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Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry

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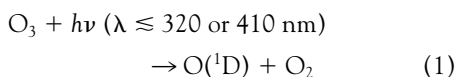
Atmospheric aerosols play important roles in climate and atmospheric chemistry: They scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions. Two important aerosol species, sulfate and organic particles, have large natural biogenic sources that depend in a highly complex fashion on environmental and ecological parameters and therefore are prone to influence by global change. Reactions in and on sea-salt aerosol particles may have a strong influence on oxidation processes in the marine boundary layer through the production of halogen radicals, and reactions on mineral aerosols may significantly affect the cycles of nitrogen, sulfur, and atmospheric oxidants.

Over the past decade, there has been intense interest concerning the role of aerosols in climate and atmospheric chemistry. The climatic effects of aerosols had already been recognized in the early to mid-1970s [for a review, see (1)], but the focus of scientific attention shifted during the 1980s to the impact of the growing atmospheric concentrations of CO₂ and other "greenhouse" gases. Scientific interest in the climatic role of aerosols was rekindled after the proposal of a link between marine biogenic aerosols and global climate (2). This proposal, which was originally limited to the effects of natural sulfate aerosols, triggered a discussion about the role of anthropogenic aerosols in climate change (3), which led to the suggestion that they may exert a climate forcing comparable in magnitude, but opposite in sign, to that of the greenhouse gases (1, 4).

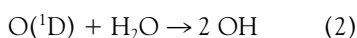
The main sources of biogenic aerosols are the emission of dimethyl sulfide (DMS) from the oceans and of nonmethane hydrocarbons (NMHCs) from terrestrial vegetation, followed by their oxidation in the troposphere (1). Carbonyl sulfide (COS), which has a variety of natural and anthropogenic sources, is an important source for stratospheric sulfate aerosol (5) and therefore indirectly plays an important role in stratospheric ozone chemistry (6). These sources are susceptible to changes in physical and chemical climate: The marine production of DMS is dependent

on plankton dynamics, which is influenced by climate and oceanic circulation, and the photoproduction of COS is a function of the intensity of ultraviolet-B (UV-B) radiation. Air-sea transfer of DMS changes with wind speed and with the temperature difference between ocean and atmosphere. The amount and composition of terpenes and other biogenic hydrocarbons depend on climatic parameters, for example, temperature and solar radiation, and would change radically as a result of changes in the plant cover due to land use or climate change. Finally, the production of aerosols from gaseous precursors depends on the oxidants present in the atmosphere, and their removal is influenced by cloud and precipitation dynamics. Consequently, the fundamental oxidation chemistry of the atmosphere is an important factor in the production of atmospheric aerosols. In turn, aerosols may also play a significant role in atmospheric oxidation processes.

The oxidation efficiency of the atmosphere is primarily determined by OH radicals (7, 8), which are formed through photodissociation of ozone by solar UV radiation, producing electronically excited O(¹D) atoms by way of



where $h\nu$ is a photon of wavelength λ , and by



Laboratory investigations have shown that reaction 1 can occur in a spin-forbidden mode at wavelengths between 310 and 325 nm (9), and even up to 410 nm (10). In the latter case, calculated O(¹D) and OH formation at low-sun conditions at mid-latitudes will increase by more than a factor of 5 compared with earlier estimates (8). Globally and diurnally averaged, the tropospheric concentration of OH radicals is about 10⁶ cm⁻³, corresponding to a tropospheric mixing ratio of only about 4 × 10⁻¹⁴ (11). Reaction with OH is the major atmospheric sink for most trace gases, and therefore their residence times and spatial distributions are largely determined by their reactivity with OH and by its spatiotemporal distribution. Among these gases, methane (CH₄) reacts rather slowly with OH, resulting in an average residence time of about 8 years and a relatively even tropospheric distribution. The residence times of other hydrocarbons are shorter, as short as about an hour in the case of isoprene (C₅H₈) and the terpenes (C₁₀H₁₆), and consequently, their distributions are highly variable in space and time.

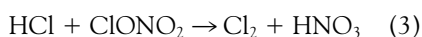
Reliable techniques to measure OH and other trace gases important in OH chemistry have recently been developed and are being used in field campaigns, mainly to test photochemical theory (12). However, because of their complexity they cannot be used to establish the highly variable temporal and spatial distribution of OH. For this purpose, we have to rely on model calculations, which in turn must be validated by testing of their ability to correctly predict the distributions of industrially produced chemical tracers that are emitted into the atmosphere in known quantities and removed by reaction with OH (such as CH₃CCl₃ and other halogenated hydrocarbons) (13). Distributions of OH derived in this way (Fig. 1) can be used to estimate the removal rates and distributions of various important atmospheric trace gases, such as CO, CH₄, NMHCs, and halogenated hydrocarbons. In the tropics, high concentrations of water vapor and solar UV radiation combine to produce the highest OH concentrations worldwide, making this area the photochemically most active region of the atmosphere and a high priority for future research.

