; this latter calculation is presented in Figure 2.6.1.2.

The authors' results indicate "the terrestrial biosphere was a source of anthropogenic carbon until the 1940s, roughly in line with previous model-based estimates, after which it turned into a sink of anthropogenic CO₂." Between the 1980s and 2000s, the strength of the global land sink grew from a value of 0.3 Pg C per year to 1.1 Pg C per year, suggesting the terrestrial biosphere has begun to "flex its muscles," likely in response to the aerial fertilization and transpiration-reducing effects of the ongoing rise in the air's CO₂ content. Others have challenged these findings, suggesting the world's oceans and terrestrial ecosystems may be gradually losing their ability to sequester CO₂ emissions (Canadell *et al.*, 2007; Le Quere *et al.*, 2007; Schuster and Watson, 2007).

Le Quere *et al.* (2009), for example, developed "a global CO₂ budget for each year during 1959–2008 and analyzed the underlying drivers of each component." In this undertaking, they say "the global increase in atmospheric CO₂ was determined directly from measurements, CO₂ emissions from fossil fuel combustion were estimated on the basis of countries' energy statistics, [while] CO₂ emissions from land-use change were estimated using deforestation and other land-use data, fire observations from space, and assumptions on the carbon density of vegetation and soils and the fate of carbon." For the time evolution of the land and ocean CO₂ sinks, they used "state-of-the-art models on which [they] imposed the observed meteorological conditions of the past few decades."

Le Quere *et al.* reported, "between 1959 and 2008, 43% of each year's CO₂ emissions remained in the atmosphere on average" and "the rest was absorbed by carbon sinks on land and in the oceans." They write, "in the past 50 years, the fraction of CO₂ emissions that remains in the atmosphere each year has likely increased, from about 40% to 45%," stating "models suggest that this trend was caused by a decrease in the uptake of CO₂ by the carbon sinks in response to climate change and variability."

Although their findings can be interpreted as indicating the uptake rate of anthropogenic CO₂ by the oceans, land, or both may have decreased with time—as they and others have suggested—they temper this conclusion with the caveat that "changes

in the CO₂ sinks are highly uncertain." It should be noted that the time evolution or temporal histories of the anthropogenic CO₂ sinks in Le Quere *et al.*'s analysis were obtained from models; they themselves admit "sink processes not considered in current models may be contributing to the observed changes" and these "sink processes" would be doing so in unknown ways not included in their calculations. In addition, the work of Khatiwala *et al.* (2009), which covers a longer span of time, reveals the existence of multidecadal variability that in a short half-century context could be interpreted as a trend, but in a much longer two-and-a-half century timeframe is readily recognized as an oscillatory variation about an essentially constant mean.

Knorr (2009) also covered a much longer time-span than Le Quere *et al.*, utilizing data on CO₂ emissions arising from fossil-fuel use, cement production, and changes in land use, as well as atmospheric CO₂ concentrations measured at Mauna Loa and the South Pole and those derived from Law Dome and Siple ice-core data, together with their associated uncertainties, to construct a history since 1850 of the airborne fraction of anthropogenic CO₂. The U.K. researcher reports, "despite the predictions of coupled climate-carbon cycle models, no trend in the airborne fraction can be found." He writes in the concluding section of his study, "the hypothesis of a recent or secular trend in the AF cannot be supported on the basis of the available data and its accuracy," indicating not only has the global ocean been increasing its uptake of anthropogenic carbon in such a way as to "keep up" with the rate at which the air's CO₂ content has risen—as has been demonstrated by Khatiwala *et al.* (2009)—so also have Earth's terrestrial ecosystems been "keeping up" in this regard.

Gloor *et al.* (2010) note Canadell *et al.* (2007) and Raupach *et al.* (2008) claimed to have detected a long-term increasing trend in the airborne fraction that they interpret as being indicative of "a decreasing trend in the efficiency of the ocean and land carbon sinks." Noting Knorr (2009) had already challenged Canadell *et al.* and Raupach *et al.* with respect to their detection of a positive AF trend, "arguing that given the noise in the data, the trend is not detectable," Gloor *et al.* (2010) proceeded to challenge the second claim of Canadell *et al.* and Raupach *et al.*; i.e., their contention that a positive AF trend is indicative of decreasing planetary carbon sink efficiency, by investigating "the question of what controls trends

and decadal scale variations in CO₂ airborne fraction using simple linear models describing the evolution of an atmospheric perturbation in CO₂.”

The three researchers first determined there is no one-to-one association between positive trends in CO₂ flux to the atmosphere due to fossil fuel emissions and changes in land use and negative trends in Earth’s carbon sink efficiency. Secondly, they found that in order to detect trends in sink efficiencies from the time course of fossil fuel-derived CO₂ emissions and temporal changes in land use, “it is necessary to disentangle the spin-up time and fossil fuel growth rate variation signatures in the airborne fraction from signatures due to other causes.” When they make the pertinent calculations for fossil-fuel and land-use changes, they say they “do indeed find a positive trend in the residuals,” but they argue this trend “is not statistically significant after correcting for known events such as the temporal distribution of the extrinsic forcings and likely omissions in the emissions (particularly from land-use change),” further noting their analysis suggests “trends in airborne fraction are not a very good diagnostic to detect changes in carbon sink efficiency because variations in the signal are complex and the signal-to-noise ratio is small.”

Thus, Gloor *et al.* conclude “atmospheric data, if analyzed adequately, do not yet reveal a statistically significant signal.” They further note, “although approximately one-half of total CO₂ emissions is at present taken up by combined land and ocean carbon reservoirs (Schimel *et al.*, 2001),” coupled climate/carbon-cycle models “predict a decline in future carbon uptake by these reservoirs, resulting in a positive carbon-climate feedback.”

In an effort to shed more light on the subject, Ballantyne *et al.* (2012) used “global-scale atmospheric CO₂ measurements, CO₂ emission inventories and their full range of uncertainties to calculate changes in global CO₂ sources and sinks during the past fifty years.” The five U.S. scientists say their mass balance analysis shows “net global carbon uptake has increased significantly by about 0.05 billion tonnes of carbon per year and that global carbon uptake doubled, from 2.4 ± 0.8 to 5.0 ± 0.9 billion tonnes per year, between 1960 and 2010.” Ballantyne *et al.* conclude, “although present predictions indicate diminished C uptake by the land and oceans in the coming century, with potentially serious consequences for the global climate, as of 2010 there is no empirical evidence that C uptake has started to diminish on the global scale.”

Other research lends confidence to the idea that the carbon-sequestering strength of the land and ocean will continue in the future, even in the face of rising temperatures. Allen *et al.* (1999) analyzed sediment cores from a lake in Italy and the Mediterranean Sea, determining that over the past 102,000 years, the warm period of the Holocene produced organic carbon content in vegetation more than double that observed for any other period in this historic record. Similarly, Velichko *et al.* (1999) reconstructed carbon storage in vegetation in Northern Eurasia, determining plant life there was more productive and efficient in sequestering carbon at higher, as opposed to lower, air temperatures. Vegetative carbon storage during the Holocene Optimum, which occurred about 6,000 years ago, was calculated to be 120 percent greater than present-day carbon sequestration in this region.

In assessing the ability of Earth’s vegetation to sequester carbon in the future, it is also important to consider the findings of Luz *et al.* (1999), who estimated the biospheric productivity of the planet as a whole is currently at its highest point in the past 82,000 years, as is the atmospheric CO₂ concentration. Xiao *et al.* (1998) used a process-based ecosystem model to compute global net ecosystem production from 1990 to 2100 based on three scenarios of atmospheric CO₂ and temperature change. In all cases where these parameters increased together, they reported positive increases in global net ecosystem productivity.

It should be clear from the observational data that Earth’s biosphere is exerting a powerful brake on the rate of rise of the air’s CO₂ content, such that the large increases in anthropogenic CO₂ emissions of the past two decades have not resulted in any increase in the rate of CO₂ accumulation in the atmosphere. The IPCC has yet to acknowledge the existence and sign of this negative feedback, choosing to rely on projections from the Coupled Model Intercomparison Project Phase 5 (CMIP5) models. Those models “consistently estimate a positive carbon cycle feedback, i.e. reduced natural sinks or increased natural CO₂ sources in response to future climate change.” The models further find “in particular, carbon sinks in tropical land ecosystems are vulnerable to climate change” (p. 21 of the Technical Summary, Second Order Draft of AR5, dated October 5, 2012).

