Provoking the air

Jonathan Williams

Max Planck Institute for Chemistry, Abt Luftchemie, J J Becher Weg 27, Mainz, Germany.
Email: williams@mpch-mainz.mpg.de

Environmental context. Understanding ozone chemistry has been the aim of atmospheric chemists for over 50 years. Although the chemical mechanisms in current models become increasingly detailed and complex, it is far from clear that our continued pursuit of ever more trace level products will improve our understanding of the underlying photochemistry. Here we suggest a new, innovative measurement approach by which the chemical component of models can be tested and on which policy strategy can be forged.

Just over 50 years ago, atmospheric chemists began to examine the trace gas composition of ambient air in earnest. In the 1950s, it was discovered that tropospheric ozone, a key constituent of urban smog, is formed through photochemistry involving NO_x (NO and NO_2) and volatile organic compounds (VOC).[1] At that time, the number of compounds being measured was rather limited, some 20–30 VOCs and ∼five inorganic species. Since then, thanks to advances in the available technology, a much larger range of compounds is routinely quantified. Recent studies have shown that approximately a thousand VOC compounds can be identified in an air sample[2,3] and ∼30 000 compounds in smoke,[4] indicating three orders of magnitude more speciation in just half a century. Interestingly, the task of understanding ozone chemistry has remained central to atmospheric research and considerable effort is spent using the more detailed chemical information to calculate ozone production rates and the dependence of ozone formation on VOC and NO_x.

In order to address the provenance of ozone (and its daughter radical OH), a cyclic research paradigm of ever-increasing chemical complexity has emerged. The cycle proceeds as follows: a new species is quantified in the air; the rate coefficient with OH (and where appropriate with NO_3 and O_3) is determined in the laboratory (as a function of temperature and pressure); and then these reactions are added to an atmospheric model so that its effect on ozone or OH can be gauged. The underlying assumption is that greater chemical detail will lead us to a better understanding of atmospheric ozone and OH. Certainly, this form of mechanistic mapping has led to the development of very explicit mechanisms for oxidation,[5] and through this approach, we have become aware of a myriad intermediates involved in the atmospheric oxidation of hydrocarbons. Such mechanisms express as fully as possible the current state of knowledge and are especially useful prognostically in assessing alternative emissions strategies. However, this explicit chemistry approach tends to ignore the fact that the ultimate goal, for example the assessment of ozone production rates, can be highly dependent on other model parameterisations (of mixing, surface uptakes, aerosol processes, etc.) and these introduce considerable additional uncertainty into the generated result. A direct result of this approach is that the mechanisms used in models have become ever more complex and hence less suitable for use in global models, which must be chemically abbreviated to be tractable. Another consequence of increasing complexity is that measurement–model comparisons that are needed to test newly implemented chemical schemes necessitate the quantification of ever more species, which involves increasing difficulty and cost. A further disadvantage of the existing paradigm is that the research forefront tends to move further away from the initial oxidation steps and towards more minor yield products, with ever decreasing impacts on the original focus, ozone. Thus it is tempting to contemplate whether any alternative approaches are available to an atmospheric chemist.

In reaction to the aforementioned trend, a different type of measurement is being initiated by several innovative field measurement specialists. Instead of simply analysing the composition of the air as exactly as possible, an air sample is subjected to a carefully controlled stimulus (such as light, or OH, or heating) and the chemical result is monitored. If the stimulus is applied carefully, an atmospherically meaningful result can be directly obtained through measurement. This active rather than passive approach can provide interesting new responses to test against models, or in some cases it can short-cut use of the model entirely by measuring a normally model-derived parameter directly. One of the earliest examples of this approach

Dr J. Williams is an atmospheric chemist. He received his B.Sc. in Chemistry and French and his Ph.D. in Environmental Science from the University of East Anglia, England. Between 1995 and 1997, he worked at the NOAA Aeronomy laboratory in Boulder, USA. He has participated in many international field campaigns on aircraft, ships and at ground stations. His present research involves investigating the chemistry of reactive organic species in the atmosphere, in particular over the tropical rainforest and in the marine boundary layer. Dr Williams leads a research group focussed on volatile organic compounds (VOC) at the Max Planck Institute for Chemistry in Mainz, Germany, and is an honorary Reader at the University of East Anglia, UK.

involved passing ambient air through a heated gold tube, before measuring NO downstream. This method, developed at the National Oceanic and Atmospheric Administration, USA,[6] was used to quantify all oxidised nitrogen compounds collectively, a quantity that became known as NO_y. It was found that the key atmospheric nitrogen species such as NO, NO_2, $RC(O)OONO_2$, HNO_3, $RONO_2$ and HONO were all efficiently converted to NO in the pre-reactor, and NO could be accurately determined by existing techniques. This technique provided a very useful budgeting tool for reactive nitrogen compounds as the individually measured species could be summed and compared with NO_y.

