The Role of Marine Biota in the Functioning of the Biosphere

Carlos M. Duarte (Ed.)

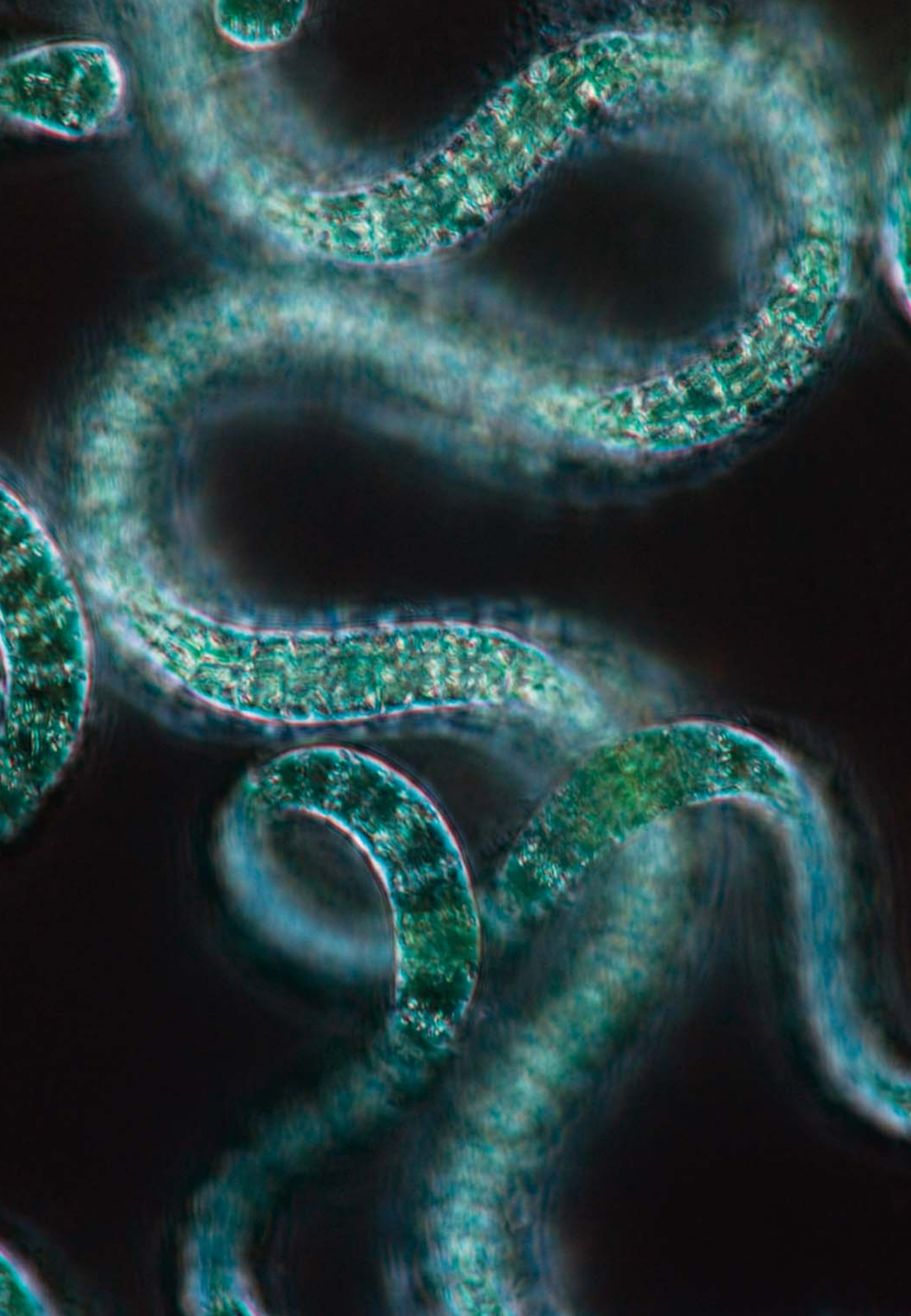
Offprint of the Chapter

Chapter 5
THE ROLE OF MARINE MICROBIOTA IN SHORT-TERM CLIMATE REGULATION

by

Rafel Simó
Institute of Marines Sciences
Spanish National Research Council (CSIC)
Barcelona, Spain

www.fbbva.es
ISBN: 978-84-92937-04-2



Chapter 5

THE ROLE OF MARINE MICROBIOTA IN SHORT-TERM CLIMATE REGULATION

Rafel Simó

Institute of Marines Sciences
Spanish National Research Council (CSIC)
Barcelona, Spain

Marine life, and particularly microscopic plankton, influence climate over long and short time scales. In the long term they do this by shaping the biogeochemical cycles of elements (such as C, O, N, P, Si, S, Fe) essential for Earth-system functioning. In the short term they do it by exchanging climate-active gases with the atmosphere. Here we focus on the short term effects. Oceans influence heat retention in the atmosphere by the exchange of greenhouse gases, regulate atmospheric photochemistry through the emission of oxidant scavengers and radical precursors, and influence the energy budget of the atmosphere (and, by extension, of the planet) through the emission of primary aerosols and secondary aerosol and cloud precursors. For example, the oceans represent the largest natural source of tropospheric sulfur, with associated significant consequences for planetary albedo, and they compete with continents as emittors of primary aerosols in the form of sea-salt crystals, organic polymers, and microorganisms. Ongoing international initiatives for global data integration, together with the invaluable information registered by remote sensing from satellites, are revealing that marine microbiota do not

Photo 5.1: Spirulina cyanobacteria. Each filament is a colony of bacterial cells. Light micrograph of *Spirulina platensis,* photosynthesising bacteria that are found in most habitats where water is present.

Photo 5.2: The *Blue Marble.* Photograph of the Earth as seen from the *Apollo 17* on December 7th, 1972. This is the original image, with Antarctica at the top. It was rotated 180º before it was distributed.

Source: NASA.

only influence the properties and behavior of their host oceans but also leave their footprint in the ocean's sky. A further evidence of the complex and fascinating architecture of our living planet.

5.1. EARTH ALBEDO AND CLIMATE

5.1.1. On the way towards a walk on the Moon

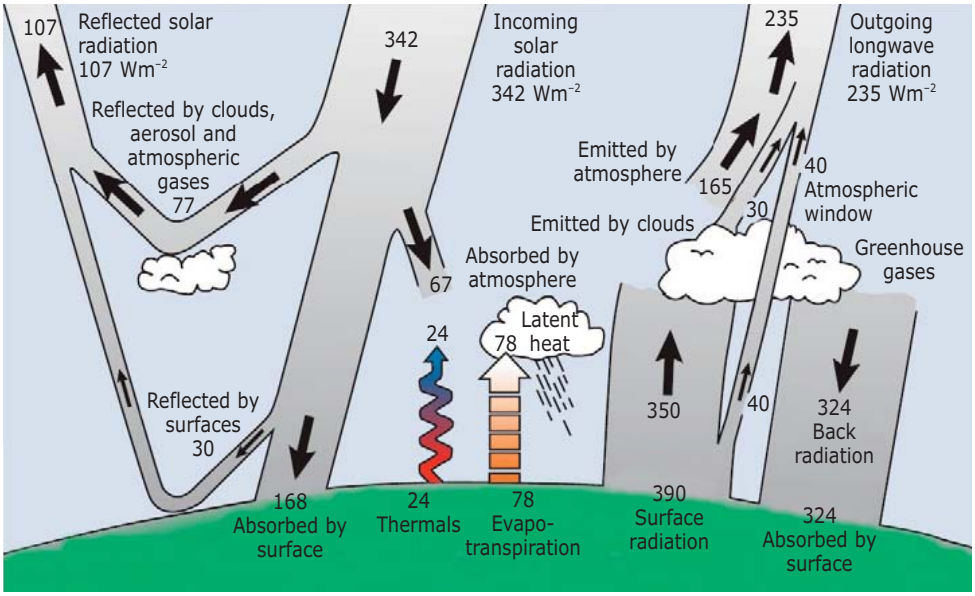
December 7th, 1972, 10:39 UTC. The *Apollo 17* had just left orbit around the Earth to begin its trajectory to the Moon, in what would be the last manned lunar mission. The crew looked at the Earth 29,000 km below and shot the *Blue Marble*, one of the most famous and widely distributed photographs of the past century (photo 5.2). The Earth appeared fully illuminated because the Sun was right behind them and the winter solstice was approaching. It looked like it was made of a bluish glass, dotted with the white and brownish textures of the clouds and the continents. To the last astronauts to walk on the Moon, their home planet was a tiny marble in the middle of the Universe.

