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Question From the Classroom

By Bob Becker

Q. Would a vacuum cleaner still work inside a vacuum?

A. Good question! If you think of a vacuum cleaner as something that pulls or sucks the dirt into it, then it should probably work in a vacuum. This way of thinking, however, is based on a belief in a force called “suction”. Unfortunately, most people don’t know that such a force does not exist.

Consider a suction cup—stick one on top of a table and ask 100 randomly chosen people what is holding it down. You will probably get the same answer: “Suction”. It is a suction cup after all. If you questioned them further about the nature of the force, they will most likely attribute it to some kind of pulling force created by the vacuum beneath the suction cup.

But when you ask, **“What is a vacuum?”** many will respond correctly, “A vacuum is nothing. It’s the absence of any matter.” “So if it’s nothing”, you say, “what’s doing the pulling?” At this point you will probably hear a whole lot of “Hmmm’s”—that’s the sound of people reexamining their ideas about how the world works. The simple truth is that a vacuum is nothing and can therefore do nothing! So what supplies the force that keeps a suction cup stuck to the table? It’s not a pulling force from within; it’s a pushing force from without. That’s right! Our atmosphere pushes with a force of 14.7 pounds per square inch. That’s like having the weight of a bowling ball pushing on every square inch, of every surface around you, all the time. It is caused by an almost unimaginably large number of molecules moving at hundreds of miles per hour, colliding constantly with each other and with every object on our planet. We take that pressure for granted. We forget it’s even there ... until it’s gone, that is, and then we start attributing strange pulling forces to its absence! Hmmm ...

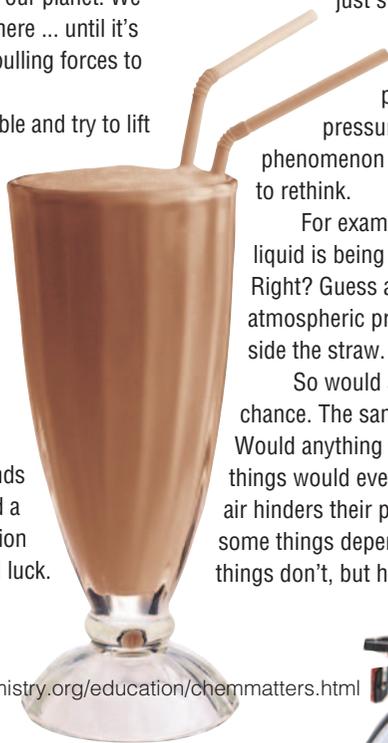
But if you simply place a suction cup on the table and try to lift it up, it comes off easily. Why is it easy with all that pressure pushing down on it? The explanation is simple: there’s also air beneath the suction cup pushing upward with an equal force. But when you push the suction cup firmly to the table, you force that air out. In this instance, when you try to lift it, you fight against atmospheric pressure but receive no help from beneath. It’s just you against the atmosphere. If it’s a small suction cup with a surface area of only one square inch, then you will need to pull upward with a force of about 14.7 pounds to break it loose. That’s assuming that you’ve created a perfect vacuum beneath the cup. If it’s a larger suction cup with a surface area of 10 square inches ... good luck.



Let’s get back to the vacuum cleaner. A dirt particle sitting on your carpet is pushed equally from all sides by atmospheric pressure. Normally, these forces cancel each other out, so the particle just sits there. A vacuum cleaner works because it creates an area of lower pressure above the particle. The dirt particle thus gets pushed (not pulled) into the vacuum cleaner by the greater air pressure on the underside of it. This means that every phenomenon you attribute to a vacuum pulling, you now have to rethink.

For example, what about a drinking straw? Certainly, that liquid is being pulled into our mouths by the suction we create. Right? Guess again! It’s being pushed up the straw by the atmospheric pressure pushing down on the liquid surface outside the straw.

So would a vacuum cleaner work inside a vacuum? Not a chance. The same goes for suction cups and drinking straws. Would anything work inside a vacuum? Most definitely! Some things would even work better because air hinders their performance. So some things depend on air and some things don’t, but how good are you at



telling which is which? Try the following activity, and find out. The first few should be easy based on what you've just read. For the rest, you're on your own. Hint: there's more to air than just pressure; just think of all the things it does that we take for granted.

So just how important is our atmosphere? Imagine you relocate to planet X, a planet just like Earth, with the exact same gravitational pull, but with

no atmosphere at all. Which of the following 50 items will still work on planet X, and which ones will not? Don't use the cop-out answer and say none of them will work because we'd all be dead. Imagine you and your friends have pressurized space suits with oxygen tanks and everything you will need to survive.

For the things that will work, will they work exactly the same, or perhaps even better? For the things that will not work, can you think of possible modifications that could enable them to work? ▲



Around the house ...

1. a suction cup
2. a vacuum cleaner
3. a drinking straw
4. a siphon
5. a light stick
6. a flashlight
7. a magnet
8. a broom
9. an aerosol spray can
10. an alarm clock



Heating it up ...

11. a match
12. a candle
13. a blow dryer
14. an electric stove
15. a gas stove
16. a pressure cooker
17. a microwave oven
18. a convection oven
19. a smoke detector



Outdoor fun ...

20. a soap bubble maker
21. a boomerang
22. a yo-yo
23. a Frisbee
24. a kite
25. a swing
26. a pogo stick
27. a bow and arrow
28. the game of golf
29. the game of baseball
30. a flower garden



Getting around ...

31. a bicycle (and tire pump)
32. a hang glider
33. a golf cart
34. a helicopter
35. a parachute
36. a hovercraft
37. an automobile (with air bag)
38. a hot air balloon
39. the Goodyear blimp
40. the space shuttle

We're talking major energy ...

41. a shot gun
42. an emergency road flare
43. dynamite (and fuse)
44. lightning (and thunder)
45. a coal-burning power plant
46. a nuclear power plant
47. a nuclear warhead
48. a shooting star
49. our sun
50. a beautiful sunset

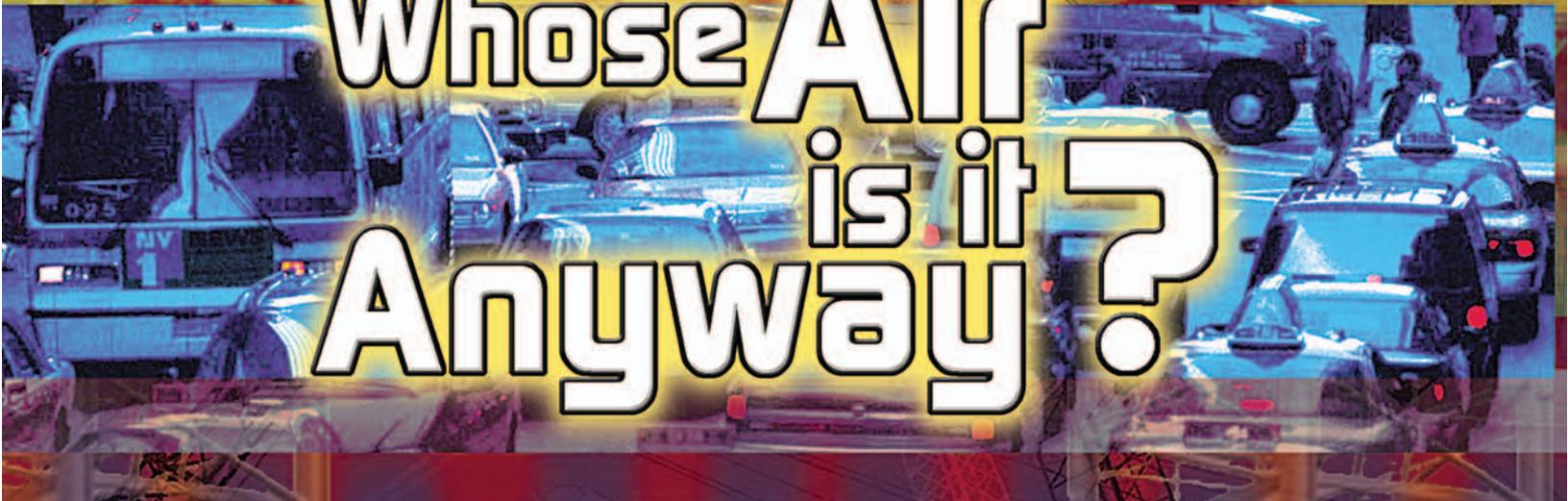


ALL PHOTOS: GETTY IMAGES/PHOTODISC





Whose Air is it? Anyway?



By Jeannie Allen

It's a fact of life. We live on the Earth and in the air. As for your share of that air—do you know where it's been?

Air is arguably the closest and most important biological connection we have with the rest of the world. We breathe air into our bodies every few seconds. Like it or not, we share the air we breathe with the people around us, whether friends or strangers.

Yuck, you may say! But it's how our world is constructed. We don't get a new air supply every day. We simply "recycle" the same air over and over. As one atmospheric chemist pointed out, "Air may not look like much, but try breathing something else!"

We share the air we breathe not only with other people but also with the rest of our environment—cars, trucks, buses, factories, airports, trees, grass, livestock and wildlife, lakes and oceans—you name it. Air is in constant motion, ever blowing and breezing from one place to another. The air we breathe and the stuff that's in it have come from somewhere else.

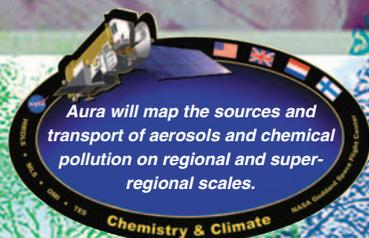
Moving air carries some interesting baggage, including moisture, dust, bacteria, fungal spores, viruses, and varying traces of chemical constituents worthy of our attention, like ozone (O_3), nitrogen oxides (NO_x), and sulfuric acid (H_2SO_4). As for any air travel, some passport checking is in

order. For our health and safety, we need to know where our air comes from, what it's carrying, and what happens to it before it reaches us.

Curious about where your air has been? So is NASA. Scientists working with data from NASA's Earth-observing satellites have been discovering, often to their amazement, that air pollution is quite an inter-continental traveler! Dust from the Sahara has turned up on coral reefs in Florida, and dust from the Asian Gobi Desert has appeared as far away as the East Coast of North America. Air pollution from the northeastern United States sometimes reaches Europe, and, occasionally, European pollution travels the opposite direction in return.

Sea salt and frozen plankton that traversed the Pacific Ocean via Hurricane Nora appeared over the midwestern United States in 1997. Satellite photos have revealed smoke from Asian fires crossing the Pacific to reach southern California. Air pollution from China often drifts directly over Japan.

All of this air travel has significant political impacts. It's becoming obvious that countries, despite their own efforts to curb pollution, won't have clean air until their neighbors do.



DIGITAL VISION



SeaWiFS satellite image of the West Coast of North America on April 25, 1998, shows the arrival of airborne dust from China. The dust is visible in the clouds at the center of the left edge of the image, and as streaks of light brown haze over Cape Mendocino on the California coast.

Tracking ozone

Ozone in the lower atmosphere is one of the pollutants of greatest concern to NASA. Ozone in the upper atmosphere (stratosphere) protects us against harmful ultraviolet radiation from the sun, but ozone where we breathe harms us. The effect of breathing ozone is somewhat akin to a slow burn. Ozone is an oxidizer, readily donating one atom of oxygen to other “willing” molecules. Over time, breathing too much ozone can permanently reduce our lung capacity.

Hate getting up early? If you're into sports, you might prefer doing your summer workouts in the cooler morning hours. You may even find breathing a little easier at that time. Ozone levels tend to be low in the morning, before the chemical soup of nitrogen oxides and hydrocarbons has time to build up from vehicle traffic and other sources. They're the chemical ingredients for ozone formation, a group of chemical reactions that really get going as sunlight becomes more intense later in the day. You can read more about that in “Chemistry in the Sunlight” on pages 22–24.

Ozone concentrations vary widely around the globe. With recent improvements in satellite technology and the availability of more data, atmospheric scientists are only now recognizing the extent of ozone's travels.

Anne Thompson is one of the trailblazers in ozone tracking at NASA Goddard Space Flight Center. She and her colleagues want to be able to predict ozone concentrations and distribution. She explains, “What we're trying to do is to parse out which ozone comes from natural causes and which ozone comes from human activity. It's extremely hard to separate natural and man-made sources of gases.

The precursors of ozone such as nitrogen oxides are not labeled ‘I came from an aircraft engine’, ‘I came from the stratosphere’, ‘I came from the ground’, or ‘I came from lightning’. You have to measure other related chemicals that fingerprint the source.”

Thompson and her colleagues recently



Anne Thompson NASA scientist, and Agnes Phahlane, a meteorologist of the South African Weather Service, prepare for a balloon launch during the SAFARI-2000 campaign in Zambia. The balloon carried both an ozonesonde instrument to measure ozone and a radiosonde to measure temperature, pressure, and relative humidity—conditions that can affect ozone concentrations and distribution.

focused on a region off the West Coast of Africa. She describes the research in these words:

“We would combine all the data we could get from various sources. We would get real-time weather data from many sources. We would get real-time satellite data on ozone concentrations from the Total Ozone Mapping Spectrometer (TOMS satellite) and the Optical Transient Detector (OTD) Lightning Sensor. Then, we would combine all of them to make our best forecast of where the ozone, dust, biomass burning, and lightning would make their impact, and so where we should direct the NASA research aircraft to make observations for us. We would forecast and fly, analyze our observations, and then forecast and fly again to extend our understanding.”

Thompson notes that she has developed a healthy respect for how variable the atmosphere is. “Weather systems in the troposphere are constantly moving and mixing the air, and at the same time, chemical reactions are changing the air's chemical composition.”

