Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry 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, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded $500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

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MEASUREMENTS AND MODELING OF GLYOXAL:
INSIGHTS INTO RURAL PHOTOCHEMISTRY AND
SECONDARY ORGANIC AEROSOL PRODUCTION

by

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Chapter 1

Introduction\footnote{This introduction will be part of a series compiled by the Wisconsin Initiative for Science Literacy (WISL) to "promote literacy in science, mathematics and technology among the general public." It is intended to "explain [this] scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress."}

1.1 Why study atmospheric trace gases?

On a very rough scale, the atmosphere is composed of 78% nitrogen (N\textsubscript{2}), 21% oxygen (O\textsubscript{2}) and 1% ‘other gases’, neglecting water vapor which may constitute up to 3% of atmospheric gas depending on the humidity. More that 90% of the unspecified ‘other gas’ is argon, a relatively unreactive gas. Both N\textsubscript{2} and O\textsubscript{2} are crucial for life in a number of ways, but atmospheric scientists tend to refer to them as ‘background gas.’ In fact, nearly all of the interesting chemistry which occurs in the atmosphere is happening within just the remaining 0.1% mixture of gases.

One of the gases in that remaining 0.1% is carbon dioxide (CO\textsubscript{2}), which is the subject of much current debate as nations and economies attempt to address the threat of global climate change. Compared to the trace gases which will be discussed below, even CO\textsubscript{2} is quite abundant, constituting a bit less than 0.04% or 400 parts per million (ppm, 1 ppm = 0.0001%) of atmospheric gases. Current efforts to address climate change are focused on CO\textsubscript{2}, in part because of its longevity in the atmosphere and in part because it is well understood and (scientifically, if not economically) easily addressable: burning less fuel will result in less emitted CO\textsubscript{2}.

There is another set of atmospheric constituents that are able to affect climate almost as powerfully as CO\textsubscript{2} while existing in much smaller quantities within the atmosphere. The gas ozone (O\textsubscript{3})
is one such substance. It is present in both the troposphere (the lowest layer of the atmosphere, which extends to 10–15 km above ground level) and the stratosphere (the next layer of the atmosphere, from the top of the troposphere to a height of 45–55 km above ground level). In the stratosphere, O₃ is produced by the photolysis (breaking apart of a molecule due to exposure to sunlight) of molecular oxygen (O₂) or the photolysis and subsequent reformation of O₃ (a null cycle). These molecules absorb ultraviolet (UV) light in the stratosphere, protecting the surface of the earth from the adverse effects of UV exposure. In the troposphere, O₃ is the byproduct of atmospheric oxidation chemistry, and is itself harmful (Seinfeld and Pandis, 2006). Ozone in the troposphere has a climate impact equal to about 1/5th that of CO₂ (Intergovernmental Panel on Climate Change, 2007), despite being over 1,000 times less abundant.

Another minor atmospheric constituent that exerts a significant influence in climate is Particulate Matter (PM). PM is composed of a complex mixture of solid and liquid particles, which may include soil, dust, metal, water, and organic compounds (US EPA, 2008a). These particles can remain aloft in the atmosphere for many days (cf. ‘atmospheric lifetime’ in US EPA, 2008a) and have a number of potential impacts on climate, both direct and indirect. First, PM can act to heat or cool the earth system like ‘greenhouse–gases’ such as CO₂, by acting upon the transfer of radiant energy. Second, PM can alter conditions in a way that indirectly affects the transfer of radiant energy. For example, PM can cause clouds to persist, and their bright white tops will cause more sunlight to be reflected back to space, causing a net cooling of the earth system. Conversely, soot that is transported to remote regions and settles on a glacier may decrease the amount of light reflected by the ice, causing heating and melting. In these cases it is not the radiative properties of the PM in the atmosphere but the altered conditions (more clouds or darker colored glaciers) which cause a climactic effect.

While the influence of CO₂ on radiant energy is reasonably well understood, the exact values for the effects of O₃ and especially PM on climate are unclear. The scientific body tasked with compiling the current understanding of climate change, the Intergovernmental Panel on Climate Change (IPCC), calculates the uncertainty in the current climactic influence of CO₂ at 10%. The IPCC calculates the potential variance in the present day climate influence of ground level O₃ at
40%, while the calculated influence of PM may vary by a factor of two. These high uncertainties in climactic effect are substantial: the present day calculated cooling from PM is roughly 80% of the expected warming from CO$_2$, and it is possible that the influence of PM is sufficient to entirely cancel the warming influence of CO$_2$ on a global scale (Intergovernmental Panel on Climate Change, 2007).