5.1.2. Earth textures and albedo

The issue of the textures of the Earth is highly relevant to climate science. The color, brightness and microstructure of the Earth surface, just like those of any body's surface, determine its albedo (i.e., the fraction of short-wave solar irradiance that is reflected back to space) and play a prominent role in the global energy balance. And it is this energy balance that ultimately drives the average climate of the planet (figure 5.1). Of the mean 342 W m^{-2} of incoming solar radiation, as much as 107 W m^{-2} is reflected back, with the remaining 235 W m^{-2} being absorbed by the atmosphere and the surface (including the biosphere) and eventually dissipated as heat and radiated out to space in the form of longwave radiation. Tiny imbalances in this tight budget (e.g., by changes in the atmospheric chemical composition) produce global warming or cooling.

Should the *Blue Marble* have been of a glassy uniform dark blue, like that of an ocean flooded planet, the energy budget would have been very different from that sketched in figure 5.1 simply because of its color. Everyone knows that wearing dark clothes or driving dark cars in hot summers are bad choices be-

Figure 5.1: The energy balance of the Earth. Incoming solar radiation that is not reflected back to space by the atmosphere and the Earth surface cycles through the components of the Earth system and eventually radiates out to space in the form of longwave (thermal) radiation.

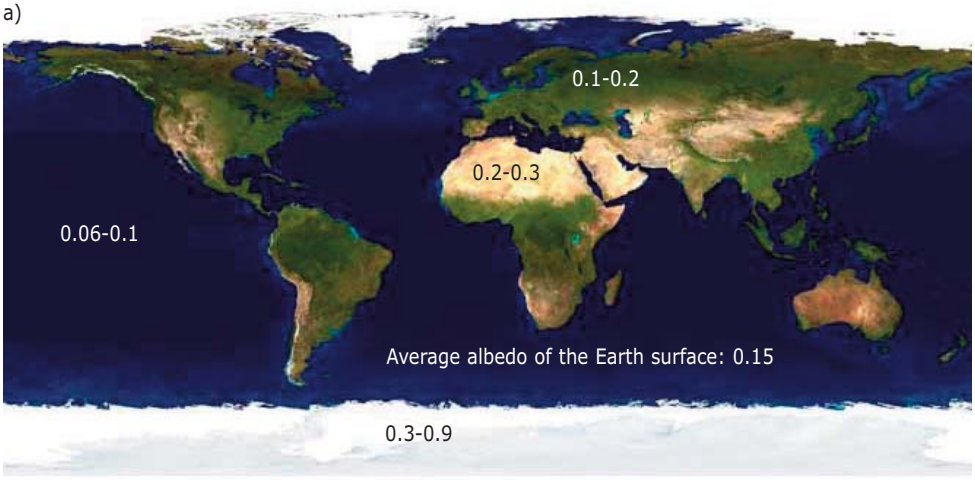


Source: Adapted from Le Treut et al. (2007).

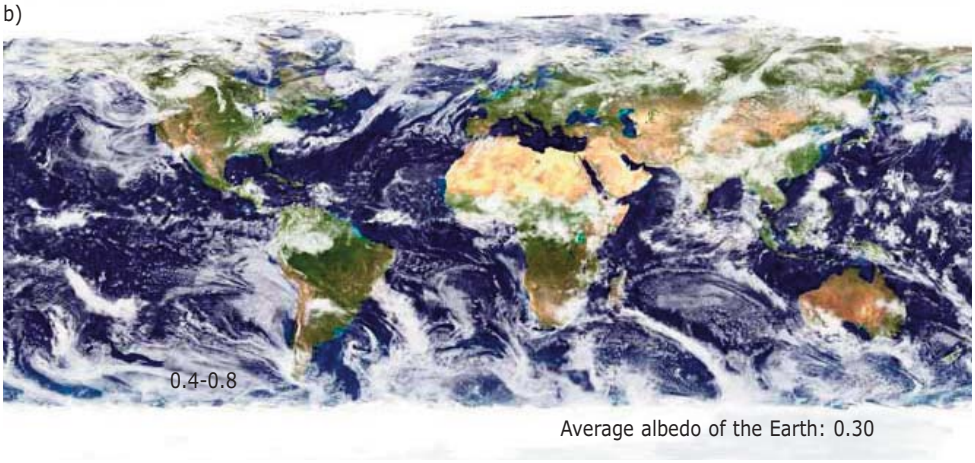
cause they absorb a lot of solar radiation and dissipate it as further warmth; clear colors reflect more, absorb less, and are highly recommended to stay comfortably cool. Likewise, the dark ocean has an albedo of 0.06 to 0.1, it therefore absorbs more than 90% of the solar energy hitting its surface. An ocean planet with a transparent atmosphere would absorb a lot more energy, and who knows how it would be dissipated. But our Earth has continents with sandy and rocky surfaces, generous vegetation covers and seasonal or per-

Map 5.1: Earth albedo. Composite of visible images taken by MODIS from NASA's satellite *Terra.* **a)** The image has been manipulated to remove clouds. Numbers are the albedo values of oceans, sea and continental ice, vegetated land, deserts, and the average of the Earth's surface. **b)** True image of the cloudy Earth, with the albedo of clouds and the resulting planetary albedo, notably higher than that of the surface.

a)



b)



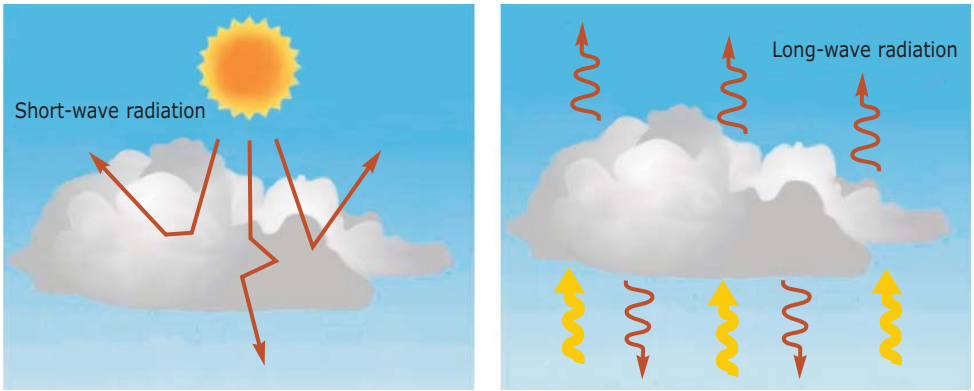
manent snow fields and ice caps (map 5.1a). Vegetated lands, including forests and crops, have albedos of 0.1-0.2, i.e., only slightly higher than that of the oceans. Exposed dry soils and sand deserts have albedos of 0.2-0.3. Only ice and snow covers have really high albedos (0.3-0.9) and reflect more sunlight than they absorb. On average, the albedo of the Earth surface is 0.15; in other words, it absorbs 85% of the solar radiation that traverses the atmosphere.

But the *Apollo 17* crew did not see the Earth as it is shown in map 5.1a. The real *Blue Marble* is a cloudy planet (photo 5.2), and its flat projection shows that ca. 60% of its surface is hidden under white clouds. Since clouds have albedos of 0.4-0.8, the actual average albedo of the Earth is 0.30, i.e., twice that of its surface (map 5.1b).

5.1.3. Clouds and solar radiation

Without clouds the Earth surface would receive far more energy from the Sun because clouds act as parasols. This sounds quite obvious, but, who has not heard weather forecasters say that cloudy nights are warmer nights? And clear winter skies bring freezing nights because heat is quickly lost upwards. So, do we regard clouds as actors playing contradictory roles: parasol clouds or greenhouse clouds? It is true that they play both roles. In general, clouds act as parasols during the day and as a greenhouse roof during the night (figure 5.2).

Figure 5.2: Role of clouds in the energy balance. *Left:* Clouds reflect part of the incoming shortwave solar radiation back to space. *Right:* Clouds retain part of the longwave (thermal) radiation coming from below, and radiate it up (out to space) and down (back to the surface).



