

Surface Ocean– Lower Atmosphere Processes



Corinne Le Quéré and Eric S. Saltzman
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Geophysical Monograph 187

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Corinne Le Quéré

Eric S. Saltzman

Editors

 American Geophysical Union
Washington, DC

Published under the aegis of the AGU Books Board

Kenneth R. Minschwaner, Chair; Gray E. Bebout, Joseph E. Borovsky, Kenneth H. Brink, Ralf R. Haese, Robert B. Jackson, W. Berry Lyons, Thomas Nicholson, Andrew Nyblade, Nancy N. Rabalais, A. Surjalal Sharma, Darrell Strobel, Chunzai Wang, and Paul David Williams, members.

Library of Congress Cataloging-in-Publication Data

Surface ocean-lower atmosphere processes / Corinne Le Quééré and Eric S. Saltzman, editors.

p. cm. -- (Geophysical monograph ; 187)

Includes bibliographical references and index.

ISBN 978-0-87590-477-1 (alk. paper)

1. Ocean-atmosphere interaction. 2. Atmospheric chemistry. 3. Climatic changes. I.

Le Quééré, Corinne . II. Saltzman, Eric S., 1955-

GC190.2.S87 2010

551.5'246--dc22

2009045024

ISBN: 978-0-87590-477-1

ISSN: 0065-8448

Cover Photo: Coastal Mediterranean waters surrounding the Cargèse Institute of Scientific Studies (Corsica, France), which hosted the summer schools of the Surface Ocean–Lower Atmosphere Study during 2001–2009. Photo courtesy of Georgia Bayliss-Brown.

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Printed in the United States of America.

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PREFACE

The need to understand global climate change and to predict climate on long time scales has focused increasing attention on the ocean-atmosphere system. Recent research on the biogeochemical linkages between the atmosphere and ocean has led to new insights about the sensitivity of the climate system to air-sea fluxes, and the potential for climate feedbacks involving atmospheric chemistry, ocean biogeochemistry, and physical climate. At the same time, there is clearly a long way to go to fully understand the nature of these feedbacks and to quantify their effects on climate.

Perhaps the most important lesson learned from several decades of research in this area is that it requires a highly multidisciplinary approach. The SOLAS (Surface Ocean–Lower Atmosphere Study, a project of the IGBP, SCOR, iCACGP, and WCRP) research program was initiated in 2004 to facilitate international research in ocean-atmosphere biogeochemical interactions. One of the goals of SOLAS was to help equip the next generation of climate scientists with broad understanding of ocean-atmosphere processes. It was recognized that many young scientists entering graduate school have strong disciplinary (chemistry, physics, biology) backgrounds but little knowledge of ocean-atmosphere processes, and little exposure to the questions driving SOLAS research or the tools needed to carry it out. The SOLAS Summer School (held in Cargèse, France, in 2003, 2005, 2007, and 2009) has helped fill this gap for about 300 postgraduate students from a wide range of backgrounds. This volume was based loosely on the SOLAS Summer School lectures. It is not intended as either a state-of-the-art review of the literature or a standard textbook. Rather, it is meant as a starting point for researchers interested in ocean-atmosphere biogeochemical exchange to obtain background in areas with which they may not be familiar and to obtain a broad perspective on the issues driving research in this challenging field. We hope it will also provide a means for experts in traditional environmental sciences to learn about SOLAS research problems and find new ways in which their expertise can contribute.

This volume consists of three types of chapters: overviews, research issues, and tools. The overview chapters

provide basic concepts in the areas of atmospheric gas-phase chemistry, aerosols and cloud processes, ocean circulation, coastal zone processes, marine ecosystems, and nutrient dynamics. The research issues chapters focus on issues of contemporary research in biogeochemistry and climate. These tend to be highly interdisciplinary, cutting across the ocean-atmosphere boundary. The topics addressed are dimethylsulfide, atmospheric dust, air-sea gas exchange, and oceanic iron and carbon cycles. A chapter on the glacial-interglacial changes in atmospheric CO₂ provides some perspective on biogeochemical cycles on longer time scales. Finally, three chapters focus on tools (remote sensing, data assimilation, and biogeochemical modeling) that are playing an increasingly important role in ocean-atmosphere research.

The editors wish to thank everyone who helped envision, organize, fund, and carry out the SOLAS Summer Schools, particularly Véronique Garçon, Peter Liss, the lecturers and Scientific Steering committees of the schools, Emilie Brévière, Georgia Bayliss-Brown and the SOLAS International Project Office, and the staff of the Cargèse Institute of Scientific Studies. The editors also wish to express their thanks to the AGU Books staff for their work in support of this project, in particular Telicia Collick and Virginia Marcum, and to the many anonymous reviewers who greatly improved the text. We wish to acknowledge financial support from more than a dozen national and international agencies, especially the support from SCOR (Scientific Committee on Oceanic Research), APN (Asia–Pacific Network for Global Change Research), CNES (Centre National d'Études Spatiales), CNRS (Centre National de la Recherche Scientifique), NASA (National Aeronautics and Space Administration), NOAA (National Oceanic and Atmospheric Administration), NERC (Natural Environment Research Council), NSF (National Science Foundation), DFG (Deutsche Forschungsgemeinschaft), IAI (Inter-American Institute for Global Change Research), and the European Union.

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Surface Ocean–Lower Atmosphere Processes
Geophysical Monograph Series 187
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10.1029/2009GM000914

Introduction to Surface Ocean–Lower Atmosphere Processes

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This introductory chapter discusses the rationale for studying the role of surface ocean–lower atmosphere processes in the context of the climate system, with an integrated, multidisciplinary approach. Accurately predicting climate change on multidecadal or centennial time scales requires an understanding of a wide range of ocean–atmosphere interactions that influence the atmospheric abundance of greenhouse gases, aerosols, and clouds. Examples of such interactions include the uptake of fossil fuel CO₂ by the oceans, perturbation of ocean ecosystems by atmospheric deposition of nutrients, and the influence of oceanic phytoplankton on cloud properties and climate by way of the ocean–atmosphere cycling of dimethylsulfide. Progress in such areas requires the understanding of processes on both sides of the ocean/atmosphere interface.

SOCIETAL IMPORTANCE

Many important science questions in climate research involve the surface ocean and the lower atmosphere. These require understanding not only the physical exchange of heat, water, and momentum between the atmosphere and ocean but also the exchange of a wide range of gases and aerosol-borne chemicals. Some of these issues, such as the idea that the oceans play an important role in the uptake of fossil fuel-derived carbon dioxide (CO₂), were first raised more than a century ago [Arrhenius, 1896]. Others are much more recent, such as the idea that aerosols generated from oceanic sulfur gases may participate in climate regulation [Shaw, 1983; Charlson *et al.*, 1987], or the recognition that deposition of iron-containing desert dust could influence the uptake of CO₂ by oceanic ecosystems [Martin, 1990]. These types of biogeochemical ex-

changes can indirectly impact the Earth's radiative balance in many different ways, on a wide range of time scales, influencing not only the global climate but also regional climate and air and water quality. One of the lessons of research in this area is that the climate system can be very sensitive to small changes in the composition of the atmosphere. Even very low levels of aerosols and trace gases can exert strong leverage on climate through their effects on ocean biology, clouds, atmospheric reactivity, and stratospheric ozone.

One of the major challenges facing climate science today is developing the capability to deliver accurate predictions about future climate change on time scales of a century or more. This requires models that capture the interactions between human activities (energy consumption; use of land, ground water, and surface water; pollution of atmosphere and oceans, and so forth) and the atmosphere, terrestrial biosphere, and the oceans. Such models will be an increasingly important tool for evaluating the long-term impacts of environmental policy options already adopted or under consideration. Another, equally important scientific challenge is to develop the observational capability to detect changes in

the ocean–atmosphere system, to be able to validate models, advance our understanding of environmental processes, and provide early warning of unanticipated events.

The imprint of human activities on the surface ocean and lower atmosphere is increasingly evident, as demonstrated by changes in atmospheric gases and aerosols, ocean acidification, ocean de-oxygenation, changing nutrients in coastal regions, surface warming, changes in sea ice distributions, and the like. At the same time, there are numerous proposals for deliberate manipulation of atmospheric and oceanic composition in order to mitigate predicted future climate change. The feasibility and wisdom of geoengineering on a global scale is a controversial topic both among scientists and among the general public [Royal Society of London, 2009]. What is clear, however, is the increasing societal need for a detailed and accurate understanding of the processes regulating the surface ocean and lower atmosphere and their interaction with the climate system.

THE RESEARCH CHALLENGE

The major goals of research on Surface Ocean–Lower Atmosphere processes are summarized in the following statement [SOLAS Science and Implementation Plan, 2004]:

To achieve quantitative understanding of the key biogeochemical–physical interactions and feedbacks between the ocean and atmosphere, and of how this coupled system affects and is affected by climate and environmental change.

Surface Ocean–Lower Atmosphere Study (SOLAS) is an international research initiative that was formed in response to the need to better understand this key region. The SOLAS initiative stemmed from the recognition that the surface ocean–lower atmosphere region is one of the keys to understanding how the Earth works, to understanding Earth’s climate history, and to predicting future changes in climate. The challenges of studying the SOLAS region are formidable, because the surface ocean and lower atmosphere consist of dynamic fluids of extraordinary chemical and biological complexity. The cartoon in Plate 1 illustrates some of the many processes and factors involved in understanding the ocean/atmosphere exchange and its impacts. These phenomena span the disciplines of physics, chemistry, and biology. They also involve an enormous range of physical dimensions, from the nanometer scales of molecules and colloids, to the micrometer scale of phytoplankton, to the kilometer scale of vertical mixing on both sides of the interface, to thousands of kilometer scales of horizontal mixing across ocean basins. The time scales involved are equally di-

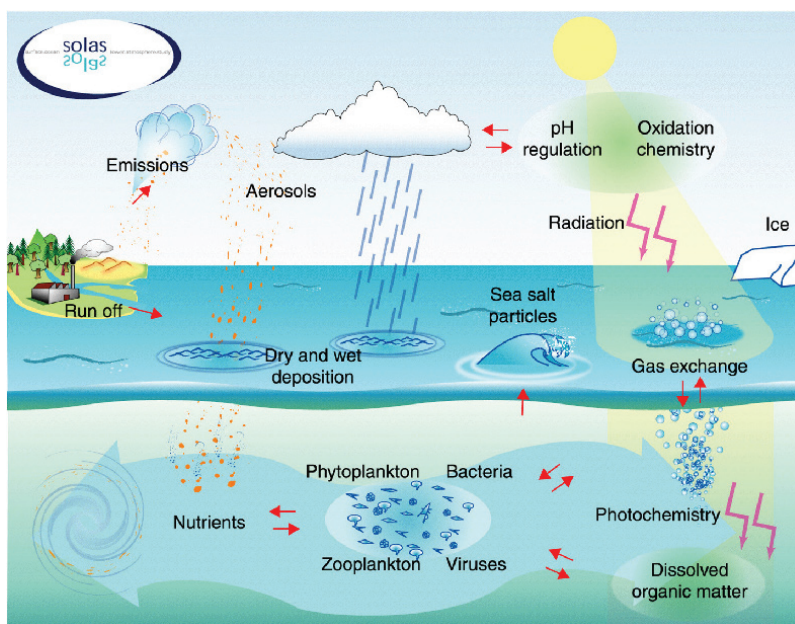


Plate 1. The SOLAS domain. An idealized cartoon illustrating the wide range of physical, chemical, and biological processes involved in ocean/atmosphere exchange (from the *SOLAS Science and Implementation Plan* [2004]). The climate system is sensitive to the abundance and types of greenhouse gases, aerosols, and clouds. These are, in turn, related to a variety of ocean processes. The exchanges between the oceans and atmosphere occur via the air/sea interface, a complex membrane whose physical, chemical, and biological properties are not well understood. Ocean/atmosphere exchanges can lead to a variety of potential climate feedbacks.