References

- Allen, J.R.M., Brandt, U., Brauer, A., Hubberten, H.-W., Huntley, B., Keller, J., Kraml, M., Mackensen, A., Mingram, J., Negendank, J.F.W., Nowaczyk, N.R., Oberhansli, H., Watts, W.A., Wulf, S., and Zolitschka, B. 1999. Rapid environmental changes in southern Europe during the last glacial period. *Nature* **400**: 740–743.
- Ballantyne, A.P., Alden, C.B., Miller, J.B., Tans, P.P., and White, J.W. 2012. Increase in observed net carbon dioxide uptake by land and oceans during the past 50 years. *Nature* **488**: 70–72.
- Bhanoo, S. N. 2009. Seas grow less effective at absorbing emissions. *The New York Times* (19 November).
- Canadell, J.G., Le Quere, C., Raupach, M.R., Field, C.B., Buitenhuis, E., Ciais, P., Conway, T.J., Gillett, N.P., Houghton, J.T., and Marland, G. 2007. Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proceedings of the National Academy of Sciences, USA* **104**: 18,866–18,870.
- Fan, S., Gloor, M., Mahlman, J., Pacala, S., Sarmiento, J., Takahashi, T., and Tans, P. 1998. A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science* **282**: 442–446.
- Fang, J., Chen, A., Peng, C., Zhao, S., and Ci, L. 2001. Changes in forest biomass carbon storage in China between 1949 and 1998. *Science* **292**: 2320–2322.
- Gloor, M., Sarmiento, J.L., and Gruber, N. 2010. What can be learned about carbon cycle climate feedbacks from the CO₂ airborne fraction? *Atmospheric Chemistry and Physics* **10**: 7739–7751.
- Harrison, R.G., Jones, C.D., and Hughes, J.K. 2008. Competing roles of rising CO₂ and climate change in the contemporary European carbon balance. *Biogeosciences* **5**: 1–10.
- Idso, S.B. 1991a. The aerial fertilization effect of CO₂ and its implications for global carbon cycling and maximum greenhouse warming. *Bulletin of the American Meteorological Society* **72**: 962–965.
- Idso, S.B. 1991b. Reply to comments of L.D. Danny Harvey, Bert Bolin, and P. Lehmann. *Bulletin of the American Meteorological Society* **72**: 1910–1914.
- Joos, F. and Bruno, M. 1998. Long-term variability of the terrestrial and oceanic carbon sinks and the budgets of the carbon isotopes ¹³C and ¹⁴C. *Global Biogeochemical Cycles* **12**: 277–295.
- Khaliwala, S., Primeau, F., and Hall, T. 2009. Reconstruction of the history of anthropogenic CO₂ concentrations in the ocean. *Nature* **462**: 346–349.
- Knorr, W. 2009. Is the airborne fraction of anthropogenic CO₂ emissions increasing? *Geophysical Research Letters* **36**: 10.1029/2009GL040613.
- Langenfelds, R.L., Francey, R.J., and Steele, L.P. 1999. Partitioning of the global fossil CO₂ sink using a 19-year trend in atmospheric O₂. *Geophysical Research Letters* **26**: 1897–1900.
- Le Quere, C., Raupach, M.R., Canadell, J.G., Marland, G., Bopp, L., Ciais, P., Conway, T.J., Doney, S.C., Feely, R.A., Foster, P., Friedlingstein, P., Gurney, K., Houghton, R.A., House, J.I., Huntingford, C., Levy, P.E., Lomas, M.R., Majkut, J., Metzl, N., Ometto, J.P., Peters, G.P., Prentice, I.C., Randerson, J.T., Running, S.W., Sarmiento, J.L., Schuster, U., Sitch, S., Takahashi, T., Viovy, N., van der Werf, G.R., and Woodward, F.I. 2009. Trends in the sources and sinks of carbon dioxide. *Nature Geoscience* 10.1038/ngeo689.
- Le Quere, C., Roedenbeck, C., Buitenhuis, E.T., Conway, T.J., Langenfelds, R., Gomez, A., Labuschagne, C., Ramonet, M., Nakazawa, T., Metzl, N., Gillett, N., and Heimann, M. 2007. Saturation of the Southern Ocean CO₂ sink due to recent climate change. *Science* **316**: 1735–1738.
- Luz, B., Barkan, E., Bender, M.L., Thieme, M.H., and Boering, K.A. 1999. Triple-isotope composition of atmospheric oxygen as a tracer of biospheric productivity. *Nature* **400**: 547–550.
- Pacala, S.W., Hurtt, G.C., Baker, D., Peylin, P., Houghton, R.A., Birdsey, R.A., Heath, L., Sundquist, E.T., Stallard, R.F., Ciais, P., Moorcroft, P., Caspersen, J.P., Shevliakova, E., Moore, B., Kohlmaier, G., Holland, E., Gloor, M., Harmon, M.E., Fan, S.-M., Sarmiento, J.L., Goodale, C.L., Schimel, D., and Field, C.B. 2001. Consistent land- and atmosphere-based U.S. carbon sink estimates. *Science* **292**: 2316–2320.
- Raupach, M.R., Canadell, J.G., and Le Quere, C. 2008. Anthropogenic and biophysical contributions to increasing atmospheric CO₂ growth rate and airborne fraction. *Biogeosciences* **5**: 1601–1613.
- Schuster, U. and Watson, A.J. 2007. A variable and decreasing sink for atmospheric CO₂ in the North Atlantic. *Journal of Geophysical Research* **112**: 10.1029/2006JC003941.
- Tans, P.P. and White, J.W.C. 1998. The global carbon cycle: In balance, with a little help from the plants. *Science* **281**: 183–184.
- Velichko, A.A., Zelikson, E.M., and Borisova, O.K. 1999. Vegetation, phytomass and carbon storage in Northern

Eurasia during the last glacial-interglacial cycle and the Holocene. *Chemical Geology* **159**: 191–204.

Wofsy, S.C. 2001. Where has all the carbon gone? *Science* **292** (5525): 2261 online.

Wolf-Gladrow, D.A., Riebesell, U., Burkhardt, S., and Bijma, J. 1999. Direct effects of CO₂ concentration on growth and isotopic composition of marine plankton. *Tellus* **51B**: 461–476.

Xiao, X., Melillo, J.M., Kicklighter, D.W., McGuire, A.D., Prinn, R.G., Wang, C., Stone, P.H., and Sokolov, A. 1998. Transient climate change and net ecosystem production of the terrestrial biosphere. *Global Biogeochemical Cycles* **12**: 345–360.

2.6.2 Carbonyl Sulfide

Idso (1990) suggested the volatilization of reduced sulfur gases from Earth's soils may be just as important as dimethyl sulfide (DMS) emissions from the world's oceans in enhancing cloud albedo, cooling the planet, and providing a natural brake on the tendency for anthropogenically enhanced greenhouse gases to drive global warming. (See Dimethylsulfide, Section 2.6.2.1.1.)

Experiments have shown soil DMS emissions to be positively correlated with soil organic matter content, and Idso noted additions of organic matter to soils tend to increase the amount of sulfur gases they emit. Because atmospheric CO₂ enrichment augments plant growth and, as a result, vegetative inputs of organic matter to Earth's soils, Idso hypothesized this phenomenon should produce an impetus for cooling, even in the absence of the surface warming that sets in motion the chain of events that produce the oceanic DMS-induced negative feedback cooling the planet.

Two years later, Idso (1992) expanded his work to include another biologically produced sulfur gas emitted from soils: carbonyl sulfide, a chemical compound with the formula OCS, but often written as COS. He noted COS is likely to be emitted in increasing quantities as Earth's vegetation responds to the ongoing rise in the air's CO₂ content. While COS is relatively inert in the troposphere, it eventually makes its way into the stratosphere, where it is transformed into solar-radiation-reflecting sulfate aerosol particles. He concluded the CO₂-induced augmentation of soil COS emissions constitutes a mechanism that can cool the planet's surface in the absence of an impetus for warming, without producing additional clouds or making them any brighter.

Researchers subsequently have learned the COS-induced cooling mechanism also operates at sea, just as the DMS-induced cooling mechanism does, and it too possesses a warming-induced component in addition to its CO₂-induced component. Andreae and Ferek (1992) demonstrated ocean-surface COS concentrations are highly correlated with surface-water primary productivity. So strong is this correlation that Erickson and Eaton (1993) developed an empirical model for computing ocean-surface COS concentrations based solely on surface-water chlorophyll concentrations and values of incoming solar radiation.

Researchers also have learned an even greater portion of naturally produced COS is created in the atmosphere, where carbon disulfide and dimethyl sulfide—also largely of oceanic origin (Aydin *et al.*, 2002)—undergo photochemical oxidation (Khalil and Rasmussen, 1984; Barnes *et al.*, 1994). The majority of the tropospheric burden of COS is ultimately dependent upon photosynthetic activity occurring near the surface of the world's oceans.

The tropospheric COS concentration has risen by approximately 30 percent since the 1600s, from a mean value of 373 ppt over the period 1616–1694 to something on the order of 485 ppt today. Aydin *et al.* (2002) have noted only a quarter of this increase can be attributed to anthropogenic sources. The rest of the observed COS increase must have had a natural origin, a large portion of which must have been derived from the products and byproducts of marine photosynthetic activity, which must have increased substantially over the past three centuries. The increases in atmospheric CO₂ concentration and temperature experienced over this period were likely driving forces for the increase in tropospheric COS concentration and its subsequent transport to the stratosphere, where it could exert a cooling influence on the Earth. This chain of events may have kept the warming of the globe considerably below what it might otherwise have been.