In addition to their action in global climate change, O$_3$ and PM have both been shown to be harmful to human health (US EPA, 2008b). For example, a study conducted by researchers at Harvard University found that people living in cities with high levels of PM, especially PM$_{2.5}$ (PM having a diameter less than 2.5 µm = 0.0000025 m), had an increased incidence of hospitalization and disease of the lung and heart (Dockery et al., 1993), and a more recent study found an increase in mortality in conjunction with elevated O$_3$ and PM$_{2.5}$ levels (Jerrett et al., 2009). Exposure to O$_3$ has been shown to cause respiratory damage, including bronchitis, emphysema, and asthma. In addition to negatively impacting human health, ground level O$_3$ is a reactive gas which can damage plants and other materials: the US Environmental Protection Agency reports that O$_3$ is responsible for an estimated $500 million in reduced crop productivity annually (US EPA, 2010).

Despite being minor components of the atmosphere by mass, trace components are profoundly influential in a number of ways. Some, like ground-level O$_3$ and PM, have adverse effects on human health, plant productivity, climate and so on. It seems reasonable that scientists should seek to control these trace species to reduce their perturbation of the natural atmosphere, but doing so is difficult because their formation in the atmosphere is not fully understood and is often quite convoluted.

1.2 What factors influence ground level O$_3$?

Ground level O$_3$ is a byproduct of the natural oxidizing action of the atmosphere. In general, a Volatile Organic Compound (VOC) in the atmosphere will be oxidized, leading to a change in chemical properties due to the addition of oxygen or altered molecule structure, and possibly the breaking apart of a molecule to form two smaller molecules. After several oxidation steps, these molecules have an increased tendency to either be washed out by rain or transferred to PM, especially if they have not been broken apart to a large degree. The oxidation of compounds within the atmosphere is beneficial in many ways, especially in that it prevents the buildup of VOCs or other emissions. Some molecules will be fully broken apart and oxidized to CO$_2$ before they are washed out by rain or transferred to
PM. Because CO₂ is not susceptible to further oxidation in the atmosphere and does not partition strongly to PM, it persists in the atmosphere for many years; this long lifetime explains part of the effectiveness of CO₂ as a greenhouse gas.

The net reaction for the atmospheric oxidation of the simplest VOC, methane (CH₄), is relatively simple:

\[
\text{CH}_4 + 8\text{O}_2 + \text{sunlight} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{O}_3. \tag{1.1}
\]

One property of this reaction is applicable to nearly all oxidation chemistry which occurs in the atmosphere: when a carbon compound is oxidized (here, CH₄ to CO₂), a corresponding reduction occurs, in this case of molecular O₂ to the oxygen in CO₂ and H₂O. Several molecules of harmful tropospheric O₃ are produced for each molecule of CH₄ which is fully oxidized.

The amount of VOC available is one factor which influences the amount of O₃, but there are other factors which influence the oxidation chemistry described in Equation 1.1 which are not immediately apparent. Oxidation in the atmosphere often occurs via a catalytic cycle, where some molecules are used and regenerated and thus are not shown in the above reaction. One such molecule is the hydroxyl radical (OH), which exists at exceedingly low concentrations (<1 part per trillion (ppt) = 0.0000000001%) but is widely acknowledged to control the oxidation chemistry occurring in the atmosphere during daylight. The OH radical, like other radical species, is highly reactive. Although it reacts very quickly – most OH radicals in the atmosphere survive less than one second before reacting – it is regenerated during the oxidation reaction, so while a given molecule is consumed by reaction with a VOC, another indistinguishable molecule will soon be made to take its place. The OH radical is regenerated from the HO₂ radical, which is formed indirectly from the reaction of OH with a VOC. OH and HO₂ (which are collectively referred to as HOₓ) exist in a catalytic cycle, each acting to re-form the other and thus neither is consumed. However, the reformation of OH from HO₂ is actually dependent on yet another catalytic cycle between nitric oxide (NO) and nitrogen dioxide (NO₂), which are collectively referred to as NOₓ.