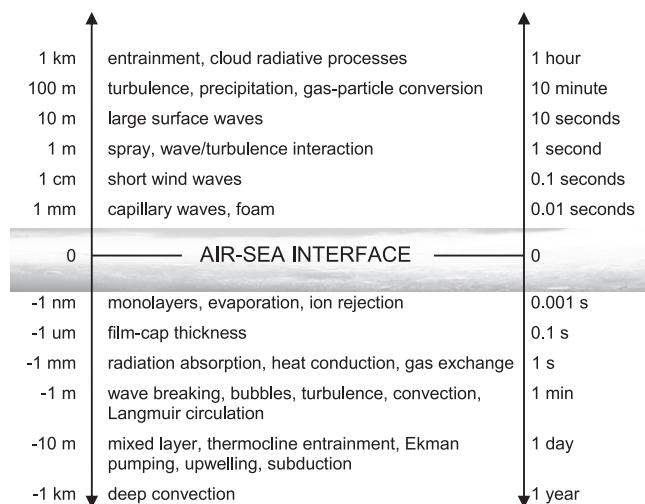


Figure 1. Spatial and temporal scales associated with physical processes in air-sea exchange and surface ocean–lower atmosphere interactions (modified from the *SOLAS Science Plan and Implementation Strategy*).

verse, ranging from nanosecond time scales of energy transfer in photochemical reactions to millisecond time scales of near surface turbulence; to days or weeks for ecosystem dynamics; and to months, years, decades, and longer in the case of climate feedbacks (Figure 1).

The scientific challenges are magnified by the fact the research community has rather limited access to this critical environment. Scientists can access the marine environment through ships and aircraft, but these provide limited spatial and temporal coverage at great expense. Buoys can provide distributed observations, but only of a very limited set of parameters. Satellite-based instruments provide near-continuous spatial/temporal coverage, but with limited sensing capabilities. For all these reasons, it is evident that progress in this area requires a highly collaborative, multidisciplinary, multinational effort.

Ongoing research in this field can be grouped into three main areas:

1. Air-sea exchange of trace gases and aerosols and its influence on atmospheric composition and reactivity, aerosols, clouds, and climate.
2. The air-sea interface itself: processes controlling air-sea exchange of gases and aerosols.
3. The role of ocean-atmosphere interactions in the cycling of CO₂ and other greenhouse gases.

Atmospheric Chemistry, Aerosols, and Clouds

The SOLAS challenge in atmospheric chemistry is to understand how the oceans influence the composition, reactiv-

ity, and radiative properties of the atmosphere. This requires a knowledge of the basic photochemistry of the atmosphere, air-sea fluxes of a wide range of chemicals (both as gases and as particles), and interactions between these chemicals and the Earth's radiation field. Trace gases can interact with the atmosphere in ways that influence tropospheric and stratospheric ozone, both of which are important to the climate system. In this volume, several chapters address the basic features of the atmosphere that are important to SOLAS research. *Atmospheric Gas Phase Reactions*, by U. Platt, outlines the fundamental processes behind our understanding of atmospheric photochemistry. This chapter lays out the basic reactions responsible for the formation and destruction of ozone and explains the key differences between stratospheric and tropospheric chemistry. The approach emphasizes the important role of gas kinetics in the field of atmospheric chemistry, which may be unfamiliar to students and researchers in oceanography. This chapter also explains the factors controlling the hydroxyl radical in the troposphere, which controls the lifetime of many climate-active gases. *Marine Aerosols*, by E. S. Saltzman, is an overview of the characteristics of principal types of aerosol over the oceans, origins of these aerosols, and some of the natural and anthropogenic processes that influence them. The chapter emphasizes the dynamic nature of the marine aerosols and the importance of both chemistry and physics in understanding their behavior. The input of terrestrially derived dust-borne iron to the oceans, and its impact on ocean productivity, is emerging as one of the most exciting and important aspects of SOLAS research. The chapter *Global Dust Cycle*, by A. Ridgwell, is an overview of the origin, transport, deposition, and climate impacts of dust. The role of humans in the dust cycle and the historical relationship between dust and climate change through the Ice Ages are explored. Marine clouds, as a result of their interactions with incoming solar and outgoing terrestrial radiation, are an extremely important part of the climate system. The radiative properties of marine clouds are intimately connected to cloud droplet microphysics, which is in turn connected to the marine aerosol. *Marine Boundary Layer Clouds*, by U. Lohmann, describes the processes controlling the behavior and climate effects of low-level clouds over the oceans. This chapter also presents the evidence for the influence of anthropogenic emissions on marine clouds.

Air-Sea Gas Exchange

The exchange of gases across the air-sea interface is a major flux in the biogeochemical cycles of many, if not most, elements. Developing accurate gas exchange models has proven to be a considerable challenge. Two major aspects

of this challenge are (1) a lack of fundamental understanding of dynamics at the interface of two turbulent fluids of very different densities, and (2) the turbulent conditions occurring in the open ocean cannot be replicated in the laboratory in a scalable way. Despite these issues, considerable progress has been made in quantifying air-sea fluxes in the oceans through use of a variety of innovative micrometeorological and geochemical approaches and then integrating these in situ approaches with satellite observations of physical surface ocean properties. *Air-Sea Gas Exchange*, by P. D. Nightingale, provides a summary of the current state of research and points out directions for future research.

Oceanic Physical and Biogeochemical Systems

The large-scale circulation of the ocean provides the backdrop for virtually all oceanographic processes; it exerts a major control on the distribution of chemicals and biota in the oceans. In the chapter *Ocean Circulation*, A. F. Thompson and S. Rahmstorf describe how ocean circulation is controlled by exchanges with the atmosphere. Special attention is given to the meridional ocean circulation, which affects the climate of the entire planet and which is projected to slow down under global warming. The chapter presents the evidence for past abrupt changes in meridional overturning circulation and explores the possible transient and equilibrium states of the global ocean circulation in the future.

Marine ecosystems play a central role in ocean biogeochemistry, dramatically influencing the rates and pathways of chemical transfers, and controlling the biological pump transporting atmospheric CO₂ into the deep ocean and sediments. In *Marine Pelagic Ecosystems*, O. Ulloa and C. Grob outline the diversity of marine microbial life and explain the basic mechanisms by which organisms influence biogeochemical cycles and climate. The availability of nutrients in the ocean exerts the strongest control on the composition and activity of marine ecosystems. In *Ocean Nutrients*, P. W. Boyd and C. L. Hurd present the marine biogeochemical cycles from the perspective of the major nutrient budgets of nitrogen, silica, and phosphorus. This chapter explains the connection between ocean physics, nutrient availability, and marine ecosystems, and ends with thoughts on future trends in nutrients, based on the authors' analysis of observed recent trends.

One of the most exciting developments in ocean biogeochemistry has been the realization that the abundance of iron can limit biological productivity over wide regions of the ocean. As noted earlier, airborne dust is a major source of iron to remote regions of the ocean. In the chapter *Ocean Iron Cycle*, P. W. Boyd explores the importance of iron as a key limiting micronutrient that indirectly influences all of the marine biogeochemical cycles. The iron cycle is extremely complex

and, in fact, not very well understood. The chapter explains our current understanding of the complex relationships that regulate the iron cycle in the ocean and presents an up-to-date estimate of the sources and sinks of surface ocean iron for all regions of the ocean. Finally, the latest information from iron fertilization experiments is presented. This chapter also explains the interest in iron fertilization as a geoengineering strategy to lower atmospheric CO₂ and presents the current position of the scientific community on this issue.

Understanding the oceanic carbon cycle is one of the major goals of climate research. It requires integrating all of our knowledge about air-sea exchange, ocean circulation, ocean biology, and biogeochemistry into a self-consistent framework. In *Ocean Carbon Cycle*, L. Bopp and C. Le Quéré examine how the interactions between physical, chemical, and biological processes influence the marine carbon cycle and discuss the implications of this cycle for the regulation of atmospheric CO₂ on time scales of thousands of years. The chapter explains very simply how the expected global climate and environmental changes may affect the natural carbon cycle in the next century and highlights the difficulties in providing quantitative numbers for the evolution of the global ocean CO₂ sink.

DMS, Clouds, and Climate

The ocean-atmosphere cycling of dimethylsulfide (DMS) is one of the classic examples of the interconnectedness of the surface ocean and atmosphere. This trace sulfur gas, produced in the surface ocean as a result of phytoplankton and bacterial metabolism, is emitted into the atmosphere, where it undergoes oxidation and conversion to sulfate aerosols. These aerosols can act as cloud condensation nuclei, affecting the extent, lifetime, and radiative properties of marine clouds. The potential of a DMS-mediated climate feedback loop between phytoplankton and clouds has inspired a considerable amount of research and controversy. Despite the considerable efforts of many scientists, the importance of this feedback is still uncertain. *Dimethylsulfide and Climate*, by M. Vogt and P. S. Liss, summarizes the current state of scientific knowledge on this issue. These authors also explore the state of knowledge of past DMS variations, of the future impact of DMS associated with climate change, and the interactions between the DMS cycle, the iron cycle, and ocean acidification.

Coastal Ocean Processes

The coastal ocean is a very active interface between the land and the open ocean, and the place where most humans are directly affected by ocean processes. Coastal ocean pro-

cesses (nutrient and carbon cycling, trace gas emissions, and so forth) are significant on a global basis, but the temporal and spatial variability in these regions makes it challenging to quantify their global impacts. In *Hydrography and Biogeochemistry of the Coastal Ocean*, S. W. A. Naqvi and A. S. Unnikrishnan describe the processes that influence coastal ocean biogeochemistry, from the physical currents specific to the coast and continental margins, to the river sources of nutrients, and the deposition and resuspension of marine sediments. The chapter compares the fluxes of CO₂, O₂, and N (in various forms) between the coast and the open ocean, thereby providing quantitative evidence of coastal activity. The chapter addresses the problems of eutrophication and hypoxia and discusses potential future changes in physical transport and biogeochemical cycles.

