

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Heterogeneous Reactions of Nocturnal Nitrogen Oxides at Atmospherically Relevant Aqueous Interfaces

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Climate Change is a Difficult Subject to Beach Breach by Sean Staudt, PhD candidate 8/2019

Our current standard of living is like a big sandy beach. It's warm. Calming. Once accustomed to this beach, it's hard to imagine life without it. This beach, representing our current lifestyle, has been decades in the making, evolving with us. But something is not quite right with this beach. Something- the truth about climate change- is buried beneath it. You can imagine strolling along this beach, basking in the warm sun as waves crash nearby. How lovely, how serene! You close your eyes to listen to waves lap when- oof! Your daze is broken. You bumped something in the sand with your foot- something hard, something... unfortunate.

In the moment, your foot aches, and you're presented with a choice: ignore it and keep walking, or explore, and find what disturbs your perfect beach. Those that are curious, they start to dig. They explore. Confronted with a problem, these explorers want to solve it. They dig and dig and dig, until they finally unearth the "unfortunate something" and it's... well... *something*. Maybe they're not sure what it is, but they know that if people hurt themselves on it, the beach might not be safe.

The explorers start combing the beach in case there are more "unfortunate somethings" in the sand. Indeed, as they excavate, more unfortunate somethings are found. It would seem the problem is larger than initially thought! What are these "somethings?" How do we fix the beach? The explorers desire more pieces to fully solve the puzzle. Unfortunately, explorers are limited by the scavenging technology of their time, and they are unable to completely unearth all of the truths hidden around the beach. Instead, they use what they've learned so far about the unfortunate somethings to predict locations, size, and shape of the "truths" still buried in the sand, in hopes that future explorers might be able to build upon their work and bring the truths to light. The explorers improve their methods. They dig up the truths buried shallow. They invent ways to better

estimate the deeply buried truths, and they start putting the puzzle together, even without all the pieces or even well-fitting pieces. The explorers are determined to uncover the full truth that hampers us, as they want a better beach (lifestyle) not only for themselves but for the future generations as well.

In this analogy, I am one explorer. I have a piece of truth that's been partially dug up. I can see that it's connected to other truths that other explorers have dug up, but even more importantly, my truth is not completely dug up- there's more under the sand. This piece is too big for me to unearth alone, but I have technologies that will allow me to clear more sand away and better estimate the shape of the puzzle piece buried. Once my time is up, I can pass on my findings so that another explorer can better guess how my piece of truth fits into solving this unfortunate something. I am an atmospheric chemist, and my work is a small part in the larger fight against climate change.

On these luxurious beaches, the first piece of truth implicating humans as a cause of climate change was dug up over 100 years ago, by "explorers" named Svante Arrhenius (famous in chemistry for a multitude of other reasons!) and Arvid Högbom.¹ They found factory emissions in their time were contributing to the total amount of gases in the atmosphere, but concluded that humans would need to put out a lot more for it to have any major impact. As they studied their truth for another decade, they realized humans were putting out more and more pollutant gas since their first conclusion, and that if the pattern continued the pollutant gas could be majorly impactful in time, dangerous or even harmful to those who encountered it in the future.¹ The explorers knew that we, the future explorers, would need to discover more to properly gauge how dangerous this piece of truth was. Ever since Arrhenius and Högbom stubbed their toes on the first piece of truth,

more and more pieces of truth have been found by curious explorers, relating to all kinds of manmade pollutants and other effects humans have been having on the climate.

My piece of truth on climate change regards a pollutant that only appears at nighttime; its name is dinitrogen pentoxide (N_2O_5 , for short). N_2O_5 is an amazing molecule. Globally, N_2O_5 appears at night anywhere there are large amounts of combustion happening: factories, energy plants, trash burning, and of course our automobiles.² N_2O_5 acts as a reservoir for these combustion products, and come sun-up breaks back down in sunlight, reverting to the smaller combustion products. N_2O_5 is known chemically to be a nitrating agent, able to perform many useful synthesis reactions- some as dangerous as the synthesis of explosives.³ Imagine the shock then, when nearly 35 years ago explorers confirmed N_2O_5 to occur naturally in our atmosphere!⁴ Now, the amount of N_2O_5 made naturally even in the most polluted cities is not enough to synthesize anything explosive, but the reactions it is capable of performing at night in the atmosphere are capable of turning normally-safe compounds into harmful products. This piece of truth connects to what I do today. I explore the interaction of N_2O_5 with a safe compound, saltwater.

