2

Feedback Factors and Radiative Forcing

Introduction

According to the Intergovernmental Panel on Climate Change (IPCC), "the combined radiative forcing due to increases in carbon dioxide, methane, and nitrous oxide is +2.30 [+2.07 to +2.35] W m^{-2}, and its rate of increase during the industrial era is *very likely* to have been unprecedented in more than 10,000 years [italics in the original]" (IPCC, 2007-I, p. 3). The IPCC calculates that this sensitivity of earth's climate system to greenhouse gases (GHG) means that if CO_2 concentrations were to double, the rise in global average surface temperature "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]" (Ibid., p. 12).

Many scientific studies suggest this model-derived sensitivity is too large and feedbacks in the climate system reduce it to values that are an order of magnitude smaller. This chapter reviews those feedbacks most often mentioned in the scientific literature, some of which have the ability to totally offset the radiative forcing expected from the rise in atmospheric CO_2.

Additional information on this topic, including reviews of feedback factors not discussed here, can be found at http://www.co2science.org/subject/f/subject_f.php under the heading Feedback Factors.

References

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., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller. (Eds.) Cambridge University Press, Cambridge, UK.

2.1. Clouds

Based on data obtained from the Tropical Ocean Global Atmosphere—Coupled Ocean-Atmosphere Response Experiment, Sud *et al*. (1999) demonstrated that deep convection in the tropics acts as a thermostat to keep sea surface temperature (SST) oscillating between approximately 28° and 30°C. Their analysis suggests that as SSTs reach 28°-29°C, the cloud-base airmass is charged with the moist static energy needed for clouds to reach the upper troposphere, at which point the cloud cover reduces the amount of solar radiation received at the surface of the sea, while cool and dry downdrafts promote ocean surface cooling by increasing sensible and latent heat fluxes there. This "thermostat-like control," as Sud *et al*. describe it, tends "to ventilate the tropical ocean efficiently and help contain the SST between 28°-30°C." The phenomenon would

also be expected to prevent SSTs from rising any higher in response to enhanced CO_2-induced radiative forcing.

Lindzen *et al*. (2001) used upper-level cloudiness data obtained from the Japanese Geostationary Meteorological Satellite and SST data obtained from the National Centers for Environmental Prediction to derive a strong inverse relationship between upper-level cloud area and the mean SST of cloudy regions of the eastern part of the western Pacific (30°S-30°N; 130°E-170°W), such that the area of cirrus cloud coverage normalized by a measure of the area of cumulus coverage decreases about 22 percent per degree C increase in the SST of the cloudy region. In describing this phenomenon, Lindzen *et al*. say "the cloudy-moist region 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 findings of Lindzen *et al.* were subsequently criticized by Hartmann and Michelsen (2002) and Fu *et al*. (2002), and then Fu *et al.* were rebutted by Chou *et al*. (2002), an exchange that is summarized in Section 1.2 of this report. The debate over the infrared adaptive iris still rages in the scientific community, but Lindzen and his colleagues are not the only scientists who believe the cooling effect of clouds has been underestimated.

Croke *et al*. (1999) used land-based observations of cloud cover for three regions of the United States (coastal southwest, coastal northeast, and southern plains) to demonstrate that, over the period 1900-1987, cloud cover had a high correlation with global air temperature, with mean cloud cover rising from an initial value of 35 percent to a final value of 47 percent as the mean global air temperature rose by 0.5°C.

Herman *et al*. (2001) used Total Ozone Mapping Spectrometer 380-nm reflectivity data to determine changes in radiation reflected back to space over the period 1979 to 1992, finding that "when the 11.3-year solar-cycle and ENSO effects are removed from the time series, the zonally averaged annual linear-fit trends show that 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." The overall long-term effect was an increase in radiation reflected back to space of 2.8 Wm^{-2} per decade, which represents a large cloud-induced cooling influence.

Rosenfeld (2000) used satellite data obtained from the Tropical Rainfall Measuring Mission to look for terrestrial analogues of the cloud trails that form in the wakes of ships at sea as a consequence of their emissions of particulates that redistribute cloud-water into larger numbers of smaller droplets that do not rain out of the atmosphere as readily as they would in the absence of this phenomenon. Visualizations produced from the mission data clearly revealed the existence of enhanced cloud trails downwind of urban and industrial complexes in Turkey, Canada, and Australia, to which Rosenfeld gave the name *pollution tracks* in view of their similarity to *ship tracks*. Rosenfeld also demonstrated that the clouds comprising these pollution tracks were composed of droplets of reduced size that did indeed suppress precipitation by inhibiting further coalescence and ice precipitation formation. As Toon (2000) noted in a commentary on this study, these smaller droplets will not "rain out" as quickly and will therefore last longer and cover more of the earth, both of which effects tend to cool the globe.

In summation, as the earth warms, the atmosphere has a tendency to become more cloudy, which exerts a natural brake upon the rising temperature. Many of man's aerosol-producing activities tend to do the same thing. Hence, there appear to be a number of cloud-mediated processes that help the planet "keep its cool."

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/f/feedbackcloud.php.

References

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.

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.

Hartmann, D.L. and Michelsen, M.L. 2002. No evidence for IRIS. *Bulletin of the American Meteorological Society* **83**: 249-254.

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.

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.

Rosenfeld, D. 2000. Suppression of rain and snow by urban and industrial air pollution. *Science* **287**: 1793-1796.

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.

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

2.2. Carbonyl Sulfide

Some time ago, Idso (1990) suggested that 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 and thereby cooling the planet and providing a natural brake on the tendency for anthropogenically enhanced greenhouse gases to drive global warming. (See Section 2.7.) On the basis of experiments that showed soil DMS emissions to be positively correlated with soil organic matter content, and noting that additions of organic matter to soils tend to increase the amount of sulfur gases they emit, Idso hypothesized that because atmospheric CO_2 enrichment augments plant growth and, as a result, vegetative inputs of organic matter to earth's soils, 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 that tends to cool the planet.

Two years later, Idso (1992) expanded this concept to include carbonyl sulfide (OCS), another biologically produced sulfur gas that is emitted from soils, noting that it too is likely to be emitted in increasingly greater quantities as earth's vegetation responds to the aerial fertilization effect of the ongoing rise in the air's CO_2 content, while pointing out that OCS is relatively inert in the troposphere, but that it eventually makes its way into the stratosphere, where it is transformed into solar-radiation-reflecting sulfate aerosol particles. He consequently concluded that the CO_2-induced augmentation of soil OCS emissions constitutes a mechanism that can cool the planet's surface (1) in the absence of an impetus for warming, (2) without producing additional clouds or (3) making them any brighter.

What have we subsequently learned about biologically mediated increases in carbonyl sulfide emissions? One important thing is that the OCS-induced cooling mechanism also operates at sea, just as the DMS-induced cooling mechanism does, and that it too possesses a warming-induced component in addition to its CO_2-induced component.

In a study contemporary with that of Idso (1992), ocean-surface OCS concentrations were demonstrated by Andreae and Ferek (1992) to be highly correlated with surface-water primary productivity. So strong is this correlation, in fact, that Erickson and Eaton (1993) developed an empirical model for computing ocean-surface OCS concentrations based solely on surface-water chlorophyll concentrations and values of incoming solar radiation. It has also been learned that an even greater portion of naturally produced OCS 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). Hence, the majority of the tropospheric burden of OCS is ultimately dependent upon photosynthetic activity occurring near the surface of the world's oceans.

This is important because the tropospheric OCS 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. This is a sizeable increase; and Aydin *et al*. (2002) note that only a fourth of it can be attributed to anthropogenic sources. Consequently, the rest of the observed OCS increase must have had a natural origin, a large portion of which must have ultimately been derived from the products and byproducts of marine photosynthetic activity, which must have increased substantially over the past three centuries. A solid case can be made for the proposition that both the increase in atmospheric CO_2 concentration and the increase in temperature experienced over this period were the driving forces for the concomitant increase in tropospheric OCS concentration and its likely subsequent transport to the stratosphere, where it could exert a cooling influence on the earth and that may have kept the warming of the globe considerably below what it might otherwise have been in the absence of this chain of events.

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

The first portion of this response can be explained by the fact that most terrestrial plants prefer much warmer temperatures than a mere 3°C, so that as their surroundings warm and they grow better, they extract more OCS from the atmosphere in an attempt to promote even more warming and grow better still. At the point where warming becomes a detriment to them, however, they reverse this course of action and begin to rapidly reduce their rates of OCS absorption in an attempt to forestall warming-induced death. And since the consumption of OCS by lichens is under the physiological control of carbonic anhydrase—which is the key enzyme for OCS uptake in all higher plants, algae, and soil organisms—we could expect this phenomenon to be generally operative over most of the earth. Hence, this thermoregulatory function of the biosphere may well 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 increases in greenhouse gas concentrations, produce an impetus for it to do so.

Clearly, this multifaceted phenomenon is extremely complex, with different biological entities tending to both increase and decrease atmospheric OCS concentrations at one and the same time, while periodically reversing directions in this regard in response to climate changes that push the temperatures of their respective environments either above or below the various thermal optima at which they function best. This being the case, there is obviously much more we need to learn about the many plant physiological mechanisms that may be involved.

State-of-the-art climate models totally neglect the biological processes we have described here. Until we fully understand the ultimate impact of the OCS cycle on climate, and then incorporate them into the climate models, we cannot be certain how much of the warming experienced during the twentieth century, if any, can be attributed to anthropogenic causes.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/c/carbonylsulfide.php.

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.

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.

Khalil, M.A.K. and Rasmussen, R.A. 1984. Global sources, lifetimes, and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS_2) 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.