Lessons From the Past

The current state of the ocean-atmosphere system offers only a snapshot of the full range of possible behaviour of the system. If we want to make robust predictions about future change, we need to test our understanding of biogeochemical processes over a wider range of climatic conditions. One way to do that is to examine past changes. A remarkable wealth of information about past conditions has been extracted from polar ice cores and marine sediments. In *Glacial-Interglacial Variability in Atmospheric CO₂*, K. E. Kohfeld and A. Ridgwell use the paleoclimate archive to assess our knowledge and understanding of the processes that have controlled the concentration of atmospheric CO₂ during the glacial-interglacial cycles.

Tools of the Trade

The challenges of studying physical and biogeochemical ocean-atmosphere processes on a large scale have led to the development and refinement of a variety of research tools. These tools help us discover new phenomena, observe variability on a variety of scales of time and space, extrapolate what we know to regions and time periods that we cannot observe, and test conceptual ideas about interactions in a physically realistic way. In this volume, we present introductions to three types of research tools that are becoming increasingly important: remote sensing, data assimilation, and biogeochemical modeling. These tools were once the exclusive domain of experts, but they are becoming increasingly available to researchers at all levels. It is important that any user have a basic understanding of the underlying principles and the strengths and limitations of the approaches they are using. *Remote Sensing*, by H. Loisel, C. Jamet, and J. Riedi, outlines the basic principles behind satellite-based observations of the

oceans and atmosphere with examples showing cloud properties, sea surface temperature, ocean color, and sea surface height. In the chapter *Data Assimilation Methods*, C. Jamet and H. Loisel explain the goals, approach, and mathematical framework used to integrate diverse data sets, in ways that both minimize and quantify uncertainties. In *Biogeochemical Modeling*, by C. Le Quéré, L. Bopp, and P. Suntharalingam, the elements of a numerical ocean-atmosphere biogeochemical model are explained. Such models encapsulate into a physically consistent numerical framework our knowledge of physical transport and mixing, air-sea exchange, chemical production and destruction, and ecosystems. Some such models have become an essential tool for hypothesis testing, guiding the design of observational experiments, and predicting the direction and magnitude of future changes in the ocean-atmosphere system.

SUMMARY

This is a brief introduction to the motivation and scope of ongoing research in the area of surface ocean–lower atmosphere processes. This broad and multidisciplinary research agenda clearly requires the involvement of scientists with a diverse range of backgrounds, expertise, and interests. This chapter is intended to provide some perspective on the need for such research. We hope that the accompanying contents of this volume will serve to inform and inspire the next generation of researchers to help tackle the challenge.

REFERENCES

- Arrhenius, S. (1896), On the influence of carbonic acid in the air upon the temperature of the ground. *Philos. Mag.*, 41, 237–276.
- Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, 326, 655–661.
- Geoengineering the Climate: Science, Governance and Uncertainty* (2009), RS 1636, The Royal Society, London.
- Martin, J. M. (1990), Glacial-interglacial CO₂ change: The iron hypothesis. *Paleoceanography*, 5, 1–13.
- Shaw, G. E. (1983), Bio-controlled thermostatism involving the sulfur cycle. *Climate Change*, 5, 297–303.
- The Surface Ocean–Lower Atmosphere Study: Science and Implementation Plan* (2004), IGBP Report 50, IGBP Secretariat, Stockholm.

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Atmospheric Gas Phase Reactions

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This chapter introduces the underlying physicochemical principles and the relevance of atmospheric gas phase reactions. In particular, reaction orders, the concept of elementary reactions, definition of and factors determining reaction rates (kinetic theory of chemical reactions), and photochemical reactions are discussed. Sample applications of the pertinent reaction pathways in tropospheric chemistry are presented, particularly reactions involving free radicals (OH, NO₃, halogen oxides) and their roles in the self-cleaning of the troposphere. The cycles of nitrogen and sulfur species as well as the principles of tropospheric ozone formation are introduced. Finally, the processes governing the stratospheric ozone layer (Chapman Cycle and extensions) are discussed.

1. ATMOSPHERIC GAS PHASE CHEMISTRY

Chemical reactions in the atmosphere are relevant for understanding of any chemical process in the atmosphere. Particular questions include the ozone formation in the troposphere, the origin of the stratospheric ozone layer, the degradation of air pollutants, and the degradation of climate gases. The latter two groups of processes facilitate the self-cleaning of the atmosphere and influence the global climate. We categorize chemical reactions in (1) homogeneous reactions, where the reactants are all in the same phase (in the atmosphere usually in the gas phase); (2) heterogeneous reactions, where the reactants are in different phases (e.g., reactions of gas molecules at aerosol surfaces, cloud droplets or ice crystals); and (3) photochemical reactions, i.e., the chemical transformation of gas molecules by solar radiation.

2. GAS-PHASE REACTION KINETICS

Gas-phase reaction kinetics explains which reactions actually proceed in the gas phase and which do not and why. Also, it gives quantitative answers about the evolution of the concentrations of the reactants as a function of time, i.e.,

Surface Ocean–Lower Atmosphere Processes
Geophysical Research Series 187
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10.1029/2008GM000767

the reaction rate (or reaction velocity). It forms the basis of incorporating the thousands of chemical reactions simultaneously occurring in the atmosphere in a numerical model. Moreover, the thermodynamics of chemical reactions allows us to determine under which conditions chemical reactions will occur spontaneously and which concentrations will prevail in equilibrium.

3. REACTION ORDER

Depending on the number of molecules interacting in an elementary reaction process, we define the “reaction order.”
Reactions of zeroth order:



A reactant (or educt) A decays with constant reaction rate. We define the reaction rate as

$$\frac{d[A]}{dt} = -k, \quad (1)$$

with the reaction rate constant k in units of molecule/(cm³ s).
Reactions of first order (unimolecular reactions):



with the reaction rate constant k in $1/s$,

$$\frac{d[A]}{dt} = -k[A]. \quad (2)$$

$[A]$ denotes the concentration, i.e., amount of matter per unit volume of the atom or molecular species A. Units are molecule/cm³ or mol/L.

Reactions of second order (bimolecular reactions):



A collides with B: (1) reactions can only occur during collisions, and (2) usually, only a small fraction of the collisions leads to reactions. Reaction rate:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = k_2[A][B]. \quad (3)$$

4. REACTION RATES

In simple cases, the temporal evolution of reactants can be calculated. For instance, a first-order reaction follows by integration of equation (2):

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = -k \int_0^t dt', \quad (4)$$

yielding (after some rearrangements)

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad (5)$$

which is equivalent to $[A] = [A]_0 e^{-kt}$. An example for the temporal evolution of $[A](t)$ in a first-order reaction is given in Figure 1.

It should be noted that many bimolecular reactions of the type



are usually pressure-dependent reactions. In reactions that have only one product, the required conservation of momentum and energy is difficult, or, in other words, the energy released by the reaction is largely stored in the excited molecule C^* and is likely to cause C^* to break up into its constituents $A + B$. However C^* may be stabilized by collision with another molecule M. At increasing concentration of M (or increasing pressure), the probability of stabilizing C^* increases up to the point where $[M]$ is so high that all C^* are stabilized.

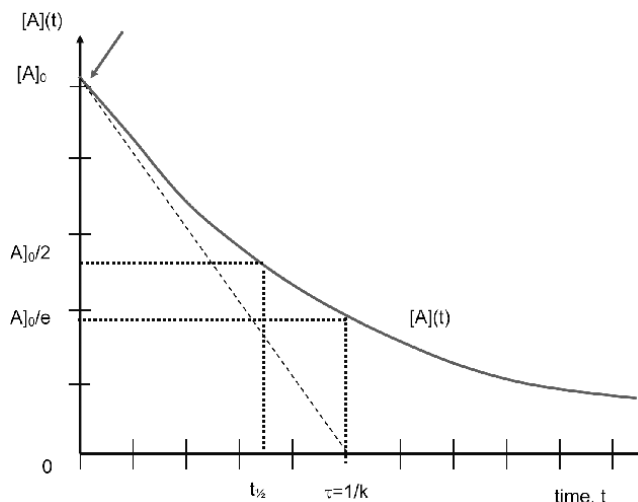


Figure 1. Temporal evolution of the concentration $[A](t)$ in a first-order reaction (solid line). $[A]_0$ denotes the initial concentration at $t = 0$. The dotted lines give the time constant $t_{1/2}$ for half completion and lifetime (time when only $1/e$ of the initial number of molecules are left, where e denotes the base of the natural logarithm). The dashed line is the tangent of the decay curve $[A](t)$ at time $t = 0$; it can be used to approximate $[A](t)$ for times $t \ll \tau$.

5. KINETIC THEORY OF CHEMICAL REACTIONS

In almost all cases, only reactions of second order of the type



are elementary reactions (note that this includes photochemical reactions, where the second reactant is a photon).

In the overwhelming number of cases any other types of reactions (in particular, the unimolecular decay and reactions of the type $A + B \rightarrow C$) are complex reactions, i.e., reactions that do not occur within a single collision but rather proceed in a series of steps. Understanding a reaction system (e.g., the formation of ozone in the atmosphere) means identifying the series of elementary reactions converting the educts into the observed products.

Elementary reactions can only occur upon collisions between atoms or molecules. A further condition for reactions to occur is the decrease of Gibbs free energy $\Delta G_R = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$, where $\Delta G = \Delta H - T\Delta S$, ΔH is the enthalpy of the molecules involved, and ΔS is entropy of the molecules involved. Simply speaking (neglecting entropy changes), we can say that reactions only occur when they are exothermic; that is, energy is released by the reaction. However, even

for exothermic reactions, normally only a small fraction of all collisions lead to chemical reactions. This is because an energy barrier usually has to be overcome (as indicated in Figure 2) and also because other conditions have to be met, e.g., the rearrangement of atoms in the product molecules, which is sometimes called the steric factor. The energy to overcome the barrier is usually taken from the kinetic energy of the colliding molecules (reactants of the reaction).

