

# Observing Systems for Atmospheric Composition

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Editors

# Observing Systems for Atmospheric Composition

Satellite, Aircraft, Sensor Web and  
Ground-Based Observational Methods  
and Strategies

With 124 Illustrations

 Springer

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# Preface

The goal of the third International Summer School on Atmospheric and Oceanic Science (ISSAOS 2004) was to bring together experts in observing systems and the atmospheric sciences to discuss the need for an observing system for atmospheric composition, its components, and the integration of components into a system. Much of the lecture material was conceptual, with the idea to provide attendees with a context to put their own component of the observing system.

The Local Committee, Guido Visconti and Piero Di Carlo, started to think about this school in the summer 2002 and asked William Brune to be a director. Prof. Brune accepted with enthusiasm and was able to get Mark Schoeberl and Andreas Wahner as co-directors. Because the director soon realized that they needed another year to put together all the speakers he had in mind, the school was held from 20–24 September 2004 in L'Aquila (Italy). The speakers were P. K. Bhartia, W. Brune, J. Burrows, J.-P. Cammas, K. Demerjian, H. Fischer, D. Jacob, P. Newman, K. Reichard, V. Rizi, M. Schoeberl, M. Schultz, U. Schumann, A. Thompson, C. Trepte, A. Wahner.

This edition of ISSAOS, for the first time, asked students to provide an evaluation of the school at its conclusion. The students generally liked the school, including the quality of the lectures, the opportunities to ask the lecturers questions, and accessibility of the lecturers for conversations. These results encouraged us to put together the lectures of the school in a book to give a larger audience the opportunity to learn about the observational and modeling techniques used to understand the atmospheric composition from satellites, aircraft, and ground-based platforms. For many lectures were two common themes: the role of each component in an observing system for atmospheric composition, and the advances necessary to improve the understanding of atmospheric composition.

For the school's organization we acknowledge the financial contribution of the Italian Ministry of the Environment, and of Center of Excellence CETEMPS.

We are also grateful to Simona Marinangeli and Manuela Marinelli for the help in the school's organization and the hard work of rearranging the lectures in an editorial format.

January 2006

G. Visconti  
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(*Editors*)

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# Introduction I

## Observing Systems for Atmospheric Composition

WILLIAM H. BRUNE

The concept of observing systems is not new. Even at the dawn of weather satellites in the mid-1960s, planners were conceiving ways to combine the new cloud pictures from satellites with information from radiosondes, aircraft, and surface sites to improve weather forecasting. A 1965 drawing from the United States National Oceanic and Atmospheric Administration illustrates such an observing system.



FIGURE 1. Schematic of a fully integrated environmental monitoring system, circa 1965. (From the United States National Oceanic and Atmospheric Administration image archive.)

Even observing systems for atmospheric composition aren't new. Ozonesondes, aircraft, ground-based networks, field-intensive studies, and lidars have often been used together to advance the understanding of atmospheric composition. Satellites have been part of the observing system for stratospheric composition related to ozone and ozone changes for more than 30 years, but typically not part of the observing systems for atmospheric composition in the troposphere, the lowest layer of Earth's atmosphere.

So, why hold an International Summer School of Oceanic and Atmospheric Sciences on observing systems for atmospheric composition in 2004? We had three main reasons. First, the advances in computer technology, data distribution, collection, and assimilation, and modeling enable the use of information from observing systems in ways that were not possible before. Second, new satellite instruments can make global observations of key atmospheric constituents in the troposphere. Third, with the new computational and observing capabilities, understanding current global atmospheric composition and being able to predict future global atmospheric composition is becoming more of a reality.

Our planet is changing. A changing atmospheric composition is coupled with changes in other Earth components to determine the consequences of those changes. An observing system for atmospheric composition will thus help improve the understanding of and predictability for these other Earth components—climate variability and change, the water cycle, human contributions and responses, land use and land cover changes, ecosystems, and the carbon cycle—as well.

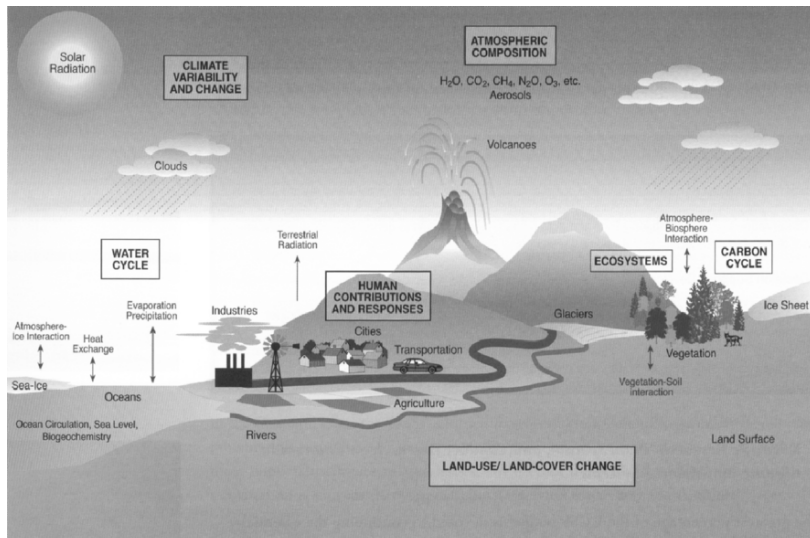


FIGURE 1. Schematic of the climate system (from *Our Changing Planet*, the U.S. Climate Change Science Program for Fiscal Years 2004 and 2005).

# Introduction II

## Needs for Sampling on Short Time and Spatial Scales

WILLIAM H. BRUNE

### Introduction

While the major constituents of the Earth's atmosphere have not changed much since the advent of humans, the minor components have varied dramatically. Humans and their activities and natural processes both exert a powerful influence on atmospheric composition, sometimes with serious consequences. Understanding the variability and mitigating these consequences require an observing system for atmospheric composition. Components of an observing system for atmospheric composition have existed for decades, although recent advances in sensor technology and computational power make an integrated observing system more realizable. The observing system for atmospheric composition consists of instruments, models, and research.