2.3. Diffuse Light

The next negative feedback phenomenon is diffused light. It operates through a chain of five linkages, triggered by the incremental enhancement of the atmosphere's greenhouse effect that is produced by an increase in the air's CO_2 content. The first linkages is the proven propensity for higher levels of atmospheric CO_2 to enhance vegetative productivity, which phenomena are themselves powerful negative feedback mechanisms of the type we envision. Greater CO_2-enhanced photosynthetic rates, for

example, enable plants to remove considerably more CO_2 from the air than they do under current conditions, while CO_2-induced increases in plant water use efficiency allow plants to grow where it was previously too dry for them. (See Chapter 7 for extensive documentation of this phenomenon.) This establishes a potential for more CO_2 to be removed from the atmosphere by increasing the abundance of earth's plants and increasing their robustness.

The second linkage of the feedback loop is the ability of plants to emit gases to the atmosphere that are ultimately converted into "biosols," i.e., aerosols that owe their existence to the biological activities of earth's vegetation, many of which function as cloud condensation nuclei. It takes little imagination to realize that since the existence of these atmospheric particles is dependent upon the physiological activities of plants and their associated soil biota, the CO_2-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 which 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 the 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 finally produces the end result: a greater biological extraction of CO_2 from the air and the subsequent sequestration of its carbon, compliments of the intensified diffuse-light-driven increase in total canopy photosynthesis and subsequent transfers of the extra fixed carbon to plant and soil storage reservoirs.

How significant is this multi-link process? Roderick *et al*. (2001) provide a good estimate based on the utilization of a unique "natural experiment," a technique that has been used extensively by Idso (1998) to evaluate the climatic sensitivity of the entire planet. Specifically, 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 the 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 concluded that the Mt. Pinatubo eruption may well 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 CO_2 concentration that year by about 1.2 ppm.

Interestingly, this reduction is about the magnitude of the real-world perturbation that was actually observed (Sarmiento, 1993). What makes this observation even more impressive is the fact that the CO_2 reduction was coincident with an El Niño event; because, in the words of Roderick et al., "previous and subsequent such events have been associated with *increases* in atmospheric CO_2." In addition, the observed reduction in total solar radiation received at the earth's surface during this period would have had a tendency to reduce the amount of photosynthetically active radiation incident upon earth's plants, which would also have had a tendency to cause the air's CO_2 content to rise, as it would tend to lessen global photosynthetic activity.

Significant support for the new negative feedback phenomenon was swift in coming, as the very next year a team of 33 researchers published the results of a comprehensive study (Law *et al*., 2002) that compared seasonal and annual values of CO_2 and water vapor exchange across sites in forests, grasslands, crops and tundra—which are 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 reported that "net carbon uptake (net ecosystem exchange, the net of photosynthesis and respiration) was greater under diffuse than under direct radiation conditions," and in discussing this finding, which is the centerpiece of the negative feedback phenomenon we describe, they noted that "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)." More importantly, they also reported that "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]." In fact, they wrote that "Hollinger *et al*. (1994) found that daily net CO_2 uptake was greater on cloudy days, even though total PPFD was 21-45 percent lower on cloudy days than on clear days."

One year later, Gu *et al*. (2003) reported that they "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," finding that in the eruption year of 1991, "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 that "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." Commenting on the significance of these observations, Gu *et al*. noted that "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."

In the preceding paragraph, we highlighted the fact that the diffuse-light-induced photosynthetic enhancement observed by Gu *et al*., in addition to likely being global in scope, was caused by volcanic aerosols acting under cloudless conditions. Our reason for calling attention to these two facts is to clearly distinguish this phenomenon from a closely related one that is also described by Gu *et al*.; i.e., the propensity for the extra diffuse light created by increased cloud cover to further enhance photosynthesis, even though the total flux of solar radiation received at the earth's surface may be reduced under such conditions. Based on still more real-world data, for example, Gu *et al*. note that "Harvard Forest photosynthesis also increases with cloud cover, with a peak at about 50 percent cloud cover."

Although very impressive, in all of the situations discussed above the source of the enhanced atmospheric aerosol concentration was a singular significant event—specifically, a massive volcanic eruption—but what we really need to know is what happens under more normal conditions. This was the new and important question addressed the following year in the study of Niyogi *et al*. (2004): "Can we detect the effect of relatively routine aerosol variability on field measurements of CO_2 fluxes, and if so, how does the variability in aerosol loading affect CO_2 fluxes over different landscapes?"

To answer this question, the group of 16 researchers used CO_2 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 CO_2 by three types of vegetation: trees (broadleaf deciduous forest and mixed forest), crops (winter wheat, soybeans, and corn), and grasslands. Their work revealed that an aerosol-induced increase in diffuse radiative-flux fraction [DRF = ratio of diffuse (Rd) to total or global (Rg) solar irradiance] increased the net CO_2 assimilation of trees and crops, making them larger carbon sinks, but that it decreased the net CO_2 assimilation of grasslands, making them smaller carbon sinks.

How significant were the effects observed by Niyogi *et al*.? For a summer mid-range Rg flux of 500 Wm^{-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 CO_2 assimilation by a broadleaf deciduous forest located in Tennessee, USA. Averaged over the entire daylight period, they further determined that 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. Hence, they concluded that natural variability among commonly present aerosols can "routinely influence surface irradiance and hence the terrestrial CO_2 flux and regional carbon cycle." And for these types of land-cover (forests and agricultural crops), that influence is to significantly increase the assimilation of CO_2 from the atmosphere.

In the case of grasslands, however, the effect was found to be just the opposite, with greater aerosol loading of the atmosphere leading to less CO_2 assimilation, due most likely, in the estimation of Niyogi *et al*., to grasslands' significantly different canopy architecture. With respect to the planet as a whole, however, the net effect is decidedly positive, as earth's trees are the primary planetary players in the sequestration of carbon. Post *et al*. (1990), for example, noted that woody plants account for approximately 75 percent of terrestrial photosynthesis, which comprises about 90 percent of the global total (Sellers and McCarthy, 1990); those numbers make earth's trees and shrubs responsible for fully two-thirds (0.75 x 90 percent = 67.5 percent) of the planet's net primary production.

What is especially exciting about these real-world observations is that much of the commonly-present aerosol burden of the atmosphere is plant-derived.

Hence, it can be appreciated that earth's woody plants are themselves responsible for emitting to the air that which ultimately enhances their own photosynthetic prowess. In other words, earth's trees significantly control their own destiny; i.e., they alter the atmospheric environment in a way that directly enhances their opportunities for greater growth.

Society helps too, in this regard, for as we pump ever more CO_2 into the atmosphere, the globe's woody plants quickly respond to its aerial fertilization effect, becoming ever more productive, which leads to even more plant-derived aerosols being released to the atmosphere, which stimulates this positive feedback cycle to a still greater degree. Stated another way, earth's trees use some of the CO_2 emitted to the atmosphere by society to alter the aerial environment so as to enable them to remove even more CO_2 from the air. The end result is that earth's trees and humanity are working hand-in-hand to significantly increase the productivity of the biosphere. This is happening in spite of all other insults to the environment that work in opposition to enhanced biological activity.

In light of these several observations, it is clear that the historical and still-ongoing CO_2-induced increase in atmospheric biosols should have had, and should be continuing to have, a significant cooling effect on the planet that exerts itself by both slowing the rate of rise of the air's CO_2 content and reducing the receipt of solar radiation at the earth's surface. Neither of these effects is fully and adequately included in any general circulation model of the atmosphere of which we are aware.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/f/feedbackdiffuse.php.

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. CO_2-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 CO_2 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 CO_2 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.

2.4. Iodocompounds

The climatic significance of iodinated compounds or iodocompounds was first described in the pages of *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." Specifically, the team used a smog chamber operated under coastal atmospheric conditions to demonstrate, as they report, that "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 that concentrations of condensable iodine-containing vapors over the open ocean "are sufficient to influence marine particle formation."

The significance of this work is that 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), which demonstrates that 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, as O'Dowd *et al*. continue, "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 that "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 picophytoprokaryotes 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." In doing so, 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 report "can account for >80 percent of the variability in the methyl iodide concentrations." They add that 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 say "is a large fraction of the total estimated global flux of iodine (10^{11}-10^{12} g I year^{-1})." This observation is extremely important, because volatile iodinated compounds, in Smythe-Wright *et al*.'s words, "play a part in the formation of new particles and cloud condensation nuclei (CCN)," and because "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." More specifically, they suggest that "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," which, as previously noted, tend to counteract global warming.

Most recently, as part of the Third Pelagic Ecosystem CO_2 Enrichment Study, Wingenter *et al*. (2007) investigated the effects of atmospheric CO_2

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 Espegrend, Norway. Three of these mesocosms were maintained at ambient levels of CO_2 (~375 ppm or base CO_2), three were maintained at levels expected to prevail at the end of the current century (760 ppm or $2xCO_2$), and three were maintained at levels predicted for the middle of the next century (1150 ppm or $3xCO_2$). During the 25 days of this experiment, the researchers followed the development and subsequent decline of an induced bloom of the coccolithophorid *Emiliania huxleyi*, carefully measuring several physical, chemical, and biological parameters along the way. This work revealed that the iodocarbon chloroiodomethane (CH_2CII) experienced its peak concentration about six to 10 days after the coccolithophorid's chlorophyll-a maximum, and that its estimated abundance was 46 percent higher in the $2xCO_2$ mesocosms and 131 percent higher in the $3xCO_2$ mesocosms.

The international team of scientists concluded that the differences in the CH_2CII concentrations "may be viewed as a result of changes to the ecosystems as a whole brought on by the CO_2 perturbations." And 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), it can be appreciated that the CO_2-induced stimulation of the 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.