Especially because of its role in producing OH, ozone (O₃) is of central importance in atmospheric chemistry. Large amounts of ozone are destroyed and produced by chemical reactions in the troposphere, particularly the CO, CH₄, and NMHC oxidation cycles, with OH, HO₂, NO, and NO₂ acting as catalysts. Because emissions of NO, CO, CH₄, and NMHC

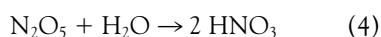
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have increased as a result of human activities, tropospheric ozone has increased as well (14). The overall effect on OH, the “detergent of the atmosphere,” is, however, less clear. On one hand, the increase in ozone will lead to more OH production, but on the other hand, the destruction of OH will also increase because reactions with CO and CH₄ are its main sinks.

Atmospheric chemical processes are not limited to the gas phase, but also occur on the surface of solid particles and within liquid particles, such as aerosols and cloud droplets. The importance of clouds as scavengers of gases and aerosols, as scattering agents for photochemically active solar radiation, as a means of transport from the lower to the upper troposphere, as producers of NO by lightning, and as media for aqueous photochemical reactions is now well recognized (15–17). In contrast, the role of nonactivated aerosol particles as a medium for chemical processes in the troposphere was given little attention until recently. It was generally assumed that the small amount of liquid water available in aerosols would prevent reactions in or on aerosols from competing successfully with reactions in cloud droplets. This assumption was recently proven to be wrong, however, for the troposphere, where, for example, substantial amounts of SO₂ can be oxidized on sea-salt aerosols (18, 19), and for the stratosphere, where the potential power of heterogeneous reactions was dramatically demonstrated in connection with studies on the stratospheric ozone hole. Studies showed that the first, critical step in a series of chemical reactions leading to rapid ozone depletion is



which leads to the formation of catalytically active Cl. This reaction only occurs on the surface or within particles of polar stratospheric clouds at low temperatures (6, 17). Earlier it had been shown that the reaction



takes place on stratospheric sulfuric acid particles, leading to the conversion of the catalytically active NO_x to the much less reactive HNO₃. Neither reaction occurs to a significant extent in the gas phase, but both are strongly facilitated by surfaces containing liquid water or ice.

In this article, we will focus on recent developments in our understanding of the biogeochemical processes that provide precursor materials for some of the climatically and chemically most important aerosol species, such as sulfate and organic particles, and on the atmospheric processes that regulate the formation of these aerosols. Be-

cause the large amounts of particulate matter in the troposphere make it likely that heterogeneous reactions are of importance for tropospheric chemistry, we will discuss the potential for active halogen chemistry in the marine boundary layer and for heterogeneous loss of NO_x and SO₂ on various types of aerosol particles.

Dimethyl Sulfide: Phytoplankton, Aerosols, Clouds, and Climate

Ten years ago, Charlson, Lovelock, Andreae, and Warren (CLAW) (2) proposed a hypothesis in which DMS is released by marine phytoplankton, enters the troposphere, and is oxidized to sulfate particles, which then act as cloud condensation nuclei (CCN) for marine clouds. Changes in CCN concentration affect the number concentration of cloud droplets, which influences cloud albedo and consequently climate. Large-scale climate change, in turn, affects the phytoplankton in the oceans and thereby closes the feedback loop. In the years since publication of the CLAW hypothesis, over 700 papers have been published discussing the biogeochemistry of DMS (and its precursors) and its link to climate. In spite of this effort, fundamental gaps remain in our understanding of key issues in this biosphere-climate interaction, such as the processes that regulate the concentration of DMS in seawater, the rate of transfer across the air-sea interface, the mechanism and rate of CCN production from DMS oxidation, and the effect of climate on DMS production in the sea. As a consequence, we are still not able to represent the CLAW hypothesis in the form of a process-based, quantitative, and predictive model. Even the overall sign of the feedback cannot be deduced with certainty, because it is not yet known if a warming climate would result in an increase or decrease of DMS emissions. Glacial-to-interglacial changes in the amounts of DMS oxidation products in polar ice cores have not answered this question unambiguously, because they may reflect variations in atmospheric transport patterns as much as differences in DMS production (20).