Another aspect of this multifaceted global “biothermostat” was revealed in a laboratory study of samples of the lichen *Ramalina menziesii* collected from an open oak woodland in central California, USA by Kuhn and Kesselmeier (2000). When the lichens were optimally hydrated, the researchers found, they absorbed COS from the air at a rate that gradually doubled as air temperature rose from approximately 3° to 25°C, whereupon their rate of COS absorption began a precipitous decline that led to zero COS absorption at 35°C.

Most terrestrial plants thrive in temperatures much warmer than 3°C; as their surroundings warm and they grow better, they extract more COS from the atmosphere, promoting more warming and growing better still. But above a certain temperature warming becomes detrimental to plants, and they begin to reduce their rates of COS absorption, resulting in cooling. The carbonic anhydrase enzyme that governs the uptake of COS in lichens also controls it in all higher plants, algae, and soil organisms, suggesting this thermoregulatory function of the biosphere likely operates across the globe.

Sandoval-Soto *et al.* (2012) reiterated the importance of COS in the atmosphere, noting, “aside from sulfur dioxide, carbonyl sulfide (COS) is the most abundant sulfur gas in the atmosphere with relative constant mixing ratios of 450–500 ppt and a lifetime of more than two years.” They point out “COS can be transported up into the stratosphere,” where it “may serve as a source of sulfur to the stratospheric aerosol layer by conversion to sulfuric acid (Junge *et al.*, 1961; Crutzen, 1976),” thereby contributing to the scattering of incoming solar radiation back to space and exerting a cooling influence on Earth. In addition, they note terrestrial vegetation “acts as the main sink for this trace gas,” and it is “heavily underestimated” in this regard, citing the work of Notholt *et al.* (2003), Mu *et al.* (2004), Sandoval-Soto *et al.* (2005), Campbell *et al.* (2008), Suntharalingam *et al.* (2008), and Van Diest and Kesselmeier (2008).

Further exploring the relationship between increasing atmospheric CO₂ and COS, Sandoval-Soto *et al.* grew three- to four-year-old holm oak (*Quercus ilex* L.) and European beech (*Fagus sylvatica* L.) trees in greenhouse chambers from March 1998 to February 2000 at atmospheric CO₂ concentrations of either 350 or 800 ppm, measuring a number of plant physiological properties and processes. In the case of holm oak, the five researchers report there was “a decrease of the COS uptake capacity induced by high CO₂ levels under long-term conditions,” and their data for beech support “a similar interpretation.” They conclude increasing levels of atmospheric CO₂ may have had a tempering effect on Earth’s rate of warming during the development of the planet’s Current Warm Period, and that cooling influence could increase in the future.

This multifaceted phenomenon is clearly complex, with different biological entities affecting atmospheric COS concentrations simultaneously but

in different ways, while periodically reversing directions in response to changing temperatures. There is obviously much to be learned about the plant physiological mechanisms that may be involved. Until the COS cycle is fully understood and incorporated into the climate models, it cannot be known just how much of the warming experienced during the twentieth century can be attributed to anthropogenic sources.

References

- Andreae, M.O. and Ferek, R.J. 1992. Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere. *Global Biogeochemical Cycles* **6**: 175–183.
- Aydin, M., De Bruyn, W.J., and Saltzman, E.S. 2002. Preindustrial atmospheric carbonyl sulfide (OCS) from an Antarctic ice core. *Geophysical Research Letters* **29**: 10.1029/2002GL014796.
- Barnes, I., Becker, K.H., and Petroescu, I. 1994. The tropospheric oxidation of DMS: a new source of OCS. *Geophysical Research Letters* **21**: 2389–2392.
- Campbell, J.E., Carmichael, G.R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D.R., Blake, N.J., Vay, S.A., Collatz, G.J., Baker, I., Berry, J.A., Montzka, S.A., Sweeney, C., Schnoor, J.L., and Stanier, C.O. 2008. Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science* **322**: 1085–1088.
- Crutzen, P.J. 1976. The possible importance of COS for the sulfate layer of the stratosphere. *Geophysical Research Letters* **3**: 73–76.
- Erickson III, D.J. and Eaton, B.E. 1993. Global biogeochemical cycling estimates with CZCS satellite data and general circulation models. *Geophysical Research Letters* **20**: 683–686.
- Idso, S.B. 1990. A role for soil microbes in moderating the carbon dioxide greenhouse effect? *Soil Science* **149**: 179–180.
- Idso, S.B. 1992. The DMS-cloud albedo feedback effect: Greatly underestimated? *Climatic Change* **21**: 429–433.
- Junge, C.E., Chagnon, C.W., and Manson, J.E. 1961. Stratospheric aerosols. *Journal of Meteorology* **18**: 81–108.
- Khalil, M.A.K. and Rasmussen, R.A. 1984. Global sources, lifetimes, and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS₂) in the Earth’s atmosphere. *Atmospheric Environment* **18**: 1805–1813.
- Kuhn, U. and Kesselmeier, J. 2000. Environmental

variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research* **105**: 26,783–26,792.

Mu, Y., Geng, C., Wang, M., Wu, H., Zhang, X., and Jiang, G. 2004. Photochemical production of carbonyl sulphide in precipitation. *Journal of Geophysical Research* **109**: 10.1029/2003JD004206.

Notholt, J., Kuang, Z., Rinsland, C.P., Toon, G.C., Rex, M., Jones, N., Albrecht, T., Deckelmann, H., Krieg, J., Weinzierl, C., Bingemer, H., Weller, R., and Schrems, O. 2003. Enhanced upper tropical tropospheric COS: Impact on the stratospheric aerosol layer. *Science* **300**: 307–310.

Sandoval-Soto, L., Kesselmeier, M., Schmitt, V., Wild, A., and Kesselmeier, J. 2012. Observations of the uptake of carbonyl sulfide (COS) by trees under elevated atmospheric carbon dioxide concentrations. *Biogeosciences* **9**: 2935–2945.

Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A., and Kesselmeier, J. 2005. Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO₂). *Biogeosciences* **2**: 125–132.

Suntharalingam, P., Kettle, A.J., Montzka, S.M., and Jacob, D.J. 2008. Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake. *Geophysical Research Letters* **35**: 10.1029/2008GL034332.

Van Diest, H. and Kesselmeier, J. 2008. Soil atmosphere exchange of carbonyl sulfide (COS) regulated by diffusivity depending on water-filled pore space. *Biogeosciences* **5**: 475–483.

2.6.3 Diffuse Light

Another negative feedback phenomenon is diffuse light. It operates through a chain of five linkages triggered by the incremental enhancement of the atmosphere's greenhouse effect produced by an increase in the air's CO₂ content.

The first linkage is the proven propensity for higher levels of atmospheric CO₂ to enhance vegetative productivity, a powerful negative feedback mechanism. Greater CO₂-enhanced photosynthetic rates, for example, enable plants to remove considerably more CO₂ from the air than they do under current conditions, while CO₂-induced increases in plant water use efficiency allow plants to grow where it was previously too dry for them. This establishes a potential for more CO₂ to be removed from the atmosphere by increasing the abundance of

Earth's plants and increasing their robustness (see Carbon Sequestration, Section 2.6.1, this volume).

The second linkage of the feedback loop is the ability of plants to emit gases to the atmosphere that are ultimately converted into “biosols”—aerosols that owe their existence to the biological activities of Earth's vegetation, many of which function as cloud condensation nuclei. Since the existence of these atmospheric particles is dependent upon the physiological activities of plants and their associated soil biota, the CO₂-induced presence of more, and more-highly-productive, plants will lead to the production of more of these cloud-mediating particles, which can then result in more clouds that reflect sunlight and act to cool the planet.

The third linkage is the observed propensity for increases in aerosols and cloud particles to enhance the amount of diffuse solar radiation reaching Earth's surface. The fourth linkage is the ability of enhanced diffuse lighting to reduce the volume of shade within vegetative canopies. The fifth linkage is the tendency for less internal canopy shading to enhance whole-canopy photosynthesis, which produces the end result: a greater biological extraction of CO₂ from the air and the subsequent sequestration of its carbon.

Roderick *et al.* (2001) provide a good estimate of the significance of this process based on a unique “natural experiment,” a technique used extensively by Idso (1998) to evaluate the climatic sensitivity of the planet. Roderick and his colleagues considered the volcanic eruption of Mt. Pinatubo in June 1991, which ejected enough gases and fine materials into the atmosphere to produce sufficient aerosol particles to greatly increase the diffuse component of the solar radiation reaching the surface of Earth from that point in time through much of 1993, while only slightly reducing the receipt of total solar radiation.

Based on a set of lengthy calculations, they conclude the Mt. Pinatubo eruption may have resulted in the removal of an extra 2.5 Gt of carbon from the atmosphere due to its diffuse-light-enhancing stimulation of terrestrial vegetation in the year following the eruption, which would have reduced the ongoing rise in the air's CO₂ concentration that year by about 1.2 ppm. The reduction they calculated is approximately the magnitude of the change in CO₂ concentration actually observed (Sarmiento, 1993).