A more recent example of this 'active' type of measurement is the 'Comparative Rate Method' developed recently to quantify total ambient reactivity to OH (loss rate of OH radicals in the atmosphere).[7] This method, developed at the Max Planck Institute for Chemistry in Germany, applies a high OH field to ambient air with and without a carefully selected reagent. The method works as follows: first an OH field is established in a reactor and a reagent gas (not present in the atmosphere) introduced. The decrease of the reagent in the OH field is noted. Then the reagent is mixed with ambient air and again the decrease noted. In the second case, the reagent must compete for the available OH with all the reactive components of ambient air, and as a result, less of the reagent is consumed. The difference in reagent loss, with and without ambient air, can be translated into a reactivity. The result, which is given in s^{-1}, represents the total loss rate of OH in the atmosphere. Again this measurement effectively brackets a large number of atmospheric species, allowing a budgeting of reactivity contributors to be performed. A similar type of measurement has also been applied by Bill Brune and coworkers in aerosol research to examine how much aerosol an airmass can potentially produce, termed the Potential Aerosol Mass (PAM).[8] This has been defined as the aerosol mass generated when precursor-gas laden air is exposed to extreme amounts of ozone (O_3), hydroxyl (OH), and hydroperoxyl (HO_2). Airborne precursors are thus oxidised rapidly to low-volatility compounds that condense onto pre-existing particles and form secondary aerosol mass. In a sense, this is an attempt to speed up naturally occurring chemistry and physics to make an effect accessible to measurement in a shorter time. In other words, it is a practical approach to predicting future chemistry.

Each of the methods described above can be used to test, constrain or validate subsections of existing atmospheric chemistry models and thereby improve our understanding of ozone chemistry. However, ultimately it would be ideal if an active measurement method could be applied to examine ozone chemistry directly. The question therefore arises whether a method of direct measurement can be devised to determine in situ ozone production rates, or whether at a particular location, ozone formation is NO_x- or VOC-limited. This represents a return to the core question posed over 50 years ago and would enable comparisons between sophisticated model predictions and a direct measurement of perturbed air. Such a system would also be a tremendous asset to the increasing number of megacities seeking the most effective strategy of ozone reduction (NO_x or VOC). Key to this measurement will be finding an acceptable method of accelerating the photochemistry in an air sample such that a meaningful, measurable result can be obtained in a reasonable time. One possible approach would be simply to increase the photon flux impinging on one of two identical air samples. Provided that the ambient light spectrum is maintained, a strong light source (e.g. a Xenon lamp with appropriate filter) can be expected to increase the rates of photolysis by factors of 10–100 relative to the control. The strong linear dependence of the OH radical production on photolysis rate[9] suggests that this would provide a reasonable mimic of the real atmosphere. Thus an air sample confined in this strongly irradiated area for 1 min would effectively be photochemically aged by 100 min ($\sim$1.5 h). Previously reported ozone production rates range from 1 to 20 ppbv h^{-1} (parts per billion per hour).[10,11] Therefore, commercially available ozone instruments that are easily capable of measuring ozone to 1 ppbv could be used to measure this perturbation. This assumes that surface losses of ozone (and OH) within the containment vessel can be kept low. Extending this measurement of ozone production rates to deliver VOC and NO_x dependencies would require that VOC and NO_x be dosed to the reaction chambers. The effect would always be measured relative to the unadulterated control. VOC could be added in the form of isoprene, which has a very high reaction rate with OH and a high recycling efficiency,[12] and NO_x should be added in the form of NO_2 rather than NO so as to avoid ozone titration and to expedite the achievement of photochemical equilibrium. Alternatively, for the VOC sensitivity assessment, a more realistic strategy would be to concentrate the suite of ambient air VOC (by cryofocussing or adsorption methods) and inject these into the reactor so as to increase the suite of VOCs in the chamber by a given factor. A range of mixing ratios of both VOC (or isoprene) and NO_2 (e.g. 50 pptv, 500 pptv and 2 ppbv) could be added to ambient air before irradiation, with each addition occurring in a separate chamber. The channels most appropriate to the ambient conditions at the time could then be selected and the relative increases of ozone with added NO_2 and VOC could be compared. Simply put, if in a given location the response of ozone was stronger to added NO_2, it would follow that reducing NO_2 would have the greatest effect on reducing ozone. A further advantage of this system is that ozone measurements can be made very rapidly, so that these sensitivity determinations could be made at high temporal resolution. It may well be that the most effective urban ozone reduction strategy would be effectively a function of time of day and then strategies could be adjusted accordingly. In essence, the aim would be to determine the ambient photochemical production rate corresponding to the specific VOC and NO_x conditions at the source, as well as the dependence of this production on VOC and NO_x levels. This instantaneous measured production rate may differ from what actually happens to the air parcel because it depends on future meteorological conditions, mixing rates, wet and dry deposition rates of VOC and NO_x, etc.; however, the proposed measurement would provide the basis on which to make policy decisions.