In conclusion, as Wingenter *et al*. sum things up, the processes described above "may help contribute to the homeostasis of the planet." And the finding of O'Dowd *et al*. that changes in cloud albedo "associated with global change" can lead to an increase in global radiative forcing that is "similar in magnitude, but opposite in sign, to the forcing induced by greenhouse gases," suggests that CO_2-induced increases in marine iodocarbon emissions likely contribute to maintaining that homeostasis.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/f/feedbackiodo.php.

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.

Laturnus, 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_2CII: Potential climate impacts. *Geophysical Research Letters* **34**: 10.1029/2006GL028139.

2.5. Nitrous Oxide

One of the main sources of nitrous oxide (N_2O) is agriculture, which accounts for almost half of N_2O emissions in some countries (Pipatti, 1997). With N_2O originating from microbial N cycling in soil—mostly from aerobic nitrification or from anaerobic denitrification (Firestone and Davidson, 1989)—there is a concern that CO_2-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 N_2O emissions from agricultural soils as the air's CO_2 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 CO_2, while measuring harvestable biomass production and N_2O evolution from the mesocosm soils over the course of three crop cuttings. This work revealed that the total harvestable biomass production of *P. pratense* was enhanced by the experimental doubling of the air's CO_2 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 that after emergence of the mixed stand and during vegetative growth before the first harvest and N fertilization, N_2O fluxes were higher under ambient CO_2 in both the low and moderate soil N treatments. In fact, it was not until the water table had been raised and extra fertilization given after the first harvest that the elevated CO_2 seemed to increase N_2O fluxes. The four Finnish researchers thus concluded that the mixed stand of *P. pratense* and *T. pratense* was "able to utilize the increased supply of atmospheric CO_2 for enhanced biomass production without a simultaneous increase in the N_2O fluxes," thereby raising "the possibility of maintaining N_2O emissions at their current level, while still enhancing the yield production [via the aerial fertilization effect of elevated CO_2] even under low N fertilizer additions."

In a similar study, Kettunen *et al*. (2007b) grew timothy (*Phleum pratense*) in monoculture within sandy-soil-filled mesocosms located within greenhouses maintained at atmospheric CO_2 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 N_2O from the mesocosms, vegetative net CO_2 exchange, and final above- and below-ground biomass production over the course of three harvests. In this experiment the elevated CO_2 concentration increased the net CO_2 exchange of the ecosystems (which phenomenon was primarily driven by CO_2-induced increases in photosynthesis) by about 30 percent, 46 percent and 34 percent at the low, moderate, and high soil N levels, respectively, while it 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. And once again, Kettunen *et al*. report that "an explicit increase in N_2O fluxes due to the elevated atmospheric CO_2 concentration was not found."

Welzmiller *et al*. (2008) measured N_2O and denitrification emission rates in a C_4 sorghum [*Sorghum bicolor* (L.) Moench] production system with ample and limited flood irrigation rates under Free-Air CO_2 Enrichment (seasonal mean = 579 ppm) and control (seasonal mean = 396 ppm) CO_2 during the 1998 and 1999 summer growing seasons at the experimental FACE site near Maricopa, Arizona (USA). The study found "elevated CO_2 did not result in increased N_2O or N-gas emissions with either ample or limited irrigation," which findings 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."

In discussing the implications of their findings, Welzmiller *et al*. say their results suggest that "as CO_2 concentrations increase, there will not be major increases in denitrification in C_4 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.

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 N_2O and methane (CH_4). This they did in the Tapajos National Forest near Santarem, Brazil, by modifying 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; then, after initiating the throughfall-exclusion treatment, they continued their measurements for an additional three years. This work revealed that the "drier soil conditions caused by throughfall exclusion inhibited N_2O and CH_4 production and promoted CH_4 consumption." In fact, they report that "the exclusion manipulation lowered annual N_2O emissions by >40 percent and increased rates of consumption of

atmospheric CH_4 by a factor of >4," which results they attributed to the "direct effect of soil aeration on denitrification, methanogenesis, and methanotrophy."

Consequently, if global warming would indeed increase the frequency and/or intensity of El Niño events as some claim it will, the results of this study suggest that the anticipated drying of the Amazon Basin would initiate a strong negative feedback via (1) large drying-induced reductions in the evolution of both N_2O and CH_4 from its soils, and (2) a huge drying-induced increase in the consumption of CH_4 by its soils. Although Davidson *et al.* envisage 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" (an extreme response that would be expected to increase N_2O and CH_4 emissions), we note that the projected rise in the air's CO_2 content would likely prohibit such a thing from ever occurring, due to the documented tendency for atmospheric CO_2 enrichment to greatly increase the water use efficiency of essentially all plants, which would enable the forest to continue to flourish under significantly drier conditions than those of the present.

In summation, it would appear that concerns about additional global warming arising from enhanced N_2O emissions from agricultural soils in a CO_2-enriched atmosphere of the future are not well founded.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/n/nitrousoxide.php

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 CO_2. *Soil Biology and Biochemistry* **34**: 1777-1784.

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 N_2O 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.

Kettunen, R., Saarnio, S., Martikainen, P.J. and Silvola, J. 2007a. Can a mixed stand of N_2-fixing and non-fixing plants restrict N_2O emissions with increasing CO_2 concentration? *Soil Biology & Biochemistry* **39**: 2538-2546.

Kettunen, R., Saarnio, S. and Silvola, J. 2007b. N_2O fluxes and CO_2 exchange at different N doses under elevated CO_2 concentration in boreal agricultural mineral soil under *Phleum pratense*. *Nutrient Cycling in Agroecosystems* **78**: 197-209.

Mosier, A.R., Morgan, J.A., King, J.Y., LeCain, D. and Milchunas, D.G. 2002. Soil-atmosphere exchange of CH_4, CO_2, NO_X, and N_2O in the Colorado shortgrass steppe under elevated CO_2. *Plant and Soil* **240**: 201-211.

Pipatti, R. 1997. Suomen metaani-ja dityppioksidipaastojen rajoittamisen mahdollisuudet ja kustannustehokkuus. VTT tiedotteita. 1835, Espoo, 62 pp.

Welzmiller, 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.

2.6. Methane

What impact do global warming, the ongoing rise in the air's carbon dioxide (CO_2) content and a number of other contemporary environmental trends have on the atmosphere's methane (CH_4) concentration? The implications of this question are huge because methane is a more powerful greenhouse gas, molecule for molecule, than is carbon dioxide. Its atmospheric concentration is determined by the difference between how much CH_4 goes into the air (emissions) and how much comes out of it (extractions) over the same time period. 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 forces are ignored by the IPCC.

2.6.1. Extraction

Early indications that atmospheric CO_2 enrichment might significantly reduce methane emissions associated with the production of rice were provided by Schrope *et al*. (1999), who studied batches of rice growing in large vats filled with topsoil and placed within greenhouse tunnels maintained at atmospheric CO_2 concentrations of 350 and 700 ppm, each of

which tunnels was further subdivided into four sections that provided temperature treatments ranging from ambient to as much as 5°C above ambient. As would be expected, doubling the air's CO_2 content significantly enhanced rice biomass production in this system, increasing it by up to 35 percent above-ground and by up to 83 percent below-ground. However, in a truly unanticipated development, methane emissions from the rice grown at 700 ppm CO_2 were found to be 10 to 45 times less 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." Indeed, they report that "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.

In checking for potential problems with their experiment, Schrope *et al*. could find none. They thus stated that their results "unequivocally support the conclusion that, during this study, methane emissions from *Oryza sativa* [rice] plants grown under conditions of elevated CO_2 were dramatically reduced relative to plants gown in comparable conditions under ambient levels of CO_2," and to be doubly sure of this fact, they went on to replicate their experiment in a second year of sampling and obtained essentially the same results. Four years later, however, a study of the same phenomenon by a different set of scientists yielded a different result in 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 FACE study where the air's CO_2 concentration was increased 200 ppm above ambient. They found that the extra CO_2 "significantly increased the CH_4 [methane] emissions by 38 percent in 1999 and 51 percent in 2000," which phenomenon they attributed to "accelerated CH_4 production as a result of increased root exudates and root autolysis products and to the increased plant-mediated CH_4 emission because of the higher rice tiller numbers under FACE conditions." With such a dramatically different result from that of Schrope *et al*., many more studies likely will be required to determine which of these results is the more typical of rice culture around the world.

A somewhat related study was conducted by Kruger and Frenzel (2003), who note that "rice paddies contribute approximately 10-13 percent to the global CH_4 emission (Neue, 1997; Crutzen and Lelieveld, 2001)," and that "during the next 30 years rice production has to be increased by at least 60 percent to meet the demands of the growing human population (Cassman *et al*., 1998)." Because of these facts they further note that "increasing amounts of fertilizer will have to be applied to maximize yields [and] there is ongoing discussion on the possible effects of fertilization on CH_4 emissions."

To help promote that discussion, Kruger and Frenzel investigated the effects of N-fertilizer (urea) on CH_4 emission, production, and oxidation in rice culture in laboratory, microcosm and field experiments they conducted at the Italian Rice Research Institute in northern Italy. They report that in some prior studies "N-fertilisation stimulated CH_4 emissions (Cicerone and Shetter, 1981; Banik *et al*., 1996; Singh *et al*., 1996)," while "methanogenesis and CH_4 emission was found to be inhibited in others (Cai *et al*., 1997; Schutz *et al*., 1989; Lindau *et al*., 1990)," similar to the polarized findings of Schrope *et al*. and Inubushi *et al*. with respect to the effects of elevated CO_2 on methane emissions. In the mean, therefore, there may well be little to no change in overall CH_4 emissions from rice fields in response to both elevated CO_2 and increased N-fertilization. With respect to their own study, for example, Kruger and Frenzel say that "combining our field, microcosm and laboratory experiments we conclude that any agricultural praxis improving the N-supply to the rice plants will also be favourable for the CH_4 oxidising bacteria," noting that "N-fertilisation had only a transient influence and was counter-balanced in the field by an elevated CH_4 production." The implication of these findings is well articulated in the concluding sentence of their paper: "neither positive nor negative consequences for the overall global warming potential could be found."