The double catalytic cycle which regenerates HOₓ and NOₓ while oxidizing VOCs is illustrated in Figure 1.1. The reaction of NO with HO₂ regenerates OH and produces NO₂, and NO is regenerated by the photolysis of NO₂. The oxygen atom which is produced when NO₂ is photolyzed will react
with \( O_2 \) to form \( O_3 \), the pollutant. Altogether, this cycle is represented by the equations

\[
\text{NO} + \text{OH} + \text{VOC} \xrightarrow{\text{several steps}} \text{NO}_2 + \text{HO}_2 + \text{Oxidized VOC} \quad (1.2)
\]

\[
\text{HO}_2 + \text{NO} \quad \rightarrow \quad \text{OH} + \text{NO}_2 \quad (1.3)
\]

\[
2 \times [\text{NO}_2 + \text{sunlight}] \quad \rightarrow \quad \text{NO} + \text{O} \quad (1.4)
\]

\[
2 \times [\text{O} + \text{O}_2] \quad \rightarrow \quad \text{O}_3 \quad (1.5)
\]

so that the net reaction (cancelling those species which are regenerated) is

\[
\text{VOC} + 2\text{O}_2 + \text{sunlight} \quad \rightarrow \quad \text{Oxidized VOC} + 2\text{O}_3. \quad (1.6)
\]

This equation is not chemically balanced (that is, the number of atoms on the left and right side is not necessarily conserved, since ‘VOC’ and ‘Oxidized VOC’ are not specified here), and we have taken the liberty of ignoring the production or consumption of \( O_2 \) and \( \text{H}_2\text{O} \), as these gases are controlled by other processes and are not significantly impacted by this chemistry. While the above set of equations lacks some chemical detail, it does illustrate the basic reaction with occurs in the atmosphere in general terms; thus Equation 1.1 which was an example of atmospheric oxidation is a specific application of Equation 1.6.

Even the level of detail shown in Figure 1.1 is greatly reduced when compared to the possibilities for reactions in the real atmosphere. The family of all alkyl peroxy radicals (\( \text{RO}_2 \), where \( R \) indicates any size hydrocarbon) provides a relevant example. The reaction pathway displayed in Figure 1.1 assumes that all alkyl peroxy radicals (\( \text{RO}_2 \)) will react with NO to form RO and \( \text{NO}_2 \) as in Equation 1.7 below. In truth, the intermediate \( \text{RO}_2 \) may react with a number of species, including NO, \( \text{HO}_2 \), or even another molecule of \( \text{RO}_2 \):

\[
\text{RO}_2 + \text{NO} \quad \rightarrow \quad \text{RO} + \text{NO}_2 \quad (1.7)
\]

\[
\text{RO}_2 + \text{NO} \quad \rightarrow \quad \text{RONO}_2 \quad (1.8)
\]

\[
\text{RO}_2 + \text{HO}_2 \quad \rightarrow \quad \text{ROOH} \quad (1.9)
\]

\[
\text{RO}_2 + \text{RO}_2 \quad \rightarrow \quad \text{RO} + \text{ROH} & \text{other products.} \quad (1.10)
\]

Here \( \text{RONO}_2 \) are alkyl nitrates, \( \text{ROOH} \) are alkyl hydroperoxides, and \( \text{ROH} \) are alcohols, each of which goes on to react with their own unique chemistries. The chemical processing shown in Fig-
ure 1.1 is accurate in neglecting Equation 1.9 and Equation 1.10 when there is an excess of NO, such that reactions of RO$_2$ with HO$_2$ or another RO$_2$ are unlikely. However, Equation 1.8 is a process which uses NO and cannot be neglected on the basis of competitive reactivity. It is omitted from Figure 1.1 because it is a low yield process, usually occurring less than 1 time in 10. However, low yield processes such as this one are important to atmospheric chemistry because they terminate the catalytic regeneration of NO$_x$ described above. The relative frequency of termination steps such and Equation 1.8 or the production of nitric acid,

\[
\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M},
\]

where M indicates any other gas, determine the number of times NO$_x$ can participate in the oxidation of VOCs before being removed from the atmosphere.