Sodium chloride (NaCl) is what makes our ocean so salty. The amount of NaCl in saltwater around the world is, for the most part, the same and unchanging. A piece of truth discovered 30 years ago by Finlayson-Pitts, Ezell, and Pitts (1989) notes that N_2O_5 can react with the salt in salty water, forming a new pollutant: nitryl chloride (let's call it ClNO_2), of which I want to describe two special traits.⁵ The first special trait about ClNO_2 is that it is not soluble in water at all! So if N_2O_5 from the atmosphere reacts with wet NaCl particles (crashing ocean waves can generate these!), ClNO_2 can form and promptly leave the water. ClNO_2 is now in the gas phase, in place of the N_2O_5 molecule from which it came. Another piece of truth put together by Behnke et al. in 1997 says that, for a reaction of N_2O_5 with just sodium chloride in water, a certain amount of

chloride (Cl) in the water will yield a certain amount of ClNO₂ that will leave the water.⁶ This information is displayed in Figure 1. The second special trait about ClNO₂ is that, like N₂O₅, it breaks down in sunlight. When N₂O₅ breaks down, it forms the simple combustion products it was before it became N₂O₅. When ClNO₂ breaks down though, it forms one combustion product (that can later again form N₂O₅,) in addition to a destructive radical chlorine atom. Historically, radical chlorine is known to be very bad for the

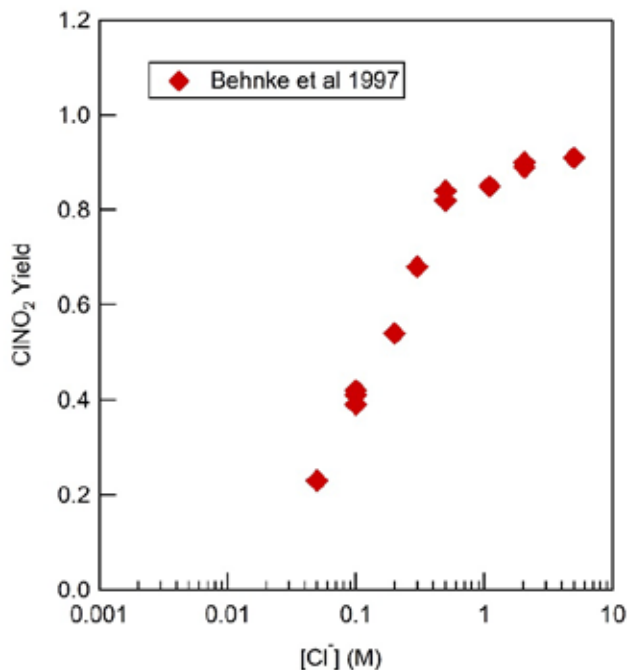


Figure 1 - Behnke and company's piece of truth: ClNO₂ synthesized is dependent on the amount of chloride in water

atmosphere. Frank Sherwood Rowland and Mario Molina discovered their piece of truth in the 1970's, pertaining to chlorine's use in coolants and refrigerants in the form of chlorofluorocarbons, more commonly known as CFC's.⁷ Noting the ozone-destroying capabilities of chlorine generated from CFC's and their long lifetimes in the atmosphere (up to 100 years- gases released in the 70's are likely still up there!), CFC's were labelled "super" greenhouse gases and their generation and use was promptly banned internationally in 1987 as part of the Montreal Protocol, an international treaty.⁸ (Rowland, Molina, and a third explorer named Paul J. Crutzen were awarded the 1995 Nobel Prize for Chemistry for this discovery!) And N₂O₅ is capable of turning harmless saltwater into this??

Thankfully it doesn't seem like a lot of ClNO₂ is generated from the reaction of N₂O₅ with Cl in water, even at the maximum reaction amount seen in Figure 1. Scientists constantly calculate

and recalculate pollutant populations over and again, compiling their results into massive reports used to help inform policy decisions.⁹ Because these reports are so largely encompassing though, it would be in our best interest to quantify this reaction to the best of our ability. Putting a number on this reaction helps other scientists understand how our piece of truth might affect theirs. (For more, lookup the Intergovernmental Panel on Climate Change. I promise you'll be drinking from the firehose!)