Bolstering the attribution of this change to diffuse light, Roderick *et al.* note the CO₂ reduction was coincident with an El Niño event, whereas “previous and subsequent such events have been associated with increases in atmospheric CO₂.” Moreover, the

observed reduction in *total* solar radiation received at Earth's surface during this period would have had a tendency to reduce the amount of photosynthetically active radiation, would have had a tendency to cause the air's CO₂ content to rise by lessening global photosynthetic activity.

Further support for the new negative feedback phenomenon came in 2002, when a team of 33 researchers published the results of a comprehensive study (Law *et al.*, 2002) that compared seasonal and annual values of CO₂ and water vapor exchange across sites in forests, grasslands, crops, and tundra—part of an international network called FLUXNET—investigating the responses of these exchanges to variations in a number of environmental factors, including direct and diffuse solar radiation. The researchers report “net carbon uptake (net ecosystem exchange, the net of photosynthesis and respiration) was greater under diffuse than under direct radiation conditions.” In discussing this finding, which is the centerpiece of the negative feedback phenomenon described in this section, they note “cloud-cover results in a greater proportion of diffuse radiation and constitutes a higher fraction of light penetrating to lower depths of the canopy (Oechel and Lawrence, 1985).” They also report “Goulden *et al.* (1997), Fitzjarrald *et al.* (1995), and Sakai *et al.* (1996) showed that net carbon uptake was consistently higher during cloudy periods in a boreal coniferous forest than during sunny periods with the same PPFD [photosynthetic photon flux density].” They also write, “Hollinger *et al.* (1994) found that daily net CO₂ uptake was greater on cloudy days, even though total PPFD was 21–45 percent lower on cloudy days than on clear days.”

Gu *et al.* (2003) “used two independent and direct methods to examine the photosynthetic response of a northern hardwood forest (Harvard Forest, 42.5°N, 72.2°W) to changes in diffuse radiation caused by Mount Pinatubo's volcanic aerosols.” In the eruption year of 1991, they found, “around noontime in the mid-growing season, the gross photosynthetic rate under the perturbed cloudless solar radiation regime was 23, 8, and 4 percent higher than that under the normal cloudless solar radiation regime in 1992, 1993, and 1994, respectively,” and “integrated over a day, the enhancement for canopy gross photosynthesis by the volcanic aerosols was 21 percent in 1992, 6 percent in 1993 and 3 percent in 1994.” Gu *et al.* write, “because of substantial increases in diffuse radiation world-wide after the

eruption and strong positive effects of diffuse radiation for a variety of vegetation types, it is likely that our findings at Harvard Forest represent a global phenomenon.”

The diffuse-light-induced photosynthetic enhancement observed by Gu *et al.* was caused by volcanic aerosols acting under cloudless conditions. That distinguishes this phenomenon from a closely related one also described by Gu *et al.*—the propensity for the extra diffuse light created by increased cloud cover to enhance photosynthesis even though the total flux of solar radiation received at Earth's surface may be reduced under such conditions. Gu *et al.* note, “Harvard Forest photosynthesis also increases with cloud cover, with a peak at about 50 percent cloud cover.”

The work reviewed above focuses on the enhanced atmospheric aerosol concentration caused by a singular significant event: a massive volcanic eruption. Niyogi *et al.* (2004) asked a more general question: “Can we detect the effect of relatively routine aerosol variability on field measurements of CO₂ fluxes, and if so, how does the variability in aerosol loading affect CO₂ fluxes over different landscapes?”

The group of 16 researchers used CO₂ flux data from the AmeriFlux network (Baldocchi *et al.*, 2001) together with cloud-free aerosol optical depth data from the NASA Robotic Network (AERONET; Holben *et al.*, 2001) to assess the effect of aerosol loading on the net assimilation of CO₂ by three types of vegetation: trees (broadleaf deciduous forest and mixed forest), crops (winter wheat, soybeans, and corn), and grasslands.

Their work revealed an aerosol-induced increase in diffuse radiative-flux fraction [DRF = ratio of diffuse (R_d) to total or global (R_g) solar irradiance] increased the net CO₂ assimilation of trees and crops, making them larger carbon sinks, but decreased the net CO₂ assimilation of grasslands, making them smaller carbon sinks. For a summer midrange R_g flux of 500 W m⁻², going from the set of all DRF values between 0.0 and 0.4 to the set of all DRF values between 0.6 and 1.0 resulted in an approximate 50 percent increase in net CO₂ assimilation by a broadleaf deciduous forest located in Tennessee, USA. Averaged over the entire daylight period, the shift from the lower to the higher set of DRF values “enhances photosynthetic fluxes by about 30 percent at this study site.” Similar results were obtained for the mixed forest and the conglomerate of crops

studied. Niyogi *et al.* conclude natural variability among commonly present aerosols can “routinely influence surface irradiance and hence the terrestrial CO₂ flux and regional carbon cycle.” For these types of land cover (forests and agricultural crops), that influence significantly increases the assimilation of CO₂ from the atmosphere. In the case of grasslands, Niyogi *et al.* found the opposite effect, with greater aerosol loading of the atmosphere leading to less CO₂ assimilation. The researchers suggest this result was most likely due to grasslands’ significantly different canopy architecture.

With respect to the planet as a whole, the net effect of diffuse light processes is decidedly positive, as Earth’s trees are key in carbon sequestration. Post *et al.* (1990) note woody plants account for approximately 75 percent of terrestrial photosynthesis, which represents about 90 percent of all photosynthesis (Sellers and McCarthy, 1990).

Moreover, much of the commonly present aerosol burden of the atmosphere is plant-derived. Woody plants are themselves responsible for emitting to the air that which ultimately enhances photosynthesis. Earth’s trees alter the atmospheric environment in a way that directly enhances their growth. And as humans release more CO₂ into the atmosphere, the globe’s woody plants respond to its aerial fertilization effect, becoming increasingly productive, leading to even more plant-derived aerosols being released to the atmosphere, further stimulating this positive feedback cycle. These effects are not adequately incorporated into the climate models.

References

- Baldocchi, D., Falge, E., Gu, L.H., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., Evans, R., Fuentes, J., Goldstein, A., Katul, G., Law, B., Lee, X.H., Malhi, Y., Meyers, T., Munger, W., Oechel, W., Paw U, K.T., Pilegaard, K., Schmid, H.P., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. 2001. FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities. *Bulletin of the American Meteorological Society* **82**: 2415–2434.
- Fitzjarrald, D.R., Moore, K.E., Sakai, R.K., and Freedman, J.M. 1995. Assessing the impact of cloud cover on carbon uptake in the northern boreal forest. In: Proceedings of the American Geophysical Union Meeting, Spring 1995, *EOS Supplement*, p. S125.
- Goulden, M.L., Daube, B.C., Fan, S.-M., Sutton, D.J., Bazzaz, A., Munger, J.W., and Wofsy, S.C. 1997. Physiological responses of a black spruce forest to weather. *Journal of Geophysical Research* **102**: 28,987–28,996.
- Gu, L., Baldocchi, D.D., Wofsy, S.C., Munger, J.W., Michalsky, J.J., Urbanski, S.P., and Boden, T.A. 2003. Response of a deciduous forest to the Mount Pinatubo eruption: Enhanced photosynthesis. *Science* **299**: 2035–2038.
- Holben, B.N., Tanré, D., Smirnov, A., Eck, T.F., Slutsker, I., Abuhassan, N., Newcomb, W.W., Schafer, J.S., Chatenet, B., Lavenu, F., Kaufman, Y.J., Castle, J.V., Setzer, A., Markham, B., Clark, D., Frouin, R., Halthore, R., Karneli, A., O’Neill, N.T., Pietras, C., Pinker, R.T., Voss, K., and Zibordi, G. 2001. An emerging ground-based aerosol climatology: Aerosol Optical Depth from AERONET. *Journal of Geophysical Research* **106**: 12,067–12,097.
- Hollinger, D.Y., Kelliher, F.M., Byers, J.N., and Hunt, J.E. 1994. Carbon dioxide exchange between an undisturbed old-growth temperate forest and the atmosphere. *Ecology* **75**: 134–150.
- Idso, S.B. 1998. CO₂-induced global warming: a skeptic’s view of potential climate change. *Climate Research* **10**: 69–82.
- Law, B.E., Falge, E., Gu, L., Baldocchi, D.D., Bakwin, P., Berbigier, P., Davis, K., Dolman, A.J., Falk, M., Fuentes, J.D., Goldstein, A., Granier, A., Grelle, A., Hollinger, D., Janssens, I.A., Jarvis, P., Jensen, N.O., Katul, G., Mahli, Y., Matteucci, G., Meyers, T., Monson, R., Munger, W., Oechel, W., Olson, R., Pilegaard, K., Paw U, K.T., Thorgeirsson, H., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. 2002. Environmental controls over carbon dioxide and water vapor exchange of terrestrial vegetation. *Agricultural and Forest Meteorology* **113**: 97–120.
- Niyogi, D., Chang, H.-I., Saxena, V.K., Holt, T., Alapaty, K., Booker, F., Chen, F., Davis, K.J., Holben, B., Matsui, T., Meyers, T., Oechel, W.C., Pielke Sr., R.A., Wells, R., Wilson, K., and Xue, Y. 2004. Direct observations of the effects of aerosol loading on net ecosystem CO₂ exchanges over different landscapes. *Geophysical Research Letters* **31**: 10.1029/2004GL020915.
- Oechel, W.C. and Lawrence, W.T. 1985. Tiaga. In: Chabot, B.F. and Mooney, H.A. (Eds.) *Physiological Ecology of North American Plant Communities*. Chapman & Hall, New York, NY, pp. 66–94.
- Post, W.M., Peng, T.-H., Emanuel, W.R., King, A.W., Dale, V.H., and DeAngelis, D.L. 1990. The global carbon cycle. *American Scientist* **78**: 310–326.
- Roderick, M.L., Farquhar, G.D., Berry, S.L., and Noble, I.R. 2001. On the direct effect of clouds and atmospheric particles on the productivity and structure of vegetation. *Oecologia* **129**: 21–30.