Early, limited data sets had suggested a possible correlation between DMS and phytoplankton concentration (21), which led to the hope that global DMS distributions could be estimated from remotely sensed chlorophyll concentrations. However, a recent statistical analysis of almost 10,000 measurements of DMS in surface seawater failed to show any useful correlations between DMS and chlorophyll or other chemical or physical parameters (22). One reason for the absence of a correlation between plankton biomass and DMS is that the intra-

cellular concentration of its metabolic precursor, dimethylsulfoniopropionate (DMSP), varies between different phytoplankton species over a range of five orders of magnitude. Although it is clear that some taxonomic groups typically contain higher amounts of DMSP, these relations are by no means clear cut (23). Biota-DMS correlations are further obscured by the complex set of interactions that regulate the concentration of DMS in the surface ocean (24) (Fig. 2). The release of DMSP into the water column is controlled by senescence or by grazing by viral, bacterial, and zooplankton (25), which in turn is influenced by the dynamics of the phytoplankton population. The subsequent breakdown of DMSP to DMS, which occurs with turnover times on the order of hours to days, is microbially mediated and can have a DMS yield between 12 and 66% (26, 27). In the marine mixed layer, DMS is subject to a number of removal mechanisms, including bacterial and photochemical decomposition, emission to the atmosphere, and downward mixing, with a total turnover time of one to a few days (24, 26). The rates of the dominant DMS sinks—biological decomposition, photodecomposition, and ventilation—are highly variable as a function of time, place, and meteorological conditions, but are of comparable overall importance for the removal of dissolved DMS. As a result of this complexity, attempts to predict the concentration of DMS in surface waters by a process model have been successful only on a regional level (28), and the construction of a global DMS concentration and emission field had to rely on a heuristic extrapolation scheme (22).

Given the concentrations of DMS in surface water and the overlying air, the

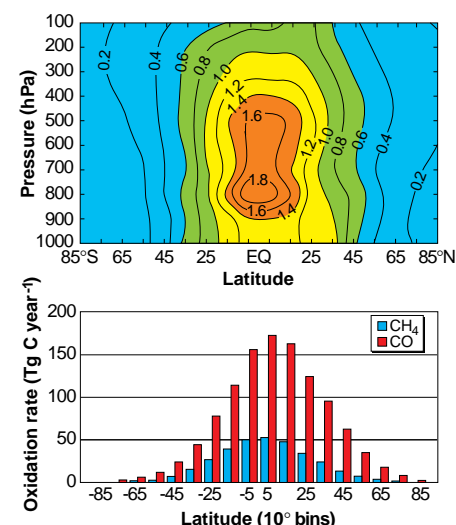


Fig. 1. (A) Model-derived longitudinally and diurnally averaged values of annual mean OH concentration (in units of 10^6 molecules cm^{-3}). (B) Estimated annual oxidation rates of CO and CH₄ by reaction with OH.

sea-air flux can be estimated from the air-sea concentration gradient and an empirically determined exchange coefficient. The formulations for the dependence of this coefficient on wind speed—based on wind-tunnel, radiocarbon, and tracer measurements—differ in their predictions by about a factor of 2 (29). Studies on DMS and sulfur cycling over the oceans (30) and a recent analysis of the oxygen distribution in and over the ocean (31) strongly support the higher estimates. However, there are also studies consistent with the lower estimates (32), and we conclude that there is at present no objective way to select one formulation over the others. Largely as a consequence of this uncertainty, estimates of global annual sea-air flux of DMS based on the Kettle *et al.* (22) database range from 20 to 40 Tg of S per year, with frustratingly little improvement in the width of this range over the last decade (33).

Extensive work on the atmospheric photooxidation of DMS has shown that the main oxidant of DMS is the OH radical, leading to the production of SO₂ and lesser amounts of methane sulfonic acid (MSA), dimethyl sulfide, and dimethyl sulfone. Especially during high-latitude winter, however, the NO₃ radical can also play an important role, even in remote regions (34). This additional reactant could explain the observed seasonal cycle in the concentration ratio of MSA to non-sea-salt sulfate, which shows a pronounced minimum in winter. A major discrepancy between the modeled and observed diurnal behavior of DMS in the marine boundary layer (MBL) remains to be resolved. When independently modeled OH concentrations and measured OH-oxidation rate constants are used, the amplitude of the

modeled diurnal cycle of DMS is much smaller than observed (19, 35, 36). The DMS removal rates calculated under these conditions are consistent with the air-sea exchange fluxes obtained using the low estimates of the sea-air exchange coefficients. However, to produce a satisfactory fit between the observed and modeled diurnal cycles, the daytime oxidation rate of DMS must be approximately doubled by increasing the oxidation rate constant or the OH concentration, or by invoking additional DMS oxidation pathways. Reactions with halogen radicals, such as BrO, Cl₂, and Br, may help to resolve this discrepancy (37, 38). Regardless of its mechanistic explanation, however, the observed large diel amplitude of DMS implies high emission fluxes from the sea surface, consistent with the higher estimates of the air-sea exchange coefficients.