The observing system is needed to develop an understanding of atmospheric composition and the processes that drive it and to provide the capability to confidently predict the interactions between atmospheric composition and changes and Earth and human activities. Two aspects of our existence are particularly affected by variations in atmospheric composition:

- air quality (human health, infrastructure and visibility degradation, ecosystem damage)
- climate (Earth's radiative balance and its cascading effects)

*Thus, we are interested in the atmospheric composition that influences either atmospheric chemistry or Earth's radiation balance*

One way to examine the observing needs for tropospheric composition is the list the issues affecting humans and the atmospheric processes that determine tropospheric composition (Figure 1). The issues range from the global scale to the regional and local scale: climate, atmospheric oxidation, global pollution, carbon balance, regional pollution and haze, and urban pollution and PM<sub>2.5</sub> (particles < 2.5  $\mu\text{m}$  in diameter). The processes are not all chemical: emissions

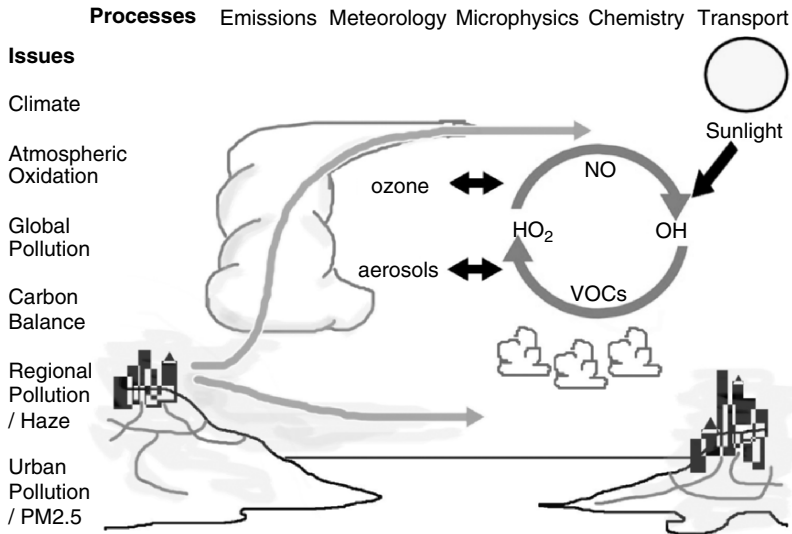


FIGURE 1. Schematic the processes and issues of atmospheric composition.

of atmospheric constituents from surface and airborne sources, meteorology, microphysics, chemistry, and transport.

We seek to answer two questions:

- How well can we describe these processes?
- Can we develop predictive capability for these issues?

The focus of this lecture will be on tropospheric composition and its behavior on short times scales and local to regional spatial scales. Of interest are water vapor ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), the pollutants ozone ( $\text{O}_3$ ), and small particles and their precursors (particularly nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), volatile organic compounds (VOCs), carbon monoxide (CO), sulfur dioxide ( $\text{SO}_2$ ), and ammonia ( $\text{NH}_3$ ), as well as acids and nitrates, toxic and carcinogenic gases. These atmospheric constituents can be either anthropogenic or natural. Even if we are only interested in pollution, we need to understand the interactions of pollutants with the environment.

Consider an atmospheric constituent that is a pollutant (e.g., an atmospheric component that has serious negative consequences for humans and their environment in trace amounts). Predicting the amount of this pollutant, which we will call A, requires observed variables, laboratory measurements of rate coefficients, and computer modeling.

Take the example of a simple box model. The time rate of change for an atmospheric constituent, A, can be determined from the equation:

$$\frac{d[A]}{dt} = \frac{q_A}{H} + P(A) - L(A)[A] - \frac{v_{dA}}{H} [A] + \frac{u}{\Delta x} ([A]_o - [A]) \quad (1)$$

where

$[A]$  is the concentration of  $A$  (molecules  $\text{cm}^{-3}$ )

$q_A$  is the emission rate (molecules  $\text{cm}^{-2} \text{s}^{-1}$ )

$H$  is the height of the mixing box (cm)

$P(A)$  is the chemical production rate of  $A$  (molecules  $\text{cm}^{-3}\text{s}^{-1}$ )

$L(A)$  is the 1st-order loss rate of  $A$  ( $\text{s}^{-1}$ )

$v_{dA}$  is the deposition velocity of  $A$  ( $\text{cm s}^{-1}$ )

$u$  is the horizontal wind velocity ( $\text{cm s}^{-1}$ )

$\Delta x$  is the width of the box in the wind direction (cm)

$[A]_o$  is the background value for  $[A]$  (molecules  $\text{cm}^{-3}$ )

At any given time, any one of these terms can be dominant, depending of the identity of  $A$  and the local meteorology. Often, several are comparable.

The amount of a pollutant that has adverse effects on humans and their environment depends on the atmospheric constituent and has changed over time as medical and public health studies improve. At present, the United States (EPA, 2004; WHO, 2000) and the World Health Organization have six pollutants whose adverse levels have been established (Table 1). Generally the ambient air-quality standards of the US, WHO, European Union, and other countries are similar, although there are differences.

Of these pollutants,  $\text{CO}$ ,  $\text{SO}_2$ , and lead are primary emissions,  $\text{NO}_2$  (nitrogen dioxide) is rapidly exchanged with  $\text{NO}$  (nitric oxide), which is a primary emission, particulate matter is both a primary emission and created by gas-to-particle conversion, while ozone is purely a secondary emission generated by atmospheric chemistry.