Sakai, R.K., Fitzjarrald, D.R., Moore, K.E., and Freedman, J.M. 1996. How do forest surface fluxes depend on fluctuating light level? In: *Proceedings of the 22nd Conference on Agricultural and Forest Meteorology with Symposium on Fire and Forest Meteorology*, Vol. 22, American Meteorological Society, pp. 90–93.

Sarmiento, J.L. 1993. Atmospheric CO₂ stalled. *Nature* **365**: 697–698.

Sellers, P. and McCarthy, J.J. 1990. Planet Earth, Part III, Biosphere. *EOS: Transactions of the American Geophysical Union* **71**: 1883–1884.

2.6.4 Iodocompounds

The climatic significance of iodinated compounds, or iodocompounds, was initially described in *Nature* by O’Dowd *et al.* (2002). As related by Kolb (2002) in an accompanying perspective on their work, the 10-member research team discovered “a previously unrecognized source of aerosol particles” by unraveling “a photochemical phenomenon that occurs in sea air and produces aerosol particles composed largely of iodine oxides.”

O’Dowd *et al.* used a smog chamber operated under coastal atmospheric conditions to demonstrate, as they report, “new particles can form from condensable iodine-containing vapors, which are the photolysis products of biogenic iodocarbons emitted from marine algae.” They also demonstrated, using aerosol formation models, that concentrations of condensable iodine-containing vapors over the open ocean “are sufficient to influence marine particle formation.”

The aerosol particles O’Dowd *et al.* discovered can function as cloud condensation nuclei (CCN), helping to create new clouds that reflect more incoming solar radiation back to space and thereby cool the planet (a negative feedback). With respect to the negative feedback nature of this phenomenon, O’Dowd *et al.* cite the work of Laturnus *et al.* (2000), who demonstrated emissions of iodocarbons from marine biota “can increase by up to 5 times as a result of changes in environmental conditions associated with global change.” Therefore, O’Dowd *et al.* write, “increasing the source rate of condensable iodine vapors will result in an increase in marine aerosol and CCN concentrations of the order of 20–60 percent.” Furthermore, they note, “changes in cloud albedo resulting from changes in CCN concentrations of this magnitude can lead to an increase in global radiative forcing similar in magnitude, but opposite in sign, to

the forcing induced by greenhouse gases.”

Four years later, Smythe-Wright *et al.* (2006) measured trace gas and pigment concentrations in seawater, while identifying and enumerating picophytoprokaroyotes during two ship cruises in the Atlantic Ocean and one in the Indian Ocean, where they focused “on methyl iodide production and the importance of a biologically related source.” They encountered methyl iodide concentrations as great as 45 pmol per liter in the top 150 meters of the oceanic water column that correlated well with the abundance of *Prochlorococcus*, which they reported “can account for >80 percent of the variability in the methyl iodide concentrations.” They further state they “have confirmed the release of methyl iodide by this species in laboratory culture experiments.”

Extrapolating their findings to the globe as a whole, the six researchers “estimate the global ocean flux of iodine [I] to the marine boundary layer from this single source to be 5.3×10^{11} g I year⁻¹,” which they state “is a large fraction of the total estimated global flux of iodine (10^{11} - 10^{12} g I year⁻¹).” Smythe-Wright *et al.* point out volatile iodinated compounds “play a part in the formation of new particles and cloud condensation nuclei (CCN),” and “an increase in the production of iodocompounds and the subsequent production of CCN would potentially result in a net cooling of the Earth system and hence in a negative climate feedback mechanism, mitigating global warming.” They suggest “as ocean waters become warmer and more stratified, nutrient concentrations will fall and there will likely be a regime shift away from microalgae toward *Prochlorococcus*,” such that “colonization within the <50° latitude band will result in a ~15 percent increase in the release of iodine to the atmosphere,” with consequent “important implications for global climate change.”

As part of the Third Pelagic Ecosystem CO₂ Enrichment Study, Wingenter *et al.* (2007) investigated the effects of atmospheric CO₂ enrichment on marine microorganisms in nine marine mesocosms maintained within two-meter-diameter polyethylene bags submerged to a depth of 10 meters in a fjord at the Large-Scale Facilities of the Biological Station of the University of Bergen in Espesgrend, Norway. Three of these mesocosms were maintained at ambient levels of CO₂ (~375 ppm or base CO₂), three were maintained at levels expected to prevail at the end of the current century (760 ppm or 2xCO₂), and three were maintained at levels

predicted for the middle of the next century (1150 ppm or $3\times\text{CO}_2$). During the 25 days of this experiment, the researchers followed the development and subsequent decline of an induced bloom of the coccolithophorid *Emiliana huxleyi*, carefully measuring several physical, chemical, and biological parameters along the way. This work revealed iodocarbon chloriodomethane (CH_2CI) concentrations peaked about six to 10 days after the coccolithophorid's chlorophyll-a maximum, and the peak estimated abundance was 46 percent higher in the $2\times\text{CO}_2$ mesocosms and 131 percent higher in the $3\times\text{CO}_2$ mesocosms.

The international team of scientists concludes the differences in the CH_2CI concentrations “may be viewed as a result of changes to the ecosystems as a whole brought on by the CO_2 perturbations.” Because emissions of various iodocarbons have been found to lead to an enhancement of cloud condensation nuclei in the marine atmosphere, as demonstrated by O’Dowd *et al.* (2002) and Jimenez *et al.* (2003), the CO_2 -induced stimulation of marine emissions of these substances provides a natural brake on the tendency for global warming to occur as a consequence of any forcing, as iodocarbons lead to the creation of more highly reflective clouds over greater areas of the world’s oceans. As Wingenter *et al.* conclude, the processes described above “may help contribute to the homeostasis of the planet.”

References

- Jimenez, J.L., Bahreini, R., Cocker III, D.R., Zhuang, H., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., O’Dowd, C.D., and Hoffmann, T. 2003. New particle formation from photooxidation of diiodomethane (CH_2I_2). *Journal of Geophysical Research* 108: 10.1029/2002JD002452.
- Kolb, C.E. 2002. Iodine’s air of importance. *Nature* 417: 597–598.
- Laternus, F., Giese, B., Wiencke, C., and Adams, F.C. 2000. Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae—The influence of abiotic factors. *Fresenius’ Journal of Analytical Chemistry* 368: 297–302.
- O’Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S.G., and Hoffmann, T. 2002. Marine aerosol formation from biogenic iodine emissions. *Nature* 417: 632–636.
- Smythe-Wright, D., Boswell, S.M., Breithaupt, P., Davidson, R.D., Dimmer, C.H., and Eiras Diaz, L.B. 2006. Methyl iodide production in the ocean: Implications for climate change. *Global Biogeochemical Cycles* 20: 10.1029/2005GB002642.
- Wingenter, O.W., Haase, K.B., Zeigler, M., Blake, D.R., Rowland, F.S., Sive, B.C., Paulino, A., Thyrhaug, R., Larsen, A., Schulz, K., Meyerhofer, M., and Riebesell, U. 2007. Unexpected consequences of increasing CO_2 and ocean acidity on marine production of DMS and CH_2CI : Potential climate impacts. *Geophysical Research Letters* 34: 10.1029/2006GL028139.

2.6.5 Stratospheric Perturbations

Few researchers have examined the influence of the stratosphere on global climate, yet several studies indicate this layer of the atmosphere has a significant impact on various climate parameters.

In an early study of the subject, Hartley *et al.* (1998) utilized meteorological data for the winter of 1992–93 to study a broad range of stratospheric polar vortex distortions for possible impacts on meteorological events in the troposphere. As they describe it, the results of their study “clearly indicate that stratospheric processes induce significant anomalies in dynamical fields at the tropopause.”

Previously, although atmospheric processes of tropospheric origin were known to have the ability to perturb the stratosphere, feedback in the opposite direction was assumed to be negligible. The results of Hartley *et al.*’s study, however, demonstrate this assumption was incorrect, leading them to suggest a more realistic representation of the stratosphere may be required to enable general circulation models (GCMs) of the atmosphere to properly simulate the troposphere.

