“Laboratory Studies of the Role of Sea Salt Bromine in Determining Tropospheric Ozone”

Grant No. DE-FG02-98ER62578

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Abstract:

I have been asked to submit a report to cover this grant's lifecycle. The purpose of this research was to elucidate the processes that release halide ions from sea salt particles into air in the form of highly reactive halogen atoms and to study the impact on tropospheric chemistry, particularly that involving the formation and loss of ozone. The research involved primarily laboratory studies of model systems, although some field studies were carried out in collaboration with other DOE investigators. These studies established that sea salt particles react with a variety of trace gases found in the troposphere to form halogen-containing gases that photolyze in sunlight to generate halogen atoms. The trace gases include NO_2 , N_2O_5 and ClONO_2 , as well as OH and O_3 . The primary component of sea salt is sodium chloride, and the chloride atoms formed from this chemistry leads to ozone formation under most tropospheric conditions. On the other hand, sodium bromide, which is a minor component of sea salt, forms bromine atoms which lead to ozone destruction. The latter was confirmed in field studies in the Arctic at polar sunrise where gas phase Br_2 and BrCl from sea salt sodium bromide were measured for the first time.

This research highlighted the importance of halogen chemistry in the troposphere, a topic that had been largely overlooked to this point. It is now universally recognized as being very important in controlling the levels of ozone, which is a greenhouse gas, important atmospheric oxidant and toxic gas. In fact, this area has become something of a "cottage industry" in the field of atmospheric chemistry and an important key to accurately modeling climate change.

Key Results:

Key results are summarized in the attached RIMS final report, and include the following:

- New techniques for measuring some unusual but potentially important halogen gases such as HOCl were developed;
- Unique "markers" for chlorine atom chemistry in coastal urban areas such as 4-chlorocrotonaldehyde were identified, some of which have now been measured in air by other research groups;
- Sea salt particles were shown to react with some trace gases via unique interface processes which are much faster than uptake and reaction inside the particles, and in addition, proceed by different mechanisms. This chemistry had not previously been recognized but now is the subject of many studies by a number of different research groups;
- The nitrogen oxide N_2O_5 was shown to be particularly important in reacting with both NaCl and NaBr in sea salt particles, generating ClONO_2 and BrNO_2 respectively. Recently ClONO_2 has been detected for the first time in mid-continental air in the U.S., suggesting that halogen chemistry elucidated in this research is not restricted to marine areas but rather, is quite ubiquitous;
- The gases Br_2 and BrCl were measured for the first time in air in the Arctic at polar sunrise in a joint collaboration with other DOE-sponsored researchers (Dr. Chet Spicer); this was published in *Science*. This confirmed that the reason for the rapid loss of O_3 at polar sunrise that had been previously observed was the formation of Br_2 and BrCl which

rapidly photolyzed to form highly reactive bromine atoms which destroyed O₃ in a chain reaction;

- Gas phase Cl₂ was measured for the first time in air on the east coast of the U.S. in a collaboration with DOE researchers (Chet Spicer, Carl Berkowitz and colleagues at PNNL). This moved the importance of chlorine chemistry in the troposphere from “hypothesized” based on laboratory studies to “confirmed” in field studies.

In summary, the research sponsored by DOE has had a major impact on our understanding of tropospheric chemistry, and in particular, that which impacts the formation and fates of ozone. This is critical for quantitatively assessing the role of ozone in climate change, health and local to regional air pollution.

FINAL REPORT

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OBJECTIVES: Sea salt particles play a key role in the chemistry of the atmosphere over oceans as well as in coastal urban areas. Thus, through reactions with trace gases in air, they can generate photochemically labile gases such as Cl_2 and Br_2 , which act as sources of highly reactive halogen atoms.¹⁻⁵ These atoms can impact ozone levels in the atmosphere both directly by reacting with O_3 as well as indirectly by participating in the VOC- NO_x cycles that lead to ozone formation. This is important because ozone is a greenhouse gas and alters the ultraviolet radiation received at the earth's surface. This makes it a major greenhouse gas. Ozone is itself an oxidant as well as a precursor to other oxidants such as the hydroxyl free radical. Because the hydroxyl radical controls the concentrations of a number of greenhouse gases such as methane, ozone has not only a direct global climate impact but an indirect one as well. Finally, ozone is an air pollutant for which air quality standards are set.⁶

