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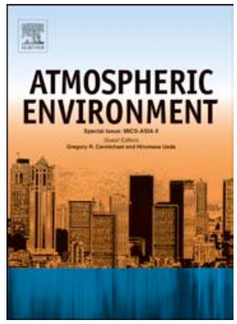

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Jon Abbatt, Christian George, Megan Melamed, Paul Monks, Spyros Pandis, Yinon Rudich

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Fundamentals of Atmospheric Chemistry: Keeping a Three-Legged Stool Balanced

Jon Abbatt,[1] Christian George,[2] Megan Melamed,[3] Paul Monks,[4] Spyros Pandis,[5] Yinon Rudich[6]

1 – Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Canada
2 – Université de Lyon, Lyon, F-69626, France; CNRS, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, F-69626, France
3 – IGAC Executive Officer, University of Colorado/CIRES, Boulder, CO 80309-0216, USA
4 – Department of Chemistry, University of Leicester , Leicester LE1 7RH, UK
5 – Department of Chemical Engineering, University of Patras, Greece
6 – Department of Environmental Sciences, Weizmann Institute, Rehovot 76100, Israel

Fundamentals and Atmospheric Chemistry

Atmospheric chemistry has required for decades, and will require moving forward, a three-legged stool approach of laboratory, ambient observations, and modeling studies to address the most pressing issues of our time. Each leg of the stool is only as stable as the fundamental chemistry that underpins it, i.e. within each leg there is the need to understand the connections that exist between the fundamental properties and reactivity of molecules and observable atmospheric phenomena. This editorial aims to underline the fact that the field of atmospheric chemistry is evolving in a manner whereby connections to fundamental atmospheric chemistry research are weakening, threatening to destabilize the approach that has worked so successfully in the past.

Atmospheric chemistry's foundation is based in chemical kinetics and thermodynamics of gaseous and condensed phases, photochemical mechanisms, and measurement technique development. Laboratory studies have routinely provided rate constants, absorption cross-sections, thermodynamic properties, quantum yields, and are the epicenter for many measurement technique developments for field, space and laboratory research. On one hand, laboratory studies provide the fundamental chemistry to determine what can be measured in the ambient atmosphere, the ability to measure it, and the inputs necessary for atmospheric chemical models. On the other hand, laboratory studies are also used to verify novel ambient observations that commonly drive the field, and theoretical mechanisms that are used in models. Similarly, ambient observations permit model evaluation and model results can promote ambient measurements that might not have occurred otherwise. It is this checks and balance system of laboratory, observations, and modeling underpinned by fundamental atmospheric chemistry that has led to the discovery and scientific understanding of some of the most pressing issues of our time such as air pollution, the ozone hole, and climate change.

As an early example of this checks and balance system, motivated by ambient measurements, Haagen-Smit and co-workers elegantly demonstrated through laboratory experiments that ozone is formed when hydrocarbon and NO_X mixtures are exposed to sunlight, ushering in the era of coupled NO_X-VOC-O_3 chemistry that is still a main focus of the field [1], i.e. a molecular-level, fundamental understanding of laboratory, modeling and field observations was developed. An example from the front lines today arises from revisions in our understanding of isoprene oxidation chemistry, both theoretical [2] and experimental [3], that indicate the potential for OH regeneration and for reaction products, including short-lived Criegee intermediates, involved in secondary organic aerosol (SOA) formation [4,5]. This work has involved gas-phase kinetics, heterogeneous uptake studies, development of reaction mechanisms, significant analytical technique development - all essential for reconciliation of models with recent measurements of both HOx and SOA in biogenically-impacted environments. Numerous other examples exist for how atmospheric chemistry depends on fundamental research: spectroscopic data constrain all optical remote sensing techniques; thermodynamic, diffusion and kinetic parameters govern the partitioning of semi-volatiles to aerosol; molecular-level nucleation processes govern rates of gas-to-particle conversion and ice formation; formation of reactive oxygen species play a role in particulate health effects, etc.

The Current Field

Despite the history and success of the field of atmospheric chemistry having such roots, the ability of the atmospheric chemistry community to deliver such fundamental insights and data is at a crossroads. In particular, resources are being increasingly allocated in a targeted manner to applied- or solution-oriented science, such as that proposed within the Future Earth initiative [6], with the underpinning, fundamental work de-emphasized. As well, a large emphasis is given to modeling necessary for international assessments. Yet, these models are only as good as the fundamental chemistry on which their code is based and whether it is evaluated against laboratory and ambient observations.

The de-emphasis of fundamental atmospheric chemistry may be due in part to the multi-disciplinary nature of atmospheric chemistry that is an amalgam of engineers, physicists, meteorologists, biologists, computer scientists, and chemists. However, much more important is the demand for solutions-oriented science that is not unique to atmospheric chemistry, but extends across many scientific disciplines that have potential societal importance. The President of the Canadian National Research Council of Canada has gone so far as to say that "Scientific discovery is not valuable unless it has commercial value" [7]. This shift coincides with the retirement of many of the field's innovators and pioneers that provided the fundamental insights necessary to discover and underpin our understanding of societally relevant issues such as the ozone hole, tropospheric ozone production, and acid rain. Will resources be present for emerging leaders in atmospheric chemistry to engage in fundamentals research or will they be pulled, increasingly, into applied studies? Will there be a pool of fundamentally trained scientists available to answer future challenges to the field?

A Path Forward

As we move forward, the fundamental science community is increasingly focused on much more complex chemical systems than the comparatively simple gas phase processes studied in the past. Emphasis is now on new particle formation, multiphase reactivity, water and ice nucleation, interactions of boundary layer gases with surfaces such as soil and snow, couplings with the biosphere and ocean, etc. The additional complexity of these systems makes the connections between fundamental studies and implementation in atmospheric models much more of a challenge, but no less important than when the field was focused solely on simpler chemistry. A fundamentals approach will decipher the most relevant aspects of this chemistry that need to be appropriately parameterized for modeling of our atmospheric environment. Emphasis should be given to reaction systems that are accurate environmental mimics and to studying processes occurring on ambient samples, i.e. by moving the lab to the field or the field to the lab. As well, the fundamentals chemistry community needs to become more aware of the rapidly changing research landscape in our community, for example, through joint workshops and collaborative lab/field/modeling proposals to funding agencies that will embrace such an approach. As well, there is scope for multi-participant campaigns held at central facilities to address the complexity of these systems, such as the very successful set of particle nucleation experiments conducted in the CLOUD program at CERN [8], or recent instrument intercomparisons (e.g. of black carbon aerosol measurements [9]). Group efforts that summarize the state of science in an area are also crucial (e.g. a review of gas-to-particle uptake [10] or atmospheric black carbon [11]).

Just as it has responded to surprises in the past, such as the discovery of the ozone hole, our community will need to address unexpected observations that will challenge our understanding of the basic chemistry of the atmosphere. At the same time, there will be increasing pressure to understand the environmental impacts of emerging energy technologies and new chemical products, many of which have yet to be studied in depth. We need to understand their environmental impacts before widespread implementation. Dedicated allocation of resources for fundamental research, whether conducted in the lab, the field or a model is needed to maintain strength in all areas, keeping the three-legged stool balanced. As well, it is appropriate that international organizations, such as IGAC and iCACGP provide leadership, by focusing on fundamentals research in their conferences and by stressing its importance within their sponsored activities.

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