To quantify this reaction, our approach is to try and replicate bits of the atmosphere in our laboratory. The atmosphere is complex, so we start with simple mimics and build up from there. Thanks to Behnke (1997) and Figure 1 (and others since then)¹⁰⁻¹², we know fairly well how N₂O₅

behaves with just chloride in water, at concentrations resembling real life ocean water. However, Ryder et al. (2009) uncovered an interesting piece of truth when testing actual ocean water: the amount of ClNO₂ seen from N₂O₅ reaction with ocean water was way lower than how much ClNO₂ was measured from N₂O₅ and simple chloride-in-water solutions, even though they contained nearly the same amount of Cl!¹² It can be seen in Figure

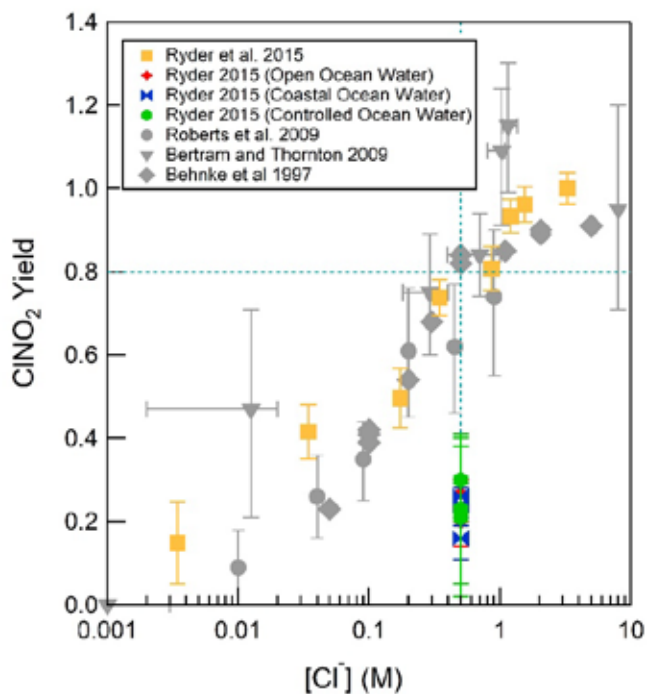


Figure 2 - Ryder et al. 2015 compared their data to other explorers, and found that their lab results were the same, but their ocean samples were very different! Dashed lines guideline expected ClNO₂ yield for Cl concentration of the ocean. Exact Cl concentrations for ocean water samples estimated to be 0.5 M.

2 that the difference between laboratory and ambient measurements is actually rather large. There

must be something else in the oceanwater causing this to happen, but this part of this piece of truth is still buried in the sand. It's my turn to start digging!

As a first step, I also followed what other explorers before me have done and measured ClNO_2 compared to the amount of Cl in water. For the purpose of my research, I purposefully generated a controlled amount of N_2O_5 and blew it over a control or simple ocean mimic (salt in water), and used an instrument called a mass spectrometer, which specializes in identifying and counting any products that might've appeared from a reaction. What I found reflected the results as seen in Figures 1 and 2 very well, but this on its own wasn't new information. We won't ever learn anything new about this piece of truth by repeating the same experiments.

My real contribution to uncovering this piece of truth pertains to some of the other chemicals found in oceanwater, and how these other chemicals affect the reaction of N_2O_5 forming ClNO_2 . My simple ocean mimics for testing were the same Cl -in-water samples, but this time mixed with: Sodium sulfate (found in waters worldwide, harmless at the found amounts), sodium acetate (represents many molecules found worldwide, with widely varying uses and backgrounds), or sodium perchlorate (very specifically **not** found naturally, makes for a good control substance). These mimics are not perfect, nor do they properly represent the complexity of oceanwater. They are simplistic and incomplete, but they are a closer representation than anything tested before. And by testing additions to NaCl one by one, we get a better feel for how each of these additives affects the overall reaction.