Another agricultural source of methane is the fermentation of feed in the rumen of cattle and sheep. 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. With respect to cattle, Boadi et al. (2004) report that existing mitigation strategies for reducing CH_4 emissions from dairy cows include the

addition of ionophores and fats to their food, as well as the use of high-quality forages and grains in their diet, while newer mitigation strategies include "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." To this end, they provide a table of 20 such strategies, where the average maximum potential CH_4 reduction that may result from the implementation of each strategy is 30 percent or more.

With as many as 20 different mitigation strategies from which to choose, each one of which (on average) has the potential to reduce CH_4 emissions from dairy cows by as much as a third, it would appear there is a tremendous potential to dramatically curtail the amount of CH_4 released to the atmosphere by these ruminants and, by implication, the host of other ruminants that mankind raises and uses for various purposes around the world. Such high-efficiency approaches to reducing the strength of the atmosphere's greenhouse effect, while not reducing the biological benefits of elevated atmospheric CO_2 concentrations in the process, should be at the top of any program designed to achieve that difficult (but still highly questionable) objective.

In view of these several observations, 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, which could take a huge bite out of methane-induced global warming. But do methane emissions from natural vegetation respond in a similar way?

We have already discussed the results of Davidson *et al*. (2004) in our Nitrous Oxide section, which results suggest that a global warming-induced drying of the Amazon Basin would initiate a strong negative feedback to warming via (1) large drying-induced reductions in the evolution of N_2O and CH_4 from its soils and (2) a huge drying-induced increase in the consumption of CH_4 by its soils. In a contemporaneous study, Strack *et al*. (2004) also reported that 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 cries out for an analysis of how lowered water tables will affect peatland emissions of CH_4.

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 CO_2 content, CH_4 emissions would decline by 74-81 percent. In an attempt to obtain some experimental data on the subject, at various times over the period 2001-2003 Strack *et al*. measured CH_4 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.

At the conclusion of their study, the Canadian scientists reported that "methane emissions and storage were lower in the drained fen." The greatest reductions (up to 97 percent) were measured at the higher locations, while at the lower locations there was little change in CH_4 flux. Averaged over all locations, they determined that the "growing season CH_4 emissions at the drained site were 55 percent lower than the control site," indicative of the fact that the biosphere appears to be organized to resist warming influences that could push it into a thermal regime that might otherwise prove detrimental to its health.

In another experimental study, Garnet *et al*. (2005) grew seedlings of three emergent aquatic macrophytes (*Orontium aquaticum* L., *Peltandra virginica* L., and *Juncus effusus* L.) plus 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 CH_4 emitted by the plant foliage, along with net CO_2 assimilation rate and stomatal conductance, which were made to vary by changing the CO_2 concentration of the air surrounding the plants and the density of the photosynthetic photon flux impinging on them.

Methane emissions from the four wetland species increased linearly with increases in both stomatal conductance and net CO_2 assimilation rate; but the researchers found that changes in stomatal conductance affected foliage methane flux "three times more than equivalent changes in net CO_2 assimilation," making stomatal conductance the more significant of the two CH_4 emission-controllers. In addition, they note that evidence of stomatal control of CH_4 emission has also been reported for *Typha latifolia* (Knapp and Yavitt, 1995) and *Carex* (Morrissey *et al*., 1993), two other important wetland plants. Hence, since atmospheric CO_2 enrichment

leads to approximately equivalent—but oppositely directed—changes in foliar net CO_2 assimilation (which is increased) and stomatal conductance (which is reduced) in most herbaceous plants (which are the type that comprise most wetlands), it can be appreciated that the ongoing rise in the air's CO_2 content should be acting to *reduce* methane emissions from earth's wetland vegetation, because of the three-times-greater negative CH_4 emission impact of the decrease in stomatal conductance compared to the positive CH_4 emission impact of the equivalent increase in net CO_2 assimilation.

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 which 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 (Steudler *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), with forest soils—especially boreal and temperate forest upland soils (Whalen and Reeburgh, 1996)—appearing to be the most efficient in this regard (Le Mer and Roger, 2001).

In an attempt to learn more about this subject, 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 that methane was absorbed by the soils of all three sites, being positively correlated with temperature, as has also 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 additionally—and even more strongly—positively correlated with the C/N ratio of the cypress plantations' soil organic matter. Based on these results, it can be appreciated that any global warming, CO_2-induced or natural, would produce two biologically mediated negative feedbacks to counter the increase in temperature: (1) a warming-induced increase in methane uptake from the atmosphere that is experienced by essentially all soils, and (2) an increase in soil methane uptake from the atmosphere that is produced by the increase in plant-litter C/N ratio that typically results from atmospheric CO_2 enrichment.

Another study that deals with this topic is that of Menyailo and Hungate (2003), who assessed the influence of six boreal forest species—spruce, birch, Scots pine, aspen, larch, and Arolla pine—on soil CH_4 consumption in the 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). They determined, in their words, that "soils under hardwood species (aspen and birch) consumed CH_4 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 CH_4 than the soils under the four conifers; under high soil moisture conditions they consumed 65 percent more. As for the implications of these findings, Pastor and Post (1988) have suggested, in the words of Menyailo and Hungate, that "changes in temperature and precipitation resulting from increasing atmospheric CO_2 concentrations will cause a northward migration of the hardwood-conifer forest border in North America." Consequently, if such a shifting of species does indeed occur, it will likely lead to an increase in methane consumption by soils and a reduction in methane-induced global warming potential, thereby providing yet another biologically mediated negative feedback factor that has yet to be incorporated into models of global climate change.

Last, we note that increases in the air's CO_2 concentration will likely lead to a net reduction in vegetative isoprene emissions, which, as explained in Section 7.7.1. under the heading of Isoprene, should also lead to a significant removal of methane from the atmosphere. Hence, as the air's CO_2 content—and possibly its temperature—continues to rise, we can expect to see a significant increase in the rate of methane removal from earth's atmosphere, which should help to reduce the potential for further global warming.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/m/methaneextract.php, http://www.co2science.org/subject/m/methaneag.php, and http://www.co2science.org/subject/m/methagnatural.php.

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.

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.

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.

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.

Dobbie, K.E. and Smith, K.A. 1996. Comparison of CH_4 oxidation rates in woodland, arable and set aside soils. *Soil Biology & Biochemistry* **28**: 1357-1365.

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.

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.

Inubushi, K., Cheng, W., Aonuma, S., Hoque, M.M., Kobayashi, K., Miura, S., Kim, H.Y. and Okada, M. 2003. Effects of free-air CO_2 enrichment (FACE) on CH_4 emission from a rice paddy field. *Global Change Biology* **9**: 1458-1464.

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 N_2O, CH_4, and CO_2 from tropical forest soils. *Journal of Geophysical Research* **91**: 11,791-11,802.

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.

Kruger, M. and Frenzel, P. 2003. Effects of N-fertilisation on CH_4 oxidation and production, and consequences for CH_4 emissions from microcosms and rice fields. *Global Change Biology* **9**: 773-784.

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.

Lindau, C.W., DeLaune, R.D., 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.

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.

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.

Mosier, A.R., Parton, W.J., Valentine, D.W., Ojima, D.S., Schimel, D.S. and Heinemeyer, O. 1997. CH_4 and N_2O fluxes in the Colorado shortgrass steppe. 2. Long-term impact of land use change. *Global Biogeochemical Cycles* **11**: 29-42.

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.

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

Pastor, J. and Post, W.M. 1988. Response of northern forests to CO_2-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.

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.

Roulet, N., Moore, T., Bubier, J. and Lafleur, P. 1992. Northern fens: Methane flux and climatic change. *Tellus Series B* **44**: 100-105.

Saari, A., Heiskanen, J., 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.

Schrope, M.K., Chanton, J.P., Allen, L.H. and Baker, J.T. 1999. Effect of CO_2 enrichment and elevated temperature on methane emissions from rice, *Oryza sativa*. *Global Change Biology* **5**: 587-599.

Schutz, H., Holzapfel-Pschorrn, A., 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., 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.

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.

Steudler, P.A., Bowden, R.D., Meillo, J.M. and Aber, J.D. 1989. Influence of nitrogen fertilization on CH_4 uptake in temperate forest soils. *Nature* **341**: 314-316.

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.

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.

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 CH_4 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. CH_4 consumption in two temperate forest soils. *Biogeochemistry* **9**: 39-52.

2.6.2. Concentrations

In Section 2.6.1, we reported on several real-world phenomena that can act to reduce or extract methane (CH_4) from the atmosphere, most of which feedbacks are enhanced as the air's CO_2 concentration rises. That those feedbacks may already be operating and having a significant impact on global methane concentrations is illustrated in a discussion of observed atmospheric methane trends.

We begin with Figure 2.6.2.1, the graph of real-world data from Simpson *et al*. (2002), which clearly shows a linear-trend decline in CH_4 growth rates since the mid-1980s. The authors contended it was "premature to believe" the rate of growth was falling, even though their own data bore witness against them.

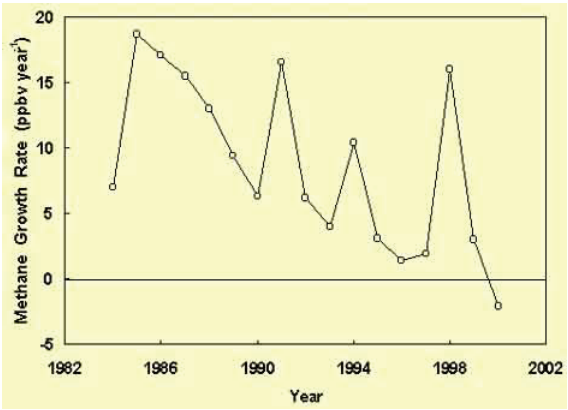

Figure 2.6.2.1. Global tropospheric methane (CH_4) growth rate vs. time. Adapted from Simpson *et al.* (2002).