The proposition here is that a new, direct and active approach to investigating ozone chemistry is desirable and feasible. The set-up, described here in concept form, can be adapted to determine in situ the dependence of ozone production on VOC and NO_x, a potentially valuable parameter for air quality specialists. By 'provoking the air' under controlled conditions as described above, a new opportunity is extended to modellers to gauge the realism of their simulations. Instead of passively comparing model and measured data as before, the measured and modelled responses to careful changes in light and temperature may be examined. The overall concept has been presented and suggestions given as to how the measurement may be made. It is hoped that this challenge will be taken up by measurement specialists worldwide.

References

[1] A. J. Haagen-Smit, M. M. Fox, Ozone formation in the photo-oxidation of organic substances. *Ind. Eng. Chem.* **1956**, *48*, 1484. doi:10.1021/IE51400A033

[2] A. C. Lewis, N. Carslaw, P. J. Marriott, R. M. Kinghorn, P. Morrison, A. L. Lee, K. D. Bartle, M. J. Pilling, A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* **2000**, *405*, 778. doi:10.1038/35015540

[3] X. Xu, L. L. P. van Stee, J. Williams, J. Beens, M. Adahchour, R. J. J. Vreuls, U. A. Brinkman, J. Lelieveld, Comprehensive two-dimensional gas chromatography (GC × GC) measurements of volatile organic compounds in the atmosphere. *Atmos. Chem. Phys.* **2003**, *3*, 665.

[4] J. Dalluge, L. L. P. van Stee, X. Xu, J. Williams, J. Beens, R. J. J. Vreuls, U. A. T. Brinkman, Unravelling the composition of very complex samples by comprehensive gas chromatography coupled to time-of-flight mass spectrometry – cigarette smoke. *J. Chromatogr. A* **2002**, *974*(*1–2*), 169. doi:10.1016/S0021-9673(02)01384-5

[5] M. E. Jenkin, S. M. Saunders, R. G. Derwent, M. J. Pilling, Construction and application of a master chemical mechanism (MCM) for modelling tropospheric chemistry. *Abstr. Pap. Am. Chem. S.* **1997**, *214*, 116.

[6] M. J. Bollinger, R. E. Sievers, D. W. Fahey, F. C. Fehsenfeld, Conversion of nitrogen dioxide, nitric acid and *n*-propyl nitrate to nitric oxide by gold-catalyzed reduction with carbon monoxide. *Anal. Chem.* **1983**, *55*, 1980. doi:10.1021/AC00262A034

[7] V. Sinha, J. Williams, J. N. Crowley, J. Lelieveld, The comparative reactivity method – a new tool to measure total OH reactivity in ambient air. *Atmos. Chem. Phys.* **2008**, *8*, 2213.

[8] E. Kang, M. J. Root, D. W. Toohey, W. H. Brune, Introducing the concept of Potential Aerosol Mass (PAM). *Atmos. Chem. Phys.* **2007**, *7*, 5727.

[9] F. Rohrer, H. Berresheim, Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. *Nature* **2006**, *442*, 184. doi:10.1038/NATURE04924

[10] L. Liu, S. Andreani-Aksoyoglu, J. Keller, C. Ordonez, W. Junkermann, C. Hak, G. O. Braathen, S. Reimann, C. Astorga-Llorens, M. Schultz, A. S. H. Prévôt, I. S. A. Isaksen, A photochemical modeling study of ozone and formaldehyde generation and budget in the Po basin. *J. Geophys. Res. – Atmos.* **2007**, *112*, D22303. doi:10.1029/2006JD008172

[11] K. Baumann, E. J. Williams, W. M. Angevine, J. M. Roberts, R. B. Norton, G. J. Frost, F. C. Fehsenfeld, S. R. Springston, S. B. Bertman, B. Hartsell, Ozone production and transport near Nashville, Tennessee: Results from the 1994 study at New Hendersonville. *J. Geophys. Res. – Atmos.* **2000**, *105*(*D7*), 9137. doi:10.1029/1999JD901017

[12] J. Lelieveld, T. M. Butler, J. N. Crowley, T. J. Dillon, H. Fischer, L. Ganzeveld, H. Harder, M. G. Lawrence, M. Martinez, D. Taraborrelli, J. Williams, Atmospheric oxidation capacity sustained by a tropical forest. *Nature* **2008**, *452*, 737. doi:10.1038/NATURE06870