The emissions of greatest interest for local-to-regional scales and times of less than a month or so are those species with lifetimes less than that of  $\text{CO}$  (Figure 2). A goal of an observing system for atmospheric composition is to develop the capability to link species like  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{NO}_x$  ( $=\text{NO}+\text{NO}_2$ ) to the atmospheric radicals  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ , and  $\text{NO}_3$ , which are the driving forces behind the atmospheric chemistry that creates secondary pollution and modifies primary pollution.

TABLE 1.1. Asian Pollutant Emissions (Gg in year 2000) &  $2\sigma$  Uncertainties

Country Pollutant	China		Japan		India		Asia total	
		%		%		%		%
$\text{SO}_2$	20.400	13	800	9	5.540	26	34.300	16
$\text{NO}_x$	11.350	23	2.200	19	4.590	48	26.770	37
$\text{CO}_2^*$	3.820	16	1.200	7	1.890	33	9.870	31
$\text{CO}$	115700	156	6.810	34	63.340	238	278560	185
$\text{CH}_4$	38.360	71	1.140	52	32.850	67	106820	65
NM VOC	17.430	59	1.920	35	10.840	149	52.150	130
BC	1.050	484	53	83	600	359	2.540	364
OC	3.390	495	74	181	2.840	544	10.420	450
$\text{NH}_3$	13.570	53	350	29	7.400	101	27.520	72

\*  $\text{CO}_2$  in Tg. From Streets et al., 2003

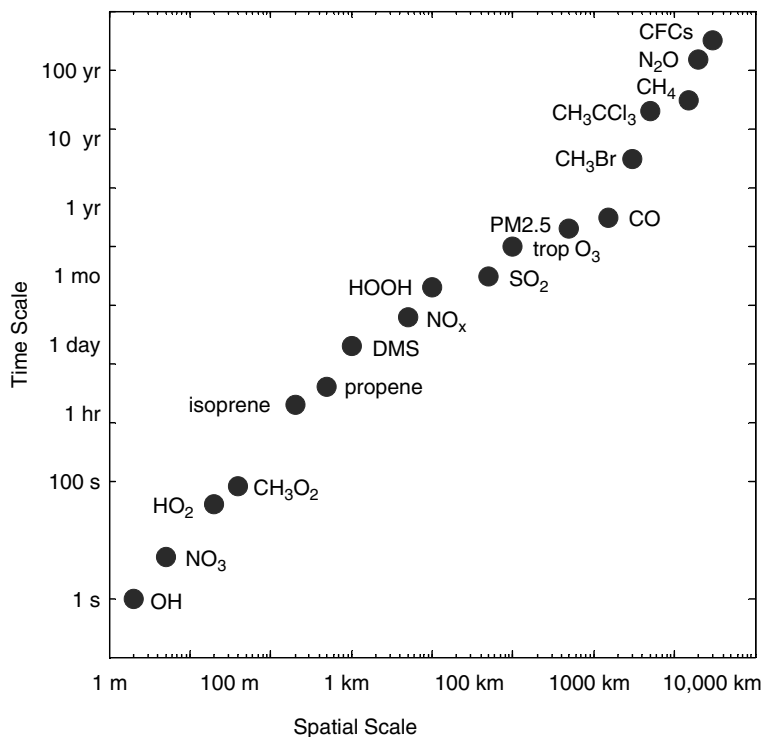


FIGURE 2. Spatial and temporal scales of atmospheric constituents.

Intensive studies show that the understanding of the processes that control atmospheric composition is reasonably good for some conditions. However, it does not yet enable the confident predictability needed for decision making regarding improved air quality, other socio-economic factors, and air-quality improvement deadlines. We examine the current understanding of each process in Figure 1.

## Emissions

Governmental environmental agencies in the US and Europe have gone to great lengths to quantify a wide range of emissions. The result is that emission inventories are probably best in these two regions. In other regions the emission inventories are less well known. For instance, the inventory of gaseous and primary aerosol emissions in Asia in the year 2000 is fairly certain for atmospheric constituents like SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub>, but is far less certain for CO,

TABLE 1.2. Emissions from Two Chemical Plants Near Houston, Texas

Plant	Emission	NO <sub>x</sub> (kmole/hr)	C <sub>2</sub> H <sub>4</sub> / NO (mole/mole)	C <sub>3</sub> H <sub>6</sub> / NO (mole/mole)
Sweeney	inventory	14	0.01	0.01
	observed	15	3.6	2.0
	obs/inventory	1.07	360	200
Freeport	inventory	31	0.03	0.01
	observed	30	1.5	0.5
	obs/inventory	0.97	50	50

nonmethane volatile organic compounds (NMVOCs), and organic carbon (OC) and black carbon (BC) aerosols (Table 2).

Even in U.S. urban areas, inventories of some emissions are found to be significantly in error. An example is Houston, Texas, in September 2000, during the TexAQS2000 intensive field campaigns (TexAQS2000). The NOAA P-3 sampled plumes from two petrochemical plants on the coast south of Houston. In the plumes were highly elevated levels of ethane (C<sub>2</sub>H<sub>4</sub>) and propene (C<sub>3</sub>H<sub>6</sub>). By applying a transport model to the plume measurements, the emission rates were derived. The resulting emissions of NO<sub>x</sub> agree with the emissions inventory (Table 3). However, the resulting ratios of ethene and propene to NO<sub>x</sub> are more than 50–200 times larger than expected from the emissions inventory. The reasons for this difference are not clear, but it could be leaks or many small spillages that are less than the level that is required to be reported. What is clear is that the emissions inventories drastically underestimated the actual alkene emissions.

This error in the emissions inventory for ethene and propene is important for Houston's pollution chemistry. The hydroperoxyl radical, HO<sub>2</sub>, is a precursor atmospheric constituent that leads to ozone production. It is mostly made during the day by processes involving sunlight, but is sometimes made at night, when ozone reacts with alkenes like propene and ethene. In Houston, a large nighttime propene spike leads to an HO<sub>2</sub> spike that is as large as HO<sub>2</sub> gets during the day (Figure 3). Thus, emission errors will propagate into errors in the modeling of radical chemistry and ozone production.