Current evidence from laboratory studies, field measurements, and modeling suggests that SO₂ is the dominant oxidation product of DMS in the MBL under most environmental conditions (34, 35, 39) and that it is the main source of non-sea-salt sulfate in the unpolluted MBL (19, 35, 36, 40). It must be remembered, however, that it is not the mass of sulfate aerosol that is relevant to climate forcing in the CLAW hypothesis, but the number concentration of CCN, which is roughly the same as the number concentration of particles above ~0.05-μm diameter (assuming the particles are completely soluble). Thus, for DMS oxidation to produce a climatic effect, it must increase the number of particles in this size range. This concentration can either be achieved by the creation of new particles from the gas phase or by the growth of existing smaller particles beyond this criti-

cal diameter. The formation of particles from gaseous H₂SO₄ molecules is a highly nonlinear process, which is also influenced by the concentrations of H₂O and NH₃. Deposition of H₂SO₄ molecules on existing surfaces (particularly sea-salt aerosols) competes with nucleation, and it has been postulated that nucleation of sulfate aerosol does not normally occur in the MBL (41, 42), a view that has been challenged by another modeling study (43). Measurements of the concentration of ultrafine particles made over the remote Southern Ocean during the IGAC Aerosol Characterization Experiment (ACE-1) provide strong evidence that, at least in this region, most of the formation of new particles does indeed take place in the free troposphere around the detrainning regions of clouds at altitudes from 2 to 6 km (44). The particles produced are initially too small to act as CCN but can be entrained from the free troposphere into the MBL and subsequently grow either by gas-to-particle deposition or by cloud processes (42, 45). In this way, DMS oxidation can lead to the formation of new CCN, both by providing the starting material for the nucleation of new particles in the free troposphere and by supporting the growth of smaller particles into CCN in the MBL. Direct evidence for the contribution of DMS oxidation to aerosol-particle and CCN production in the MBL is provided by measurements over the South Atlantic, which show strong correlations between marine DMS emission and the concentrations of total aerosol particles and CCN in particular (46).

Carbonyl Sulfide: Oceans, Trees, and Soils and Stratospheric Aerosol

In contrast to DMS, which is rapidly oxidized in the troposphere, carbonyl sulfide (COS) shows low reactivity in the gas phase and can therefore be transported into the stratosphere, where it is oxidized to H₂SO₄. This mechanism is considered the dominant source of the stratospheric sulfate-aerosol layer during periods of volcanic quiescence (5, 47), a view that has, however, been recently challenged (48). As we have become aware of the importance of aerosols in climate and stratospheric-ozone chemistry, interest in the sources and sinks of COS has intensified in recent years. With an atmospheric burden of about 5 Tg, about 15 times that of SO₂ and three times that of aerosol sulfate (on a sulfur mass basis), COS is the most abundant sulfur compound in the atmosphere. The major sources of COS are thought to be photooxidation of CS₂, biomass burning, and emissions from oceans and soils; its major sink,

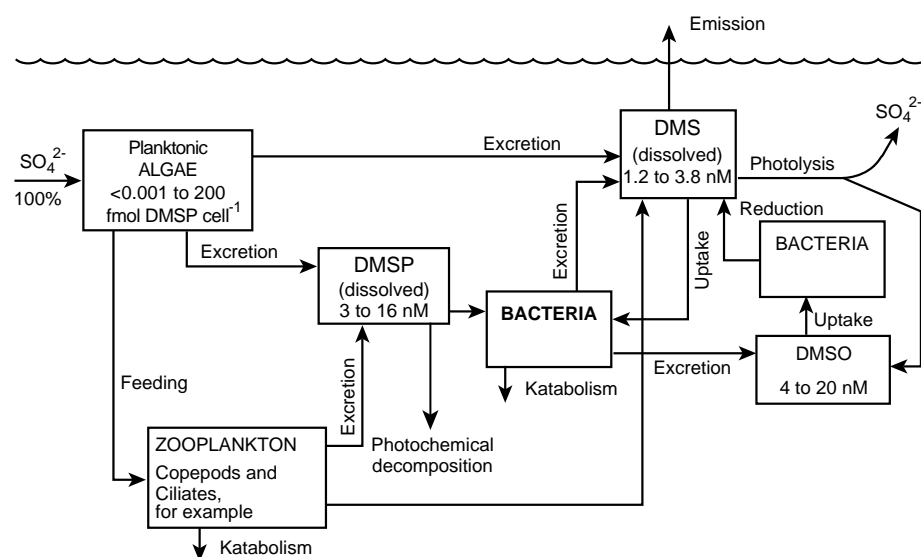


Fig. 2. Schematic representation of the processes that regulate the interactions of DMS and related sulfur species in the surface ocean.