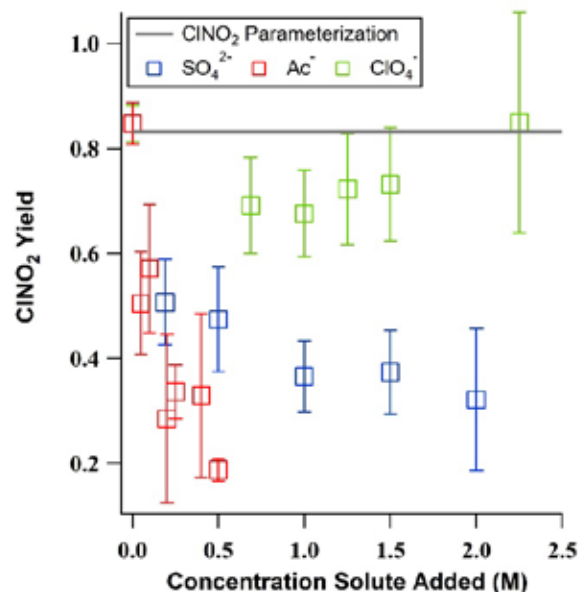


Figure 3 - My work, showing how three different additives: sulfate (SO_4^{2-}), acetate (Ac^-) and perchlorate (ClO_4^-), each affect yield of ClNO_2 from a solution containing 0.5 M Cl in water. All samples shown here contain 0.5 M Cl in water.

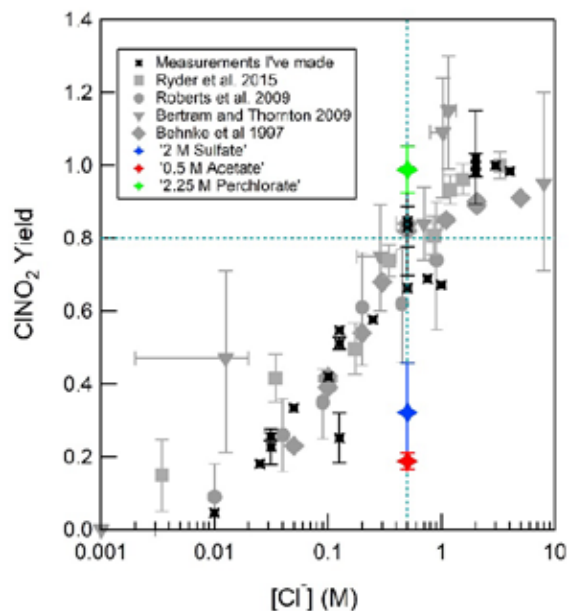


Figure 4 - The most concentrated data point for each of the salts as they appear in Figure 3: 0.5 M Cl +... 2 M sulfate, 0.5 M acetate, and 2.25 M perchlorate, respectively. Data from Figures 1 and 2 shown for comparison to the data I collected that contained only Cl in water (black points)

With all experiments run already containing the same amount of chloride in water that the ocean contains, Figure 3 shows how individually adding each of the test mix-ins affects ClNO_2 produced. It's interesting to note that both of the naturally occurring additives helped suppress the reaction of N_2O_5 with Cl , forming ClNO_2 , but not just any additive suppresses the reaction, as is shown by sodium perchlorate. Figure 4 then compares how these additives affect the yield of ClNO_2 in comparison to all the samples that contained only Cl in water. Very interesting that the 2 naturally occurring additives suppressed ClNO_2 to levels comparable to those found by Ryder et al. in 2015 (Figure 2)!

My results shown in Figures 3 and 4- my contribution to this piece of truth- can be read and referenced as Staudt et al. (2019), a manuscript recently accepted in a reputable research journal: "American Chemical Society (ACS) Earth and Space Chemistry." It contains in-depth analysis on all my results on this piece of truth, and how it connects to the pieces of truth discovered

by other explorers. If a copy is desired, or if you would enjoy a deeper discussion about this or any other “piece of truth” really, I openly invite you to reach out to me. I would be happy to discuss this paper and my results in greater detail.