Their net effect depends on the type of cloud (figure 5.3). High altitude cirrus clouds, mostly formed by ice crystals, are more efficient at retaining heat from below than at reflecting sunlight from above. They are 'warming clouds'. Low altitude clouds, stratus and stratocumulus, are better at reflecting short-wave irradiance than at retaining long-wave radiation; hence, they are 'cooling clouds'. Convective clouds like storm cumulus and cumulonimbus have a virtually neutral net effect. Altogether, clouds have a global radiative effect of net cooling, estimated at ca. –20 W m^{-2}.

The clouds that cover the largest surface of the Earth, and particularly the largest surface of dark ocean, are the low clouds, the marine stratus. Therefore, any factor having an influence on the formation and albedo of marine stratus plays a prominent role in the energy balance of the planet and, consequently, in global climate.

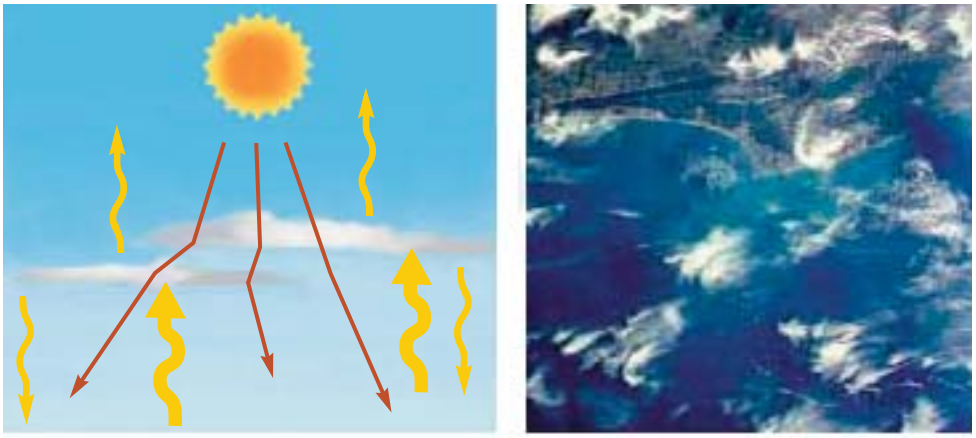
5.2. CLOUD FORMATION

For a cloud to form there must be water vapor in cooling air. This alone, however, would not be enough. Water droplets form only if there are microsurfaces for water molecules to collect and condense upon.

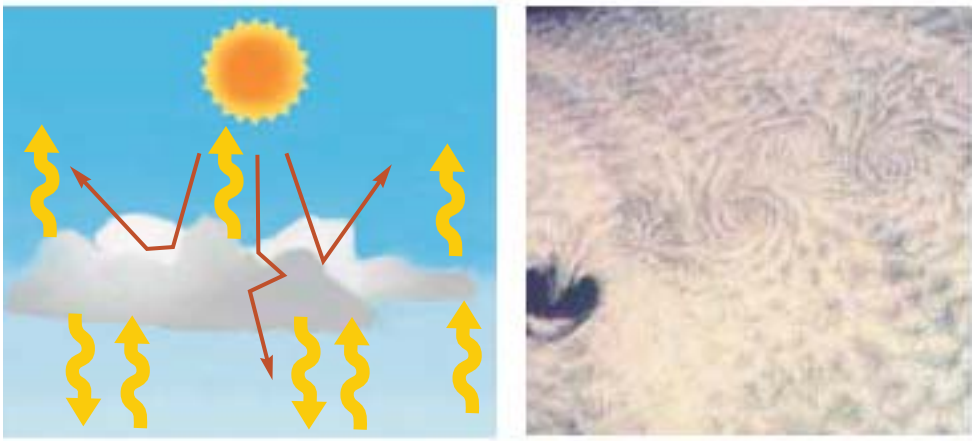
5.2.1. *Une nouvelle propriété de l'air*

In 1875, P.J. Coulier, a professor in a Paris hospital, conducted the first known laboratory experiments aimed at finding the ingredients for cloud formation (Spurny 2000). He poured a little warm water into a glass flask with an inlet and an outlet tube (figure 5.4). A rubber ball was connected to the outlet tube so that pressure changes could be applied inside the flask by hand, upon shutting off the inlet. On removing air, the pressure drop made the air remaining in the flask expand and cool rapidly. Because the air was saturated with vapor, water droplets condensed as the air cooled. These findings showed nothing really exciting simply that upon cooling, water vapor condensation formed a cloud. Nonetheless, Coulier observed that no cloud was formed if the air in the flask was too clean, e.g., if it was filtered to remove particles. Only *regular* air from the lab allowed for mist formation, and mist became dense fog if dirtier air was blown in. Coulier published an article in the *Journal de Pharmacie et de Chimie* entitled *Note sur une nouvelle propriété de l'air*. In it he stated: 'Fine solid particles suspended in the air are necessary for the production of fogs' (Coulier 1875).

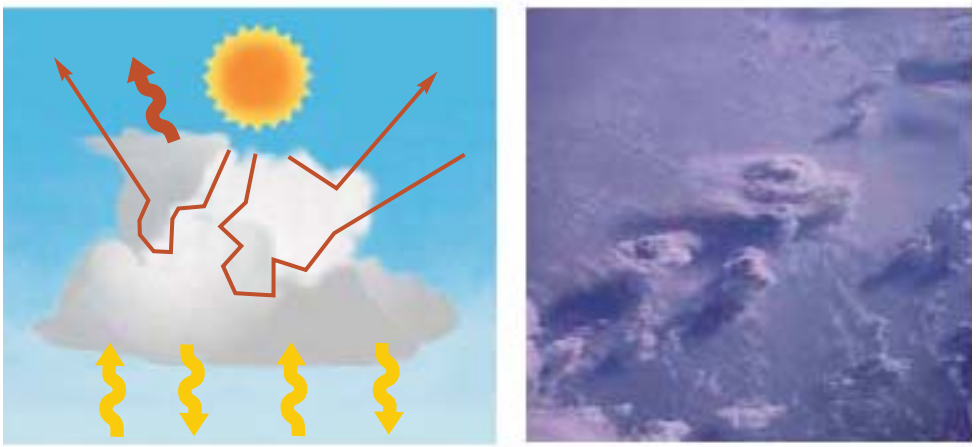
Figure 5.5: Radiative behavior of the different cloud types



High clouds (net heat retention)

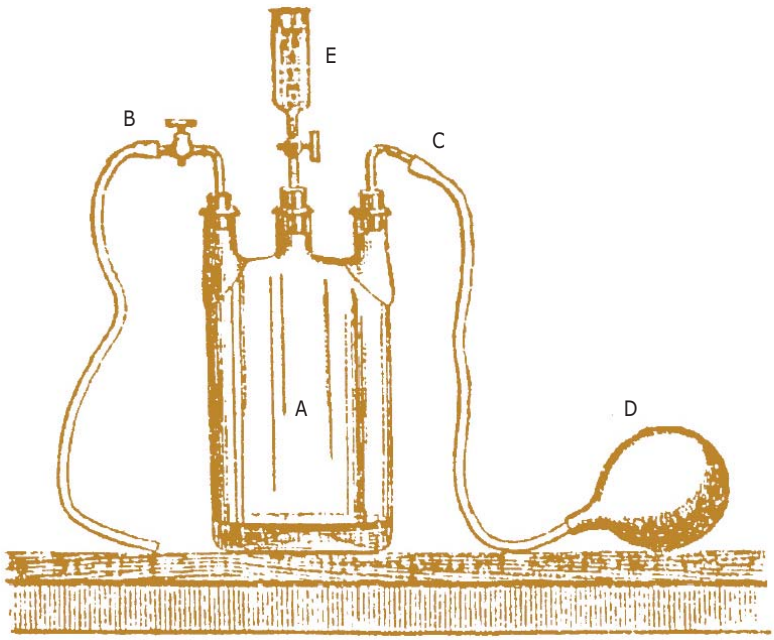


Low clouds (net cooling)



Convective clouds (neutral)

Figure 5.4: Original drawing of the apparatus used by P.J. Coulier to investigate the role of aerosol particles in water vapor condensation and cloud formation



A: glass flask; B: air inlet; C: outlet tube; D: rubber ball for lowering pressure; E: liquid water dispensor.