Organic Particles: Dominant Aerosol Fraction over the Tropical Continents

Whereas sulfate dominates the composition of marine and stratospheric submicrometer aerosols, organic matter frequently makes up the largest fraction over continental regions, especially in remote areas. One of the surprising results of the Amazon Boundary Layer Experiment (ABLE-2) was the similarity of the concentrations of particulate organic carbon and "black carbon" over the central Amazon Basin between the wet and dry seasons (65, 66). In both seasons, organic matter accounted for about 90% of the aerosol mass. During the dry season, the emission of vast amounts of smoke from forest-clearing fires at the southern perimeter of the Amazon and a predominant northward transport over the region provided an apparently satisfactory explanation for the abundance of particulate organic carbon and black carbon, especially because the aerosol also contained enhanced levels of fine particulate potassium, usually considered to be a tracer for aerosols produced by burning (67). The abundance of organic aerosols during the wet season was attributed to biogenic production (66), but without clear specification of a source mechanism. Photochemical production from gaseous hydrocarbon precursors can probably account for a significant fraction of this aerosol. Estimates for the global biogenic production of monoterpenes and other reactive volatile organics fall in the range of 300 to 500 Tg of C per year, with highest emissions in the tropics, particularly the Amazon basin (68). Aerosol yields from the reaction of these compounds with OH, O₃, and NO₃ are extremely variable, depending on the composition of the hydrocarbons as well as the circumstances under which the oxidation reactions are taking place. Yields for the daylight photo-oxidation of terpenes

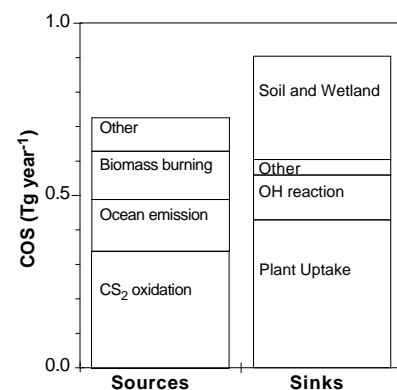


Fig. 3. Proposed budget for atmospheric carbonyl sulfide.

uptake by vegetation. In recent budgets, sources exceed sinks by about a factor of 2, in conflict with atmospheric observations, which show no sign of the secular concentration increase implied by such an imbalance (49). This disagreement suggests the presence of either one or more large, undiscovered sinks or serious overestimates of the source strengths. A recent study indicated that COS is produced during the atmospheric photooxidation of DMS, which would aggravate the imbalance (50).

Observations of a pronounced diurnal variation of COS in surface seawater and some simple laboratory experiments provided the first clues that COS was formed photochemically from biogenic precursors (51). Subsequent measurements showed COS to be supersaturated in practically all regions sampled (52); on the basis of these data, an oceanic source strength of 0.4 to 0.9 Tg of COS per year was suggested. In contrast to the previous studies, however, which had all been made during the warmer seasons or at lower latitudes, recent winter measurements in the Atlantic and Pacific (53) showed large-scale uptake of COS by the sea surface. These observations and improved models of the cycle of COS in the surface ocean have led to a drastic downward revision of the marine emission of COS to 0.15 Tg year⁻¹ (54).

Substantial progress has been made in our understanding of the mechanistic aspects of COS cycling in the sea. The dominant precursors of COS appear to be thiol (-SH) groups in biogenic organosulfur compounds: These compounds first react with photochemically or aphotically produced radicals to form thiyl radicals (-S[•]), which subsequently react with carbonyl moieties to produce COS (55). Rate constants for the photoproduction and dark production of COS have been measured in a number of environments and, when normalized to the levels of colored dissolved organic matter (CDOM) present, show remarkably little variation among different regions (56, 57). This constancy makes it possible to accurately estimate the rate of COS production in a parcel of seawater when solar UV irradiance and CDOM concentrations are known. The dominant sink for COS is its hydrolysis to bisulfide and bicarbonate, for which rate constants in seawater have been determined and verified (58). COS is lost from the photochemically active oceanic surface mixed layer by ventilation to the atmosphere and by downward mixing. These processes have been successfully incorporated into a process model of COS cycling in the upper ocean, from which sea-to-air fluxes can be predicted (56, 59). It is to be hoped that such local models can

be generalized in the future using data from remote sensing and meteorological models to produce a process-based global model of COS production.

A reexamination of the terrestrial emissions of COS has led to a reversal in our assessment of soils as a COS source. All of the soil emission studies done before 1990 used COS-free air as a sweep gas in the soil flux chambers and indicated that soils are a source of COS. However, when ambient air was used as a sweep gas, soils were consistently found to take up COS at rates of 3 to 30 ng of S per square meter per minute (60). Although the data obtained by the ambient-air method are still too sparse to derive a reliable global estimate of the soil sink for COS, they indicate that soils should not be included as a source in the budget of COS. Even at the smallest observed fluxes, the global deposition of COS to soils would be 0.3 Tg year⁻¹.

Vegetation has usually been considered to be the dominant sink of COS [see (48), and references therein]. Physiological studies showed that COS uptake by higher plants, aquatic algae, and even algal crusts on desert soils correlates with photosynthesis, and that it is mediated by enzymes in the photosynthetic pathway (61). A strong correlation between low concentrations of COS and reduced levels of CO₂ in continental air masses sampled over the Pacific Ocean supports the hypothesis of terrestrial photosynthesis as an important sink for COS (62).