Returning to the simplified chemistry of Figure 1.1, it is evident that the formation of O$_3$ requires sunlight, VOCs, and NO$_x$. This understanding of the process by which O$_3$ is formed is the gateway to controlling ground level O$_3$ pollution. Emissions of NO$_x$ along with VOC emissions are the means by which people can directly influence the chemistry occurring in the atmosphere. NO$_x$ is controlled primarily by human emissions, with some additions from natural sources such as lightning and soil microbial processes. These emissions are principally the result of high-temperature combustion: for example, the 2005 EPA assessment of Wisconsin NO$_x$ emissions estimates that well over 90% of emissions come from vehicles, electricity generation, and other fossil fuel combustion (US EPA, 2009). Near an urban center, where such NO$_x$ sources are concentrated, the reactivity of RO$_2$ is dominated by NO and the simplified conditions of Figure 1.1 are a reasonable approximation for chemical processing. Because NO$_x$ emissions in urban areas are almost entirely anthropogenic (originating from human activity) and arise from combustion, controlling the emissions and concentrations of NO$_x$ is possible to the extent that these devices can be turned off or replaced with equipment which forms less NO$_x$ while performing the same task.

The emissions of VOCs are less straightforward: some sources are obviously anthropogenic, such as a chemical spill; others are obviously biogenic (originating from the activity of non-human living things), such as the emissions of isoprene from certain species of trees. Others are difficult to assign: should the methane from cattle be considered biogenic as it originates from a cow, not a
human or a machine? The bovine emissions could also be anthropogenic, as the cattle would surely not exist in such numbers in a single locale without human influence. Another classification is to consider a VOC emissions source as being ‘controllable’ or ‘non-controllable.’ In this system, both the chemical spill and the cows would be controllable, while emissions of isoprene from trees are considered non-controllable.

The OH radical is less easily controlled: OH is generated in the troposphere when O$_3$ is photolyzed, producing a high-energy excited atomic oxygen. If this excited atomic oxygen collides with water vapor, it will produce OH radical. Thus the concentration of OH is indirectly affected by anthropogenic activity: more O$_3$ will lead to higher levels of OH, which will promote oxidation chemistry, ultimately forming more O$_3$. The concentration of ground level O$_3$ is of concern due to the deleterious effects discussed above, but very little O$_3$ is emitted directly. Instead, O$_3$ is produced in the atmosphere as described above. In many cases, more VOCs, more NO$_x$, and more HO$_x$ mean higher O$_3$ concentrations at ground level.

Any attempt to control O$_3$ concentration requires a sophisticated understanding of atmospheric chemistry along with a detailed accounting of VOC, HO$_x$, and NO$_x$, along with many other chemical compounds. For example, if there is far more NO$_x$ than actually needed to react with VOCs (as might be the case in a megacity), reducing NO$_x$ would not reduce O$_3$ concentration. In fact, because at very high NO$_x$ concentrations some new reactions which consume both NO$_2$ and OH but do not generate O$_3$ become relevant, reducing NO$_x$ may actually lead to increased O$_3$.

1.3 What factors influence Particular Matter?

Traditionally, PM (or particulates) in the atmosphere have been classified as either primary or secondary, distinguished by when particle formation occurred. Primary aerosols are emitted as particles directly from a source, such as breaking sea spray or black soot from a fire; secondary aerosols are formed when a gas condenses to form an aerosol some time after emission, and often after some chemical processing. Further, primary PM was thought to be chemically inert, meaning that it would not undergo chemical processing as described above in section 1.2. This line of thought was fruitful and provided insight into the relative importance of primary and secondary aerosol, particularly with respect to rates of formation. However, the inability of models to reproduce ambient data for
While it is not the only means of considering our current understanding of aerosol formation, the Volatility Basis Set (VBS) discussed by Donahue et al. (2009) provides a useful and concise framework for thinking about aerosols. In the VBS, all chemical compounds are assigned a volatility (that is, propensity to enter the gas–phase) based on their chemical properties. Each time a molecule is chemically oxidized, its volatility is reduced by a factor of 10 in the VBS, making it more likely to enter the aerosol phase and contribute to PM. Crucially, this framework allows a chemical to come out of the aerosol, as well as to go in; this is what allows the VBS framework to begin to explain the new measurements taken by the AMS, which indicate that primary aerosols can evaporate, react, and then recondense as secondary aerosols.