Another contribution of sea salt particles to tropospheric chemistry is that they provide an aqueous reaction medium for the uptake and reaction of gases in the atmosphere. For example, they take up SO_2 that is emitted during the combustion of fossil fuels and that is also formed during oxidation of biogenic sulfur compounds emitted from oceans.^{7,8} This sulfur dioxide is oxidized to sulfate particles that are major contributors to the aerosol loading globally, and have both direct and indirect effects on radiative forcing and hence global climate.⁹⁻¹¹

Bromine is a particularly important component of sea salt in that there is increasing evidence that it plays a role much greater than implied by the 650:1 $\text{Cl}^-:\text{Br}^-$ ratio of ions found in seawater. For example, ozone destruction *at ground level* in the Arctic and Antarctic at polar sunrise is associated with bromine chemistry,¹² and the bromine source is now recognized to be sea salt as we had originally proposed.¹³ It is highly likely that similar chemistry occurs in mid-latitudes but due to different meteorology and the lack of a long period of darkness during winter, it is not as obvious in field campaigns; even then, there is evidence of sunrise ozone destruction (SOD) from field studies in mid-latitude marine regions and it too appears to be associated with sea salt, likely bromine.^{14,15}

The overall objective of this research is to study the reactions of sea salt particles with trace gases found in air in order to elucidate their role in the formation and loss of particles and ozone from global to local scales. The specific objectives are to carry out laboratory studies on the reactions of sea salt and its components, particularly sodium bromide, in order to elucidate the

mechanisms and kinetics of the reactions in sufficient detail that the results can be input to models used to predict the effects of sea salt particles on the atmosphere.

APPROACH: Many different techniques have been applied during the course of this research: aerosol chamber studies, Knudsen cell studies, relative rate studies using GC-FID, diffuse reflectance Fourier transform mass spectrometry (DRIFTS) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX), environmental SEM (ESEM) and time of flight-secondary ion mass spectrometry (TOF-SIMS).

KEYWORDS: sea salt, sulfate, sulfur dioxide, sodium bromide, sodium chloride, ozone, halogens, troposphere, global climate.

COLLABORATIONS: The possibility of collaborating with scientists at national laboratories is one of the wonderful components of the ASP. The PI has been fortunate to participate in field studies with Carl Berkowitz and his colleagues at PNNL, and Chet Spicer of Battelle Columbus. The earlier studies carried out during the previous grant led to the first (and to date, only) measurements of Cl_2 in the troposphere; this was published in *Nature*. During the current grant, we again collaborated and measured Br_2 and BrCl at ground level at Alert, Canada. This was published in *Science* and also represents the first such measurement of these important trace gases.

In the fall of 2002, the PI spent a sabbatical leave at PNNL and developed close collaborations with the scientists at EMSL, particularly Alex Laskin, Dan Gaspar and Steve Colson. This has led to five joint publications to date, as well as a more formal partnership in an Environmental Molecular Sciences Institute in which the University component is funded by NSF.

During the course of DOE studies several years ago, we discovered that reactions occurring right at the air-water interface of sea salt particles were important for generating gaseous Cl_2 . This work benefited greatly from collaborations with theorists at UCI (Doug Tobias), the Academy of Sciences of the Czech Republic (Pavel Jungwirth) and UCI/Hebrew University of Jerusalem (R. Benny Gerber) and with an airshed modeler, Donald Dabdub at UCI. The theorists showed that halide ions in aqueous sea salt solutions were readily available at the surface to carry out these interface reactions, while Donald Dabdub and his group developed the quantitative model needed for full analysis of the chamber data. In addition, he has applied our experimental results to the chemistry occurring in coastal areas.

These collaborations have provided greatly enhanced capabilities to our DOE-funded research in terms of understanding this chemistry from the molecular scale to airshed models to field studies, but are at no additional cost to this project.