Conclusions regarding emissions:

- Some U.S. emissions are known quite well (e.g., NO<sub>x</sub> from U.S. power plants); others are known quite poorly (e.g., ethene and propene).
- In the developing world, emission inventories are generally even less well known.
- There is also a factor of 2–3 uncertainty in regional natural emissions (such as for isoprene, a highly reactive VOC emitted by trees).
- Since emissions are the fuel for tropospheric (and stratospheric) photochemistry, it is important to know well the emissions, their distributions, and variations.



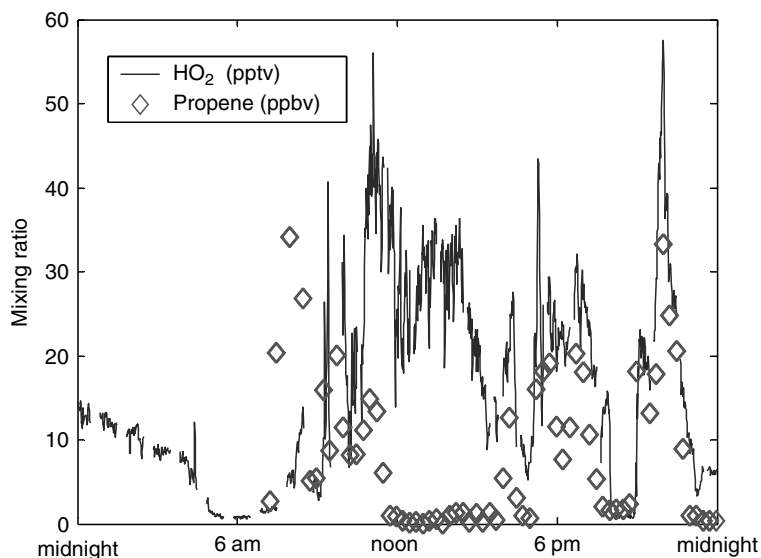


FIGURE 3. Propene emissions in the presence of ozone initiate fast atmospheric chemistry, as evidenced by the nighttime spike in propene and the reactive free radical  $\text{HO}_2$  during the TexAQS2000 intensive study.

## Tropospheric Chemistry

Where does ozone come from? In the stratosphere, ozone can result from the direct dissociation of molecular oxygen by ultraviolet light into oxygen atoms, which then join with molecular oxygen to form ozone. Ozone formation in the troposphere is more complex. It requires the presence of ultraviolet sunlight, although not as energetic as in the stratosphere, nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), and volatile organic compounds (VOCs), which are the source of the free radicals, hydroxyl ( $\text{OH}$ ), and hydroperoxyl ( $\text{HO}_2$ ).

Ozone is a secondary pollutant—its only source is in the atmosphere. It is lost, though, both on surfaces and by photochemical reactions, as given in the following equation:

$$\frac{d[\text{O}_3]}{dt} = P(\text{O}_3) - L(\text{O}_3)[\text{O}_3] - \frac{v_{d\text{O}_3}}{H} [\text{O}_3] + \frac{u}{\Delta x} ([\text{O}_3]_o - [\text{O}_3])$$

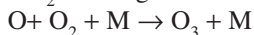
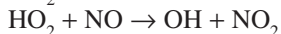
where

$$P(\text{O}_3) = k_{\text{HO}_2 + \text{NO}} [\text{NO}][\text{HO}_2] + \sum_i k_{\text{RO}_2i + \text{NO}} [\text{NO}][\text{RO}_{2i}]$$

$$L(\text{O}_3) = J(\text{O}_3)f_{\text{H}_2\text{O}} + k_{\text{HO}_2 + \text{O}_3} [\text{O}_3][\text{HO}_2] + k_{\text{OH} + \text{O}_3} [\text{O}_3][\text{OH}]$$

Ozone losses include its photodestruction, followed by reaction with  $\text{H}_2\text{O}$  to form OH, direct reaction with OH and  $\text{HO}_2$ , and deposition on surfaces. Deposition and formation of OH are often the two largest ozone destruction processes.

The instantaneous ozone production,  $P(\text{O}_3)$ , comes from a reaction that cycles  $\text{HO}_2$  to OH:



Ozone is also made by replacing  $\text{HO}_2$  in the chemical equation above with  $\text{RO}_2$ , where R is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ —a hydrocarbon with an odd number of hydrogen atoms. The instantaneous ozone production rate is determined to some extent by the cycling of  $\text{HO}_x$  between OH and  $\text{HO}_2$  where  $\text{HO}_x = \text{OH} + \text{HO}_2$  (Figure 4). Most  $\text{HO}_x$  is produced by photochemical processes as OH, although in environments where formaldehyde (HCHO) is high, a significant fraction of  $\text{HO}_x$  can come from the production of  $\text{HO}_2$  by HCHO destruction by sunlight. Once created, OH is rapidly cycled to  $\text{HO}_2$  by OH reactions with CO,  $\text{CH}_4$ , VOCs, and  $\text{O}_3$  while  $\text{HO}_2$  is cycled to OH by  $\text{HO}_2$  reactions with NO and  $\text{O}_3$ . If the sources of OH and  $\text{HO}_2$  were cut off, then OH would cycle to  $\text{HO}_2$  in about a second. The reaction of OH with VOCs typically produces  $\text{RO}_2$  before it produces  $\text{HO}_2$ . As a result,  $\text{RO}_2$  abundances are roughly equal to  $\text{HO}_2$  abundances. The amount of  $\text{RO}_2$  and  $\text{HO}_2$  produced is thus related to  $P(\text{HO}_x)$  and the amount and type of VOCs that react with OH. When NO is greater than a few 10's of pptv, the reaction of  $\text{HO}_2$  with NO dominates the reaction of  $\text{HO}_2$  with  $\text{O}_3$  and ozone is produced, not destroyed. Eventually,  $\text{HO}_x$  reacts to form more stable atmospheric constituents and the cycle is terminated. The reaction products depend on the  $\text{HO}_x$