Source: Coulier 1875.

Unfortunately, Coulier's work was not met with much excitement in the meteorological community, who probably were not subscribers to the journal in which the article was published. Five years later the Scottish meteorologist J. Aitken performed a very similar, indeed practically identical, experiment. Aitken, who was not aware of Coulier's findings, published an article in *Nature* in 1880 where he reported the same conclusions as his ignored French colleague: 'Water vapor condenses in the atmosphere on some solid nuclei; dust particles in the air form these nuclei; if there were no dust, there would be no fogs, no clouds, no mists, and probably no rain.' (Aitken 1880). When Aitken chanced upon and read Coulier's papers on the subject, he recognized publicly that 'Monsieur Coulier was the first to show the important part played by dust in the cloudy condensation of the vapour in air' (Spurny 2000). Nevertheless, and because of his later research, Aitken is considered the discoverer of so-called *cloud condensation nuclei* (CCN) and the father of subsequent investigations into the relationship between aerosols and clouds.

5.3. AEROSOLS AND CLIMATE

5.3.1. Dust in the wind

What Coulier and Aitken called *dust* in the late XIXth century, today we call *aerosols*, which is the general term used to designate any tiny particle suspended in the air. Aerosols can be of a broad size range and have very different composition and optical properties depending on their origin, formation and transformation processes. Aerosols have occurred throughout the Earth's history, as many natural sources exist (Andreae 2007). Irrespective of their source, but in reference to their formation process, aerosols can be categorized into:

Primary aerosols: Those born as particles in their very origin. These include soil dust raised by the wind, soot and ashes from wild fires, vegetal debris, or sea salt and microorganisms ejected by breaking waves.

Secondary aerosols: Those born from the transformation of gases into particles through nucleation and coalescence. These include sulfate aerosols produced by oxidation of sulfur gases from volcanoes and living beings, or organic aerosols produced by oxidation of biogenic volatile organic compounds.

Needless to say, human activities represent a major aerosol source, particularly so after the Industrial Revolution. Deforestation, land mobilization, and changes in land use are resulting in the exposure of an increasing surface of soil to wind friction, with the subsequent increase in dust loads. But above all, it is through the use of combustion energy that humankind contributes the most to aerosol levels in the atmosphere. Incomplete combustion produces, along with CO_2 and water vapor, large quantities of pyrogenic black carbon (soot –primary aerosol), and sulfur dioxide plus carbon- and nitrogen-containing volatile organics (all precursors of secondary aerosol).

5.3.2. Aerosols and solar radiation

Aerosols are an important component of the air and, as such, contribute to the configuration of the functioning of the atmosphere as a chemical reactor, substance transporter, and major actor in setting the Earth's energy balance. Depending on their size and characteristics, aerosols are involved in processes

as important as cloud formation, sulight absorption and the scattering, transport and deposition of essential elements, pollutants, allergens and disease vectors. Here I provide an overview of their main effects on climate (Penner et al. 2001; Forster et al. 2007).

Direct effect: That derived from the direct interactions between aerosols and solar or thermal radiation. Aerosols that have a low microalbedo absorb solar radiation and dissipate it as thermal radiation (heat), so that they contribute to tropospheric warming. This is the case of black carbon soot. Aerosols with a high microalbedo reflect and scatter solar radiation and contribute to cool the troposphere below. This is the case, for instance, with secondary aerosols produced from biogenic and anthropogenic sulfur emissions.

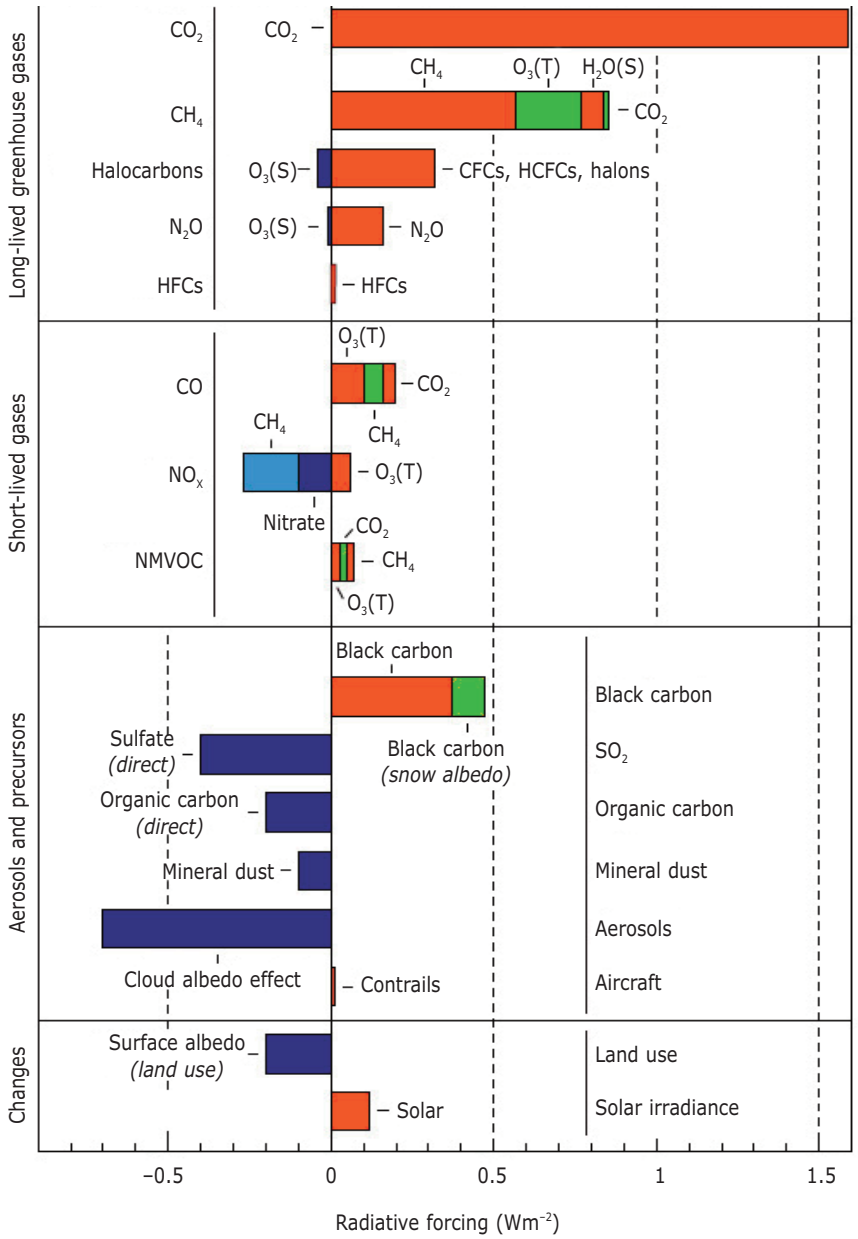
Overall, the direct radiative effect of aerosols is a net cooling estimated as –5.4 (±0.9) Wm^{-2}, and its radiative forcing since the industrial era is –0.5 (±0.4) Wm^{-2} (figure 5.5).

Indirect effects: Those derived from the influence of aerosols on the microphysical (and hence the radiative) properties, amount and lifetime of clouds.

First indirect / Cloud albedo / Twomey effect: As outlined above, aerosols play a key role in cloud formation. Aerosols in the proper size range (0.05-1 μm) and of hygroscopic nature are the most favorable for water vapor condensation into droplets. But the role of aerosols does not end with being a necessary ingredient. A cloud that condenses on few particles will be a cloud with few droplets; for a given liquid water content, fewer droplets means larger droplets. On the contrary, in the presence of high aerosol concentrations, a cloud will form with many droplets of smaller size. A cloud with more (smaller) droplets has a higher albedo than a cloud with fewer (larger) droplets (Twomey 1977). In other words, clouds 'polluted' by either anthropogenic or biogenic aerosols have higher albedos, i.e., act as better parasols.

Second indirect / Cloud lifetime / Albrecht effect: A cloud formed in the presence of high aerosol concentrations will be a longer-lived cloud because small droplets will take longer to reach their precipitable size. In other words, aerosols suppress drizzle and lengthen cloud's life as a parasol (Albrecht 2000).