NUMBERS OF UNDERGRADUATES, GRADUATE AND POSTGRADUATES: Five undergraduates (Christopher Elliott, Sarah Toal, Alisa Ezell Smith, Gennady Soskin and Monica Martinez-Aviles), five graduate students (Mike Gebel, Margaret Kaleuati, Rachel Hoffman, Matt Lakin and Huda Shaka), eight postdoctoral fellows (Krishna Foster, Sherri Hunt, Michihiro Mochida, Ann Louise Sumner, Katie Thompson, Lisa Wingen, Weihong Wang and Husheng

Yang) and a community college instructor (Mike Ezell) have worked on this project. In addition, a visitor from the University of Paris, Jean-Francois Doussin, worked with us for six months at no cost to the project.

RESULTS:

1. NO_x Reactions.

Three different approaches to studying the reactions of various oxides of nitrogen with sea salt and its components were used: a Knudsen Cell, an aerosol chamber and long path FTIR and SEM (in collaboration with Alex Laskin at PNNL). These results can be summarized as follows:

Knudsen Cell Reactions: Knudsen cells have provided a major approach for measuring uptake probabilities for gases on solids. However, a major issue has been taking into account how much of the sample surface is available for reaction since multiple layers of the sample are commonly used and diffusion into these layers can take place.

To overcome this problem, we developed a new approach in which salt at one or a fraction of a layer is used. While the net uptake of the gas is relatively small, since there is not much reactive surface available, there is no possibility of diffusion into lower layers in this case, removing that uncertainty. We applied this to the reactions of gaseous HNO₃, N₂O₅ and ClONO₂ with NaCl. Our results for HNO₃ resolve the discrepancies in previously published values and provide new insights into the mechanism. Thus, small amounts of water adsorbed to the steps and edges of the salt surfaces even under vacuum conditions control the chemistry. Initially, the entire salt surface reacts but the terrace sites on the salt that are “dry” quickly get covered by the product nitrate ion. However, the steps and edges that hold water allow the nitrate to be recrystallized into towers of NaNO₃ on the surface, exposing fresh NaCl for reaction. Thus, the salt never becomes “passivated”, and all of the chlorine in the particles, including that inside the salt particles, is ultimately available for reaction. This was published in *J. Phys. Chem. A*. [[105](#) 5178 (2003)] and *J. Phys. Chem. A*. [[107](#) 7818 (2003)].

A similar approach was applied to the N₂O₅ and ClONO₂ reactions and again has provided new insights into the kinetics and mechanisms. This was published in *Phys. Chem. Chem. Phys.* [[5](#) 1780 (2003)].

Another important finding from the Knudsen cell studies was that because synthetic sea salt has about 10% MgCl₂, which exists as the hexahydrate, it is very liquid-like in nature, even under vacuum. Thus the uptake of SO₂ was shown to behave as though it were into a liquid, rather than onto a solid salt [*Geophys. Res. Lett.*, [27](#) 887 (2000)].

Aerosol Chamber Studies: We also carried out a number of aerosol chamber studies of the reactions of N₂O₅ and NO₃ with NaCl particles. Unfortunately, reactions on the walls of the chamber and mixing issues made separation and quantification of the N₂O₅ and NO₃ reaction probabilities not possible. However, modeling of the system showed that the previously published values, including ours using a Knudsen cell, were consistent with the data.

Long Path FTIR and SEM Studies of NaNO₃: Sodium nitrate is the major particle product of the reactions of oxides of nitrogen with sea salt, so it is important to understand its properties in the atmosphere. A graduate student, Rachel Hoffman, spent about a month at PNNL working with Alex Laskin to use SEM and ESEM to study NaNO₃ hydration. In our lab, she carried out associated long path FTIR studies. We were able to show that small particles of NaNO₃ do not undergo deliquescence at the deliquescence relative humidity of 75%, but rather, form amorphous salt particles on drying which then take up water continuously as the RH is increased. This is very important for understanding the effects of particles on light scattering and global climate change. This work was published in *J. Aerosol Sci.* 35 869 (2004).