On the basis of the preceding discussion, we propose a revised budget for COS that takes into account the lowered estimate of marine emissions and the existence of a soil sink (Fig. 3). This budget is balanced within the uncertainty of the estimates, which must be considered to be as much as a factor of 2 for some of the individual sources. To calculate the atmospheric turnover time, we must take into account that the oceanic flux shown in Fig. 3 represents a net sink, which is composed of gross source and sink terms, and that the turnover time must be calculated using the gross sink term (54, 63). If we include a (gross) oceanic sink of 0.34 Tg year⁻¹ due to hydrolysis, a COS tropospheric turnover time of 3.7 years is obtained. Given such a short turnover time and the lack of any indication that the magnitude of the anthropogenic sources has increased over the last two decades, the absence of a rising trend in tropospheric COS concentrations can be explained. This budget also implies that the observed increase in the background burden of sulfate aerosol in the stratosphere (64) is not likely to be due to increased COS fluxes from the troposphere.

range from 5 to 100%, with the highest values obtained for sesquiterpenes. For most compounds, nighttime oxidation by ozone produces even higher aerosol yields than the daytime photochemical process (69). Given this wide range of yields and our limited knowledge of the mix of hydrocarbons released, especially by tropical vegetation, it is difficult to make an accurate estimate of the mean aerosol yield from hydrocarbon oxidation. Assuming a range of yields between 5 and 40% (69, 70), we obtain an estimate of 30 to 270 Tg year⁻¹ for the production of secondary organic aerosols, a magnitude comparable to the production of biogenic and anthropogenic sulfate aerosols [90 and 140 Tg year⁻¹, respectively (1)].

These production mechanisms, however, cannot explain the presence outside the burning season of black carbon (usually thought to be soot carbon from combustion), K, and Zn in both the coarse and the submicrometer fractions of Amazonian aerosols (66). These components must represent primary biogenic aerosol, which consists of microbial particles (for example, bacteria, fungi, algae, and spores), plant debris (for example, cuticular waxes and leaf fragments), and humic matter. Such a primary biogenic origin could explain the presence of K and Zn, both abundant in plant tissues. The light-absorbing properties of this aerosol may be related to the presence of humic-like substances rather than soot carbon. Unfortunately, little information is available that would allow a reliable estimate of the contribution of primary biogenic particles to the organic aerosol burden in tropical regions. However, the fact that even in an urban, temperate setting they make up some 10 to 30% of the total aerosol number and volume concentration (71) suggests that their contribution in a densely vegetated tropical region could be substantial. This view is supported by analyses of the lipid fraction of Amazonian aerosols (72), which has been shown to consist predominantly of compounds associated with microbial matter and plant waxes and makes up 10 to 20% of the total aerosol. Given that lipids represent only a fraction of the total primary biogenic aerosol, these observations are consistent with a large primary biogenic fraction in tropical aerosols.

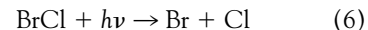
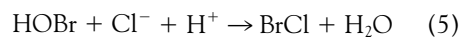
This biogenic organic aerosol may be of considerable significance for atmospheric chemistry and climate. Because both primary and secondary organic particles are effective CCN (73) and primary organic particles can be ice nuclei at temperatures as high as -4°C (71), it is likely that the optical and microphysical properties of tropical continental clouds are strongly influenced by these particles. As a considerable fraction of the planetary heat redistribution from the tropics to higher latitudes is mediated by

deep convection in the tropics, changes in the amounts or characteristics of these particles (by, for example, deforestation or biomass burning) may have far-reaching consequences. Given the high concentrations of this material in the boundary layer, they may make a considerable contribution to the free tropospheric aerosol, even if a large fraction is removed during convective transport. It is even possible that terrestrial organic particles provide surface areas for the deposition of gaseous sulfuric acid from DMS oxidation in the marine troposphere. If the nucleation of new sulfate particles is really as infrequent as has been suggested by some of the modeling studies, terrestrial biogenic particles could by this process contribute significantly to the number concentration of what would appear, on the basis of their sulfate content, to be CCN of marine biogenic origin. Finally, the presence of large amounts of soluble organic matter in the aerosol would lead to a high content of dissolved organics in cloud droplets, which would have a pronounced influence on chemical reaction sequences in these hydrometeors, and ultimately on the atmospheric budgets of important species such as O₃, OH, HO₂, and H₂O₂ (15, 74).