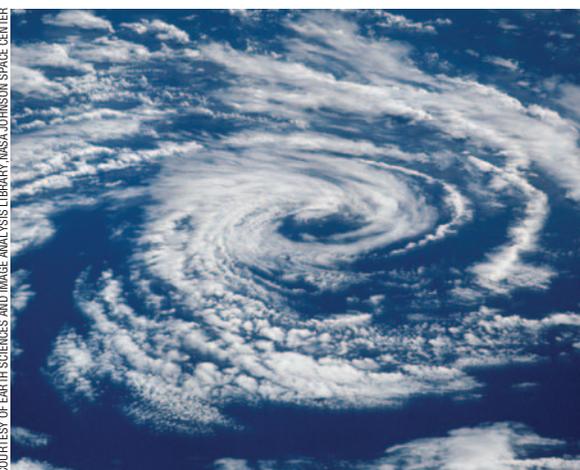
Major patterns of air circulation have enormous impacts on ozone and its precursors, the airborne chemicals that react to form it. Thompson's group was particularly interested in an anticyclone in the South Atlantic Ocean that delivers pollution from both African and South American fires over the

Atlantic. By this process, ozone from fires all across southern Africa rises up and mixes into the circulating air, which may carry the pollution hundreds of miles. Sometimes parcels of polluted air spin off, streaming out over the Atlantic, the Indian Ocean, and as far away as the Pacific.

A complete, detailed, global picture of the travels of ozone and its precursors requires more research, but some trends are

becoming clear. Background concentrations of ozone—amounts that are usually there—generally range from about 25–55 parts of ozone per billion parts of air (ppb) in surface air over the United States. Much of this ozone probably comes from outside the United States.

Keeping tabs on ozone levels is important because the U.S. National Air Quality Standard is 80 ppb over 8 hours, an amount not to be exceeded more than 3 times a year. But even if people in North America succeeded



The ever-changing and complex nature of troposphere, the lower atmosphere, makes it difficult to trace the chemical reactions that produce ozone.

Smoke Bugs

A Texas student shows us that living spores can go up in smoke and survive.

As often occurs in science, Sarah Mims's discovery happened when she wasn't really looking for it. Sarah had a good idea for a science fair project. After reading about traveling air currents and the particles they carry, she decided to sample the air near her home in Seguin, TX. Her plan was to search for fungal spores she suspected were arriving with dust from Asia.

But when she looked at a NASA SeaWiFS satellite image, Sarah found that on the day of her sampling, a large cloud of smoke from fires in Mexico had passed over Seguin. Could the smoke have delivered the *living* fungal spores she collected that day? "I was really surprised," Sarah said. She had to be sure. "Did the fungal spores I captured come from Central America?"



PHOTOS COURTESY OF SARAH MIMS

With help from friends, Sarah exposes Petrifilm to smoke from a grass fire.

What makes Sarah's research so important is that some fungal spores spread plant diseases. Farmers in tropical countries regularly set fires to clear fields of old crop residues, making room for new plantings. Sarah demonstrated that infected plants may release living fungal disease spores when they burn. Because the lightweight spores can travel vast distances on air currents, the risk of fungal infection in healthy crops seems obvious.

After reading about the project recently, Eugene Shinn, a scientist with the U.S. Geological Survey, wrote this to Sarah: "I think there is great potential in what you are doing. We have been identifying microbes including fungi in African dust that crosses the Atlantic. And, believe it or not, it reaches where you are living. One thing that has puzzled us for some time is why the number of fungal spores ... in dust fluctuates over time. We have always thought it had to do mainly with the source area. Now I wonder if it is related to fires in the Congo ... Could it be the smoke is the main source of the fungi? I encourage you to continue [your work]."

Sarah plans to submit her findings to a scientific journal. If her research is corroborated, it will provide strong evidence that agricultural diseases can spread from one continent to another—in *smoke*!

For Sarah, science research is an exciting challenge. "The reason I do science projects is because the benefits are incredible," says Sarah. "I enter competitions such as the Junior Academy of Science. You really have to understand the science ideas well to answer the judges' questions."

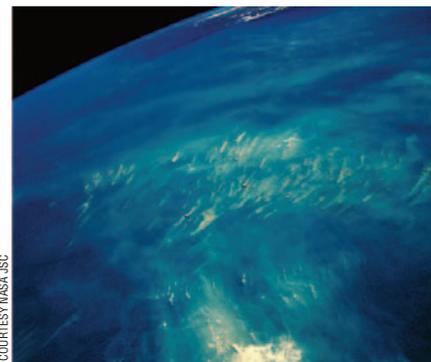
And it doesn't hurt to be organized! Sarah advises, "Doing science projects also requires a great deal of discipline. You can't wait till the last minute to do the experiment and throw a report together."

Sarah decided to do an experiment to find out if fungal spores could actually survive burning. She burned several kinds of plants—making sure to follow local fire department rules. Then she exposed pieces of a water-soluble gel, Petrifilm, to the smoke. She placed the film in culture containers and stored them at conditions favorable to fungal growth. In two or three days, she had her answer. There were colonies of at least 10 different species of fungi growing in the dishes. Clearly, fungal spores are tough enough to withstand toasting!



The presence of carbon told Sarah that the fungal spores were accompanying smoke from biomass burning.

continued from page 7.



COURTESY NASA JSC

Space Shuttle astronauts photographed these smoke plumes from the Amazon rain forest in Western Brazil in September 1984. "Slash-and-burn" techniques are sometimes used to clear forest land for agricultural purposes—for raising crops or for developing pastureland for cattle. Peak burning periods occur during the dry season, which for this Southern Hemisphere region is June through September.

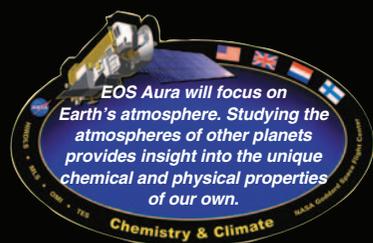
in reducing their emissions of nitrogen oxides and hydrocarbons by 25%, the ozone problem would persist. Emissions expected from Asia by 2010 could completely wipe out that gain in clean air.

"For the cooperation required to control air pollution, we need an international agreement," explains Guy Brasseur, an expert in making mathematical models of the atmosphere at the Max Planck Institute for Meteorology and the National Center for Atmospheric Research. "But before we can move to such an agreement, we need to understand the problem scientifically. Satellites are key to our research."

"NASA's Aura spacecraft will provide us with the first truly global view of tropospheric ozone... We'll be able to track ozone both regionally within continents and from one continent to another," explains Reinhold Beer, principal investigator for one of Aura's four instruments.

Daniel Jacob, atmospheric scientist at Harvard University notes that satellite observations are changing the way atmospheric chemistry is done. "Our field is undergoing a revolution, because my community is having to think about satellite observations. Interpreting satellite observations is a very difficult task ... But we need to understand what satellite observations are saying to us, because we need that global scale [perspective]." ▲

Jeannie Allen is a science writer at the NASA Goddard Space Flight Center in Greenbelt, MD. She is a frequent contributor to the Earth Observatory, NASA's award-winning website at <http://earthobservatory.nasa.gov>.



THERE'S NO PLACE LIKE HOME

Why has Mars so captured our interest? The answer might be that Earth, Mars, and Venus, along with sun-loving Mercury, are all neighbors. Also called the *inner planets*, these are the planets closest to the sun. With their solid, rocky surfaces, they're also called the terrestrial planets. That makes them different from Jupiter, Saturn, Uranus, and Neptune, which are the gas planets.

Like Earth, Venus and Mars have atmospheres. They're nice places for a probe to visit, but you probably wouldn't want to go there. How do we know? Although astronauts have yet to walk on their surfaces, robotic probes from the United States and Russia have circled and landed. They've gathered significant data and sent back pictures.

Venus

Both Venus and Mars are alien, but in very different ways. Let's start with Venus. Despite being named after the Roman goddess of love and beauty, up close Venus is hardly inviting. Superman might even find the climate more than he could bear.

Let's start with air pressure. On Venus, it's crushing! It's about 90 times the pressure you're experiencing right now. You'd have to dive to an ocean depth of more than a half-mile to duplicate the effect. In fact, when the Russian probe Venera 13 landed on the surface of Venus, it lasted about one hour before being crushed by the atmosphere.

On Venus, if the pressure doesn't kill you, the chemistry will. Consisting of 96% carbon dioxide (CO₂), about 3.5% nitrogen (N₂), no oxygen (O₂), and just trace amounts of argon (Ar) and water vapor, the Venesian atmosphere offers little chance that any kind of life as we know it could exist, let alone thrive. Do you still want to put Venus on your travel list?

When the Mars Pathfinder mission reached Mars on July 4, 1997, more than 100 million hits were made on NASA's Mars Pathfinder website in a single day. That's more than the number of people who watched Ruben beat Clay for the American Idol crown.

Here on Earth, global warming is blamed on the increase of various *greenhouse* gases in the atmosphere. On Venus, the overwhelming presence of CO₂ sets up a *runaway* greenhouse effect. Here's why. Planets receive energy from the Sun. Much of this energy is radiated back from the surface and escapes into space. But gases like CO₂ absorb some of the energy preventing its escape.

The greenhouse effect warms the atmosphere and therefore the planet. Earth's atmosphere is only about 0.036% CO₂, yet there is

concern that even small increases due to human activity may be causing the average temperature on Earth to rise.

Now imagine the greenhouse effect on Venus. It's closer to the Sun with about 260,000 times as much CO₂! We don't have to imagine. We know. The average temperature on the surface of Venus is about 467 °C (873 °F)—higher than the melting point of lead (Pb).

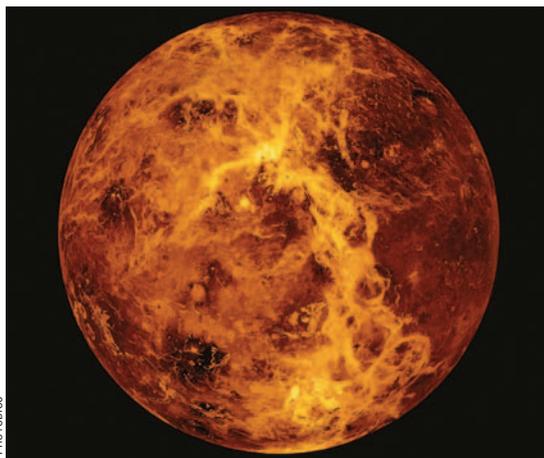
Like Earth, Venus has clouds. In fact, it is so covered with clouds that they completely obscure its surface. But don't look for our fluffy, white, water-droplet variety. Scientists think that at some point in its past, water was plentiful on Venus, but it all boiled away. The clouds on Venus are mostly sulfuric acid (H₂SO₄)! Huge volcanic eruptions release sulfur dioxide (SO₂) gas that is converted to the strong acid by photochemical reactions in the upper atmosphere.

Mars

Compared to Venus, Mars looks downright inviting. But hold off making your travel plans just yet until you've heard more about its atmosphere.



MARS ODYSSEY MISSION / NASA/JPL UNIVERSITY OF ARIZONA/AMLI



PHOTODISC

Wrapped in a dense layer of atmosphere, Venus gives new meaning to the term “greenhouse effect”. NASA’s 1990 Magellan mission used radar to penetrate the clouds and map these surface features. Colors used in this image and in the Mars image at the right are used to enhance the features; they do not represent the colors you would see using an ordinary light telescope.

Astronomers classify Mars as a planet that has an atmosphere, but compared to Earth, you might not notice. Atmospheric pressure on Mars is only about 1/100 that of Earth. Similar to Venus, Mars has an atmosphere of mostly CO₂ (95%) plus some N₂ (2.7%), Ar (1.6%), and small amounts of O₂ (0.15%), and water vapor (0.03%).

But Mars is much colder than Venus. It’s farther from the Sun, and it has a lower total concentration of CO₂—that adds up to almost no greenhouse effect at all. It has an average temperature around -63 °C (-81 °F) that varies with the seasons. Mars has winters and summers like Earth. During summer, local temperatures can get high enough to melt water, but it would quickly evaporate away at the low atmospheric pressure. Essentially, any water present on the surface is in solid form (see “The Search for Martian Water”, *ChemMatters*, Oct. 2002).

Mars is a cold and desolate place. And then there are the storms! The worst storms on Earth are only small disturbances when compared to what happens on Mars. Even a major storm on Earth only affects a specific region. Storms on Mars can encompass the entire planet. There is no escape! Huge dust storms scour the planet. Temperatures soar, then plunge as a storm subsides. Brilliant clouds of ice reappear.

The atmosphere of Mars won’t squish you like a bug on a windshield—recall Venus—but it’s no picnic either. At first glance, the Martian atmosphere seems so alien and different from Earth’s that it hardly seems relevant.

Why do we study other planets’ atmospheres?

It turns out that despite their differences, the atmospheres of Mars and Earth share some similarities. Both are mostly transparent to sunlight and are heated in similar ways—largely by infrared radiation that emanates from their surfaces. They exchange energy in a similar manner. But the climate on Mars changes more rapidly and drastically than it does on Earth. Its orbit is more elliptical than that of Earth. Its distance from the Sun varies by about 20% as it orbits once every 687 “Earth days”, about every two Earth years. It receives 40%

more sunlight at its closest approach compared to when it is most distant from the Sun. This causes rapid and significant changes in global temperatures, which produces those incredible storms.

Mars does not have oceans, unlike Earth, and because of this, study of the Martian atmosphere and climate is made much simpler. Oceans exert an effect on a planet’s climate that is very complex and difficult to predict. These complexities do not exist on Mars, making it easier for scientists to reach confident conclusions about what has caused various phenomena to occur.