2. Reactions of O₃ and OH with Sea Salt.

Three different approaches were taken to studying the reactions of O₃ and OH with sea salt and its components: aerosol chamber studies, diffuse reflectance Fourier transform infrared spectrometry (DRIFTS), and SEM-EDS and TOF-SIMS.

Aerosol Chamber Studies. We showed that OH free radicals react with deliquesced NaCl particles to generate gas phase Cl₂. In collaborative studies with theorists and airshed modelers, we showed that this was too fast to be due to known aqueous phase chemistry and must be due to a unique interface reaction. This was published in *Science* 288 301 (2000), and has led to a virtual explosion in studies of interface chemistry in the atmosphere.

In collaborative studies, the PI worked with scientists at the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory (Alex Laskin, Dan Gaspar, Jim Cowin and Steve Colson) to apply SEM-EDS and TOF-SIMS to deliquesced NaCl particles that had reacted with OH. Our previously hypothesized mechanism should generate hydroxide in the particles. We showed that OH⁻ was indeed generated in the particles, which has very important implications, for example for the uptake and oxidation of SO₂ in sea salt particles. Based on this work, we hypothesized that sea salt particles will remain basic much of the day when OH is generated by photolysis, increasing the uptake and oxidation of SO₂ to sulfate. We hypothesized that this will impact the formation of sulfate particles and their impact on radiative forcing, both direct and indirect. This was published in *Science*, 301 340 (2003) and in *Appl. Surf. Sci.* 231/232 520 (2004)]. Sander et al. and Keene et al. submitted comments on our paper to *Science* (where we published our experimental results and hypothesis) and we responded with additional analysis that was not in our original paper [*Science*, 303 5658/628d (2004)].

We then extended these studies to the reaction of deliquesced NaBr aerosols with O₃ in the dark. These studies show that the production of gas phase Br₂ in this reaction is approximately an order of magnitude larger than expected due to oxidation of bromide ions in the bulk of the particles. We propose that this reaction occurs at the air-water interface, similar to that proposed for the OH-Cl⁻ reaction. This is consistent with molecular dynamics calculations by our theoretical colleagues (Jungwirth, Tobias and Roeselova) that show that bromide ions are readily available at the interface and that O₃ in a water slab rapidly moves to the interface and remains there. However, such an interface reaction of ozone with halide ions has not before been reported. A paper is in press in *J. Phys. Chem. A* on this work, which combines the experiments and theory.

We also carried out many studies of OH with deliquesced NaBr particles to search for an interface reaction similar to that for the NaCl particles. However, after a great deal of interplay between modeling and experiment, we have concluded that in contrast to the NaCl case, the aqueous phase bromide chemistry is so fast that even if the interface reaction occurred with a reaction probability of one, it would not contribute significantly to the observed Br₂ formation. We are currently carrying out modeling studies of different systems to define the conditions and systems for which interface chemistry is expected to be important.

DRIFTS. During the past year, we have initiated diffuse reflectance Fourier transform infrared spectrometry (DRIFTS) to further investigate this impact of sea salt particles on the formation of sulfate in the troposphere. These studies clearly demonstrate that sea salt particles (represented by a 10% mixture of MgCl₂ with NaCl) that have reacted with gas phase OH take up and oxidize much more SO₂ than unreacted particles. This is in agreement with our earlier hypothesis since the particles become basic via reaction with OH and this leads both to increased uptake of SO₂ and to a more rapid oxidation of the dissolved S(IV) by O₃. Studies to quantify this are currently underway.

3. Chlorine Atom Reactions

We have carried out both kinetic and mechanistic studies to help define the importance of sea salt chemistry in the troposphere. This includes kinetics studies of chlorine atom reactions with unsaturated aldehydes and ketones which are oxidation products of biogenic hydrocarbons in air [*Phys. Chem. Chem. Phys.* 4 1824 (2002)]. In addition, studies of the mechanism of chlorine atom reactions with some unsaturated compounds (isoprene, 1,3-butadiene) were carried out to identify unique products that could be searched for in air as markers of chlorine atom chemistry [*Geophys. Res. Lett.* 27 947 (2000); *J. Geophys. Res.* 106 4939 (2001)]. It is gratifying that these markers have now been identified in field studies in coastal urban areas.