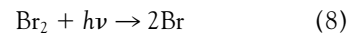
Sea-Salt Aerosol: Halogen Chemistry in the Marine Boundary Layer

Stimulated by the great significance of halogen chemistry in stratospheric ozone destruction (6) and the discovery of episodes of zero ozone concentration in the lower troposphere during polar sunrise (75), there has been growing interest in the potential role of halogen radicals in tropospheric chemistry. It has been proposed that Cl atoms can be produced in the marine boundary layer (MBL) by the reaction between HCl and OH after the volatilization of HCl from sea-salt particles that became acidified by uptake of H₂SO₄ and HNO₃ from the gas phase (76). It is, however, unlikely that this phenomenon alone can be responsible for concentrations of Cl atoms high enough to play a role in atmospheric chemistry, because these are rapidly lost from the atmosphere by reactions with hydrocarbons, including the ubiquitous CH₄. Nevertheless, the activation of both Cl and Br radicals has been observed in the Arctic lower troposphere at polar sunrise (14, 77), leading to efficient photochemical ozone loss (75). The photochemical mechanisms that are responsible for the halogen activation have not yet been firmly established, but surface catalytic reactions on sea ice may be responsible. Catalytic mechanisms for Cl and Br activation, which may also operate elsewhere

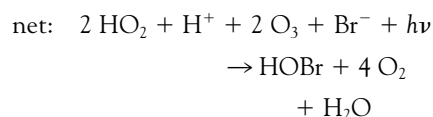
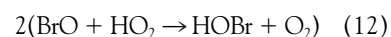
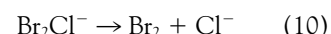
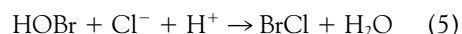
in the MBL, consist of the following reaction sequences (78, 79)



or



or



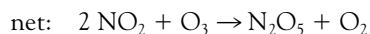
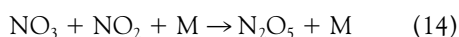
with HOBr and Cl⁻ acting as catalysts. According to Vogt *et al.* (37), the last chain may be of particular importance. It may be initialized by reaction between Br⁻ and peroxomonosulfuric (Caro's) acid, an intermediate in SO₂ oxidation: Br⁻ + HSO₅⁻ → HOBr + SO₄²⁻ (78). Model calculations for the MBL at mid-latitudes and under anticyclonic conditions indicate the possibility of Cl atom and ClO radical concentrations in the range of 1 × 10³ to 2.5 × 10³ cm⁻³ and 10⁶ to 10⁷ cm⁻³, respectively. These values would, for example, result in CH₄ loss rates by reaction with Cl of about 6 to 15% of those calculated for reaction with OH. A more interesting result of the calculation is the occurrence of substantial Br release from the aerosol phase, leading to calculated Br and BrO concentrations of 10⁵ to 10⁶ cm⁻³ and 10⁷ cm⁻³, respectively. Such BrO_x concentrations can lead to significant ozone loss in the MBL. Another interesting result of the model calculations is the possibility of substantial oxidation of S(IV) to S(VI) by HOCl and HOBr in the aerosol, which may surpass that caused by ozone and H₂O₂. If such a sulfur-oxidizing mechanism did indeed exist in the MBL, it would have important consequences, implying that relatively more SO₂ would be oxidized on preexisting sea-salt and sulfate particles, thereby reducing the production of new aerosol particles and CCN, with possible consequences for cloud microphysics and climate. These results from model calculations point to a potentially important role of gaseous halogen species in the chemistry of the MBL.



What is most urgently required at this time are observations to test these theoretical predictions.

Dust, Sea Salt, and Sulfate: Surface Reactions as Sinks for Gas-Phase NO_x and SO_x

We have already drawn attention to the potential importance of reaction 4 on water-containing aerosol as a sink for NO_x ($\text{NO} + \text{NO}_2$), the catalysts in the destruction of stratospheric ozone and the formation of ozone in the troposphere. Because NO_3 is rapidly photolyzed during daytime, N_2O_5 is mainly produced during nighttime by the reactions



Consequently the effect arising from the heterogeneous reaction 3 should be especially noticeable during the dark winter period of the year, and in particular at high latitudes of the Northern Hemisphere. This effect was predicted by global model calculations and confirmed by observations (80), showing reductions in tropospheric NO_x concentrations by more than 90% under such conditions. As a consequence, calculations indicated that ozone and OH at the surface were depleted by 25 and 20%, respectively, as far equatorward as 25°N . At higher altitudes, the effects are even larger because of the greater stability of N_2O_5 against unimolecular decomposition at lower temperatures. The calculated reduction in OH concentrations results from (i) the loss of ozone, which diminishes the production of OH radicals by reactions 1 and 2, and (ii) a lower conversion of HO_2 to OH by the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$. Sulfate aerosol was mainly responsible for this reduction in the oxidizing efficiency of the atmosphere, although reactions on sea-salt particles were also taken into account. The large effect arising from heterogeneous reactions on sulfate particles is mainly due to the fact that anthropogenic sulfur and nitrogen oxide emissions are highly correlated in space. Much less NO_x is present in the MBL, reducing the importance of sea-salt particles as sinks for NO_x . The main effects of sea salt on NO_x are, therefore, restricted to coastal areas immediately downwind of industrial regions (81).