The velocity distribution function, i.e., the number of gas molecules in the velocity interval $(v, v + dv)$, in turn, is given by the Maxwell-Boltzmann distribution:

$$f(v)dv = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B \cdot T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv, \quad (7)$$

where k_B denotes Boltzmann's constant, T is the absolute temperature, and m is the mass of the molecule (or atom). With some simplifications from (7), the fraction of molecules with $E > E_a$ is

$$n(E > E_a) = \frac{2}{\sqrt{\pi}} \sqrt{\frac{E_a}{k_B T}} \exp\left(-\frac{E_a}{k_B T}\right) \quad (8)$$

Thus, the reaction rate constant k should be proportional to $n(E > E_a)$. In 1889 Svante Arrhenius derived the following expression for the reaction rate constant:

$$k = A_R \exp\left(-\frac{E_a}{k_B T}\right) \quad (9)$$

The constant A_R is given by the product of the collision rate k_{AB} of the reactants A and B and the reaction probability per collision with sufficient energy, P_{AB} . The maximum

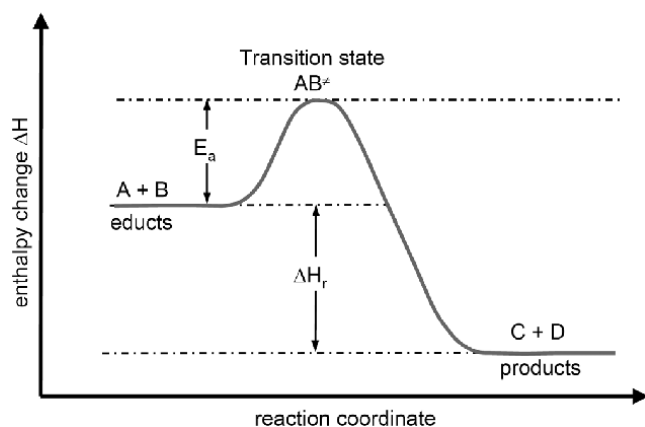


Figure 2. The energy barrier in an elementary chemical reaction.

value of the product P_{AB} times the exponential expression in equation (9) is thus unity; then $k = k_{AB}$ would just be given by the collision rate:

$$-\frac{d}{dt}[A] = k_{AB}[A][B] = P_{AB}\sqrt{2}[A][B]\sigma\bar{v}. \quad (10)$$

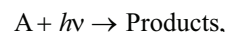
Thus,

$$k_{AB} = P_{AB}\sqrt{2}\sigma\bar{v}, \quad (11)$$

where σ denotes the collision cross section of the molecules, $\bar{v} = (8k_B T/\pi\mu)^{1/2}$ denotes their relative velocity, and $\mu = (m_1 m_2)/(m_1 + m_2)$ is the reduced mass of the reactant molecules with masses m_1, m_2 . Typical values for k_{AB} at standard conditions are about $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$.

6. PHOTOCHEMICAL REACTIONS

Absorption of a photon with frequency ν by a molecule can lead to a chemical reaction, e.g., breakup of the molecule (photolysis).



where $h\nu$ symbolizes a photon with frequency ν and thus energy $h\nu$ (h is Planck's constant). As with first-order reactions (equation (2)), we can describe the reaction rate of photolysis as

$$\frac{d[A]}{dt} = -J[A], \quad (12)$$

The reaction rate constant J (in s^{-1}) is called photolysis frequency. The absolute value of the photolysis frequency J depends on three factors.

1. The first factor is the property of the molecule to absorb radiation dI of a given frequency ν (or wavelength λ). Quantitatively, $I(\nu)$ is the intensity of the radiation field, $\sigma(\nu)$ is the absorption cross section of A at the frequency ν , and ds is the thickness of the absorbing layer.

$$dI(\nu) = -I(\nu)\sigma(\nu)[A]ds \quad (13)$$

$$dI(\lambda) = -I(\lambda)\sigma(\lambda)[A]ds$$

Note that equation (13) is the differential form of Lambert-Beer's law.

2. The second factor is the probability that the absorption of a photon will lead to a reaction (e.g., to the dissociation) of the molecule. A prerequisite is that photon energy +

internal energy exceeds the binding energy of the molecule (or the activation energy E_a). The internal energy is supplied by thermal excitation of rotational and vibrational states of the molecule; it is normally small compared to the photon energy. This probability is called quantum efficiency (quantum yield) ϕ . Frequently (when the internal energy is small), ϕ can be approximated by a step function:

$$\phi(\nu) \approx \begin{cases} 0; & h\nu < E_a \\ 1; & h\nu \geq E_a \end{cases} \quad (14)$$

The magnitude of the $F(\lambda)$ as a function of wavelength in the UV range and for different altitudes is given in Figure 3.

3. The third factor is the photon flux $F(\lambda)$ from all directions (actinic flux). F is obtained by integrating the intensity $I = I(\lambda, \vartheta, \varphi)$ (i.e., the number of photons per unit area, time, and solid angle for a given wavelength) over the entire sphere:

$$F(\lambda) = \int_0^{2\pi} \int_0^{\pi} I(\lambda, \vartheta, \varphi) \sin(\vartheta) d\vartheta d\varphi \quad (15)$$

The photolysis frequency J is then derived as

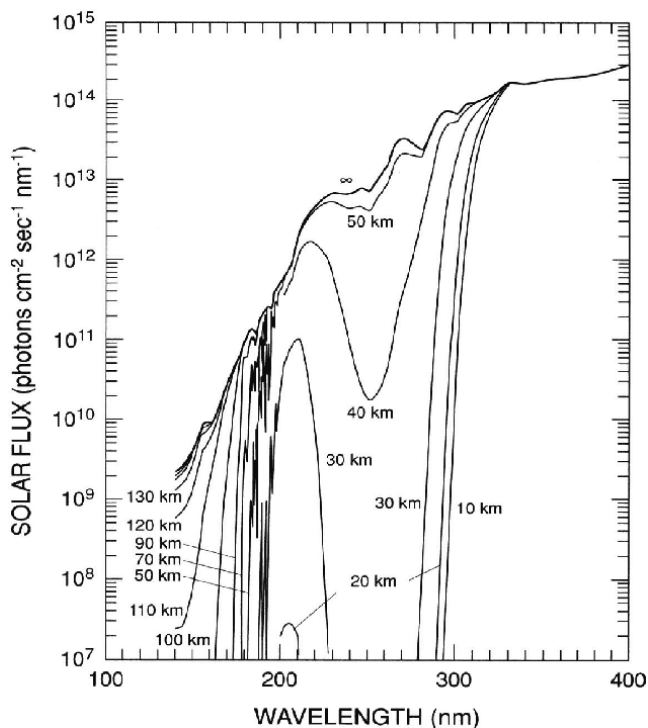


Figure 3. Solar flux $F(\lambda)$ as a function of wavelength for different altitudes (given in km). Adapted from *Brasseur et al.* [1999].

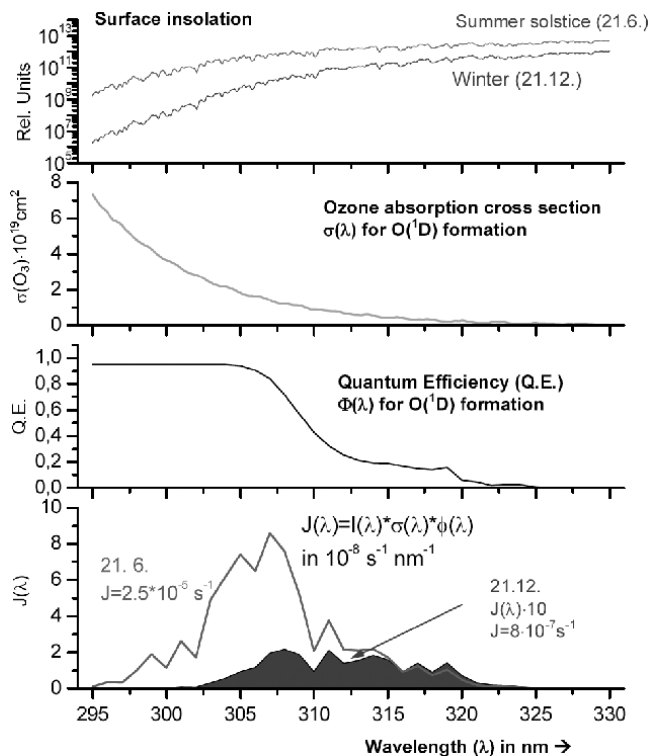
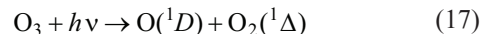


Figure 4. Solar flux $F(\lambda)$ as a function of wavelength (first panel), ozone absorption cross section (second panel), ozone quantum efficiency for formation of $O(^1D)$ atoms (third panel), and photolysis frequency (fourth panel).

$$dJ(\nu) = \phi(\nu)\sigma(\nu)F(\nu)d\nu$$

$$J = \int_0^{\infty} \phi(\nu)\sigma(\nu)F(\nu)d\nu \quad (16)$$

For an example, see Figure 4, which illustrates the conditions for the photolysis of ozone leading to electronically excited oxygen atoms $O(^1D)$.



Frequently, J is also given as function of the wavelength λ ($c = \nu\lambda$), where c is the speed of light:

$$J = \int_0^{\infty} \phi(\lambda)\sigma(\lambda)F(\lambda)d\lambda \quad (18)$$

7. TROPOSPHERIC CHEMISTRY AND SELF-CLEANING OF THE ATMOSPHERE

The capability of the atmosphere to oxidize (or otherwise degrade) trace species emitted into it is crucial for the

removal of trace species, such as oxides of nitrogen, volatile organic compounds (VOCs), or the greenhouse gas methane, and it is thus often also called the “self-cleaning” capacity of the atmosphere. Although there is no general definition, the self-cleaning capacity (or oxidation capacity [Geyer *et al.*, 2001; Platt *et al.*, 2002]) is frequently associated with the abundance of OH. However, as explained above, many other oxidants (including O₂ and O₃), as well as free radicals other than OH, can contribute to the oxidation capacity of the atmosphere. A useful concept in this context is the lifetime τ_X of a compound A against reaction with a particular degrading agent X; it is given by

$$\tau_X = \frac{1}{[X]k_{X+A}}, \quad (19)$$

where k_{X+A} denotes the reaction rate constant for reaction of radical X with species A.

8. FREE RADICALS

Free radicals are the driving force for most chemical processes in the atmosphere. Since the pioneering work of Weinstock [1969] and Levy [1971], photochemically generated HO_X radicals (hydrogen radicals are OH plus HO₂) have been recognized to play a key role in tropospheric chemistry. In particular, hydrogen radicals (1) initiate the degradation and thus the removal of most oxidizable trace gases emitted into the atmosphere, (2) give rise to the formation of strongly oxidizing agents (mostly in the troposphere), such as ozone or hydrogen peroxide, (3) catalytically destroy stratospheric ozone (see section 11), and (4) are difficult to remove once they are generated since radical-molecule reactions tend to regenerate radicals.