Figure 5.5: Main components of the radiative forcing of climate change. The columns refer to the radiative forcing (in energy units, W m^{-2}) observed or estimated since the start of the indurstrial era (about 1750) until 2005. The forcings result from the changes caused by human activies during this period. Positive forcings lead to warming of climate and negative forcings lead to a cooling. The only increase in natural forcing of any significance occurred in solar irradiance (bottom column). Note the large cooling effects of aerosols and precursors. (S) and (T) next to gas species represent stratospheric and tropospheric changes, respectively. For uncertainties associated with the estimated values, see the original source (Forster et al. 2007).



Semi-indirect effect: The presence of shortwave radiation absorbing aerosols warms the air around them, which reduces the relative humidity and stability and burns off cloud formation. In other words, soot aerosols reduce cloudiness (Ackerman et al. 2000).

Taken altogether, the indirect radiative effects of aerosols are large but very difficult to quantify. Since the industrial era, the best estimate of their radiative forcing is ca. –0.7 W m^{-2}, with an estimated range from very low to –1.1 W m^{-2} (figure 5.5). As a matter of fact, the indirect aerosol effects are one of the largest sources of uncertainty in the observation and prediction of global warming.

5.4. OCEANIC BIOSPHERE, AEROSOLS AND CLIMATE

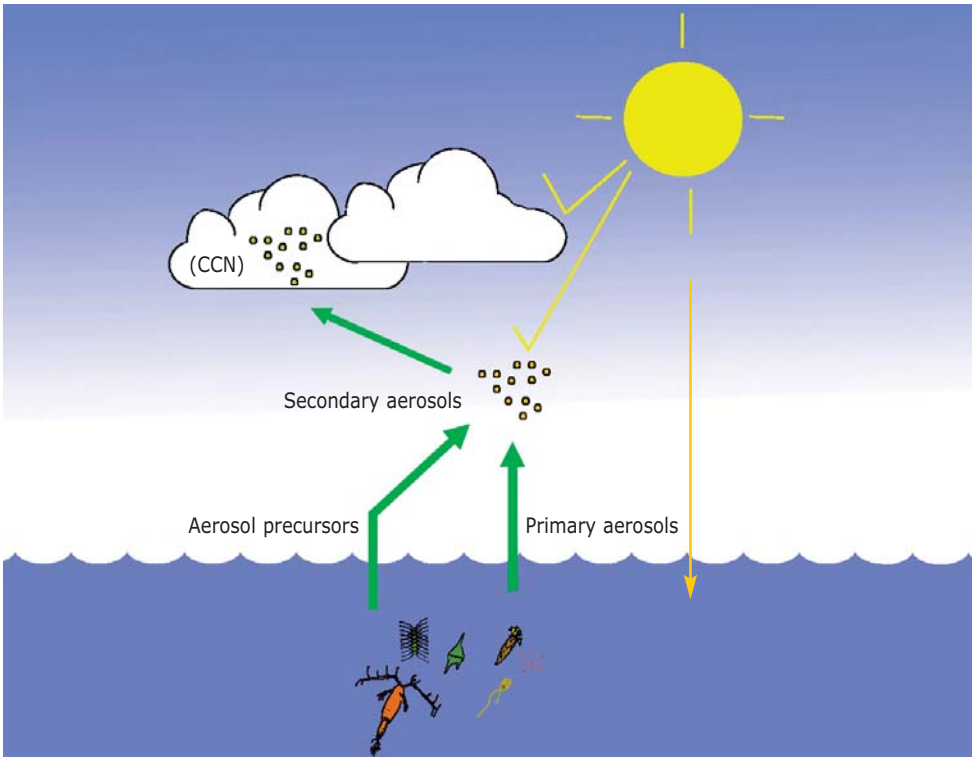
5.4.1. Marine aerosol sources

The oceans are a major aerosol source. Per unit area they are far weaker producers than the continents, where soils, vegetation and human activities represent a constant supply of airborne particles. But the oceans occupy about two thirds of the Earth surface and present little impediment to wind exposure. Marine aerosols can be either primary or secondary, and have either a biotic or an abiotic origin (figure 5.6).

Primary aerosols are produced by wind friction, bubble bursting and breaking waves releasing small seawater droplets into the air, known as sea spray (Andreae and Rosenfeld 2008). As droplets evaporate, the solid particles can coalesce and aggregate with others, absorb vapors, participate in gas-particle reactions, or serve as condensation nuclei. The main mass contributor to marine primary aerosol is sea salt. It occurs mostly in the supermicron aerosol fraction but it also makes a significant contribution to submicron particles and cloud condensation nuclei (Clarke et al. 2006). Other primary aerosols ejected by the oceans are formed by biogenic organic polymers (Leck and Bigg 2005) and microorganisms such as bacteria and viruses (Sun and Ariya 2005; Christner et al. 2008). This primary organic aerosol is very poorly characterized and its source function and mass fluxes are virtually unknown.

Secondary aerosols are generated by the oxidation and nucleation of precursor gases released by the oceans (Andreae and Rosenfeld 2008). The

Figure 5.6: The breath of the sea. The oceans, in addition to their exchange of CO_2, O_2 and water with the troposphere, emit a myriad of trace gases and particles (many of which are biogenic) that influence the chemical and optical properties of the atmosphere and act as cloud precursors.



principal known gases are dimethylsulfide (DMS, which upon oxidation gives rise to secondary sulfate aerosols, which are very efficient as cloud condensation nuclei, CCN, see below), iodomethanes, mainly produced in coastal waters (which give rise to iodine-condensable vapors and aerosols; O'Dowd et al. 2002), ammonia (which neutralizes sulfuric acid during aerosol formation and growth; Quinn et al. 1988), and a number of volatile organic compounds such as isoprene and monoterpenes (which oxidize to form organic aerosol, a main constituent of the total aerosol mass over productive waters; O'Dowd et al. 2004). The oxidation products of all these gases either nucleate to form new particles in the fine size fraction (the ones efficient as CCN) or condense on pre-existing particles and contribute to their growth and, if hygroscopic, to their activation as CCN. Actually, most remote marine aerosols examined by electron microscopy and chemical analyses are made up of mixtures of, at least, organic structures

and ammonium sulfate (O'Dowd et al. 2004, Leck and Bigg 2005). As for primary organic aerosols, the source functions for most marine secondary aerosols are not well constrained. This is because, with the exception of DMS, little is known about the concentration patterns and seasonal dynamics of most organic, iodine and nitrogen gases in the surface ocean.

5.4.2. The breath of the sea

As outlined above, the oceans exchange many more gases with the atmosphere than just CO_2, O_2 and water vapor. Volatiles of all kinds are produced in seawater by biological processes and photochemical reactions. Many of them often occur at supersaturation concentrations in surface waters and, therefore, tend to escape to the atmosphere. Some, like those mentioned in the previous section, act as aerosol and cloud precursors. Some others get involved in atmospheric chemistry and contribute to regulating the oxidative capacity of the troposphere. Some others are transported to and deposited on the continents, thus serving to compensate for the continental losses of essential elements (such as sulfur and iodine) over geological time scales. And a few survive tropospheric chemistry and reach the stratosphere, where they form aerosols or participate in ozone destruction. Altogether, marine trace gases are important actors in global biogeochemistry as they play multiple and fundamental roles in Earth system functioning. Table 5.1 shows a compilation of marine trace gases, their role in the Earth system, an estimate of the oceanic emission flux and its contribution to emissions from all sources, an enumeration of the main non-marine sources, and some selected references for further reading (see p. 122-123).

5.4.3. The smell of the sea

Dimethylsulfide (DMS) is, by far, the best studied of all the trace gases of the ocean. Several reasons lie behind the remarkable interest it has aroused in the biogeochemical and oceanographic community:

a) It is the most abundant volatile sulfur compound in the surface ocean, to the extent that it alone accounts for > 90% of the oceanic emission of sulfur; in the case of other elements, the mass fluxes are spread among a number of relative compounds.

b) It occurs at nanomolar concentrations, while other trace gases occur at picomolar levels or even less.

c) A fascinating, holistic hypothesis has been constructed on the basis of this tiny molecule. The CLAW hypothesis (so-called after the initial of its authors) postulates that, if the release of DMS by oceanic plankton and it subsequent emission to the atmosphere affects the concentration of CCN, and these affect cloud albedo over the oceans, the resulting changes in solar irradiance at the surface ocean could feed back on plankton DMS production. This feedback, postulated to be negative, would contribute to stabilize global temperatures (Charlson et al. 1987). In other words, microscopic plankton would help regulate climate through their sulfur-mediated influence on cloud albedo (figure 5.7).