Because mineral aerosol is less efficient at absorbing moisture than sea salt and sulfate, and because it is usually present in drier and warmer regions, conversion of N_2O_5 to HNO_3 on these particles by means of reaction 3 is less efficient than it is on sulfate and

sea-salt aerosol. If this process is significant at all, its influence should be confined to nighttime conditions with higher relative humidity. Nevertheless, soil dust can affect atmospheric chemistry and aerosol characteristics because its alkalinity favors uptake of SO_2 and NO_x and conversion to SO_4^{2-} and NO_3^- on the surface, as well as direct deposition of HNO_3 and H_2SO_4 from the gas phase. Preliminary model calculations indicate that 40 to 70% of aerosol sulfate can be present on mineral particles in regions with strong loadings of soil dust, particularly in large parts of Asia, Africa, and western North America (82). Because of this loss of SO_2 on particulate matter, the formation of new sulfate particles may be substantially reduced. The presence of considerable amounts of nitrate and sulfate on mineral-dust aerosols even in remote regions provides observational support for the validity of these theoretical predictions (83).

Analyses of the future climatic impact of growing SO_2 emissions, and the resulting particle formation, that do not take into account the possible deposition of a substantial fraction of the sulfur on soil dust particles may thus substantially overestimate the climate cooling effect of SO_2 emissions in several regions, such as India and China, in which major industrial developments are expected. It is estimated that 30 to 50% of the atmospheric mineral-dust loading is the result of human disturbance of Earth's surface, especially in semiarid regions (84). The overall effect on the present climate is a cooling, at least at Earth's surface. Quantitative assessments are, however, uncertain because of a severe lack of global observations of the concentration and size distributions and chemical compositions of aerosols (85). Whether reactions of O_3 , HO_2 , HNO_3 , and NO_x on dust particles affect atmospheric chemistry is not known.

Outlook

If the effects of atmospheric aerosols are to be included as interactive terms in models of climate and atmospheric chemistry, then a fundamental, quantitative understanding of their source and sink mechanisms is required. This understanding has not yet been achieved for most of the species discussed here, in spite of the considerable efforts and progress that have been made over the last decade, and such knowledge remains a major goal in biogeochemical and atmospheric research. Of particular importance in this context are the tropical and subtropical regions, where large biogenic and pyrogenic emissions of trace gases, including the NMHCs, combine with high OH concentrations to make them the photochemically most active regions of the atmosphere. They are also the

regions with the greatest and most rapidly developing part of the world's population, and we therefore strongly recommend devoting considerable attention to this much neglected part of the atmosphere.

The chemical interactions between aerosols and gas molecules are still inadequately understood. In many cases, such as the production of halogen radicals on sea-salt aerosols, modeling is far ahead of experimentation and field observations, necessitating considerable efforts to validate model predictions. Global observation programs to study the distributions of ozone and its precursors and the spatiotemporal variations in the concentration of aerosol particles and their physical and chemical properties are essential for this purpose. In other areas, such as the chemical characteristics of organic and mineral aerosols and the chemical reactions taking place on or in these particles, basic information on composition and reaction mechanisms is still needed. Here, we are at a stage at which we have tantalizing glimpses into the complexity and potential importance of these processes but not even enough information to include them in a meaningful way into models of atmospheric chemistry. Fortunately, there are exciting developments in the fields of microanalysis (86) and chemical-kinetics experimentation, which promise to shed light on these topics in the near future.

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Heterogeneous and Multiphase Chemistry in the Troposphere

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Heterogeneous and multiphase reactions on solids and in liquids, respectively, have the potential to play a major role in determining the composition of the gaseous troposphere and should be included in models for understanding this region and assessing the effects of anthropogenic emissions. Making a distinction between reactions on solids (heterogeneous reactions) and those occurring in liquid droplets (multiphase reactions) is convenient for understanding, describing, and including them in models of the troposphere. Frameworks are available for including multiphase reactions in numerical models, but they do not yet exist for heterogeneous reactions. For most of these reactions, water not only provides the medium but it is also a reactant. Other substrates such as sulfate and organic and sea-salt aerosols may also be important, but their effects cannot currently be accurately assessed because of a lack of information on their abundance, nature, and reactivities. Our ability to accurately predict the composition of the troposphere will depend on advances in understanding the microphysics of particle formation, laboratory investigations of heterogeneous and multiphase reactions, and collection of field data on tropospheric particles.

Earth's atmosphere, made up mostly of gases, has suspended in it liquid and solid particles that affect its radiation field and chemical composition. One of the most intense areas of current research in atmo-

spheric sciences is the effect of these particles, natural and anthropogenic, on the radiative balance of Earth and its climate. Here I concentrate on the changes in the composition of the gaseous atmosphere in-

Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry

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