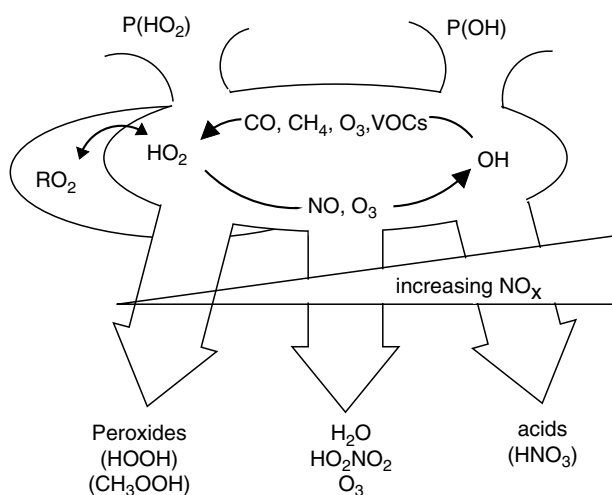
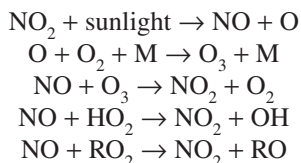


FIGURE 4. A schematic of the photochemistry of OH and  $\text{HO}_2$  as a function of  $\text{NO}_x$ .

production rates ( $P(\text{OH})$  and  $P(\text{HO}_2)$ ), and on the  $\text{NO}_x$  abundances (Figure 4). Consider a case where  $P(\text{HO}_x)$  and the  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{VOC}$  emissions are constant. At low  $\text{NO}_x$ , the  $\text{HO}_x$  is shifted to  $\text{HO}_2$  (the  $\text{HO}_2/\text{OH}$  ratio is large) and the reactions of  $\text{HO}_2$  with  $\text{HO}_2$  and  $\text{RO}_2$  produce the peroxides  $\text{HOOH}$  and  $\text{ROOH}$ . When  $\text{NO}_x$  is greater, more  $\text{HO}_x$  is shifted to  $\text{OH}$  (the  $\text{HO}_2/\text{OH}$  ratio is less) and the reaction of  $\text{HO}_2$  with  $\text{OH}$  to form  $\text{H}_2\text{O}$  slightly dominates. When  $\text{NO}_x$  is very abundant, such as in a more polluted region or in the upper troposphere and stratosphere, then  $\text{HO}_x$  is shifted even more toward  $\text{OH}$  and the reaction of  $\text{OH}$  with  $\text{NO}_2$  to form  $\text{HNO}_3$  is most important. A similar diagram can be drawn for  $\text{NO}_x$ . In this case, the primary cycling between  $\text{NO}$  and  $\text{NO}_2$  occurs by the reaction sequence:



The first two equations show how  $\text{NO}_2$  is converted into ozone. However, the reaction of  $\text{NO}$  with  $\text{O}_3$  destroys  $\text{O}_3$ ; a steady-state cycle forms during the day. No new  $\text{O}_3$  is really created by this cycle. Instead, the  $\text{O}$  atom is merely exchanged between  $\text{O}_3$  and  $\text{NO}_2$ . However, the reaction of  $\text{NO}$  with  $\text{HO}_2$  and  $\text{RO}_2$  does make new  $\text{O}_3$ .

The coupling of the  $\text{HO}_x$  and  $\text{NO}_x$  cycles produces  $\text{O}_3$  (Figure 5). As the  $\text{NO}_x$  abundance is increased,  $\text{OH}$  first rises as more  $\text{HO}_x$  is shifted from  $\text{HO}_2$  to  $\text{OH}$  and then falls, as  $\text{OH}$  is rapidly converted to  $\text{HNO}_3$ .  $\text{HO}_2$  is relatively unaffected by increasing  $\text{NO}_x$  until  $\text{NO}_x$  reaches about 1 ppbv; then  $\text{HO}_2$  decreases increasingly rapidly as  $\text{HO}_x$  is shifted from  $\text{HO}_2$  to  $\text{OH}$  and as  $\text{OH}$  (and thus  $\text{HO}_x$ ) is removed by  $\text{NO}_2$ . The resultant instantaneous ozone production rate thus increases until  $\text{NO}_x$  reaches a few ppbv and then decreases. Thus, instantaneous ozone production exhibits significant nonlinear behavior as a function of  $\text{NO}_x$ .

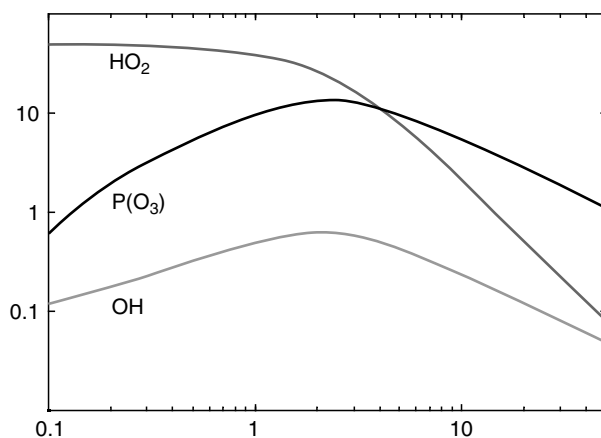


FIGURE 5. Variation of  $\text{OH}$ ,  $\text{HO}_2$ , and  $P(\text{O}_3)$  as a function of  $\text{NO}_x$ .

An example of this nonlinear behavior can be seen in observations made during the TexAQS 2000 intensive field campaign in Houston, Texas (Figure 6). The behavior of NO, NO<sub>2</sub>, and O<sub>3</sub> are shown for three days in August. Morning rush hour is marked by peaks in NO and NO<sub>2</sub>, since NO is emitted by automobile and truck engines. Evening rush hour is also seen, although the peak values are smaller. However, it is clear that O<sub>3</sub> is building up over these three days, which means that O<sub>3</sub> production is occurring.