This shortcoming of current climate models may be critical, for scientists have long suspected the upper atmosphere may amplify the effects of a number of solar phenomena. The work of Hartley *et al.* suggests the amplified perturbations of these phenomena may be propagated downward to the troposphere, where they could significantly impact Earth’s climate.

Initial evidence that such perturbations may indeed influencing climate near Earth’s surface is seen in the work of Thompson and Solomon (2002), who explored a number of different data sets in Antarctica to define the nature of climate change in Antarctica since 1969 and determine the reasons for the observed changes. The two researchers found “at the surface, the Antarctic Peninsula has warmed by several [degrees C] over the past several decades,

while the interior of the Antarctic continent has exhibited weak cooling.” In addition, they note, “ice shelves have retreated over the peninsula and sea-ice extent has decreased over the Bellingshausen Sea, while sea-ice concentration has increased and the length of the sea-ice season has increased over much of eastern Antarctica and the Ross Sea.” With respect to atmospheric circulation, they write there was “a systematic bias toward the high-index polarity of the SAM,” or Southern Hemispheric Annular Mode, such that the ring of westerly winds encircling Antarctica recently has been spending more time in its strong-wind phase.

The heightened strength and persistence of the SAM can explain most of the cooling experienced over the bulk of Antarctica over the past several decades as well as much of the warming of the Antarctica Peninsula, as the latter location experiences fewer cold-air outbreaks under such conditions while simultaneously receiving increased advective warmth from the Southern Ocean. As for what caused the strengthening of the SAM, Thompson and Solomon speculate it is related to “recent trends in the lower stratospheric polar vortex, which are due largely to photochemical ozone losses.”

Similar findings were reported in a contemporaneous study conducted by Kwok and Comiso (2002), who also report the SAM index shifted towards more positive values (0.22/decade) over the 17-year period 1982–1998, while noting a positive polarity of the SAM index “is associated with cold anomalies over most of Antarctica with the center of action over the East Antarctic plateau.” Simultaneously, the SO index shifted in a negative direction, indicating “a drift toward a spatial pattern with warmer temperatures around the Antarctic Peninsula, and cooler temperatures over much of the continent.” The authors report the positive trend in the coupled mode of variability of these two indices (0.3/decade) represents a “significant bias toward positive polarity,” which they describe as “remarkable.”

Kwok and Comiso note “the tropospheric SH annular mode has been shown to be related to changes in the lower stratosphere (Thompson and Wallace, 2000)” and “the high index polarity of the SH annular mode is associated with the trend toward a cooling and strengthening of the SH stratospheric polar vortex during the stratosphere’s relatively short active season in November, and ozone depletion,” much the same

theory put forth by Thompson and Solomon (2002).

Thejll *et al.* (2003) also demonstrated a link between stratospheric perturbations and tropospheric climate. They investigated various spatial and temporal relationships among several parameters, including the geomagnetic index (Ap), the NAO, stratospheric geopotential height, and sea level pressure. The three researchers report “significant correlations between Ap and sea-level pressures and between Ap and stratospheric geopotential heights are found for the period 1973–2000,” but “for the period 1949–1972 no significant correlations are found at the surface while significant correlations still are found in the stratosphere.” By using “Monte Carlo simulations of the statistical procedures applied to suitable surrogate data,” they conclude these correlations are due to the existence of a “real physical link.” They also note in the 1973–2000 period only the winter season series are significantly correlated, which they said “is consistent with the notion that the solar-climate link works through the stratosphere.”

Thejll *et al.* suggest their findings may be explained in two different ways: either the influence of the Sun increased through time, reaching a strong enough level in the 1970s to make the correlations they studied become statistically significant, or the state of the atmosphere changed in the 1970s, becoming more sensitive to the solar influence than it had been. In either event, their findings strengthen the argument for solar-induced perturbations being propagated downward from the stratosphere to the troposphere (Hartley *et al.*, 1998; Carslaw *et al.*, 2002).

Ineson *et al.* (2011) modeled the effects from realistic solar UV (200–320 nm) irradiance changes between solar activity minima and maxima in the stratosphere and mesosphere, finding weaker westerly winds during the winters with a less active Sun that may correspond with cold winters in Northern Europe and the United States and mild winters over Southern Europe and Canada, as observed in recent years. The observational analyses by Hood *et al.* (2013) added insight into the specific regional patterns of near-surface responses that more than likely originate from the solar UV forcing of ozone and related wind-thermal fields in the stratosphere.

Kristjansson *et al.*’s (2002) observation that “low clouds appear to be significantly inversely correlated with solar irradiance” led them to suggest a possible physical mechanism linked to the stratosphere that could explain this phenomenon. This mechanism, in

their words, “acts through UV [ultraviolet radiation] in the stratosphere affecting tropospheric planetary waves and hence the subtropical highs, modulated by an interaction between sea surface temperature [SST] and lower tropospheric static stability,” which “relies on a positive feedback between changes in SST and low cloud cover changes of opposite sign, in the subtropics.” Based on experimentally determined values of factors that enter into this process, they obtained a value for the amplitude of the variation in low cloud cover over a solar cycle that “is very close to the observed amplitude.”

Tiwari *et al.* (2005) report the Asian SouthWest Monsoon (SWM) intensity on a centennial scale “is governed by variation in TSI,” yet “variations in TSI (~0.2%) seem to be too small to perturb the SWM, unless assisted by some internal amplification mechanism with positive feedback.” They discuss a possible mechanism that “involves heating of the Earth’s stratosphere by increased absorption of solar ultraviolet (UV) radiation by ozone during periods of enhanced solar activity (Schneider, 2005).” They posit more UV reception leads to more ozone production in the stratosphere, which leads to more heat being transferred to the troposphere, which leads to enhanced evaporation from the oceans, which enhances monsoon winds and precipitation.

de Jager (2005) reviewed what is known about the role of the Sun in orchestrating climate change over the course of the Holocene, including changes that occurred during the twentieth century. Commenting on the direct effects of solar irradiance variations, de Jager reports “the fraction of the solar irradiance that directly reaches the Earth’s troposphere is emitted by the solar photosphere [and] does not significantly vary.” The variable part of this energy flux, he states, is emitted by chromospheric parts of centers of solar activity, and “it only directly influences the higher, stratospheric terrestrial layers,” which “can only influence the troposphere by some form of stratosphere-troposphere coupling.”

Solomon *et al.* (2010) point out “the trend in global surface temperatures has been nearly flat since the late 1990s despite continuing increases in the forcing due to the sum of the well-mixed greenhouse gases (CO₂, CH₄, halocarbons, and N₂O), raising questions regarding the understanding of forced climate change, its drivers, the parameters that define natural internal variability, and how fully these terms are represented in climate models.” They used observations of stratospheric water vapor concentration obtained over the period 1980–2008,

together with detailed radiative transfer and modeling information, to calculate the global climatic impact of water vapor and compare it with trends in mean global near-surface air temperature observed over the same time period.

The seven scientists found stratospheric water vapor concentrations decreased by about 10 percent after the year 2000, and their analysis indicates this decrease should have slowed the rate of increase in global near-surface air temperature between 2000 and 2009 by about 25 percent compared to what would have been expected on the basis of climate model calculations due to measured increases in carbon dioxide and other greenhouse gases over the same period. In addition, they found, “more limited data suggest that stratospheric water vapor probably increased between 1980 and 2000, which would have enhanced the decadal rate of surface warming during the 1990s by about 30% [above what it would have been without the stratospheric water vapor increase].”

Solomon *et al.* conclude it is “not clear whether the stratospheric water vapor changes represent a feedback to global average climate change or a source of decadal variability.” In either case, their findings describe a phenomenon not included in prior analyses of global climate change. They also indicate current climate models do not “completely represent the Quasi Biennial Oscillation [which has a significant impact on stratospheric water vapor content], deep convective transport [of water vapor] and its linkages to sea surface temperatures, or the impact of aerosol heating on water input to the stratosphere.”

In light of Solomon *et al.*’s findings, their identification of what current climate models do not but should do, and the questions they say are raised by the flatlining of mean global near-surface air temperature since the late 1990s, it is premature to conclude current state-of-the-art models know enough to correctly simulate the intricate workings of Earth’s climate regulatory system. The other studies cited in this section also indicate much research remains to be conducted in order to more correctly characterize and quantify the stratosphere’s influence on global climate.

References

- Carslaw, K.S., Harrizon, R.G., and Kirkby, J. 2002. Cosmic rays, clouds, and climate. *Science* **298**: 1732–1737.
- de Jager, C. 2005. Solar forcing of climate. I: Solar variability. *Space Science Reviews* **120**: 197–241.

Hartley, D.E., Villarín, J.T., Black, R.X., and Davis, C.A. 1998. A new perspective on the dynamical link between the stratosphere and troposphere. *Nature* **391**: 471–474.

Hood, L., Schimanke, S., Spanghel, T., Bal, S., and Cubasch, U. 2013. The surface climate response to 11-yr solar forcing during northern winter: Observational analyses and comparisons with GCM simulations. *Journal of Climate* **in press**: doi: 10.1175/JCLI-D-12-00843.1.