The first of the 1990s' large CH_4 spikes is widely recognized as having been caused by the eruption of Mt. Pinatubo in June 1991 (Bekki *et al*., 1994;

Dlugokencky *et a*l., 1996; Lowe *et al*., 1997), while the last and most dramatic of the spikes has been linked to the remarkably strong El Niño of 1997-98 (Dlugokencky *et al*., 2001). As noted earlier, Dlugokencky *et al*. (1998), Francey *et al*. (1999), and Lassey *et al*. (2000) have all suggested that the annual rate-of-rise of the atmosphere's CH_4 concentration is indeed declining and leading to a cessation of growth in the atmospheric burden of methane.

Dlugokencky *et al*. (2003) revisited the subject with an additional two years' of data. Based on measurements from 43 globally distributed remote boundary-layer sites that were obtained by means of the methods of Dlugokencky *et al*. (1994), they defined an evenly spaced matrix of surface CH_4 mole fractions as a function of time and latitude, from which they calculated global CH_4 concentration averages for the years 1984-2002. We have extracted the results from their graphical presentation and re-plotted them as shown in Figure 2.6.2.2.

With respect to these data, Dlugokencky *et al*. note that the globally averaged atmospheric methane concentration "was constant at ~1751 ppb from 1999 through 2002," which suggests, in their words, that "during this 4-year period the global methane budget has been at steady state." They caution, however, that "our understanding is still not sufficient to tell if the prolonged pause in CH_4 increase is temporary or permanent." We agree. However, we feel confident in suggesting that if the recent pause in CH_4 increase is indeed temporary, it will likely be followed by a decrease in CH_4 concentration, since that would be the next logical step in the observed progression from significant, to much smaller, to no yearly CH_4 increase.

Khalil *et al*. (2007) essentially "put the nails in the coffin" of the idea that rising atmospheric CH_4 concentrations pose any further global warming threat at all. In their study, the three Oregon (USA) researchers combined two huge atmospheric methane datasets to produce the unified dataset depicted in Figure 2.6.2.3.

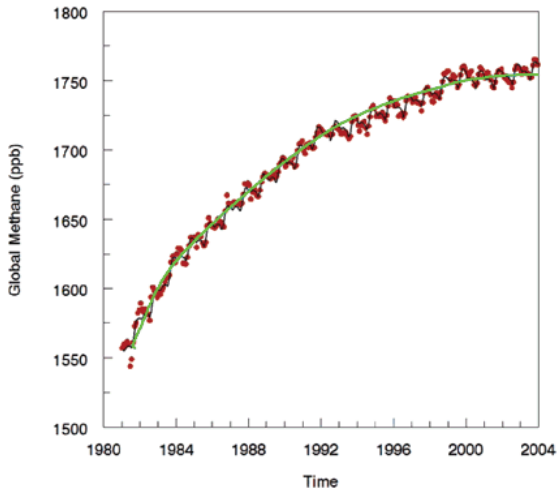

Figure 2.6.2.2. Global methane (CH_4) concentration. Adapted from Khalil *et al.* (2007).

In viewing this graph, to which we have added the smooth line, it is clear that the rate of methane increase in the atmosphere has dropped dramatically over time. As Khalil *et al*. describe it, "the trend has been decreasing for the last two decades until the present when it has reached near zero," and they go on to say that "it is questionable whether human activities can cause methane concentrations to increase greatly in the future."

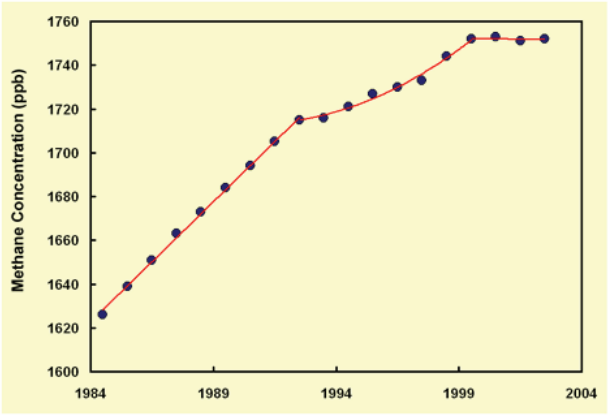

Figure 2.6.2.3. Global tropospheric methane (CH_4) concentration vs. time. Adapted from Dlugokencky *et al.* (2003).

One year later, Schnell and Dlugokencky (2008) provided 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.

Our adaptation of the graphical rendition of the data provided by the authors is presented in Figure 2.6.2.4.

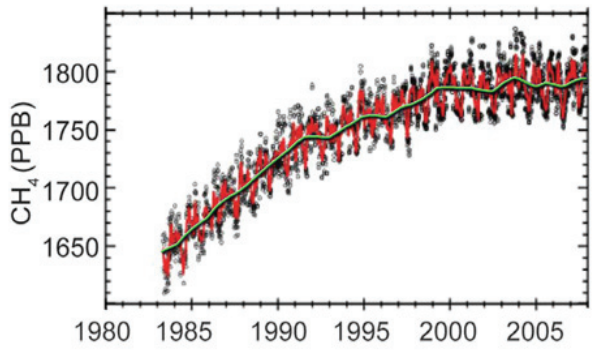

Figure 2.6.2.4. Trace gas mole fractions of methane (CH_4) as measured at Mauna Loa, Hawaii. Adapted from Schnell and Dlugokencky (2008).

In commenting on the data contained in the figure above, Schnell and Dlugokencky state that "atmospheric CH_4 has remained nearly constant since the late 1990s." This is a most important finding, because, as they also note, "methane's contribution to anthropogenic radiative forcing, including direct and indirect effects, is about 0.7 Wm^{-2}, about half that of CO_2." In addition, they say that "the increase in methane since the preindustrial era is responsible for approximately one-half the estimated increase in background tropospheric O_3 during that time."

Most recently, Rigby *et al*. (2008) analyzed methane data obtained from the Advanced Global Atmospheric Gases Experiment (AGAGE) and the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) over the period January 1997 to April 2008. The results of their analysis indicated that methane concentrations "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 mostly 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 8 and 12 ppb per year for the two measurement networks.

Although some people might be alarmed by these findings, as well as by the US, UK, and Australian researchers' concluding statement that the methane growth rate during 2007 "was significantly elevated at all AGAGE and CSIRO sites simultaneously for the first time in almost a decade," there is also reassurance in the recent findings. We note, for example, that near the end of 1998 and the beginning of 1999, both networks measured even larger methane growth rate increases of approximately 13 ppb per year, before dropping back to zero at the beginning of the new millennium. And we note that the most current displayed data from the two networks indicate the beginning of what could well be another downward trend.

Additional reassurance in this regard comes from the work of Simpson *et al*. (2002), the findings of whom we reproduced previously in Figure 2.6.2.1. As can be seen there, even greater methane growth rates than those observed by Rigby *et al*. occurred in still earlier years. Hence, these periodic one-year-long upward spikes in methane growth rate must be the result of some normal phenomenon, the identity of which has yet to be determined.

In light of these finding, it can be appreciated that over the past decade there have been essentially no increases in methane emissions to the atmosphere, and that the leveling out of the atmosphere's methane concentration—the exact causes of which, in the words of Schnell and Dlugokencky, "are still unclear"—has resulted in a one-third reduction in the combined radiative forcing that would otherwise have been produced by a continuation of the prior rates-of-rise of the concentrations of the two atmospheric greenhouse gases.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/m/methaneatmos.php.

References

Bekki, S., Law, K.S. and Pyle, J.A. 1994. Effect of ozone depletion on atmospheric CH_4 and CO concentrations. *Nature* **371**: 595-597.

Dlugokencky, E.J., Dutton, E.G., Novelli, P.C., Tans, P.P., Masarie, K.A., Lantz, K.O. and Madronich, S. 1996. Changes in CH_4 and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux. *Geophysical Research Letters* **23**: 2761-2764.

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.

Dlugokencky, E.J., Steele, L.P., Lang, P.M. and Masarie, K.A. 1994. The growth rate and distribution of atmospheric methane. *Journal of Geophysical Research* **99**: 17,021-17,043.

Dlugokencky, E.J., Walter, B.P., Masarie, K.A., Lang, P.M. and Kasischke, E.S. 2001. Measurements of an anomalous global methane increase during 1998. *Geophysical Research Letters* **28**: 499-502.

Ehhalt, D.H. and Prather, M. 2001. Atmospheric chemistry and greenhouse gases. In: *Climate Change 2001: The Scientific Basis*, Cambridge University Press, New York, NY, USA, pp. 245-287.

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 $\delta^{13}C$ 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 $\delta^{13}C$ and implications for constraints on the global methane budget. *Global Biogeochemical Cycles* **14**: 41-49.

Lowe, D.C., Manning, M.R., Brailsford, G.W. and Bromley, A.M. 1997. The 1991-1992 atmospheric methane anomaly: Southern hemisphere ^{13}C decrease and growth rate fluctuations. *Geophysical Research Letters* **24**: 857-860.

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.

2.7. Dimethyl Sulfide

More than two decades ago, Charlson *et al*. (1987) discussed the plausibility of a multi-stage negative feedback process, whereby warming-induced increases in the emission of dimethyl sulfide (DMS) from the world's oceans tend to counteract any initial impetus for warming. The basic tenet of their hypothesis was that 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 the 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 on which the droplets form (the more cloud condensation nuclei, the more and smaller the cloud droplets). And in completing the negative feedback loop, Charlson *et al*. noted that the cloud condensation nuclei concentration 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 hypothesis, much empirical evidence has been gathered in support of its several tenets. One review, for example, states that "major links in the feedback chain proposed by Charlson *et al*. (1987) have a sound physical basis," and that 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" (Ayers and Gillett, 2000).