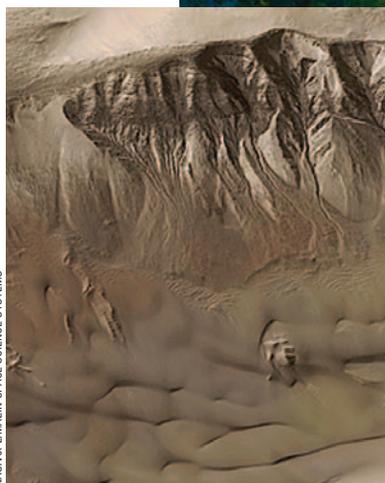
In one sense, Mars serves as a simpler natural laboratory where we can study and test various climate theories free from some of the complexities that affect the Earth’s atmosphere.

Mars of old

In the distant past, Mars may have had a more substantial atmosphere. Evidence for this comes from two different sources—geological and geochemical. The surface of Mars has erosional features that are similar to those created by rivers on Earth. It also has valley networks that look like river drainage systems. If that’s the case, then at some point, Mars must have been warm enough to support flowing water on its surface. The most proba-



Above: Without oceans, Martian weather patterns are easier to track. Here rapid heating and cooling produce incredible storms!



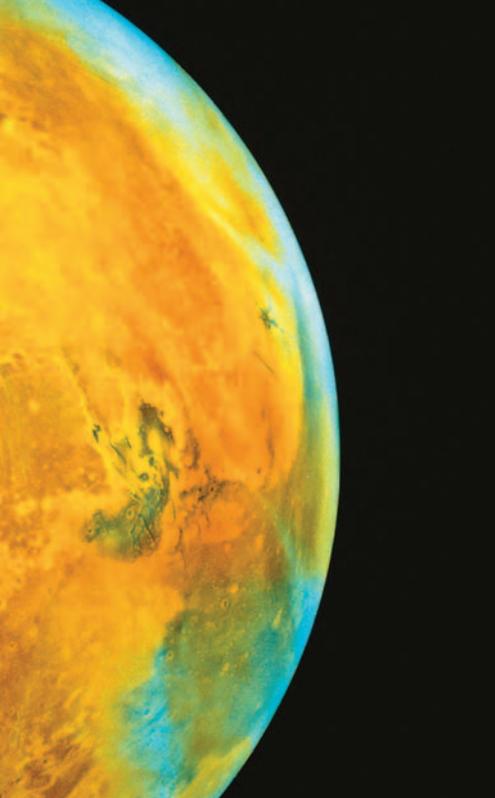
MARSAUPRIMA/IN SPACE SCIENCE SYSTEMS

Left: Mars Global Surveyor captured this image of gullies in a Mars crater at 42.4 degrees S, 158.2 degrees W. Patches of frost are visible on the crater wall

ble explanation for this evidence of water is that Mars may have had more atmosphere at one time.

Mars is also dotted with many impact craters. The older craters appear to be more heavily eroded than the younger ones. This is what we would expect if Mars had a more substantial atmosphere long ago than at present. Alternatively, the great amount of crater “erosion” may have actually resulted from “resurfacing” by lava flows and dust deposits, material that was ejected from later impacts. The jury is still out.

The geochemical evidence for an ancient atmosphere comes from isotope ratios in the present Martian atmosphere. You probably know that isotopes are atoms of the same element that differ in the number of neutrons. An atom with an extra neutron is a bit heavier. Mars is less massive than Earth. With less gravity, it is difficult for the planet to hold onto its atmosphere. If atmospheric gases were to escape into space, atoms and molecules of



How do Venus and Mars compare to Earth?



Venus

Earth

Mars

	Venus	Earth	Mars
CO ₂ (%)	96	0.036	95
N ₂ (%)	3.5	78	2.7
H ₂ O (%)	0.01	~1	0.03
O ₂ (%)	Negligible	20.9	0.13
Ar (%)	0.007	0.93	1.6
Surface temperature (°C)	464	15	-63
Atmospheric pressure (atm)	90	1	0.01
Wind speed range (km/hr)	1.1–3.6	0–360	7.2–108
Total mass (10 ²⁴ kg)	4.87	5.97	0.64
Equatorial radius (km)	6052	6378	3397
Surface gravity (m/s ²)	8.9	9.8	3.7

Source: NASA Planetary Fact Sheets at <http://nssdc.gsfc.nasa.gov/planetary/factsheet/index.html>

the lighter isotopes would tend to escape a bit more readily. This would mean that the remaining gases would contain a higher ratio of the heavier isotopes than is found on Earth. Such is the case for Mars. Isotopic ratios indicate that perhaps 90% of the Martian atmosphere has escaped.

There is still much to learn about the Martian atmosphere. In fact, as you are reading this, spacecraft are on their way to the Red Planet. The European Space Agency's first mission, Mars Express, is scheduled to enter a Martian orbit in December 2003. Part of the mission is to search the planet for water and probe the atmosphere for the presence of methane (CH₄). Because methane is destroyed by solar ultraviolet radiation and reaction with hydroxyl (OH) groups, the atmospheric lifetime of methane is only about 300 years. The presence of methane in the atmosphere would support the possibility that life exists there now.

NASA also has two rovers scheduled to land on the surface in early and late January 2004. These two 400-lb. mobile laboratories will land at very different locations to search for water and study the geological record. They can travel several meters across the Martian surface each day. These laboratories are expected to explore the surface of Mars until April 2004, or perhaps even longer. ▲

Frank Cardulla is special editions editor of *ChemMatters*.

The evolution of Earth's atmosphere

The air we breathe is mostly nitrogen (78%), oxygen (21%), some argon (<1%), and small but critical amounts of water vapor and carbon dioxide. But it wasn't always that way. The composition of Earth's atmosphere has changed dramatically over the past 5 billion years of its existence. But exactly how, when, and why remains a subject of debate and research.



Over the past 4 billion years or so, the amount of carbon dioxide appears to have dropped dramatically, while the amount of oxygen increased greatly. Indirect evidence for the change comes from what we know about stellar evolution. The Sun was about 30% dimmer 4 billion years ago. If the Earth's atmosphere had the same amount of CO₂ that it does today, the Earth should have frozen over. It didn't, so maybe CO₂ levels were higher.

Of course, other greenhouse gases such as methane (CH₄) or ammonia (NH₃) could also have provided this warming effect. One current theory argues that methane-producing ancient bacteria provided a continuous supply of methane to Earth's early atmosphere. Methane could have produced a significant greenhouse effect given that the greenhouse effect of methane is 23 times greater than that of carbon dioxide.

How did oxygen become so abundant? One theory credits an increase in photosynthesis—as plant life developed, carbon dioxide was consumed and oxygen generated. Another theory argues that early bacteria were capable of separating water into hydrogen and oxygen. The hydrogen escaped to space, whereas the oxygen was left behind. Who's right? We aren't sure. Perhaps neither theory is correct. But trying to find the answer is part of what makes science fun.



CLOUDS

By Anne M. Rosenthal

Clouds may blanket hundreds of square kilometers of marine sky or billow tens of thousands of feet above the earth. Despite these vast proportions, cloud formation actually depends on the presence of microscopic airborne particles.

In order to understand clouds, we need to think about the properties of one of earth's most abundant compounds: water. Within our atmosphere, water is the only substance that exists naturally as a gas, liquid, and solid. When it changes from water vapor—the gaseous form—to make liquid water droplets or solid ice crystals, the water molecules rely on help from tiny suspended particles, which serve as *condensation nuclei*.

On the surfaces of these tiny suspended particles, H₂O meets H₂O. As molecules continue to gather, weak hydrogen bonds form between them. The result of all this gathering and ordering is liquid water. Or if it's really cold, solid ice crystals or snowflakes form.

The temperature at which water vapor turns to droplets or crystals depends on how much water vapor there is in the air. For a given amount of saturation, water condenses at a temperature called the *dew point*. Sometimes, however, even though the dew point has been reached, nucleation particles may be lacking to initiate the phase change. As a result, nothing visible happens.

If more and more water vapor enters the air, for example by evaporation from a mountain lake, the air may become saturated. As the air cools, it may reach *supersaturation*, an overloaded state. Then, provide the water-

Finding your way out of a cave can be hard enough. Imagine if a dense “pea-soup” fog suddenly appeared! That’s what happened to the famous cloud scientist Vincent J. Schaefer as he was enjoying the refreshing waters of a cave pool.

In order to conserve flashlight batteries, his companion decided to light a lamp. But the air above the lake was supersaturated with water vapor! As soon as the match was struck, the water vapor condensed into a thick fog. Smoke particles from the match flame served as nuclei on which the fog droplets formed. Schaefer is given credit for inventing cloud seeding, a method for coaxing more rain or snow from clouds by dusting them with tiny particles.

laden air with minute particles, perhaps the exhaust from a passing vehicle and—PRESTO!—a cloud appears.

What types of particles contribute to cloud formation and exactly how minute are they? Sea salts are a major source of nuclei. Because of their water-attracting or *hygroscopic* quality, they can induce precipitation at temperatures above the dew point. Smoke, exhaust, soil, and even meteoritic dust contribute to cloud formation. Most of these particles have diameters less than one micrometer—that's about 0.0001 cm or 0.00004 inches.

Meteorologists know that increasing ice crystal formation within supercooled clouds results in increased precipitation. Weather modification companies apply a synthetic version of this phenomenon by seeding clouds with dry ice (solid carbon dioxide) or silver iodide (AgI) crystals. For relieving drought conditions, the process has met with only limited success; however, it has proved useful in dissipating cold fogs that might otherwise shut down airports.

*I've looked at clouds from both sides
From up and down, and sideways
It's cloud illusions I perceive
I really don't know clouds*

When you're lying back in the grass on a balmy day, clouds passing by might resemble ponies or even monsters—"cloud illusions", as the song says. However, it's helpful to know the scientific names too, since each type of cloud has its own interesting characteristics.

While scientists differ on exactly how clouds should be categorized, here's a classification system that is often used.

Blanket-like clouds that form thick layers are called *stratus clouds*; when they occur at ground level, we call them fog. As rain clouds, the prefix "nimbo" meaning "precipitating" is added, resulting in the term "nimbostratus."

Associated with dreary days of continuous rainfall or snowfall, nimbostratus clouds tend to be dark, low storm clouds.

Cumulus clouds, also known as heap or lump clouds, may be small fair-weather puffs dotting the sky as far as the horizon. They can also become the immense blackened *cumulonimbus* clouds jutting into the upper reaches of the troposphere, the layer of Earth's atmosphere closest to the surface. The bases of these giant storm clouds, usually at 4000-5000 feet, define the point where the air is cold enough for water to condense; the tops of these clouds touch the stratosphere, where winds may further sculpt their crests into characteristic anvil shapes.

Within these cumulonimbus giants lie numerous convection cells that feed on the heat produced when water vapor condenses. Think for a moment on how "hot-and-sweaty" after a workout quickly becomes "cold-and-clammy" as your sweat evaporates into water vapor. The opposite process occurs when water vapor changes to droplets or crystals: Heat is produced. Since hot air rises, pockets of air where condensation is occurring rapidly move upward within a cloud.

These updrafts are the beginning of a chain reaction. As the air pocket rises, it expands in the thinner air and cools.

This cooling triggers further condensation, which in turn heats the pocket. Heating ensures the pocket's continued buoyancy. As it continues its climb skyward, the pocket cools, more water condenses, and the cloud builds further.

Storm clouds and lightning bolts

Lightning sizzles throughout these large clouds as static electricity produced by the constant movement of materials within the

Nimbostratus clouds mean dreary days.



cloud discharges. When a large negative charge collects on the underside of the thundercloud, it induces an opposite charge known as an "electric shadow" on the ground below. As negative charges move downward from the cloud on a zigzagging path or "stepped leader", positive charges begin to travel upward from the earth's surface, often making use of a conductor such as a tree or a metal antenna—or even a person. Lightning flickers as opposite charges meet, and electricity travels along the stepped leader. So hot is a lightning bolt that it heats the surrounding air to temperatures greater than those at the sun's surface. Thunder is the shock wave produced as the air quickly expands from the heat and then contracts once the lightning has passed. On a single day, the thunderstorm-prone state of Colorado may receive 10,000–15,000 lightning strikes!

Besides lightning, thunderclouds often bear numerous other hazards. Ice, repeatedly coated with water and tossed to freezing heights within the cloud, drops as hail when it becomes too heavy for upward drafts to bear. Fierce downbursts can produce winds blowing over 100 miles per hour when cooler air drops suddenly from the storm cloud toward the ground. In the United States, about 1% of severe storms—those producing winds at least 58 miles/hour, hail at least 3/4 inch in diameter, or heavy rainfall—spawn tornadoes, rapidly spinning columns of air that become visible when they carry dirt and debris.

Besides the nimbostratus and nimbo cumulus clouds, another precipitating cloud is the icy web or cirrus cloud. These feathery clouds, generally composed of ice crystals, form at altitudes over 23,000 feet. Their precipitating tails are called *virgas*, which means that the precipitation never reaches the ground, but instead evaporates, changing back into water vapor.

Clouds may take particularly interesting shapes. Some of the frantic reports about aliens from outer space about to land spaceships on earth may well be related to sightings of lenticular clouds—clouds typically occurring leeward of mountain ranges when fast-moving winds tumbling over the peaks develop isolated air pockets. As the pockets move upward and cool off, "flying saucer" shapes can condense out.

Contrails— Streaks in the sky

In today's world, not all clouds result from natural causes. A significant contributor of clouds are jet airplanes, which leave linear



clouds called condensation trails, or "contrails", in their wake. Contrails form when exhaust from jets flying above 30,000 feet cools rapidly in the subzero reaches of the upper troposphere and lower stratosphere. Water vapor and liquid water droplets within the jet exhaust precipitate almost instantly into ice crystals. Additionally, the tiny particles present in the exhaust seed clouds from water vapor in the surrounding atmosphere.