Today, we have an enormous amount of direct and indirect evidence of the presence of HO_X radicals [see, e.g., Ehhalt, 1999; Platt *et al.*, 2002], and the importance of HO_X for atmospheric chemistry can be assumed to be proven beyond reasonable doubt. Nevertheless, the possible role of other radicals, beginning with the (historical) idea of the impact of oxygen atoms O(³P) or excited oxygen molecules O₂(¹Δ), has been the topic of past and current investigations. In particular, the nitrate radical, NO₃ (see section 9), and the halogen atoms and halogen oxide radicals, BrO, IO, and ClO, can make a considerable contribution to the oxidizing capacity of the troposphere. For instance, a reaction with NO₃ or BrO can be an important sink of dimethylsulfide (DMS) in marine environments. Also, nighttime reactions of nitrate radicals with organic species and NO_X play an important role for the removal of these species. In addition, NO₃ chemistry can be a source of peroxy radicals (such as HO₂ or CH₃O₂) and even OH radicals. Table 1 shows an overview over the

Table 1. Free Radical Cycles Pertinent to Tropospheric Chemistry and Key Processes Influenced or Driven by Reaction of Those Radicals

Species	Significance
<i>HO_X Cycle</i>	
OH	degradation of most volatile organic compounds (VOC) key intermediate in O ₃ formation NO _X ⇒ NO _Y conversion
HO ₂	intermediate in O ₃ formation intermediate in H ₂ O ₂ formation
RO ₂	intermediate in ROOR' formation aldehyde precursor PAN precursor intermediate in O ₃ formation
<i>NO₃ Cycle</i>	
NO ₃	degradation of certain VOC (olefins, aromatics, DMS, etc.) NO _X ⇒ NO _Y conversion (via N ₂ O ₅ or DMS reactions) RO ₂ precursor (nighttime radical formation)
<i>XO_X Cycle</i>	
XO ^a	catalytic O ₃ destruction (cause of polar tropospheric ozone hole) degradation of DMS (BrO) change of the NO ₂ /NO (Leighton) ratio
X	degradation of (most) VOC (Cl) initiates O ₃ formation RO ₂ precursor initiates particle formation (IO _X) change of the HO ₂ /OH ratio

^aX = Cl, Br, I.

most important radical species in the troposphere and their significance for atmospheric chemistry. The details of the chemistry of NO₃ and halogen oxides will be discussed in following sections. Here we will concentrate on the tropospheric chemistry of hydroxyl radicals.

9. NITROGEN AND OTHER TRACE GAS CYCLES

The oxides of nitrogen NO and NO₂ (= NO_X) are key species in atmospheric chemistry. They regulate many trace gas cycles and influence the degradation of most pollutants in clean air as well as in polluted regions. The NO_X concentration has a strong influence on the atmospheric level of hydroxyl radicals, which, in turn, are responsible for the oxidation processes of most trace gases. In addition, NO_X is a catalyst for tropospheric ozone production (see section 10). Oxides of nitrogen (or acids formed from them) can also react with hydrocarbon degradation products to form organic nitrates or nitrites (e.g., peroxy acetyl nitrate (PAN) or methyl

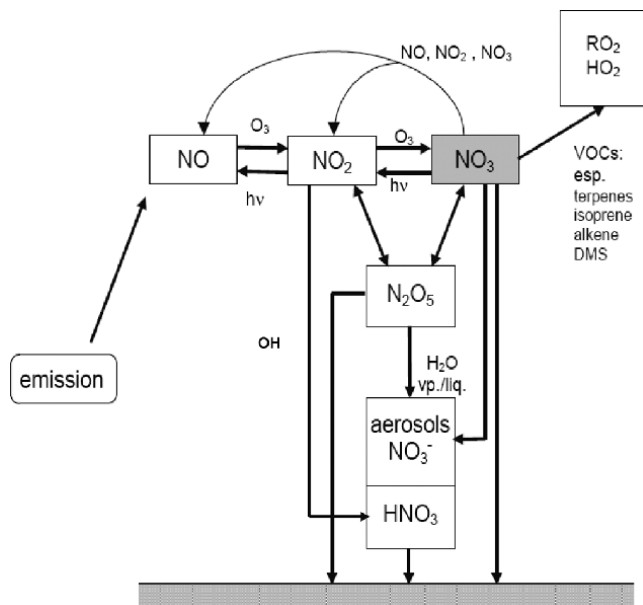


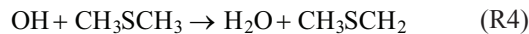
Figure 5. Simplified overview of the NO_x reaction scheme in the atmosphere. Arrows indicate main reaction pathways.

nitrite), as well as nitrosamines. These species can be much more detrimental to human health than the primary oxides of nitrogen. Finally, nitric acid, the most thermodynamically stable and ultimate degradation product of all atmospheric oxides of nitrogen, is (besides sulfuric acid) the main acidic component in “acid rain.”

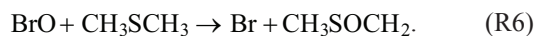
An overview of the most important oxidized nitrogen species in the atmosphere is given in Figure 5. The main reaction pathways between the various species are indicated by arrows. Oxides of nitrogen are primarily emitted in the form of NO (plus some NO_2) and N_2O . While N_2O is a very inert species and therefore plays no role for the chemical processes in the troposphere, NO reacts rapidly with natural ozone to form NO_2 (R9). Nitrogen dioxide then further reacts with OH radicals forming nitric acid. Alternatively, the reaction of NO_2 with O_3 will form NO_3 radicals (see section 8), which act as oxidizing agents or can react with NO_2 to form N_2O_5 . The latter species is the anhydride of nitric acid and thus forms HNO_3 (or nitrate aerosol) upon contact with liquid water, e.g., at the surface of the ocean or aerosol particles or of cloud droplets.

Another important species, particularly for marine chemistry, is DMS (CH_3SCH_3), which is produced by biological processes in the ocean [e.g., *Andreae et al.*, 1985]. Besides sporadic releases by volcanic eruptions, oceanic DMS emissions are the largest natural source of sulfur to the atmosphere. Because of the important role of sulfur in the formation of aerosol particles and cloud condensation nuclei,

DMS has received considerable attention. While the degradation mechanisms of DMS are not fully elucidated to date, free radical reactions are probably the dominating degrading agent. The first step in OH-initiated degradation of DMS is OH abstraction from one of the methyl groups, or OH addition to the sulfur atom.



Intermediate products in this reaction chain are dimethylsulfoxide (DMSO), CH_3SOCH_3 , and $\text{CH}_3\text{SO}_2\text{CH}_3$. Stable end-products are sulfuric acid and methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$). The involvement of NO_3 radicals has also been suggested [*Winer et al.*, 1984; *Platt and Le Bras*, 1997], where the H abstraction channel appears to be predominant. In addition, there are several reports of a possible role of halogen oxide radicals, in particular BrO [*Toumi*, 1994]. The product of the BrO-DMS reaction is DMSO:



While sulfuric acid and methane sulfonic acid form particles, DMSO does not. Thus, the fraction of DMS degraded by BrO may determine the efficiency of particle formation in marine areas, as discussed by *von Glasow and Crutzen* [2004].

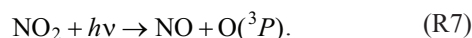
10. TROPOSPHERIC OZONE

Ozone is a key compound in the chemistry of the atmosphere. In the troposphere it is a component of smog, which is poisonous to humans, animals, and plants, and it is a precursor to cleansing agents (such as the OH radical; see section 8). Tropospheric O_3 is also an important greenhouse gas.

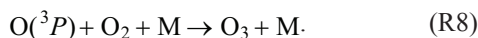
Ozone is formed by two distinctly different mechanisms in the troposphere and stratosphere. In the stratosphere, O_2 molecules are split by shortwave UV radiation into O atoms, which combine with O_2 to form O_3 . This process is the core of the Chapman Cycle [*Chapman*, 1930]. As explained in section 11, it requires shortwave UV radiation (with wavelengths shorter than about 242 nm, the threshold wavelength for O_2 photolysis). Until the late 1960s, it was believed that tropospheric ozone originated from the stratosphere. Today, we know that large amounts of O_3 are formed and destroyed in the troposphere, while influx of O_3 from the stratosphere

is only a minor contribution to the tropospheric ozone budget. Recent model calculations [World Meteorological Organization, 2002] put the cross-tropopause flux of O_3 at 390–1440 Mt/a (very recent investigations indicate that values near the lower boundary of the range are more likely), while they derive ozone formation rates in the troposphere at 2830–4320 Mt/a. The formation is largely balanced by photochemical destruction in the troposphere amounting to 2510–4070 Mt/a. Another, relatively small, contribution to the O_3 loss is deposition to the ground, modeled at 530–900 Mt/a.

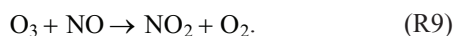
In the early 1950s it became clear that under certain conditions in the atmosphere near the ground, high concentrations of ozone are formed. In fact, it could be shown in “smog chamber” experiments that ozone is produced when mixtures of NO_X ($= NO + NO_2$) and VOC are exposed to solar UV radiation. While the phenomenon of ozone formation as a function of VOC and NO_X in illuminated mixtures was empirically found in the 1960s, the exact mechanism could only be explained in the 1970s by Weinstock [1969], Crutzen [1970], and Levy [1971]. Ozone formation in the troposphere is initiated by the production of $O(^3P)$ from NO_2 photolysis, which is facilitated by relatively long wavelength radiation (threshold wavelength about 420 nm) available in the troposphere. Under clear-sky conditions at noontime, the average lifetime of the NO_2 molecule is only on the order of 2 min ($j_{NO_2} = j_7 \approx 8 \times 10^{-3} s^{-1}$):



This reaction is followed by the rapid recombination of O with O_2 :



At high pressure (and thus M and O_2 concentrations) in the troposphere, other reactions of $O(^3P)$, in particular, reaction with O_3 , are negligible. Therefore, for each photolyzed NO_2 molecule, an ozone molecule is formed. Reactions (R7) and (R8) are the only relevant source of ozone in the troposphere. However, ozone is often rapidly oxidized by NO to back NO_2 :



Reactions (R7)–(R9) lead to a “photostationary” state between O_3 , NO , and NO_2 . The relation between the three species can be expressed by the Leighton relationship [Leighton, 1961]:

$$\frac{[NO]}{[NO_2]} = \frac{j_7}{k_9[O_3]}, \quad (20)$$

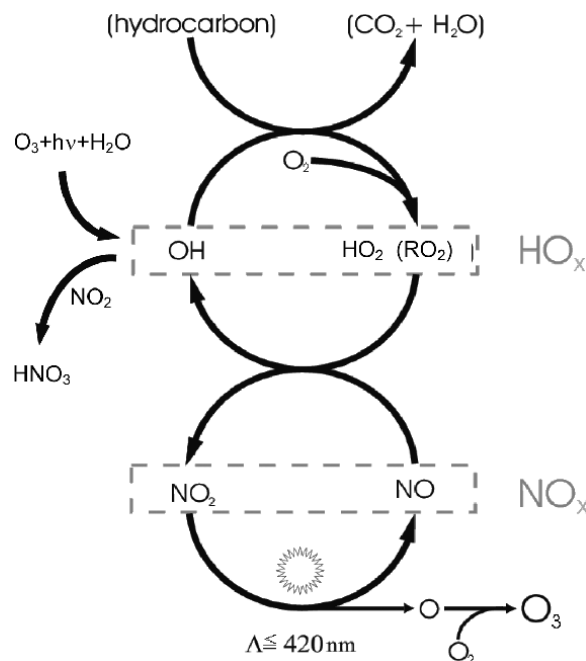


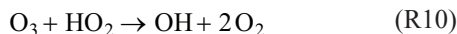
Figure 6. Ozone formation in the troposphere is catalyzed by hydrogen radicals ($OH + HO_2 = HO_X$), peroxy radicals, and NO_X .

where j_7 denotes the photolysis frequency of NO_2 and k_9 is the rate constant for the reaction of ozone with NO . For typical ozone mixing ratios of 30 ppb (1 ppb $\approx 10^{-9}$ mixing ratio) the $[NO]/[NO_2]$ ratio during daytime near the ground is on the order of unity. The reaction cycle formed by (R7)–(R9) does not lead to a net formation of ozone. However, any reaction that converts NO into NO_2 without converting an O_3 molecule interferes with this cycle and leads to net ozone production. The key factor in tropospheric O_3 formation is thus the chemical conversion of NO to NO_2 .