But just how strong is the negative feedback phenomenon proposed by Charlson *et al*.? Is it powerful enough to counter the threat of greenhouse gas-induced global warming? According to the findings of Sciare *et al*. (2000), it may well be able to do just that.

In examining 10 years of DMS data from Amsterdam Island in the southern Indian Ocean, these researchers found that 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 that the degree of warming typically predicted to accompany a doubling of the air's CO_2 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.

Other research has shown that this same chain of events can be set in motion by means of phenomena not discussed in Charlson *et al*.'s original hypothesis. Simo and Pedros-Alio (1999), for example, discovered that the depth of the surface mixing-layer has a substantial influence on DMS yield in the short term, via a number of photo-induced (and thereby mixing-depth mediated) influences on several complex physiological phenomena, as do longer-term seasonal variations in vertical mixing, via their influence on seasonal planktonic succession scenarios and food-web structure.

More directly supportive of Charlson *et al*.'s hypothesis was the study of Kouvarakis and Mihalopoulos (2002), who measured seasonal variations of gaseous DMS and its oxidation products—non-sea-salt sulfate (nss-SO_4^{2-}) 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, 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. Such was also the case in the diurnal studies: DMS concentrations were lowest when it was coldest (just before sunrise), rose rapidly as it warmed thereafter to about 1100, after which they dipped slightly and then experienced a further rise to the time of maximum temperature at 2000, whereupon a decline in both temperature and DMS concentration set in that continued until just before sunrise. Consequently, because concentrations of DMS and its oxidation products (MSA and nss-SO_4^{2-}) rise dramatically in response to both diurnal and seasonal increases in SST, there is every reason to believe that the same negative feedback phenomenon would operate in the case of the long-term warming that could arise from increasing greenhouse gas concentrations, and that it could substantially mute the climatic impacts of those gases.

Also of note in this regard, 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, in their words, "further confirms the findings of Sciare *et al*. (2000)." In addition, the MS- anomalies in the rainwater were found to be closely related to SST anomalies; and 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, one of the most important DMS sources of the world."

In a newer study of this phenomenon, Toole and Siegel (2004) note that it has been shown to operate as described above 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 that modeled surface DMS concentrations are independent of chlorophyll and are a function of the mixed layer depth alone, which they call the "stress-forced regime." So how does the warming-induced DMS negative feedback cycle operate in these waters?

For oligotrophic regimes, Toole and Siegel find that "DMS biological production rates are negatively or insignificantly correlated with phytoplankton and bacterial indices for abundance and productivity while more than 82 percent 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)," who demonstrated that 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 that was 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 say that "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 that "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 within bounds conducive to the continued existence of life, in all its variety and richness. In addition, it has been suggested that a DMS-induced negative climate feedback phenomenon also operates 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 that additions of organic matter to a soil tend to increase the amount of sulfur gases emitted therefrom, Idso (1990) hypothesized that because atmospheric CO_2 is an effective aerial fertilizer, augmenting its atmospheric concentration and thereby increasing vegetative inputs of organic matter to earth's soils should also produce an impetus for cooling, even in the absence of surface warming.

Nevertheless, and in spite of the overwhelming empirical evidence for both land- and ocean-based DMS-driven negative feedbacks to global warming, the effects of these processes have not been fully incorporated into today's state-of-the-art climate models. Hence, the warming they predict in response to future anthropogenic CO_2 emissions must be considerably larger than what could actually occur in the real world. It is very possible these biologically driven phenomena could entirely compensate for the warming influence of all greenhouse gas emissions experienced to date, as well as all those anticipated to occur in the future.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/d/dms.php.

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.

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.

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.

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.

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.

Idso, S.B. 1990. A role for soil microbes in moderating the carbon dioxide greenhouse effect? *Soil Science* **149**: 179-180.

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.

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.

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.

2.8. Aerosols

2.8.1. Total Aerosol Effect

The IPCC estimates the net effect of all aerosols is to produce a cooling effect, with a total direct radiative forcing of -0.5 Wm^{-2} and an additional indirect cloud albedo forcing of -0.7 Wm^{-2} (IPCC, 2007-I, p. 4). However, the scientific literature indicates these estimates are too low. Many studies suggest the radiative forcing of aerosols may be as large as, or larger than, the radiative forcing due to atmospheric CO_2.

Vogelmann *et al*. (2003) report that "mineral aerosols have complex, highly varied optical properties that, for equal loadings, can cause differences in the surface IR flux between 7 and 25 Wm^{-2} (Sokolik *et al*., 1998)," and "only a few large-scale climate models currently consider aerosol IR [infrared] effects (e.g., Tegen *et al*., 1996; Jacobson, 2001) despite their potentially large forcing." In an attempt to persuade climate modelers to rectify this situation, they used high-resolution spectra to obtain the IR radiative forcing at the 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. As a result of this work, the scientists determined that "daytime surface IR forcings are often a few Wm^{-2} and can reach almost 10 Wm^{-2} for large aerosol loadings." These values, in their words, "are comparable to or larger than the 1 to 2 Wm^{-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."

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 major oceans. In general, this effort revealed that "aerosols reduce the annual-mean net downward solar flux by 5.4 Wm^{-2} at the top of the atmosphere, and by 5.9 Wm^{-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 Wm^{-2}, while it was more than 25 Wm^{-2} at the surface of the sea in the vicinity of Indonesia.

These latter results are similar to those obtained earlier by Wild (1999), who 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. This work revealed that 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 Wm^{-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 Wm^{-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, which is 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."

So which approach do climate models typically employ? "Unfortunately," according to Anderson *et al*., "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."

How significant is this choice? Anderson *et al*. report that the negative forcing of anthropogenic aerosols derived by forward calculation is "considerably greater" than that derived by inverse calculation; so much so, in fact, that if forward calculation is employed, the results "differ greatly" and "even the sign of the total forcing is in question," which implies that "natural variability (that is, variability not forced by anthropogenic emissions) is

much larger than climate models currently indicate." The bottom line, in the words of Anderson *et al*., is that "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 that the National Research Council (1979) concluded that "climate sensitivity [to CO_2 doubling] is likely to be in the range 1.5-4.5°C" and that "remarkably, despite some two decades of intervening work, neither the central value nor the uncertainty range has changed," Schwartz opined that this continuing uncertainty "precludes meaningful model evaluation by comparison with observed global temperature change or empirical determination of climate sensitivity," and that it "raises questions regarding claims of having reproduced observed large-scale changes in surface temperature over the 20th century."

Schwartz thus contends that 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 that 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." Indeed, he says "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," which surely suggests that even the best climate models of the day are wholly inadequate for this purpose.

Coming to much the same conclusion was the study of Jaenicke *et al*. (2007), who 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 lump together under the category of "dead biological matter."

With respect to the meteorological and climatic relevance of these particles, they note that 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 say "have now been carried out at several geographical locations covering all seasons of the year and many characteristic environments," Jaenicke *et al*. report that "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 that "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 say "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," and, consequently, that "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." However, they note that "the IPCC-Report of 2007 does not even mention these particles," and that "this disregard of the biological particles requires a new attitude."

We agree. Over much of the planet's surface, the radiative cooling influence of atmospheric aerosols (many of which are produced by anthropogenic activities) must prevail, suggesting a probable net anthropogenic-induced climatic signal that must be very close to zero and incapable of producing what the IPCC refers to as the "unprecedented" warming of the twentieth century. Either the air temperature record they rely on is in error or the warming, if real, is due to something other than anthropogenic CO_2 emissions.

Our review of important aerosol studies continues below with a separate discussion of four important aerosol categories: (1) Biological (Aquatic), (2) Biological (Terrestrial), (3) Non-Biological (Anthropogenic), and (4) Non-Biological (Natural). Additional information on this topic, including reviews of aerosols not discussed here, can be found at http://www.co2science.org/subject/a/subject_a. php under the heading Aerosols.

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.

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.

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.

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

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.

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. *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.

2.8.2. Biological (Aquatic)

Charlson *et al*. (1987) described a multi-stage negative feedback phenomenon, several components of which have been verified by subsequent scientific studies, that links biology with climate change. The process begins with an initial impetus for warming that stimulates primary production in marine phytoplankton. This enhanced process leads to the production of more copious quantities of dimethylsulphoniopropionate, which leads in turn to the evolution of greater amounts of dimethyl sulphide, or DMS, in the surface waters of the world's oceans. Larger quantities of DMS diffuse into the atmosphere, where the gas is oxidized, leading to the creation of greater amounts of acidic aerosols that function as cloud condensation nuclei. This phenomenon then leads to the creation of more and brighter clouds that reflect more incoming solar radiation back to space, thereby providing a cooling influence that counters the initial impetus for warming.

Several recent studies have shed additional light on this complex hypothesis. Simo and Pedros-Alio (1999) used satellite imagery and *in situ* experiments to study the production of DMS by enzymatic cleavage of dimethylsulphoniopropionate in the North Atlantic Ocean about 400 km south of Iceland, finding that 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 observations led them to conclude that "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 that 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 say, "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."

Ayers and Gillett (2000) summarized relevant empirical evidence collected at Cape Grim, Tasmania, along with pertinent evidence reported in many peer-reviewed scientific papers on this subject. They conclude that "major links in the feedback chain proposed by Charlson *et al*. (1987) have a sound

physical basis." More specifically, they noted 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."