NO<sub>x</sub> reaches several 10's of ppbv during rush hour. Thus, NO and HO<sub>2</sub> should anticorrelate. They do (Figure 7). However, since  $P(O_3) \sim [NO][HO_2]$ , it can be large even when a small amount of HO<sub>2</sub> reacts with a large amount of NO, and vice versa. P(O<sub>3</sub>) remains between 40 ppbv/hr and 60 ppbv/hr from the hours of about 8:00 to 14:00. In this period, roughly 300 ppbv of ozone is created, which is proportional to the total ozone observed. Obtaining a more accurate ozone balance requires knowledge not only of the photochemistry, but also of the height of the mixed layer, the ozone loss on Earth's surface, and the ozone transport to and away from the region of interest.

The NO abundance is related to the NO<sub>x</sub> abundance, and the RO<sub>2</sub> and HO<sub>2</sub> abundances are related to the VOC abundance. Because NO<sub>x</sub> and VOCs are the primary emissions that contribute to ozone production, an ozone isopleth plot as a function of VOCs and NO<sub>x</sub> abundance should provide guidance for the optimum regulatory actions to reduce ozone pollution. An early diagram (Figure 8) met the following conditions:

- It was chosen for a particular region, or box, which could be moving.
- The time duration of the run was chosen to capture the maximum ozone production.

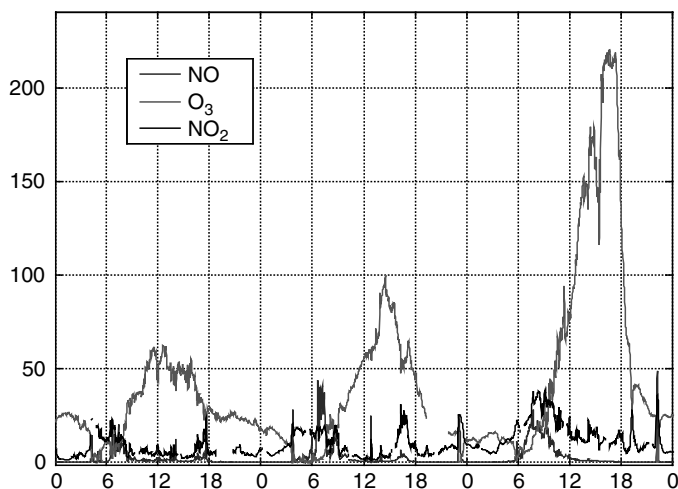


FIGURE 6. NO, NO<sub>2</sub>, and O<sub>3</sub> during a pollution episode in Houston, Texas, during the TexAQS 2000 air-quality study.

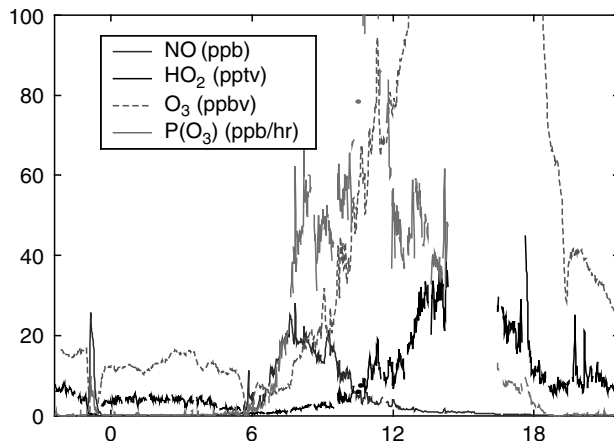


FIGURE 7. NO, HO<sub>2</sub>, and P(O<sub>3</sub>) during a pollution episode in Houston, Texas, during the TexAQS 2000 intensive field campaign.

- The entire plot was generated by changing the VOC/NO<sub>x</sub> mixture while leaving the meteorological conditions constant.

Regions above the ridgeline at VOC/NO<sub>x</sub> = 8 are “VOC-limited”; more VOCs are needed to produce more ozone. Regions on the plot below the ridgeline are “NO<sub>x</sub>-limited”; more NO<sub>x</sub> is needed to produce more ozone. Urban areas are typically

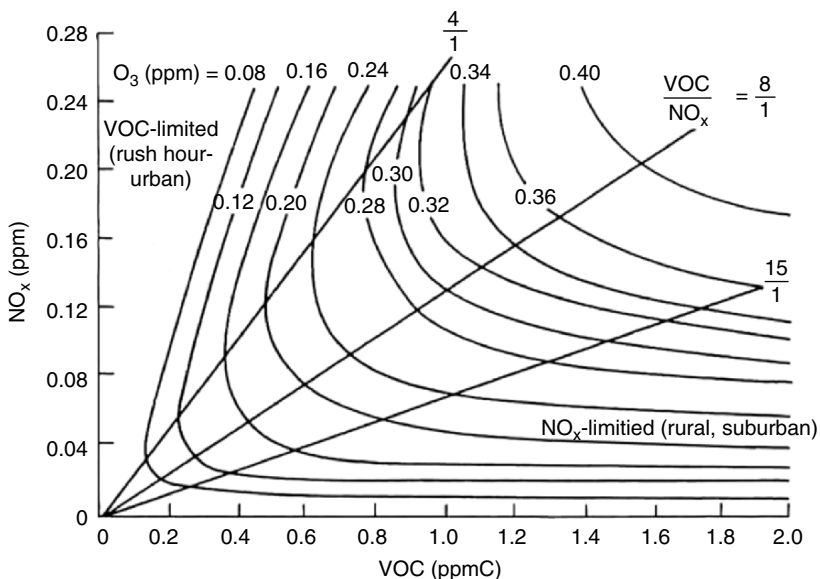


FIGURE 8. An example of an ozone isopleth diagram (adapted from NRC, 1990).