So progress was made on my piece of truth. What happens now? What action happens next? Ultimately, there’s still a lot of work to do. Between my progress and the progress of thousands of other explorers, we are still uncovering pieces of truth, and we are still trying to tie the puzzle pieces together. For the puzzle pieces still very buried, we are still estimating their location, size, and shape, using knowledge gained from nearby pieces of truth to guide current and future explorers to a fuller, more complete truth. This “truth,” climate change, can no longer be denied. It has a very real presence on our beach, and if unchecked will continue hurting people.

All of us explorers know the truth in full is down there, and we know that digging it up is probably going to disturb the beach. But we must. We have to try our best to enjoy our beach as it goes through the climate change-related changes, fixing it as we go. We can still live a good lifestyle. More importantly, we can shape the beach to suit our future generations, that they may enjoy it as much as we do, possibly more. They might be able to enjoy the beach without the worry of stubbing their toes on an unfortunate something under the sand.

References:

- (1) Weart, S. The Carbon Dioxide Greenhouse Effect <https://history.aip.org/climate/co2.htm> (accessed Jun 24, 2019).
- (2) Fibiger, D. L.; McDuffie, E. E.; Dube, W. P.; Aikin, K. C.; Lopez-Hilfiker, F. D.; Lee, B.

- H.; Green, J. R.; Fiddler, M. N.; Holloway, J. S.; Ebben, C.; et al. Wintertime Overnight NO_x Removal in a Southeastern United States Coal-Fired Power Plant Plume: A Model for Understanding Winter NO_x Processing and Its Implications. *J. Geophys. Res. Atmos.* **2018**, 1412–1425.
- (3) Bachman, G. B.; Dever, J. L. The $\text{BF}_3 \cdot \text{N}_2\text{O}_5$ Complex. Its Use as a Nitrating Agent. *J. Am. Chem. Soc.* **1958**, 80 (21), 5871–5873.
- (4) Toon, G. C.; Farmer, C. B.; Norton, R. H. Detection of Stratospheric N_2O_5 by Infrared Remote Sounding. *Nature* **1986**, 319 (13), 570–571.
- (5) Finlayson-Pitts, B. J.; Ezell, M. J.; Pitts, J. N. Formation of Chemically Active Chlorine Compounds by Reactions of Atmospheric NaCl Particles with Gaseous N_2O_5 and ClONO_2 . *Nature*. 1989, pp 241–244.
- (6) Behnke, W.; George, C.; Scheer, V.; Zetzsch, C. Production and Decay of ClONO_2 from the Reaction of Gaseous N_2O_5 with NaCl Solution: Bulk and Aerosol Experiments. *J. Geophys. Res. Atmos.* **1997**, 102 (D3), 3795–3804.
- (7) Molina, M. J.; Rowland, F. S. Stratospheric Sink of Chlorofluoromethanes: Chlorine Atom-Catalyzed Destruction of Ozone. *Nature* **1974**, 249 (6), 810.
- (8) *Handbook for the Montreal Protocol on Substances That Deplete the Ozone Layer Thirteenth Edition (2019)*; Nairobi, 2019.
- (9) Pachauri, R. K.; Meyer, L.; Van Ypersele, J.-P.; Brinkman, S.; Van Kesteren, L.; Leprince-Ringuet, N.; Van Boxmeer, F. *Climate Change 2014 Synthesis Report*; 2014.
- (10) Bertram, T. H.; Thornton, J. a. Toward a General Parameterization of N_2O_5 Reactivity on Aqueous Particles: The Competing Effects of Particle Liquid Water, Nitrate and Chloride. *Atmos. Chem. Phys. Discuss.* **2009**, 9 (4), 15181–15214.

- (11) Roberts, J. M.; Osthoff, H. D.; Brown, S. S.; Ravishankara, a. R.; Coffman, D.; Quinn, P.; Bates, T. Laboratory Studies of Products of N₂O₅ Uptake on Cl⁻ Containing Substrates. *Geophys. Res. Lett.* **2009**, *36* (20), 1–5.
- (12) Ryder, O. S.; Campbell, N. R.; Shaloski, M.; Al-Mashat, H.; Nathanson, G. M.; Bertram, T. H. Role of Organics in Regulating ClNO₂ Production at the Air–Sea Interface. *J. Phys. Chem. A* **2015**, *119* (31), 8519–8526.