The VBS enables scientists to computationally simulate the formation of aerosols, providing insight into the formation and dynamic processes of PM. The VBS predicts that PM will be formed when a compound is present in the gas–phase above its volatility limit. This could occur when a fire emits compounds which are only volatile at high temperatures and subsequent cooling of the smoke provides an opportunity for those gases to condense to the liquid phase on an aerosol particle; or when an otherwise volatile chemical is chemically oxidized to produce a less–volatile compound, which then goes on to condense, adding to PM. Broadly, such an understanding of aerosols correctly predicts that PM will form when there is ‘too much’ of a compound in the gas–phase compared to the amount in the aerosol phase (based on its volatility). In this way, PM formation is favored by the same conditions which favor $O_3$ formation, as $O_3$ formation indicates oxidative chemistry and thus the presence of molecules with reduced volatility. However, PM has dependencies beyond the factors which control the formation of $O_3$, such as reactions of the compounds within the particle.

1.4 A role for glyoxal in understanding $O_3$ and PM

Glyoxal, the smallest $\alpha$–dicarbonyl, is a molecule of interest to the field of atmospheric science because its behavior in the atmosphere is illustrative of the difficulties faced in understanding both the formation of $O_3$ and PM. Glyoxal is formed by the oxidation of both biogenic and anthropogenic
emissions. It is produced as a first–generation (from oxidation of the primary emissions) and second–
generation (from oxidation of the products of first–generation oxidation) product. Typically, glyoxal
exists at concentrations below 1000 ppt, and often below 200 ppt in rural regions. Because glyoxal
is formed both by prompt (first–generation) and latent (second–generation) oxidation chemistry, it
provides a useful test of computational models which seek to simulate atmospheric chemistry. It
has a lifetime of a few hours in the troposphere (Volkamer et al., 2005), which allows modelers to
examine processes occurring on a commensurate timescale. In particular, glyoxal can be used to test
the ability of a model to reproduce higher–generation chemistry and the associated production of O₃
and propensity to form PM.

Despite a high vapor pressure, glyoxal has been shown to partition to the aerosol phase several
orders of magnitude (one order of magnitude is a factor of 10, two orders of magnitude is a factor
of 100, etc.) more strongly than its volatility would otherwise suggest (Kroll et al., 2005). Put
another way, glyoxal should not form PM because it is volatile, but experiments have shown that
it forms large, polymer–like molecules in significant quantities along with other chemically distinct
compounds. There are many known reactions of glyoxal in the particle phase (depicted schematically
in Figure 1.2, which was adapted with permission from Galloway et al., 2009), some of which are
reversible (such as hydration, glyoxal + H₂O ⇌ glyoxal•H₂O), and others of which are permanent
(such as glyoxal → nitrogen–containing compounds). The stronger than expected partitioning of
glyoxal to the aerosol phase can be partially explained by appealing to these reactions including
especially the formation of low–volatility oligomers, but it is also possible that glyoxal can react to
form oxidation products which will then enter the gas–phase and continue to react. The propensity
of glyoxal to form PM is interesting not only because it contributes to the total mass of PM but
because it may be used as a tracer for molecules which behave similarly, adding to our understanding
of the formation of PM.

This thesis will describe the construction of the Madison Laser–Induced Phosphorescence (LIP)
Instrument, which enables high–speed (∼ 1 min), in situ measurements of glyoxal with previously
unattainable sensitivity. The data collected by this instrument has been used to study aerosol forma-
tion (including showing for the first time that glyoxal partitioning to the aerosol phase is reversible),
to study photochemistry in both rural and urban sites, and to gain insight into the reaction mechanisms of VOCs. To progress beyond a simple description of observed glyoxal concentrations, a model was constructed, providing a means to test current understanding of photochemistry against measurements from a research site in California.

1.4.1 Measurement: The Madison LIP Instrument

The Madison LIP Instrument makes high-sensitivity, selective measurements of glyoxal by exploiting the unique properties of gaseous glyoxal interacting with light. Glyoxal will absorb light (in this case, 440.3 nm, blue) and emit it at a different color (520 nm, green). Crucially, the light is emitted on a relatively slow timescale of around 15 µs (= 0.000015 s) compared to most other processes (< 0.05 µs), meaning that the green light emitted by glyoxal is separated in time and in energy from the blue laser light which is used for excitation. Thus, the combination of an optically coated filter which rejects blue light and a digital filter which rejects signal which comes too soon after the laser effectively renders the instrument blind to the blue laser and to scattered light. The amount of green light reaching the detector is directly proportional to the amount of glyoxal in the sample cell, allowing straightforward quantification. Because the detector rejects nearly all light except the green light emitted by glyoxal, it is able to measure glyoxal at very low concentrations.