Although contrails often fade quickly from the sky, the opposite is also true: Some contrails have staying power. The narrow

both sides now,
still somehow,
I recall,
clouds, at all.

Joni Mitchell (1969)

CORBIS

PHOTODISC



High, feathery cirrus clouds reflect heat back to the surface.

linear cloud tracing the airliner's path may tear into wispy cirrus or widen to a sheet of cirro-stratus clouds. Observing contrails helps us to understand a portion of our atmosphere where it is difficult to use weather instruments. Contrails are more likely to form and linger in air already saturated with water vapor.

An important aspect of clouds is their reflectivity of sunlight. Like cirrus clouds, contrails block rays that would otherwise warm the earth's surface. On the other hand, they trap radiant energy emitted by the ground, retaining heat in the atmosphere. Scientists aren't sure exactly how the equation adds up—whether contrails help cool or heat the earth's atmosphere.

A research opportunity arrived in September 2001 when commercial jets were temporarily grounded in the United States following the terrorist attacks. Atmospheric scientist David J. Travis at the University of Wisconsin-Whitewater reported in the journal *Nature* (August 8, 2002) that the average difference between daytime and nighttime temperatures during the three-day period when jets and their contrails were absent was one Celsius degree larger than normal. This occurred even though ranges for the three-day periods immediately preceding and following the hiatus were smaller than normal. The data bolstered the view that contrails may be affecting the earth's climate.

Cloud research

To help answer questions about cloud reflectivity and the trapping of infrared heat, NASA has launched two instruments called

CERES (Cloud and the Earth's Radiant Energy System). The first instrument orbiting the earth on NASA's EOS Terra satellite consists of three telescopes. The first telescope measures how much solar radiation is reflected, while the other two are sensitive to longer-wavelength infrared radiation.

The second instrument launched on NASA's EOS Aqua satellite carries similar telescopes. Because Terra flies over the equator at about 10:30 a.m. and Aqua flies over at 1:30 p.m., tropical clouds are observed at two different times of day. The separated times provide an opportunity for scientists to observe how clouds build.

Then at night, Terra and Aqua cross the equator at 10:30 p.m. and 1:30 a.m. respectively. In the darkness, they continue to measure infrared radiation. Taken together, the two instruments provide better coverage of the planet than a single instrument and make it easier to study variations in earth's energy balance between day and night.

Another important area of NASA cloud research is related to ozone depletion or "ozone holes" over the two polar areas, which has left high-latitude populations especially vulnerable to increases in UV radiation and skin cancer. It is the ozone layer in the stratosphere that absorbs much of the damaging ultraviolet light and makes life on earth possible.

The primary culprits in ozone destruction are CFCs, or chlorofluorocarbons. These human-made chemicals were produced for many years as effective spray-can propellants, refrigerants, solvents, and blowing agents for plastic foams. CFCs were initially

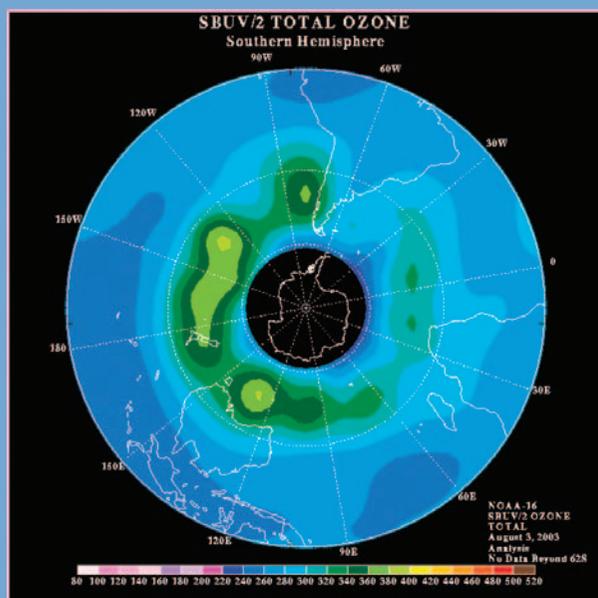
promoted because they were stable and, therefore, safe for use at the ground level. However, it was this very stability that made them dangerous over the long term. Their persistence made it possible for CFCs to rise into the stratosphere. There, solar ultraviolet radiation splits the CFC molecules, releasing ozone-destroying chlorine. Mounting evidence of the role of CFCs in destroying ozone led to unprecedented international cooperation to phase out the use and production of the chemicals by industrial nations in the 1987 Montreal Protocol and its amendments.

But why is ozone most likely to be depleted over the Earth's poles? And why do "holes" appear and disappear? The answers to both questions may be in the clouds.

The complete story of ozone depletion involves a type of cloud called a PSC, or polar stratospheric cloud. Normally, the air over the poles is so dry that clouds don't form. But during the polar winters, temperatures become extremely low and ice crystal clouds form from the minute amounts of water vapor present in the stratosphere. The surfaces of these ice crystals are sites for chemical reactions that produce *free radicals*. Chemists define these as atoms or molecules that contain a single unpaired electron—a feature that causes them to be extremely reactive. Unfortunately, some of these reactions result in the destruction of ozone.

The seasonal appearance of ozone holes at the South Pole is further explained by long periods of light and darkness. Since ozone destruction is dependent on UV radiation, it doesn't occur until daylight reappears.

SOURCE: NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION / NATIONAL WEATHER SERVICE. WWW.NWS.NOAA.GOV



This map shows the August 2003 Southern Hemisphere total ozone from the Solar Backscattering UltraViolet (SBUV/2) instrument on board the NOAA polar orbiting satellite. In austral spring the analysis shows the "ozone hole" (values below 220 Dobson Units) over Antarctica and the Antarctic Ocean. This area of low ozone is confined by the polar vortex. Usually circular in August and September, the vortex tends to elongate in October, stretching toward inhabited areas of South America. By November, the polar vortex begins to weaken and ozone-rich air begins to mix with the air in the "ozone hole" region. The "ozone hole" is usually gone by late November/early December. The SBUV/2 instrument cannot make observations in the polar night region because it relies upon backscattered sunlight. The blackened area centered over the pole represents the latitudes in which no observations can be made.

Land masses tend to deflect and divert winds into vertical north-south pathways. With little land-mass interference in the Southern Hemisphere, air circulates in a strong circumpolar or "horizontal" fashion. At the South Pole, the strong circulation creates a *vortex*, a whirlpool of air which prevents warm northerly air from reaching the pole. As a result, the stratosphere over the South Pole becomes very cold—cold enough to allow the formation of PSCs which accelerate the catalytic destruction of ozone. When the vortex weakens in the late spring, the ozone depleted air disperses in the atmosphere.

Ozone depletion in the Southern Hemisphere was the first to capture scientists'

attention. Then, during the 1999–2000 season, scientists observed record ozone losses of 70% over the Arctic. NASA's Arctic campaign, involving over 350 scientists from around the world, studied the problem during

the winter of 2003 with a combination of satellite instruments, measurements from aircraft, remote sensing, and research balloons, as well as ground-based instrumentation.

What interests atmospheric scientists the most is whether we're making any progress with our efforts to save Earth's fragile ozone layer. Is the Montreal Protocol having any effect? Or are there already so many ozone-destroying chemicals on the loose that the risk is spreading? Finding these answers may be the focus of many NASA missions to come. NASA's EOS Aura mission scheduled to launch in early 2004 will gather the most accurate information on chemistry and dynamics to date. With four instruments on board, Aura will orbit the Earth from pole to pole gathering ozone data 24 hours a day. ▲

Anne M. Rosenthal is a science writer from the San Francisco Bay Area. Her most recent *ChemMatters* article, "Nanotechnology—The World of the Super Small", appeared in the December 2002 issue.

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Activity

**“Nature is a mutable cloud,
which is always and never
the same.”**

Ralph Waldo Emerson (1803–1882)

By Bob Becker

We’ve all done it: lain back on a grassy hillside staring up at a multitude of puffy white clouds—one looking like an elephant, the next like Abraham Lincoln. But how often do we stop and consider why clouds form in the first place?

We know that clouds comprise small suspended droplets of water and that they have a great influence on weather patterns. But what causes their appearance and subsequent disappearance in the sky overhead? The following activity will enable you to make your own clouds in a plastic bottle and then to explore some of the factors responsible for their formation.

Safety:

Use standard precautions for any use of open flames. Strike match on safety strip; be sure the area is free of flammable material; wear safety goggles in the laboratory; be sure to have fire extinguishing equipment handy.

You will need:

- One empty 2-L soda bottle, preferably colorless, rinsed out, and allowed to dry
- 50 mL of room-temperature tap water
- One match
- One dark-colored backdrop such as a black tabletop or notebook cover
- Safety goggles

What to do:

1. Remove the label from the bottle to ensure an unobstructed view. Screw the cap on to the bottle securely. Then, using a dark backdrop to provide greater contrast, squeeze the bottle and release three to five times near the bottom as you observe the air space in the upper portion of the bottle. Since nothing has been added to the bottle, this can serve as a control for future observations.
2. Now remove the cap, and pour in 50 mL of water. Screw the cap back on

securely and swirl the water around inside the bottle for 10–15 seconds. This should ensure that the air inside the bottle is well saturated with water vapor. Or, in other words, that the inside humidity is 100%. Now, repeat the squeezing technique used in step 1. What do you observe inside the bottle after the repeated squeezing?

3. Remove the cap again. In one hand, hold the bottle sideways with a slight upward tilt. In the other hand, take a lit wooden match and insert it partially into the bottle. Immediately give the bottle a quick squeeze to extinguish the match. You should see a small amount of smoke from the match trapped in the bottle. Withdraw the match, screw the cap back on, and set the bottle upright. Repeat

the squeezing technique used in step 1. What do you observe inside the bottle when you squeeze? When you release the squeeze?

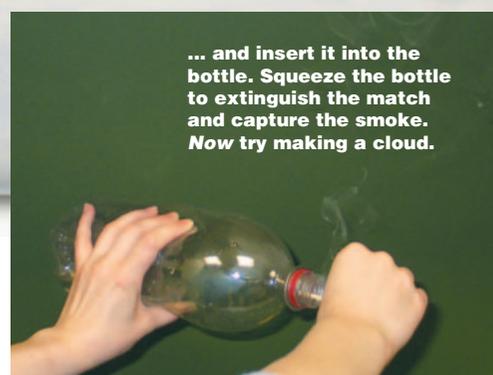
What’s going on?

Although you couldn’t tell from looking at it, there were two important changes occurring when the air-filled bottle was squeezed in **the first trial**: (1) a substantial increase in pressure, which should be obvious, because you were decreasing the volume of the bottle by squeezing it, and (2) a slight increase in temperature, although you probably didn’t observe this change. This happens whenever a gas is compressed in this fashion.

When the squeeze is released, the gas molecules suddenly occupy a larger volume. Again you probably didn’t notice it, but there was a slight decrease in



Cloud in a Bottle



STAFF PHOTOS

temperature. This type of cooling is quite noticeable whenever you let the air out of a pressurized tire. It cools off quite substantially, and the valve stem can become quite cold. When you increase the pressure in a tire, the exact opposite occurs.

During **the second trial**, you introduced water vapor. As you might imagine, the amount of moisture that air can hold greatly depends on the temperature; the higher the temperature, the more water evaporates. 100% humidity at 32 °C (90 °F) translates into twice as much moisture content in the air as 100% humidity at 20 °C (68 °F). Thus, when the bottle was squeezed and the temperature increased slightly, so did the moisture content of the air as the water at the bottom and on the sides of the bottle evaporated a bit more. When the squeeze was released and the temperature

dropped slightly, that extra vapor had to condense back into a liquid.

Water condenses best when it has a place to condense. The only surfaces available were the sides of the bottle and the water layer at the bottom. The total amount of moisture condensing would have been just a fraction of a drop, so this evaporating and condensing went pretty much unnoticed.

Then in **the third trial**, you introduced smoke into the bottle: not much—probably only a few millionths of a gram—but enough to create microscopic condensation sites throughout the bottle. This time when the squeeze was released and the temperature dropped, the water could condense onto the smoke particles and form miniscule water droplets suspended throughout the bottle. In other words, it formed a *cloud*. When the bottle was resqueezed

and the temperature went back up, these droplets evaporated, but the smoke particles were still there, and so the whole process could be repeated. Eventually, the smoke precipitates out—onto the sides of the bottle or into the liquid layer below—and the cloud effect wears off.

In our atmosphere, clouds

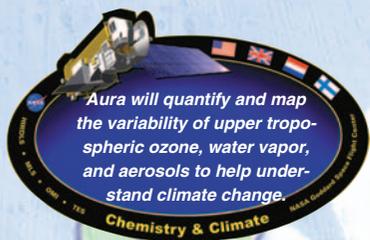
can form whenever warm moisture-rich air comes in contact with cooler air. There, the tiny dispersed solid particles—referred to as aerosols—act as nucleation sites for cloud formation. Although they are quite small, these particles can have huge effects on global climates and weather patterns.

Further investigation

The water you used in this activity was at room temperature. Experiment with water at a variety of temperatures and see what effect it has on the cloud formation. Also try other sources of condensation sites such as smoke from a candle, chalk dust, talcum powder, etc. Does the size and type of particle make a difference in cloud formation?

Using a slide projector or strong flashlight, shine some bright light through the bottle. Have the room as dark as possible and view the bottle from various angles. The scattering and diffraction may cause different colors to emerge, and these colors can change over time as the clouds in the bottle start to thin out.

Reprints of this activity may be purchased by calling 1-800-635-7181, ext. 8158.



Life
in
a

Greenhouse

**Hot out?
Blame it on the
greenhouse
effect.**

You've probably heard about the greenhouse effect and how it has something to do with global warming. And despite your thoughts last January, all of that sounds like bad news.