Sciare *et al*. (2000) made continuous measurements of atmospheric DMS concentration over the 10-year period 1990-1999 at Amsterdam Island in the southern Indian Ocean. Their study revealed "a clear seasonal variation with a factor of 20 in amplitude between its maximum in January (austral summer) and minimum in July-August (austral winter)." In addition, they found DMS anomalies to be "closely related to sea surface temperature anomalies, clearly indicating a link between DMS and climate changes." They found that a temperature increase of only 1°C was sufficient to increase the atmospheric DMS concentration by as much as 50 percent on a monthly basis, noting that "this is the first time that a direct link between SSTs [sea surface temperatures] and atmospheric DMS is established for a large oceanic area."

Another pertinent study was conducted by Kouvarakis and Mihalopoulos (2002), who investigated the seasonal variations of gaseous DMS and its oxidation products—non-sea-salt sulfate (nss-SO_4^{2-}) 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 in September 1997. In the seasonal investigation, 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. Such was also the case in the diurnal study: DMS concentrations were lowest just before sunrise, rose rapidly thereafter to about 1100, were followed by a little dip and then a further rise to 2000, whereupon a decline set in that continued until just before sunrise. MSA concentrations exhibited a similar seasonal variation to that displayed by DMS, ranging from a wintertime low of 0.04 nmol m^{-3} to a summertime high of 0.99 nmol m^{-3}. The same was also true of aerosol nss-SO_4^{2-} which varied from 0.6 to 123.9 nmol m^{-3} in going from winter to summer.

A related study of methanesulfonate (MS^-) in rainwater at Amsterdam Island, by Baboukas *et al*. (2002), in the authors' words, "further confirms the findings of Sciare *et al*. (2000)." For more about that study and a newer study by Toole and Siegel (2004), see Section 2.7 of this report.

As time passes, more studies confirm the Charlson *et al*. hypothesis that as marine phytoplankton are exposed to rising temperatures, they give off greater quantities of gases that lead to the production of greater quantities of cloud condensation nuclei, which create more and brighter clouds, that reflect more incoming solar radiation back to space, and thereby either reverse, stop, or slow the warming that initiated this negative feedback phenomenon. The normal hour-to hour, day-to-day, and season-to-season behaviors of the phytoplanktonic inhabitants of earth's marine ecosystems seem to be effectively combating extreme environmental temperature changes.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/a/aerosolsbioaqua.php.

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.

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

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.

Hopke, P.K., Xie, Y. and Paatero, P. 1999. Mixed multiway analysis of airborne particle composition data. *Journal of Chemometrics* **13**: 343-352.

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.

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.

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.

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**: 10.1029/2004 GL019581.

2.8.3. Biological (Terrestrial)

Just as marine phytoplankton respond to rising temperatures by giving off 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 CO_2 content rises.

A good introduction to this subject is provided by the review paper of Peñuelas and Llusia (2003), who say 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 say 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." If this is indeed the case, it can be appreciated that with respect to the claimed ill effects of CO_2-induced global warming on earth's vegetation, there are likely to be two strong ameliorative phenomena that act to protect the planet's plants: (1) the aerial fertilization effect of atmospheric CO_2 enrichment, which is typically more strongly expressed at higher temperatures, and (2) the tendency for rising air temperatures and CO_2 concentrations to spur the production of higher concentrations of heat-stress-reducing BVOCs. With respect to temperature, Peñuelas and Llusia calculate that "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."

There may also be other phenomena that favor earth's plants within this context. Peñuelas and Llusia note that "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, since Peñuelas and Llusia report that additional numbers of "*Populus*, *Eucalyptus* or *Pinus*, which are major emitters, might greatly increase BVOC emissions."

Most intriguing of all, perhaps, is how increased BVOC emissions might impact climate change. Peñuelas and Llusia say that "BVOCs generate large quantities of organic aerosols that could affect climate significantly by forming cloud condensation nuclei." As a result, they say "there should be a net cooling of the Earth's surface during the day because of radiation interception," noting that 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 CO_2 concentrations, one example being Constable *et al*. (1999), who found no effect of elevated CO_2 on monoterpene emissions from Ponderosa pine and Douglas fir trees. Some studies, in fact, 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.

On the other hand, Staudt *et al*. (2001) observed CO_2-induced *increases* in BVOC emissions in the identical species of oak studied by Vuorinen *et al*. 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 CO_2 concentrations ranging from 250 to 750 ppm in 100-ppm increments for a period of four years—concluded that "BVOC emission can remain nearly constant as rising CO_2 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 tend to increase with atmospheric CO_2 enrichment; and the increases are often large.

Jasoni *et al*. (2003) who grew onions from seed for 30 days in individual cylindrical flow-through growth chambers under controlled environmental conditions at atmospheric CO_2 concentrations of either 400 or 1,000 ppm. At the end of the study, the plants in the CO_2-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 CO_2-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*. make a point of noting, "confer insect resistance against a major agricultural pest, spider mites." More generally, they conclude that "plants grown under elevated CO_2 will accumulate excess carbon and that at least a portion of this excess carbon is funneled into an increased production of BVOCs," which have many positive implications in the realms of both biology and climate, as noted above.

Raisanen *et al*. (2008) conducted an experiment designed to see to what extent a doubling of the air's CO_2 content and a 2°—6°C increase in air temperature might impact 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 CO_2 and ambient temperature, ambient temperature and elevated CO_2, ambient CO_2 and elevated temperature, elevated temperature and elevated CO_2—for the prior five years.

Over the five-month growing season of May-September, the three Finnish researchers found that total monoterpene emissions in the elevated-CO_2-only treatment were 5 percent greater than those in the ambient CO_2, ambient temperature treatment, and that emissions in the elevated-temperature-only treatment were 9 percent less than those in ambient air. In the presence of both elevated CO_2 *and* elevated temperature, however, 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."

A number of studies suggest that the phenomena discussed in the preceding paragraphs do indeed operate in the real world. Kavouras *et al*. (1998), for example, measured a number of atmospheric gases and particles in a eucalyptus forest in Portugal and analyzed their observations to see if there was any evidence of biologically produced gases being converted to particles that could function as cloud condensation nuclei. Their work demonstrated that certain hydrocarbons emitted by vegetation (isoprene and terpenes, in particular) do indeed experience gas-to-particle transformations. In fact, aerosols (or *bio*sols) 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. This work demonstrated, in their words, that 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 vapours released from the canopy."

Commenting on this finding, O'Dowd *et al*. note that "aerosol particles produced over forested areas may affect climate by acting as nuclei for cloud condensation," but they say there remain numerous uncertainties involving complex feedback processes "that must be determined if we are to predict future changes in global climate."

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 (OCS) in a dynamic cuvette system under controlled conditions in the laboratory. When optimally hydrated, OCS 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 OCS absorption dropped precipitously, reaching a value of zero at 35°C. Why is this significant?

OCS is the most stable and abundant reduced sulfur gas in the atmosphere and is thus 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 the earth as more and more of them collect above the tropopause. This being the case, biologically modulated COS concentrations may play a role in keeping earth's surface air temperature within bounds conducive to the continued existence of life, exactly what is implied by the observations of Kuhn and Kesselmeier.

Once air temperature rises above 25°C, the rate of removal of OCS from the air by this particular species of lichen declines dramatically. When this happens, more OCS remains in the air, which increases the potential for more OCS 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 the earth. Since the consumption of OCS by lichens is under the physiological control of carbonic anhydrase—which is the key enzyme for OCS uptake in all higher plants, algae, and soil organisms—we could expect this phenomenon to be generally operative throughout much of the plant kingdom. This biological "thermostat" may well 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 OCS, see Section 2.2 of this report.

Although BVOCs emitted from terrestrial plants both small and large are important to earth's climate, trees tend to dominate in this regard. Recent research suggests yet 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 the earth's surface (Suraqui *et al*., 1974; Abakumova *et al*., 1996), which is followed by the ability of enhanced diffuse lighting to reduce the volume of shade within vegetative canopies (Roderick *et al*., 2001), which is followed by the tendency for less internal canopy shading to enhance whole-canopy photosynthesis (Healey *et al*., 1998), which finally produces the end result: a greater photosynthetic extraction of CO_2 from the air and the 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 2.3 of this report. For example, Roderick *et al*. concluded that the Mt. Pinatubo eruption—a unique natural experiment to evaluate the overall climatic sensitivity of the planet—may well 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 CO_2-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 (O_3) (Chameides *et al*., 1988; Harley *et al*., 1999), but it is also responsible for *destroying* a lot of O_3. With respect to the latter phenomenon, Goldstein *et al*. mention three major routes by which O_3 exits the air near the 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 percent to 90 percent of total ecosystem O_3 uptake from the atmosphere (that is, O_3 destruction), while the remainder has typically been attributed to deposition on non-stomatal surfaces. However, they note that "Kurpius and Goldstein (2003) recently showed that the non-stomatal flux [from the atmosphere to oblivion] increased exponentially as a function of temperature at a coniferous forest site," and that "the exponential increase with temperature was consistent with the temperature dependence of monoterpene emissions from the same ecosystem, suggesting O_3 was lost via gas phase reactions with biogenically emitted terpenes before they could escape the forest canopy."

In a study designed to take the next step towards turning the implication of this observation into something stronger than a mere suggestion, Schade and Goldstein (2003) demonstrated that forest thinning dramatically enhances monoterpene emissions. In the current study, Goldstein *et al*. take another important step towards clarifying the issue by measuring the effect of forest thinning on O_3 destruction in an attempt to see if it is enhanced in parallel fashion to 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. Simultaneously, monoterpene mixing ratios and fluxes were measured hourly within the plantation canopy, while total ecosystem O_3 destruction was "partitioned to differentiate loss due to gas-phase chemistry from stomatal uptake and deposition."