In the troposphere the conversion of NO to NO_2 without O_3 occurs through a combination of the reaction cycles of hydroxyl HO_X ($= OH + HO_2$), peroxy radicals, and NO_X (Figure 6). In these cycles, OH radicals are converted to HO_2 or RO_2 radicals through their reaction with CO or hydrocarbons. The peroxy radicals HO_2 and RO_2 , on the other hand, react with NO to reform OH , thus closing the HO_X/RO_X cycle. This reaction also converts NO to NO_2 (see also section 9), which is then photolyzed back to NO (R7). The oxygen atom formed in the NO_2 photolysis then reacts with O_2 to form ozone (R8). The process shown in Figure 6 therefore acts like a chemical reactor that in the presence of NO_X and sunlight, converts the “fuel” CO and hydrocarbons into CO_2 , water, and ozone. Because HO_X and NO_X are recycled, this catalytic ozone formation can be quite efficient. The cycles are only interrupted if either a NO_X or a HO_X is removed

from the respective cycles, for example, by the reaction of OH with NO₂ or the self-reactions of HO₂ and RO₂. Even in background air (e.g., remote marine areas), fuel for ozone formation is always present in the form of methane (mixing ratio of ≈1.8 ppm) and CO, which is formed as a degradation product of CH₄. However, in clean air the NO_x level might be very low and thus insufficient to act as catalyst.

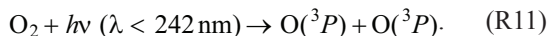
In fact, at very low NO₂ levels destruction of ozone by the reaction with HO₂ radicals



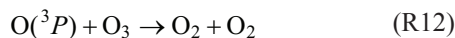
can become faster than the production of O₃ by the reaction sequence described above (and shown in Figure 6). Since the rate constant of the reaction NO + HO₂ is about 3000 times higher than k_{1,10}, the rates of both reactions (the former leading to O₃ production, the latter destroying O₃) become about equal at 3000[NO] < [O₃]. For a typical O₃ level around 30 ppb, this corresponds to NO mixing ratios of about 10 ppt (NO_x about 30 ppt); higher NO_x levels lead to net O₃ production, and lower NO_x levels lead to net O₃ destruction. This explains the sometimes very low O₃ levels in the remote marine atmosphere.

11. STRATOSPHERIC OZONE

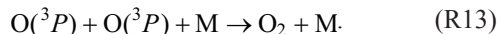
The first chemical cycle in the atmosphere was discovered by Sidney Chapman in the late 1920s; it explained the observed vertical profile of ozone, with relatively low mixing ratios in the troposphere and a maximum around 25 km altitude, which is known as the “Chapman mechanism.” The initial process is the photolysis of O₂ to form two oxygen atoms in their ground state (indicated by the spectroscopic notation ³P). In the stratosphere, sufficiently energetic UV light (i.e., light with wavelengths below 242 nm) is available to photolyze oxygen molecules:



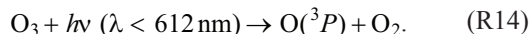
The oxygen atoms can react in three ways: (1) they can recombine with an oxygen molecule to form ozone (R8). Since two particles (O and O₂) combine to make one (O₃), collision with a third body (M, likely N₂ or O₂) is required to facilitate simultaneous conservation of energy and momentum. The reaction is therefore pressure dependent. (2) Alternatively, the oxygen atom can react with an existing ozone molecule:



(3) Finally, the recombination of two oxygen atoms to form molecular oxygen is possible but largely unimportant in the stratosphere:



In addition to the “primary” production of O atoms by the photolysis of O₂, the photolysis of O₃ also provides “secondary” O atoms. In fact, photolysis of ozone molecules occurs at a much higher rate than that of oxygen molecules:



Note this photolytic reaction leading to a ground state oxygen atom and molecule should not be confused with the ozone photolysis shown in Figure 4 leading to excited oxygen atoms (O¹D), which requires photons of much higher energy (shorter wavelength). In summary, the above reactions, also known as the “Chapman reactions,” lead to a steady-state O₃ level in the stratosphere, in which the O atom production via reactions (R11) and (R14) is in balance with their destruction via recombination with O₂ and reaction with O₃.

The above set of reactions explains the formation of a layer of ozone with a maximum concentration in the lower

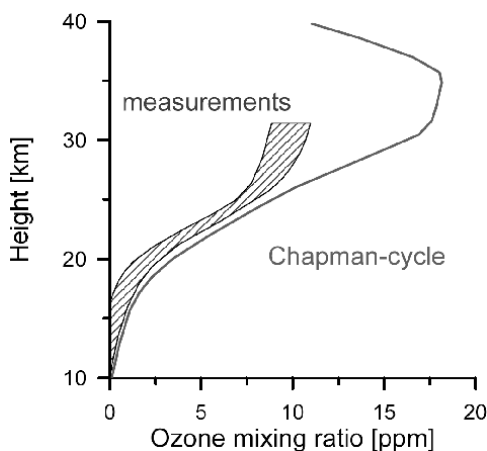
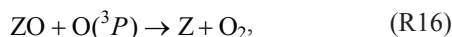
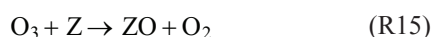


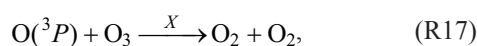
Figure 7. The stratospheric ozone profile according to the Chapman mechanism (solid line). In the lower stratosphere the rate of O₂ photolysis, and thus ozone formation, becomes extremely low. Since O₃ destruction occurs via O₃ photolysis (which takes place at much longer wavelengths) and subsequent reaction of O + O₃, the ozone concentration increases strongly with height. In the upper part of the stratosphere the recombination of O + O₂ (R8) becomes slower since the concentration of air molecules necessary as “third body” (M) in the recombination of O + O₂ reduces with atmospheric pressure. Thus, despite increasing levels of UV radiation, the O₃ concentration (and also the mixing ratio) will eventually decrease with altitude. The measurements (hatched area) are considerably lower than the predictions by the Chapman mechanism, which is due to additional ozone destruction reactions. Adapted from Röh [1994].

stratosphere. In the lower stratosphere the rate of O₂ photolysis, and thus the ozone formation rate, becomes extremely low (despite the much higher O₂ concentration there). However, O₃ destruction still occurs via O₃ photolysis, which takes place at much longer wavelengths, and the reaction of O + O₃. This explains why the ozone concentration should increase with height (in fact, the Chapman mechanism predicts zero O₃ formation in the troposphere). On the other hand, in the upper part of the stratosphere the recombination of O + O₂ (R8) becomes slower since the concentration of air molecules necessary as a “third body” (M) in the recombination of O + O₂ (R8) reduces proportionally to the atmospheric pressure. Thus, despite increasing levels of UV radiation, the O₃ concentration (and also the mixing ratio) will eventually decrease with altitude. Figure 7 depicts the ozone profile predicted by the Chapman cycle.

As can also be seen in Figure 7, actual measurements show the same shape of the ozone profile but much less ozone than predicted by the Chapman mechanism. Detailed investigation during the 1960s of the elementary reactions and photolysis processes involved revealed that, quantitatively, the mechanism overestimates the O₃ levels by about a factor of three. It subsequently became clear that there are many other trace gas cycles affecting stratospheric O₃ levels. In particular, a group of reactions were found to catalyze the elementary reaction of O + O₃ (R12). These reaction sequences follow the general scheme



with the net result



where Z (and ZO) denotes a species acting as catalyst for (R12). The main pairs of catalytic species Z (ZO) are Cl (ClO), Br (BrO), NO (NO₂), or OH (HO₂). The individual cycles vary in relative importance with altitude. Inclusion of these reactions brings observations and model calculations in very good agreement.

REFERENCES

Andreae, M. O., R. J. Ferek, F. Bermond, K. P. Byrd, R. B. Chatfield, R. T. Engstrom, S. Hardin, P. D. Houmere, F. LeMarrec, and H. Raemdonck (1985), Dimethylsulfide in the marine atmosphere, *J. Geophys. Res.*, *90*, 12,891–12,900.

Brasseur, G., J. J. Orlando, and G. S. Tyndall (1999), *Atmospheric Chemistry and Global Change*, 654 pp., Oxford Univ. Press, New York.

Chapman, S. (1930), On ozone and atomic oxygen in the upper atmosphere, *Philos. Mag., Ser. 7*, *10*, 369–383.

Crutzen, P. J. (1970), The influence of nitrogen oxides on the atmospheric ozone content, *Q. J. R. Meteorol. Soc.*, *96*, 320–325.

Ehhalt, D. H. (1999) in *Global Aspects of Atmospheric Chemistry*, edited by R. Zellner, Springer, New York, ISBN 3-7985-1127-6, pp. 21–109.

Geyer, A., B. Alicke, S. Konrad, T. Schmitz, J. Stutz, and U. Platt (2001), Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, *J. Geophys. Res.*, *106*(D8), 8013–8025.

Leighton, P. A. (1961), *Photochemistry of Air Pollution*, Academic, New York.

Levy, H. (1971), Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, *173*, 141–143.

Platt, U., and G. Le Bras (1997), Influence of DMS on the NO_x-NO_y partitioning and the NO_x distribution in the marine background atmosphere, *Geophys. Res. Lett.*, *24*, 1935–1938.

Platt, U., et al. (2002), Free radicals and fast photochemistry during BERLIOZ, *J. Atmos. Chem.*, *42*, 359–394.

Röth, E. P. (1994), *Ozonloch, Ozonsmog: Grundlagen der Ozonchemie*, Meyers Forum Ser., vol. 26, 127 pp., BI-Taschenbuchverlag, Mannheim, Germany.

Toumi, R. (1994), BrO as a sink for dimethylsulphide in the marine atmosphere, *Geophys. Res. Lett.*, *21*, 117–120.

von Glasow, R., and P. J. Crutzen (2004), Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, *4*, 589–608.

Weinstock, B. (1969), Carbon monoxide: Residence time in the atmosphere, *Science*, *166*, 224–225.

Winer, A. M., R. Atkinson, and J. N. Pitts (1984), Gaseous nitrate radical: Possible night-time atmospheric sink for biogenic organic compounds, *Science*, *224*, 156–159.

World Meteorological Organization (2002), Scientific assessment of ozone depletion, *Global Ozone Res. Monitor. Proj. Rep. 47*, Geneva, Switzerland.