The greenhouse effect on the planetary scale is actually a good thing—a *very* good thing. Scientists estimate that without some surrounding greenhouse gases, the Earth's average temperature would be a freezing $-18\text{ }^{\circ}\text{C}$ ($-0.4\text{ }^{\circ}\text{F}$). Tucked inside our security blanket of heat-absorbing gas molecules, we enjoy an average global temperature of $15\text{ }^{\circ}\text{C}$ ($59\text{ }^{\circ}\text{F}$), and it's rising!

"Greenhouse" is an interesting term for our planetary arrangement. If you've ever wandered through one of those glassed-in greenhouses on a bright sunny day, you were probably happy when the tour was over. Plants appeared to be thriving, but the air temperatures you felt were well above your comfort zone.

The explanation behind a greenhouse effect is actually pretty clear—transparent, in fact. Greenhouse gases allow light to enter, but are far less transparent to the lower-frequency light reflected back toward the atmosphere by objects warmed by the sun.

Light is described as waves of radiant energy with various frequencies and wavelengths. The most abundant molecules in the atmosphere, nitrogen (N_2), oxygen (O_2), and argon (Ar), compose 99% of the atmosphere and offer only minimal obstacles to the passage of radiant energy. As far as those molecules are concerned, radiant energy can pass through in either direction.

When radiant energy strikes the earth, much of it is absorbed and the surface gets hotter as a result. Warm objects emit radiant energy with a set of wavelengths that are collectively called infrared (IR).

For certain molecules in the atmosphere, the frequency of the radiant energy they encounter makes an enormous difference. For these so-called *greenhouse* gases, some frequencies in the IR region of the spectrum are absorbed temporarily before being re-emitted, often in a direction that sends the IR right back where it came from—the warm surface of the earth.

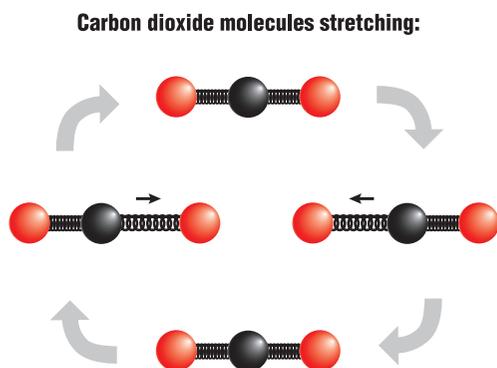
What determines whether an atmospheric gas is an IR energy absorber? You might be able to come up with a hypothesis yourself if you take a close look at the formulas for these non-greenhouse gases— N_2 , O_2 , and Ar; and then a look at the formulas for a few greenhouse gases— CO_2 , O_3 , H_2O , and CH_4 . Notice something interesting? Hold that thought!

The fact that molecules are in motion is nothing new to you. That's what explains liquid rising in a thermometer, the smell of fresh bread coming out of the oven, and steam rising from a kettle. But what you might not know is that individual molecules move in another way. They stretch and bend with a kind of vibration unique for each molecule type.

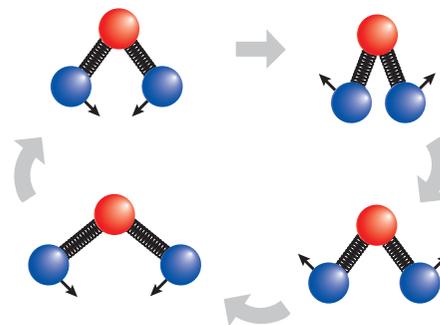
All molecules vibrate, greenhouse and non-greenhouse gas molecules included. Likewise, all molecules are made up of atoms with positive charges centered in the nuclei. When atoms bond together, their collective electrons form a negatively charged cloud surrounding the whole molecule.

When a molecule consists of only two atoms, the only way it can vibrate is for the bond connecting those two atoms to expand and contract. If the two atoms are the same, as in N_2 or O_2 , then this symmetrical stretching motion leaves the positive and negative charges evenly distributed. Isolated atoms, like Ar, cannot vibrate at all.

But for molecules with more than two atoms, there are lots of possible ways that the molecule can stretch, bend, or wiggle. Although some of these vibrations may not distort the charges, there are always some that do. In these, the electron cloud first concentrates more negative charge in one direction before swinging the negative charge in another direction—and then back again.



Water molecules bending

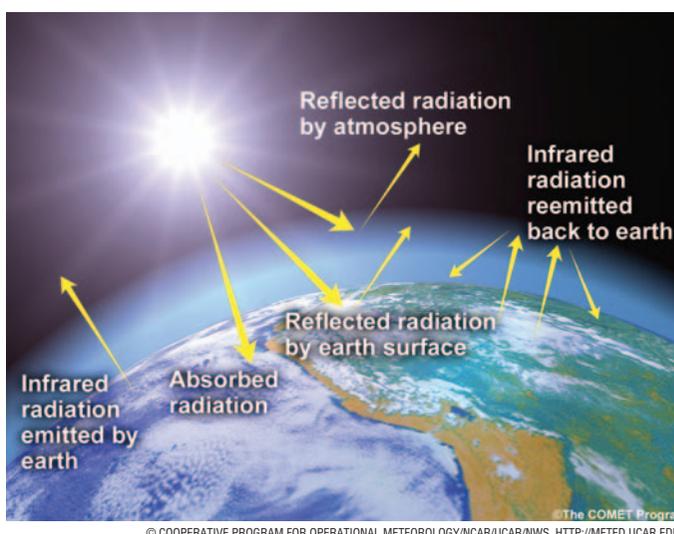


What does this have to do with energy capture? The shifting charges for each of these mixed molecules occurs at a certain frequency. If the frequency happens to match that of radiant energy in the region, the molecule, with its charges already oscillating at that frequency, absorbs that energy in much the same way that someone pushing a swing with just the right frequency adds to the motion of that object.

The earth's warm surface emits the right frequencies of IR for our greenhouse gas molecules. Although they differ slightly in their preferences, these molecules absorb and re-emit IR energy as they stretch and bend.

So, if the gases re-emit the energy, why is there a net warming effect at the earth's surface? Think about a game of ice hockey. The puck skims off in one direction only to be struck with equal force by another player. It may maintain its movement at the same speed, but the direction has changed.

The energy that the greenhouse gas re-emits has a good chance of being directed back down to the earth's surface, or in any other random direction for that matter.



All but about 30% of the solar energy striking our planet gets through the atmosphere to the surface. The other 30% is either reflected back into space by clouds, or in the case of ultraviolet light, absorbed by our fragile layer of atmospheric ozone. Even at the surface, some light is reflected, but much of the energy is absorbed and later radiated as heat.

Greenhouse gases

Any molecule that vibrates as it absorbs IR is a potential greenhouse gas. But that's where the similarities end and the differences begin. Greenhouse gases vary widely in their effectiveness at absorbing IR. Some excellent absorbers are, fortunately, not very abundant in the atmosphere. But their presence bears some careful watching since a little goes a long way toward retaining heat at the earth's surface.

Greenhouse gas	Relative effectiveness	Abundance in troposphere (%)
Carbon dioxide (CO ₂)	1 (assigned value)	3.6×10^{-2}
Methane (CH ₄)	30	1.7×10^{-3}
Nitrous oxide (N ₂ O)	160	3×10^{-4}
Water (H ₂ O)	0.1	1
Ozone (O ₃)	2000	4×10^{-6}
Trichlorofluoromethane (CCl ₃ F)	21,000	2.8×10^{-8}
Dichlorodifluoromethane (CCl ₂ F ₂)	25,000	4.8×10^{-8}

SOURCE: CHEMISTRY IN CONTEXT: APPLYING CHEMISTRY TO SOCIETY, AMERICAN CHEMICAL SOCIETY © 2000

The table above compares both the effectiveness and the relative abundance of some well-known greenhouse gases in the earth's troposphere—the lowest atmospheric layer in which we live and breathe. For the sake of comparison, we'll assign a "1" to the effectiveness of carbon dioxide (CO₂). Then, we'll assign a "1" to the abundance of water (H₂O), since it is the greenhouse gas that makes up nearly one percent of the tropospheric mix.

Now, let's take a look at each of these greenhouse gases, realizing as we do so that they act together to form a climate-warming effect as they interact with the earth's systems.

Water

We mentioned water making up about 1% of the troposphere, but we didn't mention that it is unevenly distributed around our planet—more concentrated over warm bodies of water and equatorial forests, less over the poles and stretches of deserts. Although gaseous water is an effective IR absorber, its total presence in the atmosphere gives us a mixed bag of effects. Water droplets in clouds can actually work in two ways. Depending on the location and the type of cloud, water in lower-altitude clouds is good at reflecting incoming light of all wavelengths back into space, thus shielding the earth. The opposite is true of higher clouds. Their net effect is to trap outgoing IR radiation on its way out of the atmosphere.

Carbon dioxide

Carbon dioxide may not be the most effective greenhouse gas on the chart, but its collective abundance in the atmosphere results in the capture and retention of nearly half of the outgoing energy in the peak IR wavelength region of the spectrum. Carbon dioxide does not typically react with other molecules in the atmosphere. As a result, it forms a stable gaseous mantle, its concentration tapering off gradually with increased altitude.

Like water, carbon dioxide is intimately involved with all living and formerly living matter on the surface of the planet. In preindustrial eras, atmospheric CO₂ mainly cycled in and out of this biosphere, as plants took in CO₂ to make complex carbon compounds and all living things returned the gas as the organic carbon molecules were consumed. Add forest fires and the occasional volcano eruption to the picture, and you have the historical outlines of the earth's carbon cycle.

Not all carbon dioxide returned directly to the atmosphere. Over many eons of earth's history, deposits of plant and animal remains settled in bogs and other areas where decay organisms failed to thrive. As millions of years passed, these remains formed vast energy-abundant deposits. Today, we're completing that interrupted carbon cycling by burning these deposits of oil, natural gas, and coal as fossil fuels. In doing so, we rapidly reload the atmosphere with enormous quantities of carbon. In fact, current estimates show that industrial countries release one metric ton (1000 kg or 2200 lb.) of carbon per person, per year as a result of fossil fuel consumption. In developing countries, the release rate is about one-tenth as large, but it is growing.

Searching for the sinks

To learn more about the rates at which the earth releases and *sequesters* (stores) its carbon, scientists are actively measuring the carbon dioxide levels at numerous global sites. Measuring concentrations during various growing seasons and at various temperatures, light intensities, altitudes, and humidities, they are beginning to uncover some interesting riddles.

The earth as a whole is actually sequestering more carbon than expected.

The search for natural carbon *sinks* is on. A carbon sink is a location at which the net effect is in favor of removing more carbon from the atmosphere than is being released. Although tropical rain forests are known to absorb enormous amounts of CO₂ as the abundant plants carry out photosynthesis, they are not proving to be the carbon sinks that scientists once predicted.

Rain forest scientists Deborah and David Clark and their research team recently reported some unexpected findings in the April 25, 2003, online version of the *Proceedings of the National Academies of Science* (PNAS). They shared data showing that when equatorial temperatures surpass a certain mean, tree growth and CO₂ intake actually slow down.

If tropical forests are not the important sinks once thought, where might others be located? Currently, northern forests called *boreal* forests and colder areas of the ocean are under study for their contributions—now thought to be significant.



PHOTO: DISC

Tropical forests are CO₂ absorbers. But are they "sinks"?

Can we make our own sinks? A more radical line of research investigates ways to use technology for sequestering carbon dioxide. For the past 30 years, oil companies have been injecting pressurized CO₂ into wells in order to enhance their pumping capacities. Although much of this CO₂ comes from carbon dioxide-filled pockets that are already underground, the technology might be applied toward devising strategies for draining off some excess carbon from the atmosphere.

The United States Department of Energy is conducting geological surveys for locating rock formations with underlying briny water deposits into which CO₂ might be injected. But extreme care must be taken to find stable sites for this potential use. An abrupt release of CO₂ like the one from volcanic Lake Nyos in the African country of Cameroon in August of 1986 can have deadly consequences. The Lake Nyos disaster released 1 billion cubic meters of carbon dioxide in one blast, silently killing 1724 people and countless cattle and other animal life over a 24-hour period. (See "The Lake Nyos Disaster" in the February 1996 issue of *ChemMatters*.)

Other greenhouse gases

Carbon dioxide and water are literally facts of life on earth. Their cycling in and out of the atmosphere is only partially under human control. The remaining greenhouse gases appearing in the table may be on the increase, but at least they have this going for them: Because we know how they got there, we can probably do something to control their rate of increase in the troposphere.

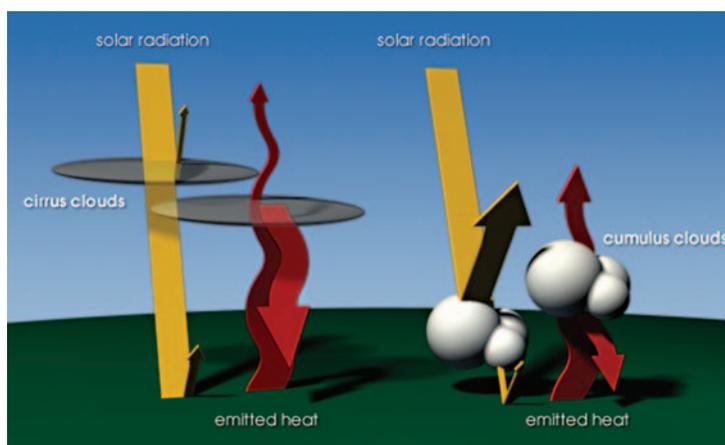
Methane, currently present in the atmosphere at 1.7 ppm, has increased to more than twice its level of preindustrial times. A part of the natural "exhaust" from the digestive systems of animals, additional methane is generated by our modern human activities. Petroleum refining releases vast quantities; decaying organic matter in garbage dumps, and large herds of grazing animals are all sources over which we have some control.