The process described above provides excellent sensitivity (amount of signal per molecule) but does not necessarily ensure that the signal originates from glyoxal: any molecule which shared the ability of glyoxal to absorb blue light and to slowly emit green light would be detected by this scheme. Full selectivity for glyoxal is achieved by using a knowledge of the amount of light glyoxal will absorb as a function of light energy. The tendency of glyoxal to absorb light varies by a factor of ∼3 over a very narrow range of wavelengths, so the laser may be tuned on to and off of the area of strong absorption, allowing an extraction of glyoxal signal from any background light uncorrelated to the change in laser energy. This is a bit like measuring the total amount of light in a room while turning on and off a light bulb; the signal of interest here can be turned up and down (like a light bulb is turned on and off), so that the difference between measurements (i.e. with lights–on and lights–off) is the actual signal of interest. The background (amount of light in the room not from that lightbulb) can be subtracted and discarded, or it may yield some additional information through
further analysis.

The Madison LIP Instrument is unique in its ability to provide in situ measurements of glyoxal at high speed. Other techniques for measuring glyoxal may require long averaging times to accumulate signal, or may be unable to go faster than a certain speed (this is the case with techniques that rely on trapping glyoxal in a cartridge and measuring it later in the laboratory). This measurement speed opens doors to new experiments, such as flux measurements which will provide insight into the rapid chemical reactions which may occur within a forest canopy or airborne measurements to study the exchange of air from the troposphere to the stratosphere during strong storms and other convective events. Such observations are most useful when they are interpreted in the context of a model which incorporates known chemistry, allowing a comparison of observations to the output of a state–of–the–science computational prediction. In such an analysis, disparities between measurement and model indicate areas of deficiency in scientific understanding and suggest future experiments.

1.4.2 Model: A Zero–Dimensional Box Model

One of the difficulties in extracting meaningful insight from atmospheric experiments is the sheer volume of data which instruments generate. For example, during the BEARPEX 2007 campaign 16 research groups operated at a research station in the foothills of the Sierra Nevada for around two months. Many groups operated several instruments, producing a data point at a regular interval as short as a few seconds or as long as a half–hour. The measurements needed for basic photochemistry were made, including levels of many VOCs, HO\textsubscript{x}, NO\textsubscript{x}, and O\textsubscript{3}, as well as several measurements of PM. Beyond the very useful simple comparisons which can be made by examining the data, searching for trends and correlations, and so on, the utility of these data is only realized in the context of a model.

The model will attempt to reproduce the measurements using the known chemistry and driving some molecules to follow measurements. For example, a photochemical model (like the one described here) has no way to estimate the amount of isoprene (a VOC emitted by many plants including broad–leaf oaks), as this would require a plant emissions model and an inventory of land use for the area – so the amount of isoprene in the model is forced to follow the measurement. However, the oxidation products of isoprene are not forced to measurement, so the model can be compared to measured
values, allowing the modeler to test the ability of known chemistry to explain the observations.

Building a model is an exercise in trade-offs, both of the modeler’s time and the computational time required to compile and run the model. For example, a model which covered the entire globe at high resolution and used all known chemistry would be far too slow to produce useful results, due to the number of calculations required. The model described here is able to use a very large (>3500) number of chemical reactions, providing a high level of chemical detail, but does so at the expense of spatial detail. The zero-dimensional (0-D) box model does not treat differences in terrain, land cover, or emissions, and thus is limited by the assumption that the air which arrives at the measurement site has been experiencing a similar environment for a time at least as long as the lifetime of the molecule of interest. Thus a 0-D box model is reasonable for study of the OH radical, which has a lifetime of <10 seconds, but it must be used carefully for molecules with a longer lifetime, such as glyoxal (lifetime ~1 hr during daytime).

Despite the limitations of the model, it can be used to gain insight into physical processes (such as the deposition of glyoxal to surfaces) and chemical processes (such as the speed with which glyoxal is produced from various source molecules). In the event that a model is unable to reproduce measurements using known chemistry, the operator may propose new chemistry or new processes and test them in the computation before attempting an experiment, or may even perform an experiment that would be impossible, such as reducing the air temperature without altering any other factor to examine the influence of lower temperatures on chemistry. The synergy of model and measurement enables more complete knowledge of the processes at work in the atmosphere, ultimately allowing a more complete understanding of the factors governing O$_3$ and PM.