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Marine Aerosols

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The aerosol over the world oceans plays an important role in determining the physical and chemical characteristics of the Earth's atmosphere and its interactions with the climate system. The oceans contribute to the aerosols in the overlying atmosphere by the production and emission of aerosol particles and precursor gases. The marine aerosol, in turn, influences the biogeochemistry of the surface ocean through long distance transport and deposition of terrestrial and marine-derived nutrients and other chemicals. This chapter is an introduction to the physical and chemical properties of marine aerosols, to processes determining their composition and behavior, and to some of the issues driving current research in this field.

1. INTRODUCTION

The aerosol over the world oceans plays an important role in determining the physical and chemical characteristics of the Earth's atmosphere and its interactions with the climate system. For the purposes of this chapter, the "marine aerosol" is defined broadly as including all various types of particles found over the oceans. This includes particles generated mechanically at the sea surface as well as those formed chemically, from the atmospheric reactions of gases emitted from the sea surface. Terrestrial aerosols derived from fossil fuel combustion, biomass burning, dust, and biogenic compounds also contribute to the marine aerosol because atmospheric transport times across the major ocean basins are comparable to the atmospheric lifetime of many aerosols. There is extensive interaction between marine and continentally derived gases and particles. As a result, it can be difficult to strictly segregate aerosols into "marine" and "continental" types.

The marine aerosol is of considerable importance to the biogeochemical state of the underlying ocean. A notable

example is the deposition of iron and other micronutrients from dust. Dust deposition is a major factor influencing surface ocean biological productivity in high nutrient, low chlorophyll regions of the oceans [*Duce and Tindale*, 1991; *Falkowski et al.*, 1998]. The aerosol also reflects the biogeochemical state of the underlying oceans. A notable example is the distribution of biogenic sulfate aerosols over the oceans, reflecting production and emissions of dimethylsulfide arising from phytoplankton [*Andreae*, 1990; *Savoie and Prospero*, 1989]. This coupling of the marine aerosol to biogeochemistry raises the potential for numerous feedback mechanisms between climate and ocean biota.

The first major survey of marine aerosols was carried out by the Sea-Air Exchange (SEAREX) program, a 10-year multi-investigator study of the transport of natural and anthropogenic substances to the Pacific ocean [*Duce*, 1989]. To a large extent, the SEAREX program defined the modern view of marine aerosol chemical properties and raised many of the questions driving marine aerosol research today. SEAREX and other research programs clearly demonstrated two important points: (1) that there is a distinct marine aerosol with characteristics related to the underlying ocean and (2) that the marine aerosol is episodically and dramatically influenced by long distance transport from continental regions.

Since that time, considerable progress has been made in terms of documenting the physical and chemical properties

of the marine aerosol and in understanding the processes that influence it. The last decade has seen a great expansion in the field of environmental aerosol science, in general, driven by the recognition of the impact of airborne particulates on global climate change and human health. This has spawned a new generation of field and laboratory instrumentation. However, many fundamental questions remain, and aerosols remain a focus of active research and discovery. Aerosol science has historically been observationally limited. New methods are needed for physical/chemical characterization of marine aerosols from all sources and at all size ranges. New tools for mapping the spatial/temporal distribution of aerosols over the oceans are needed.

This chapter is intended as a basic introduction to the physical and chemical properties of marine aerosols, to some of the processes important in determining their evolution and characteristics, and to current areas of study relevant to the Surface Ocean Lower Atmospheric Studies (SOLAS).

2. AEROSOL BASICS

2.1. Terminology

Aerosol—a dispersion of solid and liquid particles suspended in gas. Note that the strict definition of the word “aerosol” refers to a mixture of particles and gas, but in common practice, it is used to refer to the particles only. Often the term “aerosol particles” is used to refer to the solid/liquid phases only. In this chapter, the term “aerosol” is also used to refer to the suspended particles.

Primary aerosol—atmospheric particles that are emitted or injected directly into the atmosphere. Examples are particles formed in the combustion process or smoke stack, including sulfuric acid, soot, and fly ash particles. Natural examples include, Saharan dust, pollen, and sea spray (salt and organic) from the ocean.

Secondary aerosol—atmospheric particles that are created by in situ aggregation or nucleation from gas phase molecules (gas to particle conversion). These can be formed from both anthropogenic and natural gaseous emissions.

Internal versus external mixture—this term refers to the mixing state of the aerosols. An externally mixed aerosol is composed of particles with varying chemical or mineral composition. For example, in an externally mixed aerosol, sulfate and sea salt might occur in different particles. In an internally mixed aerosol, the different aerosol components are mixed within individual particles.

Homogeneous versus heterogeneous chemistry—in atmospheric chemistry, the term homogeneous chemistry refers to reactions occurring in the gas phase. Heterogeneous chemistry refers to processes involving transfer of chemicals

between the gas and particulate phases and usually reaction in or on the particulates.

Hygroscopicity—the tendency of a substance to absorb water vapor from surrounding environment.

2.2. Physical Size Distributions: Number, Surface Area, Volume

Much of what is known about atmospheric aerosols has been learned by examining how the number of particles in air varies as a function of size (diameter). Such physical size distributions are obtained using a variety of instrumentation, including particle counters, electrostatic classifiers, and optical particle analyzers. These devices take advantage of a number of aerosol properties: (1) aerosols are effective light scatterers, being similar in size to the wavelength of visible light, (2) in a supersaturated environment, aerosols will absorb material from the gas phase and grow to larger sizes, and (3) aerosols can be electrically charged and electrostatically steered.

Atmospheric aerosol particle concentrations typically exhibit a log-normal size distribution, i.e., a Gaussian distribution when plotted against the log of the diameter. Figure 1 illustrates the size distribution of the marine aerosol in terms of the number, surface area, and volume, with D_p referring to particle diameter. The left side of Figure 1 is plotted on a

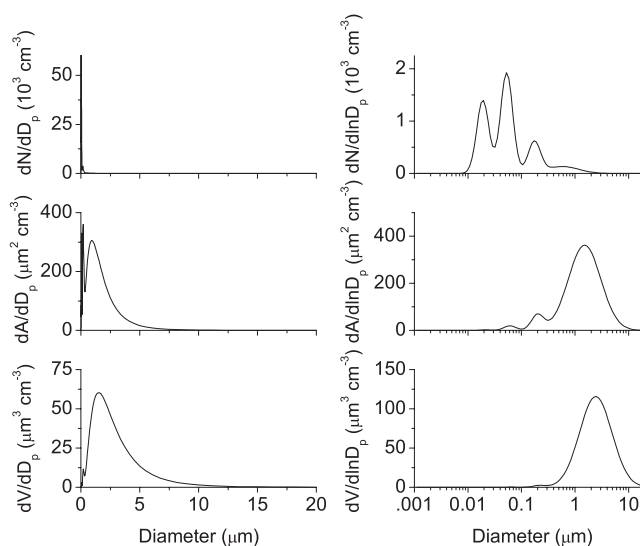


Figure 1. Model marine aerosol size distribution of aerosol number, surface, and volume distributions versus particle size. Left, linear size scales; right, logarithmic size scales. Adapted from Seinfeld and Pandis [1998] using aerosol parameters from Heintzenberg et al. [2004].

linear size scale, and the units of the number size distribution are given as *number of particles per micron per cm³*. This is commonly called dN/dD_p , and is actually the *number of particles per cm³ of air in a 1- μ m-wide size bin*. The integrated area under the size distribution therefore represents the total number of particles. The surface area and volume distributions are expressed as dA/dD_p and dV/dD_p , respectively. The gross features of the distributions are obvious. Most of the particles are in the small size range, while most of the mass is in the larger particles. However, the details of the size distribution are not clear in this view. Aerosol sizes vary over such a large dynamic range that plotting properties on a linear scale is not very illuminating.

Aerosol size distributions are usually plotted against the natural logarithm of the particle diameter. Here, the number size distribution is expressed as $dN/d\ln D_p$, or the *number of particles per cm³ of air in a size bin 1 lnDp wide*. Because $\ln D_p$ is unitless, the number distribution has units of *numbers of particles per cm³* or simply cm^{-3} . The surface area and volume distributions have analogous units. Figure 1b clearly shows that the aerosols are concentrated in distinct modes, or peaks in the distributions, with minima between them. Three major aerosol modes are commonly observed in marine air: the Aitken mode, in the size range $D_p < 0.1 \mu\text{m}$, the accumulation mode in the size range from 0.1 to 1 μm , and the coarse mode consisting of particles with $D_p > 1 \mu\text{m}$. A fourth, nucleation mode is sometimes observed, containing very small particles, $D_p < 0.01 \mu\text{m}$. The major aerosol modes have different mechanisms of formation, and removal, and often very different chemical characteristics.

Figure 2 is a process-oriented view of the aerosol size distribution. This view links the size distribution of the aerosols to the source/removal processes that affect it. The diagram is rather simple and hides the extraordinary complexity of the myriad of chemical reactions and physical processes involved in determining the nature of the atmospheric aerosol. The diagram emphasizes three basic aspects of atmospheric aerosols. First, primary aerosols are generated in the nucleation mode by condensation of vapors. In industrial settings, this may involve the cooling of heated gases. In the marine environment, it involves the gas phase production of low volatility compounds such as sulfuric or nitric acid, which readily condense onto preexisting particles. If few preexisting particles are present, these acids may form clusters with water vapor to form new particles. Nucleation mode aerosols grow into accumulation mode aerosols via further condensation of gas phase species, coagulation of particles, and processing in clouds. Coarse mode aerosols are result from mechanical aerosol generation processes, including sea spray and bubble bursting, the weathering and erosion of soils, and the ejection of volcanic material.

Major aerosol modes:

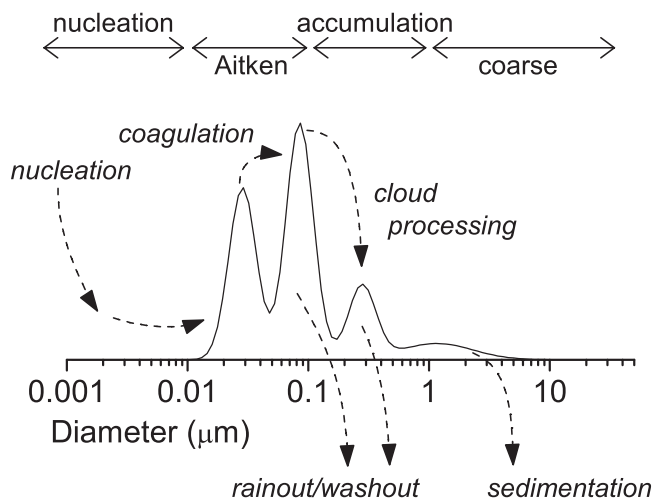


Figure 2. Schematic illustrating particle number in the major aerosol modes as a function of diameter and the relationships to sources, transformation, and removal processes.