Ozone, a molecule known for its dual reputation in the atmosphere is also an effective greenhouse gas. Most of the news about ozone is discouraging. In the stratosphere where it is needed for absorbing incoming UV light, it is decreasing. At the same time, it is increasing at ground level as a result of the complex chemical interac-

tions of transportation exhaust chemicals on hot sunny days. Its presence in the resulting photochemical smog is blamed for various health problems and material damages.

As if that isn't bad enough, ozone's effectiveness as a greenhouse gas, particularly noticed in the higher troposphere, is 2000 times greater than CO₂. Scientists hope that with the widespread use of alternative fuels and better transportation options, tropospheric ozone can be controlled. In fact, many of these measures are already stemming the crisis. Modest attempts to reduce ozone pollution in the United States have resulted in small reductions over the past few decades despite the huge increase in total vehicle miles driven.

The two **chlorofluorocarbons (CFCs)** listed in the table are extremely effective greenhouse gases and are clearly of human origin. Unfortunately, once CFCs are released into the atmosphere, they stay there for a long time. Add that to their IR-absorbing capacities, and you have a dangerous greenhouse gas, even at low concentrations. Today, the net effect of CFCs on global warming is small. Their collective greenhouse gas effect is partially balanced by their infamous



Clouds have different effects depending on their altitudes. Near the surface, they reflect light. High above, they reflect heat back to the surface.

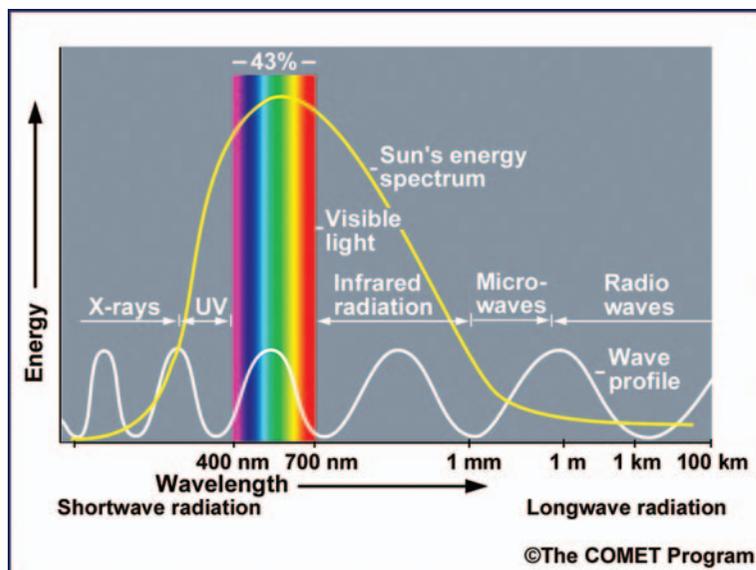
appetite for stratospheric ozone. By reducing ozone's greenhouse effect, they in turn partially cancel their own contribution to global warming. But their ozone destruction comes at a terrible price. Without Earth's thin layer of protective stratospheric ozone, people are at risk for skin cancers and other ailments caused by increased exposure to damaging UV radiation.

Controlling CFCs is already well under way, as the result of the Montreal Protocol, which banned their production in developed countries after 1995. Once valued as effective coolants for refrigeration, CFCs have been replaced by less hazardous alternatives. As a result, they pose much less of a threat to global climate than they did 10 years ago.

As our global population continues to increase, the human contributions to these gases, largely from the burning of fossil fuels, continues to rise. At this time, scientists are resigned to a warming earth over the next century regardless of how we limit our use of fossil fuels. Public policy attention is shifting in the direction of coping with all-but-certain climate changes at the same time that we attempt to slow the rate of warming. ▲

Helen Herlocker is administrative editor of *ChemMatters*.

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Chemistry in the Sunlight

By Jeannie Allen

Our lives are wholly entwined with the sun. We depend utterly on sunlight for light and warmth. Changes in the sun's energy output kick off a myriad of important biological changes, from a monarch butterfly's migration to the ripening of fruit on an apple tree.

The awesome power in sunlight streams down on us at a variety of wavelengths. Different wavelengths of light carry different amounts of energy and so impact us in different ways. The shorter wavelengths carry more energy, and some are energetic enough to initiate chemical changes in the air we breathe.

Different wavelengths of sunlight impact us in different ways. For example, in the upper atmosphere, ultraviolet radiation at wavelengths smaller than 242 nanometers can split molecular oxygen (two atoms bonded together) into atomic oxygen (individual atoms). Then when some of these energetically excited individual oxygen atoms encounter molecular oxygen, they can bond to form three-oxygen molecules called ozone.

Ozone packs a punch in our lives that's out of proportion to its low concentrations in the atmosphere. It acts as hero or villain depending on *where* it is. Ozone far above us in the upper atmosphere (stratosphere) absorbs and protects us from deadly ultraviolet radiation; however, in the lower atmosphere (troposphere), where we live, the toxicity of ozone makes its presence undesirable. It is the active ingredient of air pollution commonly known as smog. Ozone reacts easily with biological tissue, donating oxygen atoms in the process known as oxidation—not a good thing!

Breathing too much ozone over time results in something like a slow burn inside our lungs. Over time, it lowers human lung capacity and causes illness and, for a few people, it causes death. Whole forests and fields of crops respond to ozone overexposure with reduced productivity.

If having too much ozone around is so bad, why do we put up with it? Unfortunately, one by-product of our dependence on the use of fossil fuels such as coal and oil is the production of tropospheric ozone. If we want cleaner air, we have to control our consumption of these fuels, either by using them more efficiently, switching to alternative sources of energy, or both.

Left photo: Solar ultraviolet (UV) radiation (invisible to us) drives the chemical reactions that produce ozone in both earth's upper atmosphere (stratosphere) and its lower atmosphere (troposphere).

To control anything, it helps to know how it works. Most of the ozone in the troposphere forms with two groups of chemical compounds: nitrogen oxides (NO_x) and volatile organic compounds (VOCs). VOCs consist of carbon-containing gases and the gaseous vapors emitted from volatile materials such as gasoline. NO_x and VOCs occur both naturally and as by-products of fossil

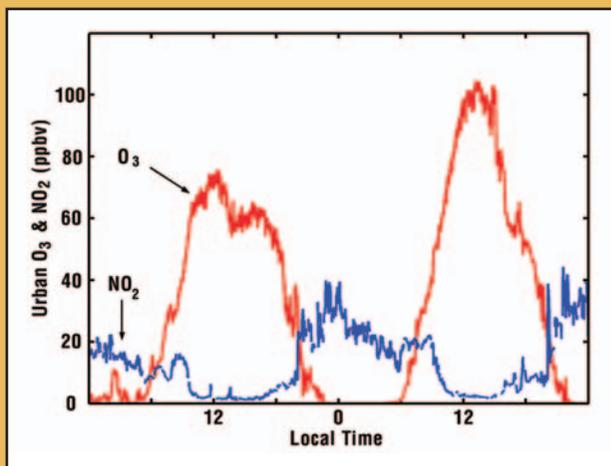
fuel combustion. Carbon monoxide also plays a role in some ozone formation reactions. Sunlight must be present for ozone to form, hence the term, photochemical smog.

Nitrogen oxides (NO_x). Nitric oxide (NO) and nitrogen dioxide (NO_2) are together known as NO_x and often pronounced “nox.” Sources of NO_x include lightning, chemical processes in soils, forest fires, and the inten-

Ozone amounts vary in space and time

The amount of ozone in the air around you depends, in part, on where you are on the earth's surface. Assuming the presence of NO_x and VOCs, the more direct the angle of sunlight, the greater its intensity, so the more ozone tends to form. Places closer to the equator tend to harbor more ozone in the lower atmosphere. Another thing to think about is that ozone formation takes place over time, and winds can carry air parcels far downwind of NO_x and VOC sources. If you live in a rural area, you may be breathing more ozone than people in some urban areas. It all depends on what's going on upwind from you (where your air comes from).

Ozone concentrations also vary through time. The highest concentrations generally occur during summer, when sunlight is most intense. On a 24-hour timescale, as industrial and motor vehicle activity rises throughout the morning, concentrations of NO_x and VOCs also rise. Ozone concentrations therefore reach their maximum shortly after the peak in vehicle traffic, about noon or soon thereafter. But downwind from urban areas, ozone may peak later in the afternoon or even after dark. After sunset, no sunlight initiates ozone formation, so ozone concentrations fall as ozone reacts with other chemicals and settles onto various surfaces.



Measurements of nitrogen dioxide (NO_2) [in blue] and ozone (O_3) [in red] show rise and fall over a 48-hour period. Because NO_2 participates in O_3 formation, its peak concentration does not coincide with peak O_3 concentrations. Ozone concentration peaks during hours of maximum sunlight, around the middle of the day.

COURTESY OF WILLIAM BRUNE, PENNSYLVANIA STATE UNIVERSITY, EARTH SYSTEMS SCIENCE CENTER



Without sunlight initiating ozone formation, nighttime ozone levels fall as it reacts with other compounds and settles on various surfaces.

PHOTODISC

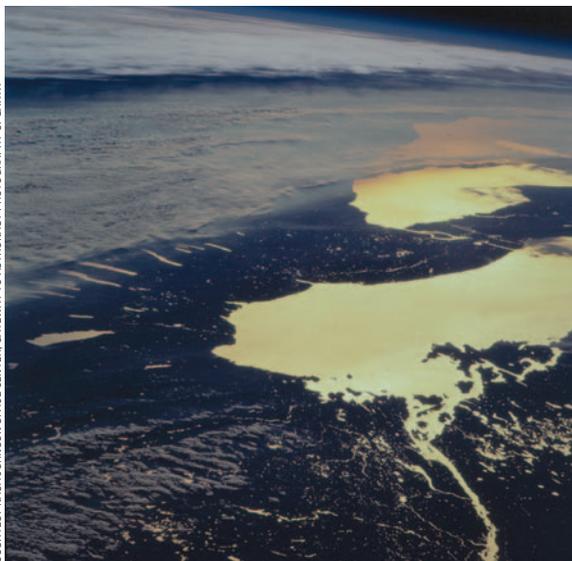
tional burning of vegetation to make way for new crops (biomass burning). NO_x emissions also come from smokestacks and tailpipes as by-products of the combustion of fossil fuels (coal, oil, and natural gas) at high temperatures. Coal-fired power plants are the primary sources of NO_x in the United States. Automobiles, diesel trucks and buses, and nonroad engines (farming and construction equipment, boats, and trains) also produce NO_x .

Volatile organic compounds

(VOCs). Volatile organic compounds, such as hydrocarbons, vaporize easily. Some plants emit VOCs, and some bacterial processes in soils also produce VOCs. The smell of a pine forest comes from a hydrocarbon called alpha-pinene. VOCs also come from gasoline combustion and from the evaporation of liquid fuels, solvents, and organic chemicals, such as those in some paints, cleaners, barbecue starter, and nail polish remover.

Atmospheric chemists should be given hero awards for even being willing to tackle ozone research, because it is maddeningly complex. NO_x and VOCs together include about 120 different chemical compounds, and hundreds of chemical reactions can take place. Some of the participating chemicals may be intercepted part of the way through the process by reactions with other chemicals in the atmosphere and may form intermediate compounds that act as temporary reservoirs for varying amounts of time. Many of the chemicals involved have very short lifetimes before they react with other chemicals to form new compounds.

An additional challenge arising for anyone seeking to track ozone-forming reactions is that they involve interactions between dif-



COURTESY NASA/JOHNSON SPACE CENTER, GATEWAY TO ASTROPHYSICS PHOTOGRAPHY OF EARTH

The STS-92 Space Shuttle astronauts photographed upstate New York at sunset on October 21, 2000. The view looks toward the southwest from southern Canada and captures a regional smog layer extending across central New York, western Lake Erie and Ohio, and further west. Winds bring ozone and some chemicals that participate in its formation to rural areas downwind of emission sources. Ozone itself is invisible.

ferent phases of matter (gases, liquids, and particles known as aerosols) and can occur on various kinds of aerosol surfaces in the atmosphere. Changing environmental conditions such as air temperature and humidity also affect ozone chemistry.

Formation of ozone at ground level has some parallels with stratospheric ozone formation. Again, the key step involves photochemical formation of oxygen atoms, this time from NO_2 . Because the N–O bond in

NO_2 is weaker than the O–O bond in O_2 , longer-wavelength UV light is sufficiently energetic to lead to formation of atomic oxygen, which can then combine with molecular oxygen to form ozone.

VOCs are not directly involved in ozone formation, but they play a crucial role in regenerating NO_2 from NO and oxygen, in a complex series of reactions, some of which are catalyzed by the hydroxyl radical (OH). The details of these reactions vary with the exact nature of the VOCs present. The ratio of NO_x to VOCs determines the efficiency of the ozone formation process.