Ineson, S., Scaife, A.A., Knight, J.R., Manners, J.C., Dunstone, N.J., Gray, L.J., and Haigh, J.D. 2011. Solar forcing of winter climate variability in the Northern Hemisphere. *Nature Geoscience* **4**: 753–757, doi:10.1038/NGEO1282.

Kristjansson, J.E., Staple, A., and Kristiansen, J. 2002. A new look at possible connections between solar activity, clouds and climate. *Geophysical Research Letters* **29**: 10.1029/2002GL015646.

Kwok, R. and Comiso, J.C. 2002. Spatial patterns of variability in Antarctic surface temperature: Connections to the South Hemisphere Annular Mode and the Southern Oscillation. *Geophysical Research Letters* **29**: 10.1029/2002GL015415.

Schneider, D. 2005. Living in sunny times. *American Scientist* **93**: 22–24.

Solomon, S., Rosenlof, K., Portmann, R., Daniel, J., Davis, S., Sanford, T., and Plattner, G.-K. 2010. Contributions of stratospheric water vapor to decadal changes in the rate of global warming. *Scienceexpress*: 10.1126/science.1182488.

Thejll, P., Christiansen, B., and Gleisner, H. 2003. On correlations between the North Atlantic Oscillation, geopotential heights, and geomagnetic activity. *Geophysical Research Letters* **30**: 10.1029/2002GL016598.

Thompson, D.W.J. and Solomon, S. 2002. Interpretation of recent Southern Hemisphere climate change. *Science* **296**: 895–899.

Tiwari, M. Ramesh, R., Somayajulu, B.L.K., Jull, A.J.T., and Burr, G.S. 2005. Solar control of southwest monsoon on centennial timescales. *Current Science* **89**: 1583–1588.

2.6.6 Volcanism

Volcanic forcings are not a function of human activities. Their impact on climate and human history is well documented and takes many forms, especially with major events with a global impact such as Tambora, Laki, and more recently Pinatubo.

In general, large volcanic eruptions eject particulate and aerosol materials into the stratosphere. These aerosols, primarily sulfate type, increase the

albedo of the planet, which means less solar radiation coming in. The result is a cooling of the lower troposphere and surface. Generally, the greater the eruption, the stronger this effect will be and the longer it will last. Smaller volcanic eruptions confined to the troposphere have little effect on the climate, as the troposphere is more efficient in scavenging out the relatively large particulates. Still, much remains to be learned about this external forcing of the climate, and as the research highlighted below indicates, not all scientists are in agreement regarding the long-term importance of this forcing on climate.

Briffa and Jones (1998) used tree-ring wood density data from more than 380 boreal forest locations in the Northern Hemisphere as surrogates for summertime temperatures, looking for effects of large volcanic eruptions on climate since 1400 AD. This exercise indicated major volcanic eruptions seemed to produce significant Northern Hemispheric cooling the year after their occurrence, with the largest of the temperature declines they detected estimated to be 0.81°C in 1601, the year following the eruption of Huaynaputina in Peru.

Of the six centuries examined, the seventeenth century experienced the greatest number (six) of climatically significant eruptions. Strong temperature anomalies suggested there were three other major volcanic eruptions during the late seventeenth century not reported in historical accounts. The researchers also found every Northern Hemispheric temperature departure of 0.3°C or more since 1400 (19 total events) followed a confirmed major volcanic eruption. This study thus suggests there is a strong link between volcanic activity and large-scale temperature variability, and it may help to explain the cool temperatures of the Little Ice Age by illustrating how closely spaced multiple eruptions could reduce hemispheric temperatures on decadal and multidecadal time scales, as well as how a lack of such eruptions could result in periods of warmer global temperatures.

Building on this perceived relationship, Hyde and Crowley (2000) analyzed statistical properties of climatically significant volcanic eruptions over the past 600 years in an effort to estimate the probability of future eruptions. They conclude there was a 35 to 40 percent probability of a volcanic eruption occurring with the capability of producing a radiative perturbation of -1 W m⁻² or larger in the following 10 years. Such an eruption was estimated to produce a

0.1°C to 0.15°C cooling over a two- to three-year period, while the probability of a larger Mt. Pinatubo-scale eruption with a radiative perturbation of -3 W m^{-2} was estimated to be 15 to 25 percent. The two scientists note if a major volcanic eruption were to occur in the next decade (which seems a reasonable possibility), it could “mask the CO₂ effect and complicate discussions on a greenhouse gas protocol.”

Sadler and Grattan (1999) examined a number of issues related to the linking of volcanic activity with spatial and temporal events in climatic, historical, and palaeoecological records. Although volcanoes can have a significant effect on proximal climates, they conclude, their global impact is less well understood. The message of their paper is thus one of caution in drawing conclusions about climate change and its connection to volcanic explosions. They report, for example, “a run of bad summers, an increase in sea ice off America, narrow rings in dendrochronological sequences, and neoglaciations can all be linked to temporally convenient climate forcing by volcanic aerosols.” In addition, they note “speculation as to the likely effect of these eruptions on fauna and flora and human societies may involve further supposition.” They also note “the role of precursor climatic and/or environmental conditions is frequently overlooked” and “it is valid to question whether the relationships established are fortuitous rather than dependent.” As one of the scientists they quote has aptly phrased it, “an eruption here, a destruction there, a plague somewhere else—all are too easily linked in hasty surmise.”

Yet another indication the climatic effects of volcanic eruptions may not be well established is provided by Douglass and Knox (2005), who “determined the volcano climate sensitivity and response time for the Mount Pinatubo eruption, using observational measurements of the temperature anomalies of the lower troposphere, measurements of the long wave outgoing radiation, and the aerosol optical density.” Their analysis revealed “a short atmospheric response time, of the order of several months, leaving no volcano effect in the pipeline, and a negative feedback to its forcing.”

One of the issues raised by these results, according to Douglass and Knox, concerns “the origin of the required negative feedback.” With respect to this question, they report “negative feedback processes have been proposed involving cirrus clouds (Lindzen *et al.*, 2001)” and “Sassen (1992) reports that cirrus clouds were produced during the Mt.

Pinatubo event.” In addition, they note the adaptive infrared iris concept of Lindzen *et al.* (2001) “yields a negative feedback factor of -1.1, which is well within the error estimate of the feedback found by us.” They also observe the short intrinsic response time they derived (6.8 ± 1.5 months) “confirms suggestions of Lindzen and Giannitsis (1998, 2002) that a low sensitivity and small lifetime are more appropriate” than the “long response times and positive feedback” characteristic of the reigning climate paradigm.

Tuffen (2010) writes “there is growing evidence that past changes in the thickness of ice covering volcanoes have affected their eruptive activity.” He further states “the rate of volcanic activity in Iceland accelerated by a factor of 30–50 following the last deglaciation at approximately 12 ka (Maclennan *et al.*, 2002)” and “analyses of local and global eruption databases have identified a statistically significant correlation between periods of climatic warming associated with recession of ice and an increase in the frequency of eruptions (Jellinek *et al.*, 2004; Nowell *et al.*, 2006; Huybers and Langmuir, 2009).” Thus he asks the next logical question: “Will the current ice recession provoke increased volcanic activity and lead to increased exposure to volcanic hazards?”

Tuffen—a researcher at the Lancaster Environment Centre of Lancaster University in the United Kingdom—“analyze[d] our current knowledge of how ice thickness variations influence volcanism” and “identif[ied] several unresolved issues that currently prevent quantitative assessment of whether activity is likely to accelerate in the coming century.” He found “ice unloading may encourage more explosive eruptions” but “melting of ice and snow may decrease the likelihood and magnitude of meltwater floods.” On the other hand, he writes, there is “uncertainty about the time scale of volcanic responses to ice unloading,” “poor constraint on how ice bodies on volcanoes will respond to twenty-first century climate change,” and “lack of data on how past changes in ice thickness have affected the style of volcanic eruptions and associated hazards.” He also notes “the sensitivity of volcanoes to small changes in ice thickness or to recession of small glaciers on their flanks is unknown,” “it is not known how localized ice withdrawal from stratovolcanoes [tall, conical volcanoes with many layers (strata) of hardened lava, tephra, and volcanic ash] will affect shallow crustal magma storage and eruption,” and “broader feedbacks between volcanism and climate change remain poorly understood.”

The U.K. researcher concludes by stating, “in

order to resolve these problems, both new data and improved models are required.” With respect to data, he adds, “existing databases of known volcanic eruptions need to be augmented by numerous detailed case studies of the Quaternary eruptive history of ice-covered volcanoes.” Regarding models, he notes, “improved physical models are required to test how magma generation, storage and eruption at stratovolcanoes are affected by stress perturbations related to the waxing and waning of small-volume ice bodies on what is commonly steep topography.” Finally, he states, “feedbacks between the mass balance of ice sheets and glaciers and volcanic activity need to be incorporated into future Earth-system models.”