The CLAW hypothesis has stimulated an enormous research effort into the oceanic and atmospheric sulfur cycle over the last two decades. However, ultimate proof has eluded researchers. Facts (observations) tell us that DMS is a by-product of the tight cycling of an abundant, and physiologically and ecologically important organic sulfur compound, dimethylsulfoniopropionate, DMSP (Simó 2001). Facts also tell us that the oceanic DMS emission represents the main natural source of atmospheric sulfur, four times larger than volcanic emissions, but just 40% of the huge sulfur emissions made by mankind during the industrial era (table 5.2). With such a large emission, DMS makes up one of the components of the smell of the sea and seafood. This would not be relevant if we had not discovered that some marine birds can detect the smell of DMS and use it as a foraging cue (Nevitt et al. 2002). Nevertheless, the observations that DMS is produced abundantly by plankton in the surface ocean, that it is a major source of atmospheric sulfate, and that sulfate is a main component of the cloud condensation nuclei of stratus, is not sufficient to accept or rebut the CLAW hypothesis.

At the Institute of Marines Sciences, Barcelona (ICM-CSIC), and in collaboration with international colleagues, for the last 10 years we have been investigating the DMS cycle at local to global scales, its significance for the ecology of microbial plankton and for sulfur fluxes in the pelagic marine ecosystem, and its participation in atmospheric processes. By the use of molecular biology analyses, community-level experiments, ecosystem observations at sea, and analyses of satellite data and oceanographic climatologies, we have been

Table 5.1: The breath of the sea. Volatile compounds (other than CO_2 and O_2) produced in the surface ocean by biological and photochemical reactions, which are emitted into the atmosphere and affect its chemical properties and dynamics.

Compound	Main environmental role[a]	Oceanic emission		Other sources[c]	Token references
		Magnitude	contribution to total emision[b]		
CH_4	Greenhouse	0.6-15 Tg/yr	0.1-2%	Wetlands, livestock, rice fields, landfills, natural gas	Bates et al. 1996; Denman et al. 2007; Rhee et al. 2009
N_2O	Greenhouse	0.9-7 TgN/yr	4-20%	Soils, fertilizers, combustion	Nevison et al. 1995; Bange 2006; Rhee et al. 2009
Sulfur volatiles: Dimethylsulfide (DMS)	Global sulfur budget Aerosol precursor: atmospheric acidity and cloud nucleation	20-35 TgS/yr	90%	Soils, plants	Kettle and Andreae 2000; Simó and Dachs 2002
COS	Precursor of stratospheric aerosol	0.60 TgS/yr	20%	Soils, combustion	Kettle et al. 2002; Uher 2006; Sutharalingam et al. 2008
CS_2	COS precursor	0.15 TgS/yr	?	Soils, wetlands	Xie and Moore 1999; Kettle et al. 2002
Selenium volatiles (methyl selenides)	Global selenium budget	£35 GgSe/yr	50-75%	Soils, plants, wetlands	Amoroux et al. 2001
Halogenated volatiles: CH_3I, CH_2I_2	Global iodine budget, tropospheric photochemistry, coastal aerosol precursor, cloud nucleation	1 TgI/yr	>50%	Rice fields, combustion	Moore and Groszko 1999; O'Dowd et al. 2002

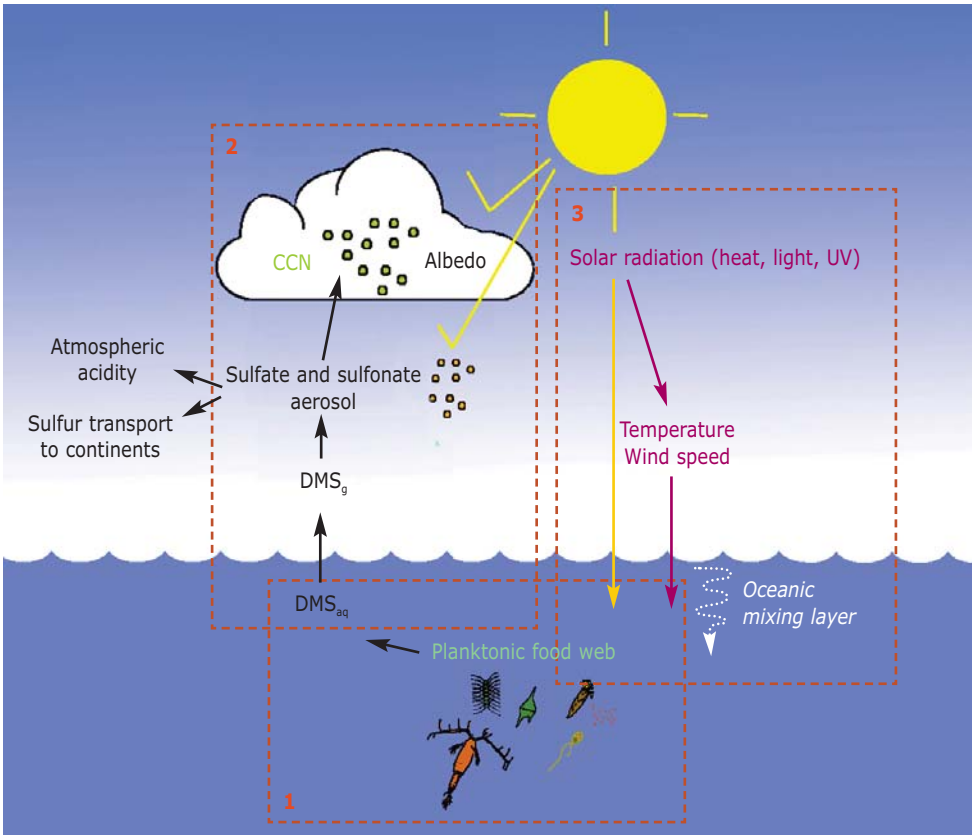
Table 5.1 *(cont.)*: The breath of the sea. Volatile compounds (other than CO_2 and O_2) produced in the surface ocean by biological and photochemical reactions, which are emitted into the atmosphere and affect its chemical properties and dynamics.

Compound	Main environmental role[a]	Oceanic emission		Other sources[c]	Token references
		Magnitude	contribution to total emision[b]		
CH_3Br	Stratospheric ozone destruction	20-46 GgBr/yr	10-40%	Agriculture, combustion, salt marshes	Lobert et al. 1995; Pilinis et al. 1996; Butler 2000; Yvon-Lewis et al. 2009
HCH_3Cl	Tropospheric photochemistry, acidity, stratospheric ozone destruction	0.1-0.3 TgCl/yr	10%	Combustion, industrial	Moore et al. 1996; Khalil and Rasmussen 1999; Butler 2000
Other halomethanes and haloethanes	Tropospheric photochemistry, acidity, stratospheric ozone destruction	?	?	Combustion	Moore et al. 1995; Butler 2000
NH_3 and methylamines (mono-, di-, tri-)	Aerosol acidity-alcalinity	?	?	Soils, wetlands, plants?	Quinn et al. 1988; Gibb et al. 1999; Jickells et al. 2003; Facchini et al. 2008
Alkyl nitrates	Tropospheric photochemistry	?	?	Combustion, poto-reactions	Chuck et al. 2002; Moore and Blough 2002
Volatile hydrocarbons (e.g., C2-C4, isoprene, monoterpenes)	Tropospheric photochemistry, aerosol precursors	2.1 TgC/yr	minor	Plants, combustion	Plass-Dülmer et al. 1995; Broadgate et al. 1997; Yassaa et al. 2008; Arnold et al. 2009; Gantt et al. 2009

In most cases a 'positive' net annual flux has been observed, but this does not mean that the surface ocean is always supersaturated in these traces everywhere. In some cases, such as COS or CH_3Br, throughout the year the oceans change their role as a source or a sink depending on the accumulation rates in the troposphere caused by variability in all sources. The list is intended to be comprehensive but not complete.