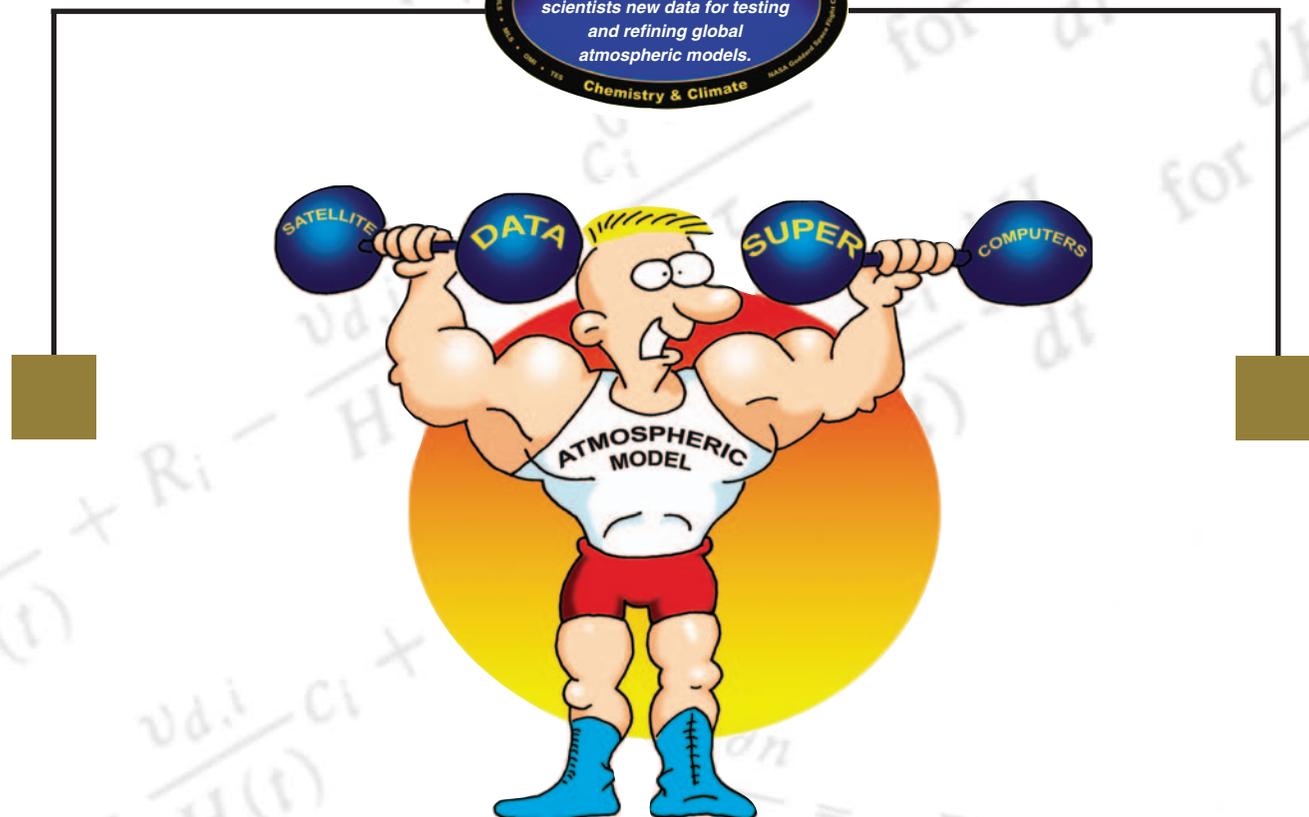
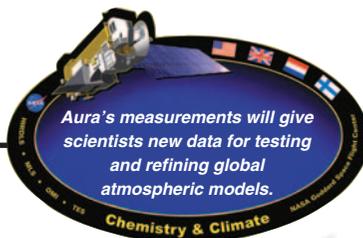
As if it wasn't complicated enough, scientists don't have a good understanding of the chemical reactions taking place after the sun goes down. Without sunlight initiating ozone formation, ozone levels fall as it reacts with other chemicals and settles onto various surfaces. Data from some recent nighttime sampling missions over Boston and Portland suggest that some pollutants might significantly decrease nighttime ozone levels.

"We don't have a good idea about what's going on at night," said one lead researcher. "And if we don't understand what goes on at night, we can't have confidence that we know the best way to fight smog during the day."

For scientists willing to tackle ozone research, the problem promises to be maddeningly complex for years to come. ▲



Jeannie Allen is a writer for NASA Goddard Space Flight Center in Greenbelt, MD. She is a frequent contributor to the Earth Observatory, NASA's award-winning website at <http://earthobservatory.nasa.gov>.



BEEFING UP ATMOSPHERIC MODELS

*“A model is just a mathematical description
of our physical understanding”*

—Daniel Jacob, atmospheric chemist at Harvard University

Models. Now there's a word that might figure into one of those personality-type tests. Read “model”, and what do you think of? Tall, slim, *very* fashionable types “walking the walk” on a runway? The very latest version of the Corvette? Small rocket kits you assemble and launch? The extra-credit project you made in eighth grade?

Let's add another idea to the model mix: *mathematical* models created by scientists to describe atmospheric processes. Although they seem complex to most of us, scientists depend on them to simplify their understanding of atmospheric processes. Describing how a great many factors

combine to affect our global climate, models allow scientists to make predictions.

How good is a model at making predictions? It is only as good as the information on which it is based. Until recently, models were weakened by the limited means for collecting measurements and by a lack of a computing power.

In fact, it wasn't too long ago that atmospheric chemistry models were the scientific equivalent of 98-pound weaklings. The other sciences with more easily obtained laboratory data would kick sand in their face at the beach—it wasn't pretty. But satellite observations and supercomputers are changing all that.

Mathematical models

So, what does a mathematical model look like? You probably rely on mathematical models without thinking about it. Just imagine what it takes to estimate the time a long car trip will take. Let's say your destination is 1000 kilometers away and your average speed will be about 100 kilometers per hour. You don't anticipate traffic. You plan to make three stops lasting about 20 minutes each. After a little calculation, you realize the trip will take 11 hours. This is a simple mathematical model.

If you insist that a model has to be something with moving parts that you construct with materials, you could have built an elaborate small-scale *physical* model—complete with a moving car. But in this case, why bother? The effort would have been time consuming, and you had your information without lifting a paintbrush or a bottle of glue.

Now let's suppose that instead of estimating the time it takes for your car trip, you're wondering about other things like, How warm will the Earth be in 25 years? What will be the status of the ozone layer in 10 years? Will smog increase in my hometown? Is annual rainfall likely to increase?

Even if you haven't asked these questions, you are probably glad that *someone* is asking them. They're important! Concerned about the environment, you understand the value of recycling and the need to protect the local water supply from potential hazards of a new landfill. But when it comes to adding relatively small amounts of odorless and invisible gases to the atmosphere, it's hard for us to see the harm.

Models help us make the connections between our behavior today and long-term global consequences.



A BIG question

Chemistry is the study of matter and its transformations. So it makes sense that the fundamental question atmospheric chemists ask is “What is the chemical composition of the atmosphere and what kinds of transformations is it undergoing?”

Ultimately, many climate and pollution issues are reduced down to a question of how the concentrations of certain chemical species vary over time. What is the collective concentration of greenhouse gases? What will their concentration be in 50 years? What is the concentration of ozone in the stratosphere and on the ground? What is the concentration of pollutant *x*?

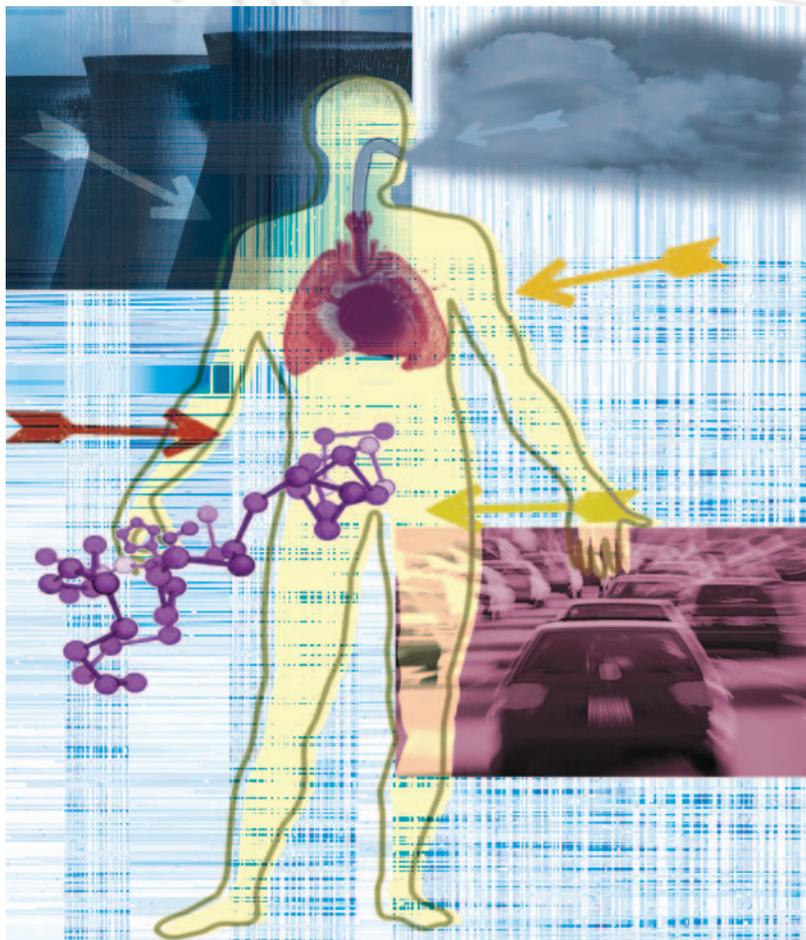
Before constructing an atmospheric model, scientists have to consider factors that will affect the concentrations of chemical species in the atmosphere. What goes into the air? What comes out of the air? How does it move through the air? Does it undergo any chemical transformations?

Some key factors getting a lot of attention from atmospheric modelers are these:

Emissions. Every process that adds chemical species to the atmosphere is an emission. Boiling water on a stove and evaporation from the ocean add water to the atmosphere. Burning fossil fuels for energy and decomposing plant materials add CO₂. Notice that some emissions are the result of human activity. Our ability and willingness to control these *anthropogenic* (human-made) emissions is the subject of many public policy debates.

Deposition. This time, we are talking about taking chemicals out of the atmosphere. Examples include uptake of CO₂ by plants during photosynthesis and a variety of chemical processes, some under human control, that trap and deliver some chemical species—including water itself—back to land and sea.

Transport. How does a species travel in the system? Like most gaseous mixtures, the atmosphere is not a homogenous or static system. Chemical species can and do travel at different speeds. As a result, they are unequally distributed throughout our atmosphere.



Chemistry. Think of the atmosphere as a huge reaction vessel, a reaction vessel filled with nitrogen, oxygen, water, carbon dioxide, and hundreds of trace chemical species. Chemical species can react with each other to form new products. The products, in turn, can react to create still more compounds.

What transformations are taking place in the atmosphere? To answer that, you'd need to know the chemicals present and the conditions under which they are reacting. Chemists are familiar with these *descriptive* models. First, they make a model based on what is known. Then they compare its predictions with experimental observations—laboratory results or even spectral data observed by satellite. If the results do not match the predictions, the model requires some adjustment. The goal of any good model is to improve the agreement of its predictions with observations.

Some of the *simplest* models that atmospheric chemists prepare are those that describe and predict the concentration of trace gases over small regions and short timescales. But even these models can require a computer to solve anywhere from a few dozen to a hundred simultaneous equations that include as many as a hundred chemical species.

Mathematical models quickly become even more complicated as additional factors are brought into the picture and as the region and timescale examined are expanded. These systems and the equations used to describe them are frequently chaotic, meaning that arbitrarily small differences in the initial state can lead to arbitrarily large differences in the final state. Perhaps the most complex of these models are the coupled atmosphere–ocean general circulation models (AOGCMs). AOGCMs are three-dimensional global models that represent the toughest problem of all—climate. They include equations that take into account the role of oceans, land vegetation, weather, and many other factors.

Models that predict future climate changes are arguably the most complex. They are also the ones with the greatest potential value. Predicting the future is extremely important, but it is a much trickier exercise than describing the present. For one thing, you don't have data to check your predictions against—they are, after all, in the *future*. Furthermore, any small errors in the model are potentially magnified by the number of years you project into the future. Inevitable problems arise when you base your predictions of the future on the data you gather today.

The first atmospheric modeler?

Better known by chemists and some chemistry students for the Arrhenius concept of acids and bases and his work on the behavior of solutions, Svante August Arrhenius also took an interest in the role of CO₂ in global warming.

A visionary of his time, he realized that our increasing reliance on fossil fuels would continue to increase atmospheric CO₂ levels. He was also aware of the role of CO₂ as a greenhouse gas. From this idea, he developed a simple mathematical model that predicted that doubling the amount of CO₂ in the atmosphere would raise global temperatures by 5.49 °C. Taking into account the CO₂ output trends at the time, he assumed it would take 1000 years to double CO₂ levels.

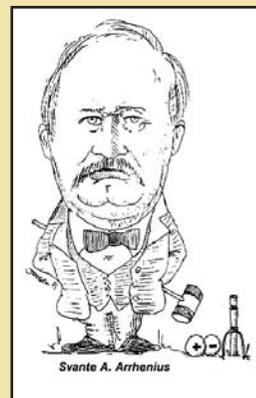
The year was 1896. Would his prediction hold up over time?

Over the next 100 years, CO₂ levels increased 23%—a much a larger increase than he had foreseen. One reason: in 1900, there were fewer than 10,000 cars on the road worldwide and many were electric. Today, there are hundreds of millions of vehicles on the road.

Given this new CO₂ concentration, Arrhenius's model predicts about 1.5 °C increase in global temperature. Average temperatures went up by only 0.59 °C. What happened?

Although his calculations were fairly accurate for just CO₂, his model was just too simple. For one, it didn't include complex processes such as increased cloud formation that cool the earth and modify the effect.

Don't be too hard on Arrhenius for his "weak" model—if he had been given access to a supercomputer and today's satellite and directly measured data, who knows what he might have come up with?



Hungry for data

So what "beefs up" a model and makes it useful? Harvard atmospheric chemist Randall Martin puts it this way: "We are VERY hungry for data." That's because global measurements, especially in remote areas, have been hard to come by. Even when they've been taken, it is difficult to get a feeling for how the various components change over time.