4. Field Studies

A unique aspect of the ASP program has been the opportunity to develop collaborations with other team members. For this PI, it has been a real highlight and has led to some outstanding science with broad impacts that could not have been done otherwise. During this grant period, we collaborated with Chet Spicer in the measurement of gaseous Br₂ and BrCl at Alert, Canada during the winter and at polar sunrise. While bromine had been hypothesized to be responsible for the ground-level ozone destruction first reported about 20 years earlier, the gases had not actually been measured. These were the first (and to date, only) such measurements and were published in *Science* 291 471 (2001) and *Atmos. Environ.* 36 2721 (2002).

We also developed a method for measuring HOCl using atmospheric pressure ionization mass spectrometry [*J. Phys. Chem. A.*, 103 8231 (1999); *Phys. Chem. Chem. Phys.* 1 5615 (1999)]. Although this has not yet been applied, it should prove useful in future field studies, since HOCl is another sea salt reaction product that has never been measured in the troposphere but should be present.

5. Other Contributions.

In addition to the above studies, the PI prepared detailed reviews of sea salt chemistry [*J. Phys. Chem.* 104 11463 (2000); *Chem. Rev.* 103 4801 (2003)].

DELIVERABLES:

The following papers acknowledging DOE support have been published:

1. Characterization of HOCl using Atmospheric Pressure Ionization Mass Spectrometry
J. Phys. Chem. A, 103, 8231 (1999)
T.E. Caldwell, K.L. Foster, Th. Benter, S. Langer, J.C. Hemminger and B.J. Finlayson-Pitts
2. Techniques for Quantifying Gaseous HOCl Using Atmospheric-Pressure-Ionization Mass Spectrometry
Phys. Chem. Chem. Phys., 1, 5615 (1999).
K.L. Foster, T.E. Caldwell, Th. Benter, S. Langer, J.C. Hemminger and B.J. Finlayson-Pitts
3. 4-Chlorocrotonaldehyde as a Unique Chlorine-Containing Compound from the Reaction of Atomic Chlorine with 1,3-Butadiene in Air at Room Temperature
Geophys. Res. Lett., 27, 947 (2000).
W. Wang and B.J. Finlayson-Pitts
4. The Uptake of SO₂ on Synthetic Sea Salt and Some of Its Components
Geophys. Res. Lett., 27, 887 (2000).
M.E. Gebel, B.J. Finlayson-Pitts and J.A. Ganske
5. Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols
Science, 288, 301 (2000).
E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias R. B. Gerber, D. Dabdub and B. J. Finlayson-Pitts
6. Physical Chemistry of Airborne Sea Salt Particles and Their Components
J. Phys. Chem., 104, 11463 (2000).
B. J. Finlayson-Pitts and J. C. Hemminger
7. Unique Markers of Chlorine Atom Chemistry in Coastal Urban Areas: The Reaction with 1,3-Butadiene in Air at Room Temperature
J. Geophys. Res., 106, 4939 (2001).
W. Wang and B. J. Finlayson-Pitts