[a] Impact of the oceanic emission on the Earth System, mainly through atmospheric chemistry
[b] Estimated contribution of the oceans to the global emission from all sources (natural + anthropogenic)
[c] Main sources to the atmosphere, other than the ocean.

Figure 5.7: The ocean/atmosphere biogeochemical cycle of dimethylsulfide (DMS) and the plankton-climate feedback hypothesis. Plankton produce DMS that escapes tight cycling and vents to the atmosphere, where it is oxidized to sulfate aerosols that can serve as cloud condensation nuclei (CCN). Associated changes in cloud albedo and below-cloud irradiance would feed back to plankton activity, in what could constitute a mechanism by which plankton help regulate climate (Charlson et al. 1987). Numbers 1, 2, 3 (in red) refer to the three major steps in this hypothetical feedback gear, to which research contributions have recently been made at the ICM-CSIC (see text).



able to make contributions that have produced a significant advance towards deciphering the feasibility of the CLAW hypothesis. Here I will briefly outline these contributions, providing a few example references for each. The numbers refer to the boxes in the diagram in figure 5.7.

1) DMS is produced by interactions among microbial plankton components, and among plankton and solar radiation. Phytoplankton acclimation to higher doses of visible and UV radiation, plus the deleterious effects of UV on bacterial DMS consumers, seem to be behind the higher

DMS concentrations generally observed in summer (Simó and Pedrós-Alió 1999; Vallina et al. 2008; Vila-Costa et al. 2008).

2) DMS emission, and not sea salt emission, correlates with the numer of CCN in the atmosphere over most of the global remote oceans. Even though the largest mass fraction of CCN is probably contributed by sea salt, monthly variability seems to be driven by DMS emission and oxidation fluxes (Vallina et al. 2007a).

3) Over most of the global oceans and on the seasonal scale, surface DMS concentrations are proportional to the daily dose of solar radiation received by plankton in the surface mixing layer (Vallina and Simó 2007). This proportionality, when projected to predicted changes in solar radiation doses with global warming, estimates a very low global increase in DMS concentrations by mid 21st century (Vallina et al. 2007b).

Our results seem to support the negative feedback of the CLAW hypothesis (more solar radiation causes more DMS, which leads to increased CCN numbers and increased cloud albedo). The outcome of our studies, however, points to the need for a significant revision of the hypothesis as it was postulated. There is no evidence yet that the strength of the feedback is of enough magnitude to buffer cloudiness and cloud albedo in the short term over a particular oceanic region; and there is no evidence yet that long term (decades to

Table 5.2: Contribution of natural and anthropogenic sources to the global emission and the atmospheric burden of sulfur

Source	Global S emission ($TgS\ yr^{-1}$)		Contribution to emission %	Contribution to S burden[a] %	
	Mean	Range			
Humans	70	60-100	67	37	
Volcanos	7	4-16	7	18	
Biota[b]	27	17-34	26	42[c]	<4% Northern mid-latitude continents <20-30% extratropical oceans NH >33% Tropics and SH

[a] Contribution to the total amount of SO_4^{-2} in the atmosphere.
[b] Includes all terrestrial and oceanic biogenic emissions, of which >90% is oceanic DMS.
[c] The biogenic (mostly DMS) contribution to sulfate burden averages 42% but varies greatly among large regions, as detailed in the right column.

NH: Northern hemisphere; SH: Southern hemisphere.

Source: Adapted from Simó 2001.

hundreds of throusands years) changes in DMS emissions could help counteract large climate shifts. There is only evidence for a seasonal negative feedback in solar irradiance: summer plankton produce more DMS that reduces irradiance, and the opposite occurs in winter. Further work should include quantitative calculations of the radiative effect of this *seasonal CLAW*, and combine this with rapidly mounting observations and models of the dynamics of other secondary aerosol precursors.

Irrespective of whether we will ever be able to prove or refute the CLAW hypothesis, it will have left the invaluable legacy of the never-quite-enough joint efforts of physiologists, ecologists, biogeochemists, atmospheric chemists and physicists, experimentalists and modelers to provide an answer to a common question, and highlighted the need to continue this line of investigation, if we are to address the complex and fascinating architecture of our living planet.

ACKNOWLEDGEMENTS

I wish to thank the BBVA Foundation and C.M. Duarte for inviting me to this Colloquium and to write this book chapter. I also thank A. Lana for her assistance with the history of the discovery of cloud condensation nuclei, and J. Corbera for help with some of the illustrations. This work is a contribution of the Research Group on Marine Biogeochemistry and Global Change of the ICM-CSIC, sponsored by the Generalitat de Cataluna, and of the MICINN projects MIMOSA and PRISMA.

REFERENCES

Ackerman, A.S. et al. "Reduction of tropical cloudiness by soot". *Science* 288 (2000): 1042-1047.

Aitken, J. "On dusts, fogs and clouds". *Nature* Feb. (1880): 384-385.

Albrecht, B. "Aerosols, cloud microphysics and fractional cloudiness". *Science* 245 (1989): 1227-1230.

Amoroux, D., P.S. Liss et al. "Role of oceans as biogenic sources of selenium". *Earth and Planetary Science Letters* 189 (2001): 277-283.

Andreae, M.O. "Aerosols before pollution". *Science* 315 (2007): 50-51.

Andreae, M.O., and D. Rosenfeld. "Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of clou-active aerosols". *Earth-Science Reviews* 89 (2008): 13-41.

ARNOLD, S.R., D.V. SPRACKLEN, J. WILLIAMS, N. YASSAA, J. SCIARE, B. BONSANG, V. GROS et al. "Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol". *Atmospheric Chemistry and Physics* 9 (2009): 1253-1262.

BANGE, H.W. "New Directions: The importance of oceanic nitrous oxide emissions". *Atmospheric Environment* 40 (2006): 198-199.

BATES, T.S., K.C. KELLY, J.E. JOHNSON, and R.H. GAMMON. "*A reevaluation of the open ocean source of methane to the atmosphere". Journal of Geophysical Research-Atmospheres 101 (1996);* D3: 6953-6961.

BROADGATE, W.J., P.S. LISS, and S.A. PENKETT. "Seasonal emissions of isoprene and other reactive hydrocarbons gases from the ocean". *Geophysical Research Letters* 24 (1997): 2675-2678.

BUTLER, J.H. "Better budgets for methyl halides?" *Nature* 403 (2000): 260-261.

CHRISTNER, B.C., C.E. MORRIS, C.M. FOREMAN, R. CAI, and D.C. SANDS. "Ubiquity of biological ice nucleators in snowfall". *Science* 319 (2008): 1214.

CHUCK, A.L., S.M. TURNER, and P.S. LISS. "Direct evidence for a marine source of C_1 and C_2 alkyl nitrates". *Science* 297 (2002): 1151-1154.

CLARKE, A.D., S.R. OWENS, and J.C. ZHOU. "An ultrafine sea-salt flux from breaking waves: implications for cloud condensation nuclei in the remote marine atmosphere". *Journal of Geophysical Research-Atmospheres* 111 (2006); D06202. doi:10.1029/2005JD006565.

COULIER, P.J. "Note sur une nouvelle propriété de l'air". *Journal de Pharmacie et de Chimie ,* Paris, Ser. 4 (1875); 22: 165-173.

DENMAN, K.L. et al. "Couplings between changes in the climate system and Biogeochemistry". In: Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor, and H.L. Miller, eds. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge and New York: Cambridge University Press, 2007.

FACCHINI, M.C., S. DECESARI, M. RINALDI, C. CARBONE, E. FINESSI, M. MIRCEA, S. FUZZI et al. "Important Source of Marine Secondary Organic Aerosol from Biogenic Amines". *Environmental Science and Technology* 42 (2008): 9116-9121.

FORSTER, P. et al. (2007). "Changes in atmospheric constituents and in radiative forcing". In: Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor, and H.L. Miller, eds. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge and New York: Cambridge University Press, 2007.

GANTT, B., N. MESKHIDZE, and D. KAMYKOWSKI. "A new physically-based quantification of marine isoprene and primary organic aerosol emissions". *Atmospheric Chemistry and Physics* 9 (2009): 4915-4927.