“VOC-limited,” while rural and suburban areas and midday urban areas are often “NO<sub>x</sub>-limited.” This diagram indicates that reducing VOCs will result in reduced produced ozone, while reducing NO<sub>x</sub> for areas above the ridgeline can result in an increase in ozone until the VOC/NO<sub>x</sub> ratio drops below 8. This behavior results from the nonlinear coupling between HO<sub>2</sub> and NO.

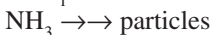
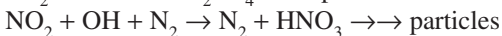
Conclusions regarding atmospheric chemistry.

- The nonlinear behavior of HO<sub>x</sub>-NO<sub>x</sub> chemistry complicates the analysis of ozone production rates from observing systems that have low spatial and temporal resolution.
- Other products of tropospheric oxidation have effects on human health and climate, such as formaldehyde (HCHO), peroxyacetyl nitrate (PAN).
- The NO<sub>3</sub> radical plays a nighttime role similar to OH’s daytime role.

## Particle Microphysics and Chemistry

Particles have severe impacts on both human health and climate. Particles can be emitted directly from sources, such as diesel engines, or created in the atmosphere by gas-to-particle conversion. Particles less than 2.5 μm in diameter are particularly important for human health. They are small enough to navigate the respiratory system’s passageways and are deposited deep within the lungs, where they can enter the bloodstream. PM2.5 has been linked to severe cardio-respiratory problems such as chronic asthma and bronchitis and even sudden heart attacks. At the same time, they are also important for Earth’s radiation budget because they are about the size of the wavelength of the incoming solar radiation and are thus efficient at scattering or absorbing light.

In gas-to-particle conversion, volatile gases react with OH, O<sub>3</sub>, or NO<sub>3</sub> to form gases that have low vapor pressures. These either condense on pre-existing aerosols or nucleate to form new ones. The main reactions involve SO<sub>2</sub>, NO<sub>2</sub>, VOCs, and NH<sub>3</sub>:



The emission of primary particles and the gas-to-particle conversion of secondary particles lead to particle size distributions, which because of microphysics tend to have certain characteristics (Figure 9). Primary particles tend to be larger than 0.01 μm, while secondary particles are created at sizes in the 0.001–0.01 range when nucleation of low-vapor-pressure gases. Both types of particles grow by coagulation, condensation of both low-vapor-pressure gases and water vapor. These processes create particle size distributions: the nucleation mode (diameter < 0.01 μm), the Aiken mode (0.01 μm < diameter < 0.08 μm), the accumulation mode (0.08 μm < diameter < 2.5 μm), and the coarse mode (*d* > 2.5 μm). The nucleation and Aiken modes are rapidly lost by coagulation; the coarse mode is

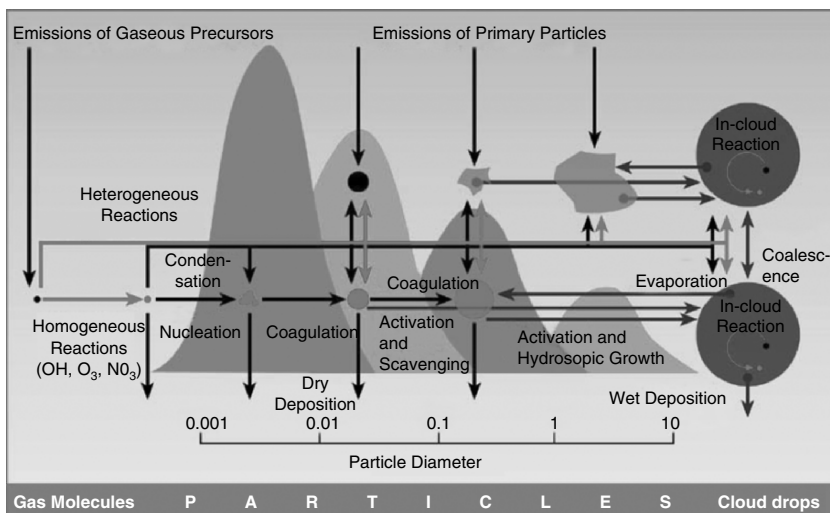


FIGURE 9. A schematic of atmospheric particles processes and size distributions (from US CCSP, 2004).

rapidly lost by deposition; the accumulation mode has a lifetime of a few weeks or so.

Equally important to the particle size distributions is the chemical composition. While no direct link has yet been made between the chemical composition of PM<sub>2.5</sub> to human health, chemical composition has a major impact on climate. For example, some particles, such as sulfate (H<sub>2</sub>SO<sub>4</sub>), reflect incoming solar light, while other particles, such as soot from diesel exhaust, absorb incoming solar light. The impact on Earth's radiative balance is not trivial.

Small particles also have indirect effects on Earth's radiative balance. The nucleation of cloud drops and ice from pure water vapor is unrealistic in Earth's atmosphere. Instead, nucleation starts with particles. However, only a small subset of atmospheric particles are good cloud condensation nuclei and even a smaller subset are good ice nuclei. The chemical composition, along with the particle size, determines a particle's ability to be a cloud condensation nuclei (CCN) or an ice nuclei (IN).

In the troposphere, particles often contain a combination of sulfate, nitrate, organic or black carbon, and ammonia. The sulfate content in the U.S. East Coast is much greater than it is on the US West Coast, primarily because of the use of sulfur-containing coal in Midwest power plants. Organic content appears to be fairly ubiquitous, even in very remote regions of the Pacific Ocean.