Goldstein *et al*. report that both the destruction of ozone due to gas-phase chemistry and emissions of monoterpenes increased dramatically with the onset of thinning, and that these phenomena continued in phase with each other thereafter. Hence, they "infer that the massive increase of O_3 flux [from the atmosphere to oblivion] during and following mastication is driven by loss of O_3 through chemical reactions with unmeasured terpenes or closely related BVOCs whose emissions were enhanced due to wounding [by the masticator]." Indeed, they say that "considered together, these observations provide a conclusive picture that the chemical loss of O_3 is due to reactions with BVOCs emitted in a similar manner as terpenes," and that "we can conceive no other possible explanation for this behavior other than chemical O_3 destruction in and above the forest canopy by reactions with BVOCs."

Goldstein *et al*. say 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." If this proves to be the case, it will be a most important finding, for it would mean that 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 that the ongoing rise in the air's CO_2 content may well lead to an overall reduction in vegetative isoprene emissions, while at the same time enhancing vegetative productivity, which may well lead to an overall increase in vegetative terpene emissions. As a result, there is reason to believe that the ongoing rise in the air's CO_2 content will help to reduce the ongoing rise in the air's O_3 concentration, which should be a boon to the entire biosphere.

In conclusion, a wealth of real-world evidence is beginning to suggest that both rising air temperatures and CO_2 concentrations significantly increase desirable vegetative BVOC emissions, particularly from trees, which constitute the most prominent photosynthetic force on the planet, and that this phenomenon has a large number of extremely important and highly beneficial biospheric consequences.

These findings further demonstrate that the biology of the earth influences the climate of the earth. Specifically, 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 CO_2 and an increase in diffuse solar radiation, which leads to increased photosynthetic extraction of CO_2 from the air. In each case, the relationship is one that is self-protecting of the biosphere. This being the case, we wonder how anyone can presume to decide what should or should not be done about anthropogenic CO_2 emissions.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/a/aerosolsterr.php.

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 CO_2 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 CO_2 concentration and climate warming. *Global Change Biology* **5**: 255-267.

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., 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.

Idso, S.B. 1998. CO_2-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 CO_2 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.

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 O_3 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 CO_2 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 CO_2 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 vapours. *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 CO_2 and temperature on monoterpene emission of Scots pine (*Pinus sylvestris* L.). *Atmospheric Environment* **42**: 4160-4171.

Reichenau, T.G. and Esser, G. 2003. Is interannual fluctuation of atmospheric CO_2 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 CO_2 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 CO_2 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.

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 CO_2 concentration. *Atmospheric Environment* **38**: 675-682.

2.8.4. Non-Biological (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 that nearly all of the surface warming observed over the United States between 1975 and 1994 (0.54°C) may well be explained by aircraft-induced increases in cirrus cloud coverage over that period. If true, this result would imply that little to none of the observed U.S. warming over that period could be attributed to the concomitant increase in the air's CO_2 content.

Ship tracks, or bright streaks that form in layers of marine stratus clouds, are another example. They are created by emissions from ocean-going vessels; these persistent and highly reflective linear patches of low-level clouds generally tend to cool the planet (Ferek *et al*., 1998; Schreier *et al*., 2006). Averaged over the surface of the earth both day and night and over the year, Capaldo *et al*. (1999) calculated that this phenomenon creates a mean negative radiative forcing of -0.16 Wm^{-2} in the Northern Hemisphere and -0.06 Wm^{-2} in the Southern Hemisphere, which values are to be compared to the much larger positive radiative forcing of approximately 4 Wm^{-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 various competing hypotheses, finding that 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) found that 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." Likewise, outside of, but adjacent to, industrial complexes in the Po Valley of Italy, Facchini *et al*. (1999) found that water vapor was more likely to form on aerosols that had been altered by human-produced organic solutes, and that 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.

In a similar vein, Rosenfeld (2000) studied pollution tracks downwind of urban/industrial complexes in Turkey, Canada and Australia. His findings indicated that 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) pointed out that when clouds are composed of smaller droplets, they will not "rain out" as quickly and will therefore last longer and cover more of the 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 that droplet clouds "are the most important factor controlling the albedo (reflectivity) and hence the temperature of our planet." They say man-made 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 man-induced impetus for cooling] and its magnitude may be even larger than anticipated." They rightly warn that lack of inclusion of the consequences of 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."

Another assessment of the issue was provided by Ghan *et al*. (2001), who studied both the positive radiative forcings of greenhouse gases and the negative radiative forcings of anthropogenic aerosols and reported that current best estimates of "the total global mean present-day anthropogenic forcing range from 3 Wm^{-2} to -1 Wm^{-2}," which represents everything from a modest warming to a slight cooling. After performing their own analysis of the problem, they reduced the magnitude of this range somewhat but the end result still stretched from a small cooling influence to a modest impetus for warming. "Clearly," they concluded, "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."

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 the 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 ± 0.05 Wm^{-2} per year, equivalent to a reduction of 2.7 percent per decade, [which] now totals 20 Wm^{-2}." They also concluded that 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."

Although this surface-cooling influence is huge, it falls right 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 that "mean clear-sky solar radiative heating for the winters of 1998 and 1999 decreased at the ocean surface by 12 to 30 Wm^{-2}." Hence, the decline in solar radiation reception discovered by Stanhill and Cohen could well be real. And if it is, it represents a *tremendous* counter-influence to the enhanced greenhouse effect produced by the contemporaneous increase in atmospheric CO_2 concentration.

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."

In consequence of the observed decline in aerosol concentration of up to 60 percent, the authors state there was "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 Wm^{-2}; and when combined with the concomitant cloud-induced radiative forcing of about 0.16 Wm^{-2}, it led to a total radiative surface climate forcing over mainland Europe of about 1 Wm^{-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 that is concurrently emitted to them, as has apparently been the case over mainland Europe for the past quarter-century.

Anthropogenic aerosols plainly have a major effect on climate. The evidence is dear contrails created by emissions from jet aircraft, ship tracks created by ocean-going vessels, and air pollution from terrestrial sources all have effects on temperatures that rival or exceed the likely effect of rising CO_2 levels. With the progress that has been made in recent years in reducing air pollution in developed countries, it is possible the lion's share of the warming has likely been produced by the removal from the atmosphere of *true* air pollutants.

Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/a/aerononbioanthro.php.

References

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., Seinfeld, J.H., Nenes, A., Kulmala, M., Laaksonen, A. and Facchini, M.C. 2001. Reshaping the theory of cloud formation. *Science* **292**: 2025-2026.

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.

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

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

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., Wehrli, 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.

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.

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.

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

2.8.5. Non-Biological (Natural)

We conclude our section on aerosols 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 think we would have a pretty good handle on what it does to earth's climate as it is moved about by the planet's ever-active atmosphere. But such is not the case, as was made strikingly clear by Sokolik (1999), who with the help of nine colleagues summarized the sentiments of a number of scientists who have devoted their lives to studying the subject.

Sokolik notes state-of-the-art climate models "rely heavily on oversimplified parameterizations" of many important dust-related phenomena, "while ignoring others." As a result, the group concludes. "the magnitude and even the sign of dust net direct radiative forcing of climate remains unclear."

According to Sokolik, there are a number of unanswered questions about airborne dust, including: (1) How does one quantify dust emission rates from both natural and anthropogenic (disturbed) sources with required levels of temporal and spatial resolution? (2) How does one accurately determine the composition, size, and shape of dust particles from ground-based and aircraft measurements? (3) How does one adequately measure and model light absorption by mineral particles? (4) How does one

link the ever-evolving optical, chemical, and physical properties of dust to its life cycle in the air? (5) How does one model complex multi-layered aerosol stratification in the dust-laden atmosphere? (6) How does one quantify airborne dust properties from satellite observations?

In discussing these questions, Sokolik makes some interesting observations, noting that: (1) what is currently known (or believed to be known) about dust emissions "is largely from micro-scale experiments and theoretical studies," (2) 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, (3) improvements in methods used to determine some of these parameters are also "sorely needed," (4) how to adequately measure light absorption by mineral particles is still an "outstanding problem," and (5) 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 says "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," for until this challenge is met, we will but "see through a glass, darkly," especially when it comes to trying to discern the effects of airborne dust on earth's climate.

Vogelmann *et al*. (2003) reiterate 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 Wm^{-2} (Sokolik *et al*., 1998)," while at the same time acknowledging that "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 that "daytime surface IR forcings are often a few Wm^{-2} and can reach almost 10 Wm^{-2} for large aerosol loadings," which values, in their words, "are comparable to or larger than the 1 to 2 Wm^{-2} change in the globally averaged surface IR forcing caused by greenhouse gas increases since pre-industrial times." And in a massive understatement of fact, Vogelmann *et al*. say that these 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 ever 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, and so on (Otterman, 1974; Charney, 1975). This scenario, however, 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 suggested that 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 conclude that "the recent drying trend in the semi-arid Sahel is attributed 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 concluded that "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 that 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 say 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 say, and their findings demonstrate why: The IPCC assumptions are wrong.

Clearly, much remains to be learned about the climatic impacts of dust before anyone can place any confidence in the climatic projections of the IPCC. Additional information on this topic, including reviews of newer publications as they become available, can be found at http://www.co2science.org/subject/a/aerononbio nat.php.

References

Charney, J.G. 1975. Dynamics of desert and drought in the Sahel. *Quarterly Journal of the Royal Meteorological Society* **101**: 193-202.

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., Noguer, M., van der Linden, P.J., Xiaosu, D., Maskell, K. and Johnson, C.A. (Eds.). 2001. *Climate Change 2001: The Scientific Basis*. Cambridge University Press, Cambridge, UK. (Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change.)

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.

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.

Vogelmann, A.M., Flatau, P.J., Szczodrak, M., Markowicz, K.M. and Minnett, P.J. 2003. *Geophysical Research Letters* **30**: 10.1029/2002GL016829.

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