GIBB, S.W., R.F.C. MANTOURA, P.S. LISS, and R.G. BARLOW. "Distributions and biogeochemistries of methylamines and ammonium in the Arabian Sea". *Deep-Sea Research II* 46 (1999): 593-615.

JICKELLS, T.D., S.D. KELLY, A.R. BAKER, K. BISWAS, P.F. DENNIS, L.J. SPOKES, M. WITT, and S.G. YEATMAN. "Isotopic evidence for a marine ammonia source". *Geophysical Research Letters* 30 (2002); 7: 1374. doi:10.1029/2002GL016728.

KETTLE, A.J., and M.O. ANDREAE. "Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models". *Journal of Geophysical Research-Atmospheres* 105 (2000); D22; 26: 793-808.

KETTLE, A.J., U. KUHN, M. von HOBE, J. KESSELMEIER, and M.O. ANDREAE. "Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks". *Journal of Geophysical Research-Atmospheres* 107 (2002); D22: 4658. doi:10.1029/2002JD002187.

KHALIL, M.A.K., and R.A. RASMUSSEN. "Atmospheric methyl chloride". *Atmospheric Environment* 33 (1999): 1305-1321.

LECK, C., and E.K. BIGG. "Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer". *Tellus* 57B (2005): 305-316.

LE TREUT, H., R. SOMERVILLE, U. CUBASCH, Y. DING, C. MAURITZEN, A. MOKSSIT, T. PETERSON, and M. PRATHER, 2007: "Historical overview of climate change". In Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, and H.L. Miller, eds. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge and New York: Cambridge University Press, 2007.

LOBERT, J.M., J.H. BUTLER, S.A. MONTZKA, L.S. GELLER, R.C. MYERS, and J.W. ELKINS. "A net sink for atmospheric CH_3Br in the East Pacific Ocean". *Science* 267 (1995): 1002- 1005.

MOORE, R.M., and N.V. BLOUGH. "A marine source of methyl nitrate". *Geophysical Research Letters* 29 (2002): 10.1029/2002GL014989.

MOORE, R.M., and W. GROSZKO. "Methyl iodide distribution in the ocean and fluxes to the atmosphere". *Journal of Geophysical Research-Atmospheres* 104 (1999); C5: 11,163-11,171.

MOORE, R.M., R. TOKARCZYK et al. "Marine phytoplankton as a source of volatile organohalogens". In A. Grimvall, and E.W.B. De Leer, eds. *Naturally-Produced Organohalogens.* Netherlands: Kluwer Academic Publications, 1995: 283-294.

MOORE, R.M., W. GROSZKO, and S. NIVEN. "Ocean-atmosphere exchange of methyl chloride: results from N.W. Atlantic and Pacific Ocean studies. *Journal of Geophysical Research-Atmospheres* 101 (1996): 28,529-28,538.

NEVISON, C.D., R.F. WEISS, and D.J. ERICKSON III (1995). "Global oceanic emissions of nitrous oxide". *Journal of Geophysical Research-Atmospheres* 100 (1995); C8: 15,809-15,820.

NEVITT, G.A., R.R. VEIT, and P. KAREIVA. "Dimethyl sulphide as a foraging cue for Antarctic Procellariiform seabirds". *Nature* 376 (2002): 680-682.

O'DOWD, C.D., J.L. JIMÉNEZ, R. BAHREINI, R.C. FLAGAN, J.H. SEINFELD, K. HÄMERI, L. PIRJOLA, M. KULMALA, S.G. JENNINGS, and T. HOFFMANN. "Marine aerosol formation from biogenic iodine emissions". *Nature* 417 (2002): 632-636.

O'DOWD, C.D., M.C. FACCHINI, F. CAVALLI, D. CEBURNIS, M. MIRCEA, S. DECESARI, S. FUZZI, Y.J. YOON, and J.-P. PUTAUD. "Biogenically driven organic contribution to marine aerosol. *Nature* 431 (2004): 676-680.

PILINIS, C., D.B. KING, and E.S. SALTZMAN. "The oceans: A source or a sink of methyl bromide?". *Geophyical Research Letters* 23 (1996); 8: 817-820.

PLASS-DÜLMER, C., R. KOPPMANN, M. RATTE, and J. RUDOLPH. "Light nonmethane hydrocarbons in seawater". *Global Bilogeochemical Cycles* 9 (1995): 79-100.

QUINN, P., R.J. CHARLSON, and T.S. BATES. "Simultaneous observations of ammonia in the atmosphere and ocean". *Nature* 335 (1988): 336-338.

RHEE, T. S., A. J. KETTLE, and M. O. ANDREAE. "Methane and nitrous oxide emissions from the ocean: A reassessment using basin-wide observations in the Atlantic". *Journal of Geophysical Research* 114 (2009): D12304, doi: 10.1029/2008 JD011662.

SIMÓ, R. "Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links". *Trends in Ecology & Evolution* 16 (2001): 287-294.

SIMÓ, R., and J. DACHS. "Global ocean emission of dimethylsulfide predicted from biogeophysical data". *Global Biogeochemical Cycles* 16 (2002): 1078, doi: 10.1029/ 2001GB001829.

SIMÓ, R., and C. PEDRÓS-ALIÓ. "Role of vertical mixing in controlling the oceanic production of dimethyl sulphide". *Nature* 402 (1999): 396-399.

SPURNY, K.R. "Atmospheric condensation nuclei. P.J. Coulier 1875 and J. Aitken 1880 (Historical Review)". *Aerosol Science and Technology* 32 (2000): 243-248.

SUN, J., and P.A. ARIYA. "Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review". *Atmospheric Environment* 40 (2005): 795-820.

SUNTHARALINGAM, P., A.J. KETTLE, S.M. MONTZKA, and D.J. JACOB. "Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake". *Geophysical Research Letters* 35 (2008): L19801, doi: 10.1029/2008GL034332.

TWOMEY, S.A. "The influence of pollution on the shortwave albedo of clouds". *Journal of the Atmospheric Science* 34 (1977): 1149-1152.

UHER, G. "Distribution and air–sea exchange of reduced sulphur gases in European coastal waters". *Estuarine, Coastal and Shelf Science* 70 (2006): 338-360.

VALLINA, S.M., and R. SIMÓ. "Strong relationship between DMS and the solar radiation dose over the global surface ocean". *Science* 315 (2007): 506-509.

VALLINA, S.M., R. SIMÓ, S. GASSÓ, C. de BOYER-MONTÉGUT, E. del RIO, E. JURADO, and J. DACHS. "Analysis of a potential 'solar radiation dose–dimethylsulfide–cloud condensation nuclei' link from globally mapped seasonal correlations". *Global Biogeochemical Cycles* 21 (2007a): GB2004, doi: 10.1029/2006GB002787.

VALLINA, S.M., R. SIMÓ, and M. MANIZZA. "Weak response of oceanic dimethylsulfide to upper mixing shoaling induced by global warming". *Proceedings of the National Academy of Sciences of the United States of America* 104 (2007b): 16004-16009.

VALLINA, S.M., R. SIMÓ, T.R. ANDERSON, A. GABRIC, R. CROPP, and J.M. PACHECO. "A dynamic model of oceanic sulfur (DMOS) applied to the Sargasso Sea: Simulating the dimethylsulfide summer-paradox". *Journal of Geophysical Research – Biogeosciences* 113 (2008), G01009, doi: 10.1029/2007JG000415.

VILA-COSTA, M., R.P. KIENE, and R. SIMÓ. "Seasonal variability of the dynamics of dimethylated sulfur compounds in a coastal northwest Mediterranean site". *Limnology and Oceanography* 53 (2008): 198-211.

XIE, H., and R.M. MOORE. "Carbon disulfide in the North Atlantic and Pacific Oceans". *Journal of Geophysical Research* 104 (1999); C3: 5393-5402.

YASSAA, N., I. PEEKEN, E. ZÖLLNER, K. BLUHM, S. ARNOLD, D. SPRACKLEN, and J. WILLIAMS. "Evidence for marine production of monoterpenes". *Environ Chem* 5 (2008): 391-401.

YVON-LEWIS, S.A., E.S. SALTZMAN, and S.A. MONTZKA. "Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability". *Atmospheric Chemistry and Physics* 9 (2009): 5963-5974.