Measurements were made with an aerosol mass spectrometer (AMS) in Scotland and Korea (Figure 10). In the Scotland sample, the size distribution is mostly in the Aiken mode and is dominated by the organic and nitrate components. In the Korean sample, the particle size distribution shows a growing accumulation mode and is dominated by the sulfate component. Peaks in the organic

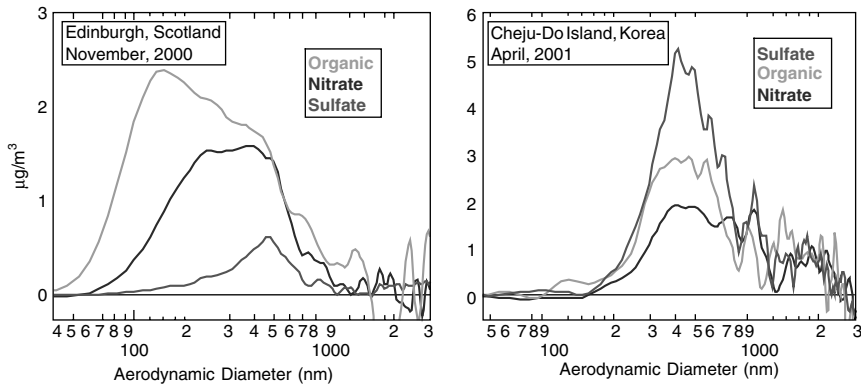


FIGURE 10. Particle size distributions and chemical composition in a city (Edinburgh, Scotland) and in a remote region downwind of urban and industrial regions (Cheju-Do Island, Korea). (from Hugh Coe, private communication, 2003).

component of the mass spectrum indicate that in Scotland the organic component consists primarily of hydrogen and carbon, while in Korea, the organic component has been oxygenated in the transit from the source regions. This oxidation process alters the particles' capability to act as CCN.

It was generally thought that there were always enough particles present in urban areas that low-vapor-pressure gases would always condense on pre-existing particles and not form new particles. However, recent measurements in Pittsburgh, PA, and other cities have shown that under certain meteorological conditions, such as recent frontal passages, new particles can nucleate (Figure 11). At 9 a.m., OH was created and reacted with  $\text{SO}_2$  and VOCs to form new particles. This burst of new particles then rapidly coagulated, creating fewer, larger particles in a few hours. That new, small particles are formed may have implications for human health.

Conclusions for microphysics.

- Airborne particles participate in both air quality and Earth's radiative balance.
- Particle distribution usually consists of particles emitted directly from sources and particles created by gas-to-particle conversion.
- Particles' roles in human and health and climate are determined by both the particle size distribution and the particles' chemical composition
- Particles containing organics are widespread.
- $\text{PM}_{2.5}$  is a major research thrust—for reasons of both health effects and climate.

## Meteorology

Meteorology affects the distribution of atmospheric constituents and atmospheric composition on spatial scales from turbulence to global transport and on temporal scales from seconds to decades. Without a knowledge of meteorology, it is



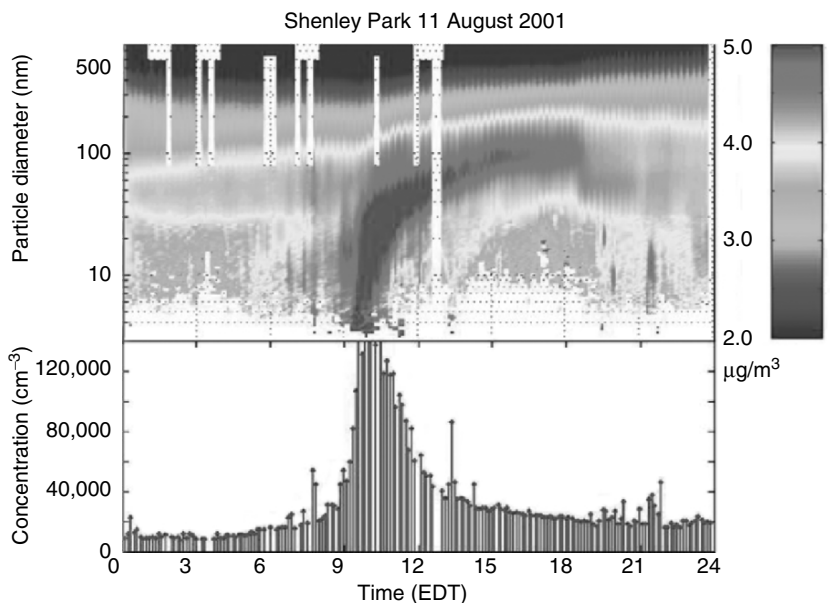


FIGURE 11. New particle formation & growth, 11/08/2001, Pittsburgh, PA. (From S. Pandis, private communication, 2003).

impossible to understand measurements of almost all atmospheric constituents, with the possible exception of the short-lived radicals  $\text{CH}_3\text{O}_2$ ,  $\text{NO}_3$ ,  $\text{HO}_2$  in most conditions and  $\text{OH}$  in essentially all conditions (Figure 2). The  $\text{OH}$  lifetime is a second or less; its abundance and behavior are defined exclusively by reactions involving  $\text{NO}_x$ , VOCs,  $\text{CO}$ , and a few other constituents, and  $\text{P}(\text{HO}_x)$ . However, for  $\text{OH}$ , solar photolysis must be well known, and that depends on clouds. The interaction between meteorology and atmospheric composition continues to be an active research topic.

To illustrate the impact of meteorology on atmospheric composition, and its measurement, consider the planetary boundary layer, or PBL (Figure 12). During the day, surface heating generates convection, which raises and mixes surface gaseous and particulate emissions throughout the convective mixed layer, which is typically 1 to 4 km high and capped by a cloud layer. The circulation time constant is about an hour. While PBL constituents are vented into the free troposphere, especially by convective systems, the PBL can often be considered to be a box into which the surface emissions are mixed.

As sunset approaches, convection becomes less active and a lower, stable PBL forms. Atmospheric constituents that were higher in the convective mixed layer when convection ceased remain in the residual layer, disconnected to the surface. Any surface emissions occurring at night remain in the nocturnal boundary layer.

During rush hour near sunrise, high levels of vehicle exhaust, including  $\text{NO}_x$ , VOCs, and particulates, build up in the shallow boundary layer. As the sun heats