In terms of aerosol number and size distribution, marine aerosols differ significantly from continental aerosols. Marine aerosols consist of Aitken particles, accumulation mode particles, and a coarse mode consisting primarily of sea salt. Away from continental sources, marine aerosol numbers (dominated by the nuclei and accumulation modes) are an order of magnitude lower than in typical continental air masses. The database of measurements of the size distribution of marine aerosol has increased greatly in recent years. Heintzenberg *et al.* [2004] compiled more than 10,000 marine aerosol size distributions from several field campaigns (Figure 3). This database provides a statistically robust characterization of the marine aerosol for several regions. One striking aspect of the aggregated data set is that aerosol numbers drop steeply at the low end of the size distribution. This reflects the fact that nucleation mode aerosols are only occasionally observed in the marine boundary layer. In other words, the marine aerosol does not appear to be continuously supplied by the formation of new nucleation mode particles. This differs from many continental aerosol measurements, which show flatter or more “open” distributions at the lowest size ranges. The evidence suggests that nucleation in the marine boundary layer is not a dominant process.

2.3. Removal Processes

Aerosol removal processes exert a major effect on the size distribution and composition of aerosols. Aerosols are removed from the atmosphere by both dry and wet processes.

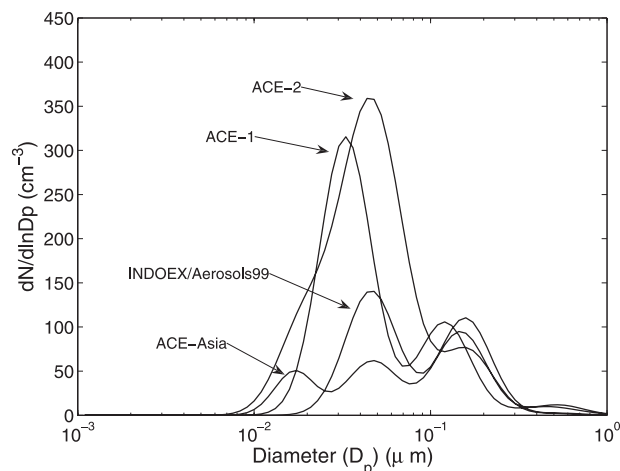


Figure 3. Marine aerosol number distributions as a function of dry particle diameter, derived from several thousand measured aerosol size distributions from four major field campaigns conducted in the Southern Ocean (ACE-1), North Atlantic (ACE-2), Indian Ocean (INDOEX, Aerosols99), and Western Pacific (ACE-Asia). The curves shown represent the median size distribution from each data set, fit to four log-normal modes. From *Heintzenberg et al.* [2004].

The most important physical processes involved in aerosol removal are gravitational settling, impaction, diffusion, and hygroscopic growth with subsequent rainout. The rates of these processes are strong functions of particle size, as illustrated in Figure 4.

The rate at which particles settle out of the atmosphere is a function of their size, shape, and density. All aerosol particles are denser than air, but gravitational settling must compete against the tendency for turbulent motions of the atmosphere to keep particles suspended. As a result, settling is important only for coarse mode particles. These larger particles are also subject to inertial forces, so they tend to impact on surfaces (like the ground or raindrops). Particles of several micrometers in diameter or larger tend to have a short lifetime in the atmosphere. For example, a 10- μm particle has a settling velocity of about 1000 cm h^{-1} or 240 m d^{-1} . So, a large aerosol particle in the boundary layer (lowermost 1–2 km) would have a lifetime of a few days or less.

Particles in air diffuse by Brownian motion, caused by the random collisions with surrounding gas molecules. This motion is important only for smaller particles, while the motion of larger particles is dominated by fluid drag and gravity. Typical diffusion length scales for aerosol particles range from 0.2 cm s^{-1} for a 1-nm particle to 0.0001 cm s^{-1} for a 10- μm particle. As a result, very fine particles tend to collide frequently, and for those particles, coagulation is an important process (Figure 2). This process transfers mass into the larger size range.

Accumulation mode aerosols (0.1–1 μm) are large enough that diffusion is slow, and the collision rate is low. As a result, coagulation is not important for this mode. This size range is small enough that gravitational settling and inertial impaction are not fast removal processes either. As a result, they tend to have a long residence time in the atmosphere and therefore tend to accumulate (hence the name). Wind tunnel studies show that the accumulation mode aerosols lie at the minimum in dry deposition rate, between gravitation settling of larger particles and diffusional loss of smaller particles (Figure 4, right panel).

For accumulation mode particles, cloud scavenging and precipitation is the major removal route. For these particles, removal occurs primarily via hygroscopic activation and growth in the slightly supersaturated conditions occurring in-cloud, followed by rainout. Aerosols of larger and smaller sizes interact with cloud droplets via Brownian diffusion and impaction, both in cloud and below cloud.

2.4. Aerosol Hygroscopicity

Aerosols containing highly soluble ionic constituents, like sulfate or ammonium sulfate salts, interact strongly with atmospheric water. The tendency to absorb moisture from the surrounding atmosphere is known as hygroscopicity. Hygroscopic aerosols grow under conditions of increasing relative humidity (RH) and shrink as RH decreases. The hygroscopic behavior of aerosols means that they are constantly shifting in size, as they adjust to changes in ambient RH. This effect

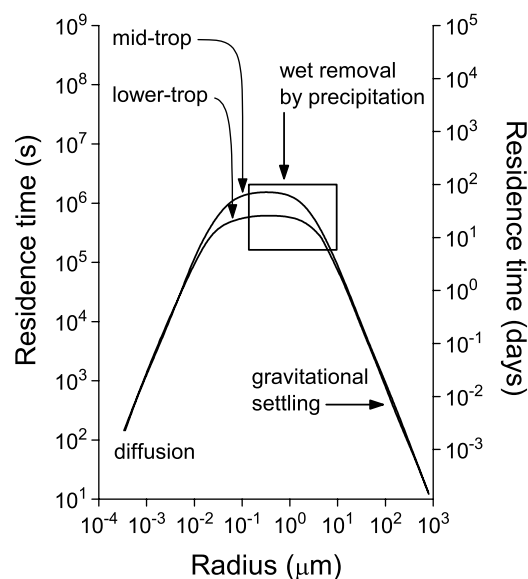


Figure 4. Atmospheric lifetimes of aerosols as a function of particle size [modified from *Kreidenweis et al.*, 1999].

is of considerable importance, in that it affects aerosol size, chemical composition (pH, ionic strength, etc.), light scattering, cloud droplet nucleation, and lifetime. These effects can significantly alter aerosol and cloud properties and their interactions with the climate system.

The hygroscopic growth behavior of pure or mixed salt aerosols can be predicted from thermodynamic properties. The growth curve can be predicted from the solubility of the various salts, their activity coefficients, and RH. In the laboratory, dry salt aerosols exposed to increasing RH exhibit a deliquescence point or threshold at which water is rapidly absorbed by the aerosol, and the dry aerosol becomes an aqueous solution. At relative humidities above the deliquescence point, the aerosol grows to a size which maintains the vapor pressure or activity of water in equilibrium with the surrounding air. For particles of diameter less than about 30 nm, the Kelvin effect of droplet curvature on surface tension exerts a significant effect on the equilibrium particle size at a given RH. The Kelvin effect is discussed further in the chapter by Lohmann, this volume (Marine Boundary Layer Clouds).

Under conditions of decreasing RH, the aqueous aerosol droplet loses water along the same equilibrium vapor pressure curve. However, rather than drying out at the deliquescence point, as one might expect, the aerosols remain hydrated and supersaturated to a much lower RH. Eventually, a second critical RH is reached, called the efflorescence or crystallization point, at which the “excess” water is lost from the particle. This supersaturation reflects the energy barrier involved in nucleation of salt crystals in an aqueous solution with no surfaces or preexisting nuclei. The efflorescence and deliquescence points can be widely separated, leading to hysteresis in particle diameter as RH is cycled. For example, the deliquescence point of pure NaCl occurs around 78% RH, while the efflorescence point is near 45% RH. An example of sea salt aerosol behavior during hydration/dehydration is shown in Figure 5. Sea salt aerosol behavior is slightly different from that of pure NaCl. Sea salt deliquesces and effloresces at slightly lower RH than pure NaCl. In fact, sea salt does not dry out completely even at very low RH. These differences in behavior are attributable to the presence of other salts, particularly MgSO_4 and MgCl_2 [Tang *et al.*, 1997]. Sulfuric acid solutions do not crystallize as they dry, and as a result, they exhibit symmetrical behavior during growth and drying.

Atmospheric aerosol particles are complex mixtures of ionic, organic, and insoluble species, and they exhibit behavior which may be difficult to model based on laboratory studies of pure compounds. A very useful resource for information on aerosol thermodynamics is the Aerosol Inorganic Model developed by S.L. Clegg, P. Brimblecombe, and

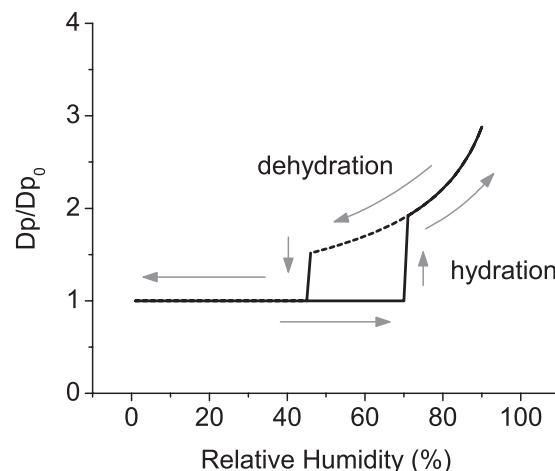


Figure 5. Change in diameter of a sea-salt particle with increasing and decreasing relative humidity. Note that the particle follows different paths during hydration and dehydration [after Tang *et al.*, 1997].

A.S. Wexler (<http://www.aim.env.uea.ac.uk/aim/aim.php>). In general, aerosols composed primarily of ionic solutions exhibit larger hygroscopic growth factors, and the presence of neutral and insoluble compounds such as soot or mineral dust tends to reduce their hygroscopicity.

In the marine boundary layer, RH levels generally range from 70% to 90%, well above the efflorescence point of most sulfate and sea-salt aerosols, so they remain in the aqueous state. The hygroscopicity of ambient aerosols is usually reported as a *hygroscopic growth factor*, defined as the ratio of aerosol diameter at a given RH to that at a lower reference RH (e.g., $D_p(90\% \text{ RH})/D_p(\text{dry})$). Accumulation mode aerosols in clean marine air masses typically exhibit growth factors at 90% RH ranging from about 1.6 to 2.0. Sea-salt aerosols have larger growth factors, typically greater than 2. Anthropogenically influenced air masses over the oceans typically exhibit lower growth factors, in the range of 1.2 to 1.5 [Berg *et al.*, 1998; Massling *et al.*, 2003]. Even lower growth factors are associated with freshly polluted air containing very high levels of elemental carbon, recently advected over the ocean. These differences point to the importance of polluted air mass “aging” in which the aerosols increase their hygroscopicity with time. This can occur via the heterogeneous oxidation of sulfur dioxide, leading to an increase in aerosol sulfate or via the oxidation of less polar organic compounds to more soluble organic acids.

2.5. Cloud Processing

Cloud processing plays an important role in the evolution of marine aerosols [Hoppel *et al.*, 1986, 1990]. Cloud drop-