8. The Role of Br₂ and BrCl in Surface Ozone Destruction at Polar Sunrise
Science, 291, 471 (2001).
K. L. Foster, R. A. Plastridge, J. W. Bottenheim, P. B. Shepson, B. J. Finlayson-Pitts and C. W. Spicer
9. Uptake and Reaction of ClONO₂ on NaCl and Synthetic Sea Salt
J. Phys. Chem. A 105, 5178 (2001).
M.E. Gebel and B.J. Finlayson-Pitts
10. Molecular Halogens Before and During Ozone Depletion Events in the Arctic at Polar Sunrise: Concentrations and Sources
Atmos. Environ. 36 2721 (2002).
C.W. Spicer, R.A. Plastridge, K.L. Foster, B.J. Finlayson-Pitts, J.W. Bottenheim, A.M. Grannas and P.B. Shepson
11. Rate Constants for the Reactions of Chlorine Atoms with a Series of Unsaturated Aldehydes and Ketones at 298 K: Structure and Reactivity
Phys. Chem. Chem. Phys., 4, 1824 (2002).
W. Wang, M.J. Ezell, A.A. Ezell, G. Soskin and B.J. Finlayson-Pitts
12. Knudsen Cell Studies of the Reactions of N₂O₅ and ClONO₂ with NaCl: Development and Application of a Model for Estimating Available Surface Areas
R. C. Hoffman, M. E. Gebel, B. S. Fox and B. J. Finlayson-Pitts
Phys. Chem. Chem. Phys., 5, 1780 (2003).
13. Reactions at Interfaces as a Source of Sulfate Formation in Sea Salt Particles
Science, 301 340 (2003)
A. Laskin, D. J. Gaspar, W. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson and B. J. Finlayson-Pitts
14. Knudsen Cell Studies of the Reaction of Gaseous HNO₃ with NaCl Using Less than a Single Layer of Particles at 298 K: A Modified Mechanism
J. Phys. Chem. A., 107 7818 (2003)
R. C. Hoffman, M. A. Kaleuati and B. J. Finlayson-Pitts
15. The Tropospheric Chemistry of Sea Salt: A Molecular Level View of the Chemistry of NaCl and NaBr
Chem. Rev. 103 4801 (2003)
B. J. Finlayson-Pitts
16. Response to Comments on "Reactions at Interfaces as a Source of Sulfate Formation in Sea Salt Particles"
Science 303 5658/628d (2004)
A. Laskin, D. J. Gaspar, W. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson and B. J. Finlayson-Pitts

17. Sodium Nitrate Particles: Physical and Chemical Properties During Hydration and Dehydration and Implications for Aged Sea Salt Aerosols
J. Aerosol Sci. **35** 869 (2004)
R. C. Hoffman, A. Laskin and B. J. Finlayson-Pitts

18. TOF-SIMS Analysis of Sea Salt Particles: Imaging and Depth Profiling in the Discovery of an Unrecognized Mechanism for pH Buffering
D. J. Gaspar, A. Laskin, W. Wang, S. W. Hunt and B. J. Finlayson-Pitts
Appl. Surf. Sci. **231/232** 520 (2004)

19. Formation of Molecular Bromine from the Reaction of Ozone with Deliquesced NaBr Aerosol: Evidence for Interface Chemistry
S. W. Hunt, M. Roeselová, W. Wang, L. M. Wingen, E. M. Knipping, D. J. Tobias, D. Dabdub and B. J. Finlayson-Pitts
J. Phys. Chem. A., **108** 11559 (2004)

EDUCATIONAL ASPECTS:

This project has also contributed significantly to the education and career development of students and postdoctoral fellows. Alisa Ezell Smith is now teaching high school chemistry, and is using her research experience in her teaching. Sara Toal is in the Ph.D. program at UCSD and Monica Martinez-Aviles is in the Ph.D. program at Purdue. Chris Elliott is working as a software consultant for Hewlett Packard. Gennady Soskin is in pharmacy school. Rachel Hoffman and Margaret Kaleuati are working for environmental consulting firms and Mike Gebel is working for the California Air Resources Board. Matt Lakin is working for the EPA. Krisha Foster is on the faculty at Cal State LA and Katie Thomposon is a lecturer at a university in London. Sherri Hunt is a AAAS Fellow and is working with the EPA in Washington. Husheng Yang is working as a scientist in industry. Michihiro Mochida is a research scientist in Hokkaido, Japan. Ann Louise Sumner is a researcher at Battelle Memorial Labs. Mike Ezell retired from the Department of Chemistry at Orange Coast College, and is now a full-time researcher at UCI. Lisa Wingen is a Project Scientist in our newly funded (NSF) Environmental Molecular Sciences Institute at UCI. Weihong Wang was a research scientist at UCI and is currently devoting herself to family. A majority of the recent participants in this research program are from underrepresented groups in science, particularly women.

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