Kravitz *et al.* (2011) focused on the ability of climate models to correctly represent volcanic aerosol forcing of climate. In June 2009, the Sarychev volcano in the Kamchatka Peninsula erupted explosively for a period of approximately five days. It injected 1.2 terragrams (Tg) of material into the atmosphere to an estimated height of as much as 16 km, nearly 10 miles. It was the second such eruption within a year. Taking advantage of this opportunity, Kravitz *et al.* studied measurements of the optical depth of the aerosol sulfates from the eruption and compared them with the projected output from a 20-member GCM ensemble, aiming to provide suggestions for improving the model’s capabilities. They used the National Aeronautics and Space Administration (NASA) Goddard Institute for Space Studies Model-E, a coupled atmosphere-ocean GCM with fairly coarse resolution in the horizontal (4° by 5° lat/lon) and vertical (23 layers). The model contained levels up to 80 km, necessarily including the stratosphere.

The control model run consisted of a 20-member suite globally over the period 2007–2010. In this experiment, 1.5 Tg of volcanic material was injected into the atmosphere at a point near Sarychev in 2008 of the model year. The observed aerosol measurements came from ground-based LIDARS at six locations around the world as well as satellite-based measurements that profile the aerosol concentration using scattered sunlight (Optical Spectrograph and Infrared Imaging System (OSIRIS)).

The model did a reasonably good job spreading the volcanic material around the Northern Hemisphere, but there were some important discrepancies between the model and observations

(see Figure 2.6.6.1). The model transported the material too quickly into the tropics and too slowly into the high latitudes. The authors speculate this error may highlight the need to improve the model’s stratospheric circulation. The model also tended to remove aerosols too quickly from the atmosphere, especially in the high latitudes, which may have been a function of the model overestimating particulate size. As shown in Figure 2.6.6.1, the modeled peak aerosol values occur one month earlier than observed and then decrease in concentration too quickly. The work of Kravitz *et al.* highlights the difficulty of developing climate models that accurately represent the influence of volcanic-induced aerosols on climate, where the likely impact on surface temperature from the Kravitz *et al.* experiment would be a bias toward warm temperatures on the time scale of months.

Clearly there remain significant uncertainties and disagreements about the climatic effects of volcanic eruptions, showing a need for further research into this topic.

References

- Briffa, K.R., Jones, P.D., Schweingruber, F.H., and Osborn, T.J. 1998. Influence of volcanic eruptions on Northern Hemisphere summer temperature over the past 600 years. *Nature* **393**: 450–454.
- Douglass, D.H. and Knox, R.S. 2005. Climate forcing by the volcanic eruption of Mount Pinatubo. *Geophysical Research Letters* **32**: 10.1029/2004GL022119.
- Huybers, P. and Langmuir, C. 2009. Feedback between deglaciation, volcanism, and atmospheric CO₂. *Earth and Planetary Science Letters* **286**: 479–491.
- Hyde, W.T. and Crowley, T.J. 2000. Probability of future climatically significant volcanic eruptions. *Journal of Climate* **13**: 1445–1450.
- Jellinek, A.M., Manga, M., and Saar, M.O. 2004. Did melting glaciers cause volcanic eruptions in eastern California? Probing the mechanics of dike formation. *Journal of Geophysical Research* **109**: 10.1029/2004JB002978.
- Kravitz, B., Robock, A., Bourassa, A., Deshler, T., Wu, D., Mattis, I., Finger, F., Hoffmann, A., Ritter, C., Bitar, L., Duck, T.J., and Barnes, J.E. 2011. Simulation and observations of stratospheric aerosols from the 2009 Sarychev volcanic eruption. *Journal of Geophysical Research—Atmospheres* **116**: D18211, doi:10.1029/2010JD015501.

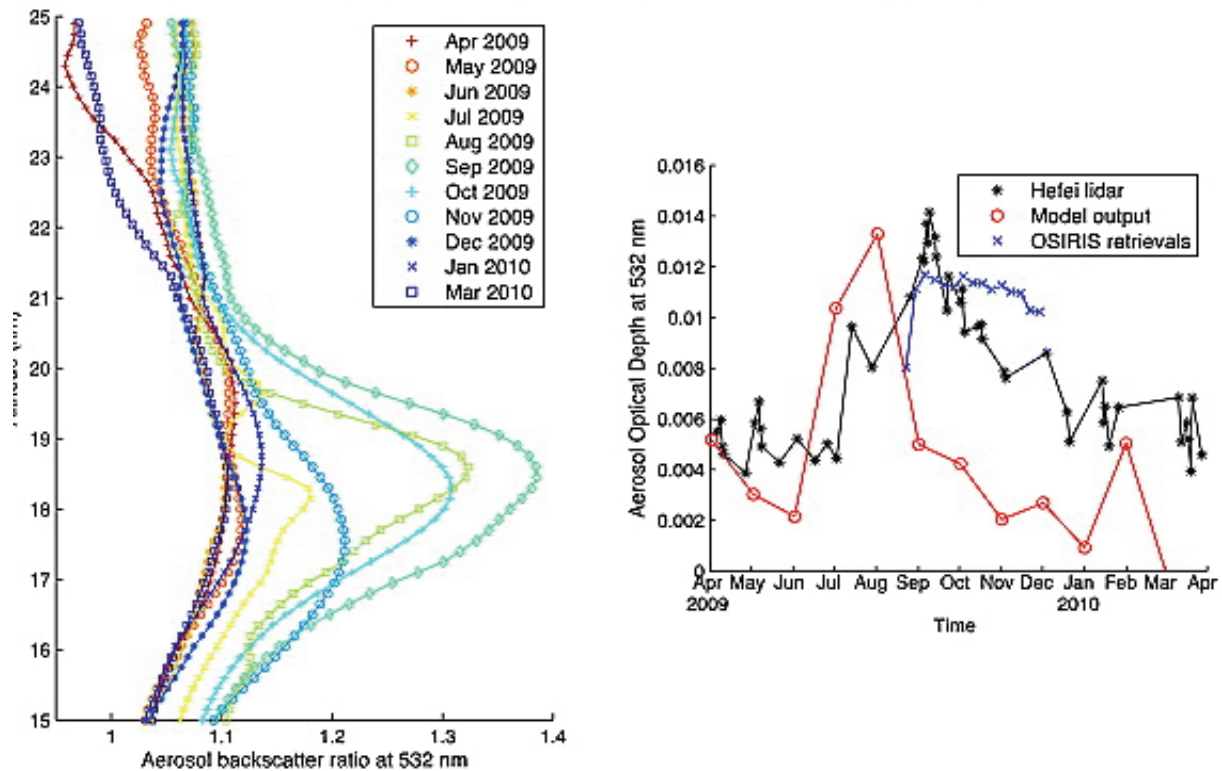


Figure 2.6.6.1. The LIDAR retrievals from Hefei, China as compared to model output and OSIRIS retrievals. (left) The monthly averages of backscatter as a function of altitude maximizing in September 2009. (right) The integrated (15–25 km) optical depth through the stratosphere for the LIDAR data (black), zonally averaged stratospheric aerosol optical depth calculated by the model in the grid latitude containing the Hefei LIDAR (28°–32°N) (red), and OSIRIS retrievals zonally averaged over the latitude band 30°–35°N (blue). Reprinted with permission from Kravitz, B., Robock, A., Bourassa, A., Deshler, T., Wu, D., Mattis, I., Finger, F., Hoffmann, A., Ritter, C., Bitar, L., Duck, T.J., and Barnes, J.E. 2011. Simulation and observations of stratospheric aerosols from the 2009 Sarychev volcanic eruption. *Journal of Geophysical Research—Atmospheres* **116**: D18211, doi:10.1029/2010JD015501, Figure 11.

Lindzen, R.S., Chou, M.-D., and Hou, A.Y. 2001. Does the Earth have an adaptive infrared iris? *Bulletin of the American Meteorological Society* **82**: 417–432.

Lindzen, R.S. and Giannitsis, C. 1998. On the climatic implications of volcanic cooling. *Journal of Geophysical Research* **103**: 5929–5941.

Lindzen, R.S. and Giannitsis, C. 2002. Reconciling observations of global temperature change. *Geophysical Research Letters* **29**: 10.1029/2001GL014074.

MacLennan, J., Jull, M., McKenzie, D.P., Slater, L., and Gronvold, K. 2002. The link between volcanism and deglaciation in Iceland. *Geochemistry, Geophysics, Geosystems* **3**: 10.1029/2001GC000282.

Nowell, D., Jones, C., and Pyle, D. 2006. Episodic quaternary volcanism in France and Germany. *Journal of Quaternary Science* **21**: 645–675.

Sadler, J.P. and Grattan, J.P. 1999. Volcanoes as agents of past environmental change. *Global and Planetary Change* **21**: 181–196.

Sassen, K. 1992. Evidence for liquid-phase cirrus cloud formation from volcanic aerosols: Climate indications. *Science* **257**: 516–519.

Tuffen H. 2010. How will melting of ice affect volcanic hazards in the twenty-first century? *Philosophical Transactions of the Royal Society A* **368**: 2535–2558.