1.5 Conclusion: using glyoxal for broader science

Glyoxal is a contributor to the formation of O$_3$ and PM, but its utility goes beyond predicting its incremental addition to these two pollutants. Glyoxal can be used to represent an entire class of compounds which have similar chemical and physical properties. Instead of measuring each individual compound which contributes to O$_3$ and PM at a site, it may be possible to use the measurement of glyoxal to account for one or more classes of compounds. The goal of these measurements is to understand the chemistry behind the behavior of glyoxal, and determine to what extent it may be
used in other situations.

One example of glyoxal being used to understand a larger process comes from satellite measurements. Space–borne measurement platforms are uniquely suited to measure global distributions of atmospheric constituents, providing not only a map of their concentrations but a clue to the overall chemistry which is occurring on a continental or even global scale. Satellite measurements of glyoxal can be used to evaluate and predict PM as well as the oxidation chemistry of VOCs. However, satellite measurements require validation by comparing the satellite measurement to another measurement technique such as the Madison LIP Instrument. In particular, the vertical profile of glyoxal is currently unknown, so airborne measurements which map out this distribution are needed.

In addition to measurements for use in satellite validation, more information is needed about the role glyoxal plays in PM and to what extent it may be used as a tracer for or indicator of PM. Glyoxal can be used as a proxy for higher–generation chemistry to improve our understanding of the oxidation chemistry and the accompanying formation of O$_3$ and potential for PM formation. Measurements in the field setting and experiments in the laboratory setting will reveal additional information about the link between glyoxal and PM, especially regarding the utility of glyoxal as a surrogate for aerosol–phase reactions for other chemical compounds. A more complete understanding of the chemistry occurring in aerosols may be accessible through the use of glyoxal as a reduced–complexity model system, and should assist global modelers and scientists who use satellite measurements.

Laboratory experiments and field measurements are examples of the way the atmosphere will work in certain cases, but ultimately it is the behavior of the true atmosphere which is of interest. The knowledge generated through laboratory experiments, collaborative field campaigns, flight missions and the interpretation of smaller models such as the one described here are used to enable global models accurately represent chemical and physical processing of VOCs. When such models are in agreement with observations from ground sites, ships, and airborne or spaceborne platforms, we have confidence that they are adequately representing the chemistry occurring in the real atmosphere. The improved regional and global models can then be used to more fully predict how the atmosphere will respond to short– and long–term perturbations, in this case especially with respect to levels of
$O_3$ and PM and their impact on climate and health.
Bibliography


Fig. 1.1.— Simplified schematic of photochemical reactions under high NOx conditions, typical of an urban environment. A VOC (here abbreviated R) is oxidized by reaction with OH, O2, NO, and O3 [left cycle]. This cycle consumes OH and NO, producing HO2 and NO2, along with an oxidized VOC (here abbreviated R'). The oxidized VOC may re-enter the VOC oxidation cycle (dash-dotted line) or could be lost to other processes (not shown). The OH and NO radicals are regenerated [right cycle] by the photolysis of NO2. Note that NO and NO2 appear in two places in the diagram (highlighted orange and blue); thus the radical regeneration cycle must run twice for each instance of the left cycle; once to regenerate the NO used to transform RO2 in to RO, and again to regenerate the NO used to transform HO2 into OH. Both instances of the radical regeneration cycle produce O3, the pollutant; photolysis of O3 has a roughly 1% yield of OH (dashed lines).
Fig. 1.2.— Simplified schematic of aerosol–phase reactions of glyoxal. Glyoxal can reversibly enter particulates, whereupon it is subject to photochemistry (forming e.g., glyoxylic acid) and may form nitrogen–bearing compounds. It may be hydrated (forming glyoxal•H$_2$O). Some oxidation products may be more volatile than glyoxal, and re-enter the gas phase. Hydrated glyoxal may form sulfate compounds, or short–chain polymers called oligomers. Formation of oligomers is reversible, while formation of sulfate compounds may be permanent. These reactions of glyoxal are an example of the chemistry that is possible in the aerosol phase, and can be used to understand the chemistry of other similar compounds. Figure adapted with permission from Galloway et al. (2009)