Having plenty of reliable data is also important in reducing both the number and type of assumptions made in the models. For example, when modelers use the model to forecast the concentration and location of chemical *x* on a particular date, it is helpful to know the actual concentration of *x* at the present time. With good data, they minimize errors by refining the model.

Beefing up! It's the computers ...

When making a forecast, modelers test their models by running simulations on powerful computers. In many ways, these simulations are similar to video games like SimEarth or WarCraft that let you change conditions and then run automatically. Whether a village or fighting unit, elements of the game respond based on the mathematical results of equations. It's really just a mathematical model built into the programming game. Of course, the models behind games are built more for entertainment value than for their descriptive or predictive ability. One other thing, if you haven't noticed it, these games have gotten *way* cooler in the past 10 years. Games are faster and can include more detailed elements, in part, because computers have *way* more memory and speed.

Until a few years ago, it was both difficult and slow to make predictions based on complex atmospheric models. Using computers with limited speed, scientists were forced to oversimplify their models. Using the speed available on today's supercomputers, climate and atmospheric chemistry models are dramatically better at delivering solutions to complicated problems.

Some of the supercomputers now running models can perform trillions of simple calculations per second. At peak performance, Japan's new Earth Simulator supercomputer—modeling global environmental problems such as global warming, El Niño, and atmospheric pollution—can perform over 40 trillion operations per second (teraflops).

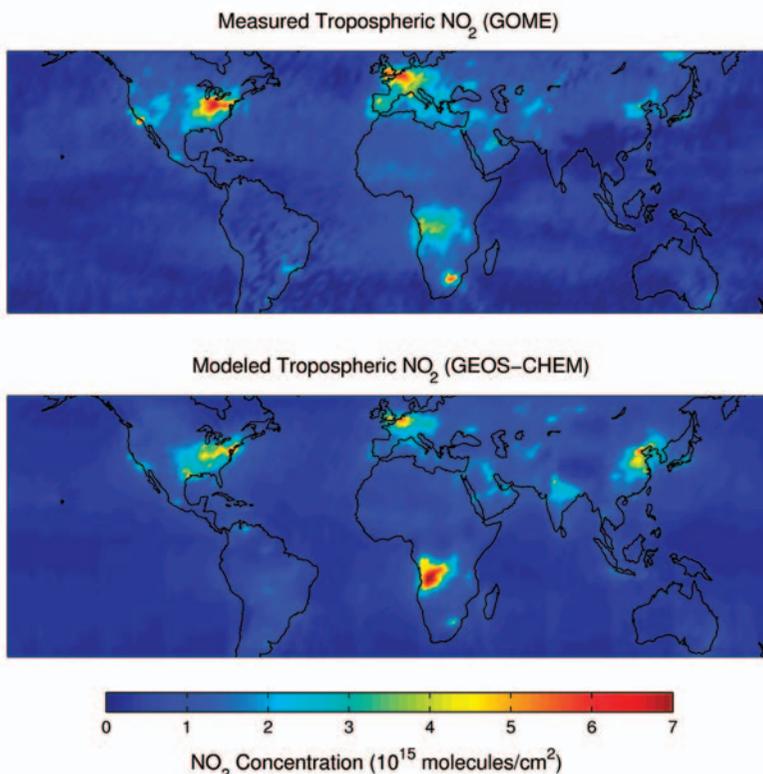
... and satellites that are driving the, uh, weight gain!

When NASA launches the Earth Observatory System Aura in early 2004, atmospheric modeling scientists will have a new tool for refining their models. The Aura satellite will carry an instrument package for making quantitative measurements of atmospheric ozone, water vapor, and other chemical species with state-of-the-art accuracy.

Among the fundamental questions Aura is designed to answer is "What is happening to the stratospheric ozone?" Currently, several models suggest that stratospheric ozone—that's the good ozone—is recovering, but it has not been confirmed by measurements. Are they correct? Aura will be able to track the global distribution of ozone and also the chemicals that participate in ozone formation.

"If we want to monitor compliance with international agreements on emissions," says Daniel Jacob, an atmospheric chemist also at Harvard, "It would be nice to observe the gases from space and detect rogue nations that are emitting more than they should."

Models are key to interpreting the data stream delivered by the



The GEOS-CHEM mathematical model of atmospheric chemistry successfully predicts concentrations of nitrogen dioxide, a compound involved in ozone's formation. In a comparison of actual observations for July 1996 by the European Space Agency's Global Ozone Monitoring Experiment (GOME, above) with the GEOS-CHEM model (below), geographic regions with high concentrations of nitrogen dioxide appear in yellows, oranges, and reds.

satellites. "A satellite is seeing a spectrum [of light] and you need to interpret this spectrum in terms of chemical concentrations in the atmosphere," says Jacob, "so what that means is that you have to say 'I think the atmosphere should look like this' and then I look at the spectrum. Does it fit with my knowledge?"

Particularly helpful are the two Aura instruments, the Ozone Monitoring Instrument (OMI) and the Tropospheric Emission Spectrometer (TES), which will view the same scene at the same time. "That's critical," says Martin, "because they'll both be using different techniques to monitor the same pollutant in some cases." Comparing the results will give the scientists a better handle on what the actual concentrations are.

"There's always a point in a science" says Jacob, "where the models can explain the observations. At that point, you say 'we don't need more observations'. But we're very far from that in atmospheric chemistry. We probably won't be there in my lifetime."

With many challenges ahead, it's an exciting time to become an atmospheric chemist. ▲

Kevin McCue is the editor of *ChemMatters*



The Earth Simulator Center

Taking on such problems as global warming, El Niño, and atmospheric pollution—the Earth Simulator can perform over 40 trillion operations per second.

Nobel Prize Winner Sherwood Rowland:

A C O N V E R S A T I O N



COURTESY OF SHERWOOD ROWLAND

Nobel Prize-winning chemist F. Sherwood Rowland probably never intended to be an environmental whistle-blower. But in the 1970s, when he and his postdoctoral associate Mario Molina at the University of California-Irvine studied a set of compounds called chlorofluorocarbons, or CFCs, they realized that they had uncovered a problem. They found that, if left unchecked, CFCs posed a serious threat to life on earth.

In 1974, they published their findings in the journal *Nature*. They reported that long-lived volatile CFCs, unreactive compounds here at ground level, gradually rise into the stratosphere. There in the presence of ultraviolet radiation, they set about destroying our thin protective shield of ozone molecules with an alarming chemical appetite. In fact, a single chlorine atom released from one of these molecules could destroy tens of thousands of ozone molecules.

Scientists from other countries extended the research. Paul Crutzen of the Max Planck Institutes in Germany studied nitrogen oxide emissions and warned of properties similar to CFCs. Finally, in 1987, world leaders ratified the Montreal Protocol, which effectively eliminated the use of CFCs after 1995—coincidentally, the year that Rowland, Molina, and Crutzen shared the Nobel Prize for their work in atmospheric chemistry.

Recently, National Chemistry Week Manager David Harwell asked Dr. Rowland to reflect on how his career in science developed. Was he always focused on science alone? His answers might surprise you.

DH: You started high school when you were only twelve! What was that like?

SR: A few years ago, after the Nobel award, someone sent me an old clipping from the hometown newspaper, the Delaware, Ohio, Gazette. It was mostly about my older brother who had done exceptionally well as a high school freshman on the Ohio State test in first year latin and had essentially aced the second year latin test as well. A footnote mentioned that his 7-year old brother had scored the highest mark among third



graders in the city. When school resumed in the fall, I was placed in the 5th grade.

I was always among the tallest in my age group, so I was not physically smaller than my classmates in high school—although they were on the average 2.5 years older. By my senior year, I was the tallest person in the school, but you must realize that this was when somebody 6'1" in a school with roughly 100–150 students in each grade could be the tallest. Then I grew another four inches in the next two years while in college!

DH: What sports did you play growing up?

SR: I played basketball and softball from a young age; I was a good player for my age group in basketball, but not for my class in school, so I was a nonplaying “scrub” for two years. I played JV in my junior year and varsity in my senior year, but was definitely not a star—just a player.

The basketball coach was a math teacher. In fact, he majored in math under my father at the local college, Ohio Wesleyan University. The coach persuaded me to take up tennis in the spring of my sophomore year, and I lettered in tennis in junior and senior years. I also lettered in debate in my senior year. I took part in extracurricular activities but was not socially active until after I entered college.

I think athletics were important for me in high school, although I was still in many ways a loner. After high school, I organized, managed, and played third base on a softball team. This was long before our present “Little League” era in which the adults organize and supervise what the kids do from pre-kindergarten on. During the summer after my second year in graduate school, I was the playing manager of the Oshawa Merchants, which won the semi-pro baseball championship of Canada that year.

People who play sports get a unique “non-ivory tower” experience when what you do every day is printed in the





newspaper the next day, along with comments about where you succeeded or failed or where your opponent did likewise—not to mention hearing it all on the local radio news. Question asked of a sports-playing scientist whose name had appeared in the newspaper: “What did it feel like when someone asked you for an autograph?” My response: “Do you mean, after I became a scientist?”

DH: Did you always want to be an atmospheric chemist?

SR: Atmospheric chemistry didn't exist as a subject when I was in graduate school. Radiochemistry—application of radioisotopes to chemistry—was very new in the immediate post-World War II period, and it had many applications.

As for my classes in atmospheric chemistry—I didn't take them; I taught them! I taught chemical kinetics in the 1950s and atmospheric chemistry in the 1970s. Radiochemistry was given at the University of Chicago by Professor Willard Libby, my research supervisor and a subsequent Nobel Prize winner (Chemistry, 1960) for the invention of carbon-14 dating. Since carbon-14 is produced in the atmosphere by cosmic ray bombardment, I became aware of the possibilities of applications of radioactivity outside the laboratory.

DH: Why did you focus on chlorofluorocarbons as the topic of your research?

SR: My research group had for several years used CFCs in the laboratory as “inert” targets for making radioactive chlorine and radioactive fluorine—although the fact that we used them as targets indicates they weren't completely inert. So when they were discovered in the atmosphere, I wondered what might happen to them there. The only chemicals my postdoctoral associate Mario Molina and I looked at initially were CCl_3F and CCl_2F_2 , two of the CFCs. Later on, of course, we looked at many others.

DH: Is teamwork important in your research? Is it ever more “comfortable” to work alone?

SR: One of the primary reasons, maybe the only one, for being a research scientist is to push yourself beyond your “comfort zone”. When you are asking questions for which you have reasonably good answers, then you aren't really doing experiments—you are just applying what you already know in a situation slightly different from before. Clearly, having a new idea sometimes arises from solitary thinking about areas of uncertainty. And sometimes it arises from interactions between colleagues.

Partnerships and collaborations bring together people with different backgrounds—or “comfort zones” if you want—and these different viewpoints may very well help you zero in on the correct answer to your new problem.

I had a small bit of experience in atmospheric chemistry, and Mario Molina basically had none when we began collaborating on the fate of chlorofluorocarbons. The problems were well outside both of our comfort zones.

DH: Did your life change after winning the Nobel Prize?

SR: Certainly! Every scientist grows up hearing about the achievements of Nobel Prize winners. But I think that it may have changed less for Crutzen, Molina, and myself than for many Nobel Prize winners because each of us had already become “public scientists”—scientists whose work had been described regularly on the front pages of the New York Times, Time Magazine, the New Yorker, People Magazine, and Rolling Stone; and on the TV networks. Because of the global importance of our work, we began receiving extensive media attention in the early 1970s, 20 years before being awarded the Nobel.

DH: Has the ban on the release of CFCs had any effect on the atmosphere?

SR: The first controls on the release of chlorofluorocarbons to the atmosphere were enacted in Oregon in 1975, and in the next year, for the entire United States, and thereafter for Canada and Scandinavia. After the discovery of the Antarctic Ozone Hole in 1985, the controls became international with the Montreal Protocol in 1987, and then, as modified later, with a total ban on the further manufacture and use of CFCs.

We know from the continuing measurements in the atmosphere that the countries of the world are obeying this ban, and the growth in CFC concentrations has stopped and has begun to reverse. However, because these molecules have long lifetimes in the atmosphere, they will still be measurably present for many decades. But the reversal has taken place already.

In fact, there are many simultaneous stories going on in the atmosphere, and if you study the amounts and locations of various gases, you can tune in on these stories. ▲

David Harwell is the manager of National Chemistry Week, a program of the Membership Division of the American Chemical Society.

The GLOBE Program:

Science in the Sunshine

It was the perfect idea for a science fair project, and Gianna D'Emilio had no trouble convincing several of her friends at the Edmund Burke School in Washington, DC, to help. Basically, they agreed to go out on the lawn and take air quality readings. They would go out every sunny day at a time when the NASA satellite Terra passed over the area to assess the amount of sunlight reaching the ground.

The commitment paid off when the group was 1 of 12 teams selected to present their findings at the 2003 GLOBE Learning Expedition held in Sibenik, Croatia, in early July. There, they met students and teachers from 22 countries who gathered to present their projects and to think about ways they could work together collecting more data for environmental research.

Gianna's initial idea was to find out how pollution affects the color of the sky. Her science teacher, Frank Niepold suggested that she begin by studying how aerosols, tiny airborne particles from a variety of natural and human-generated sources, affect not only sky color, but also weather and climate.



Gianna D'Emilio and Chris Hanawalt take aerosol measurements using a handheld sun photometer.

When Dr. David Brooks, a GLOBE scientist at Drexel University in Philadelphia heard about the project, he suggested another idea to Gianna and her team. How about validating aerosol measurements taken by a NASA satellite? While the satellite measured from the sky downward, simultaneous measurements made from the ground up would add value and meaning to the data.

GLOBE (Global Learning and Observation to Benefit the Environment) is an international organization of students and teachers who collect and share data about the health of the environment. In the United States, GLOBE is sponsored by several scientific and government agencies, including NASA, the National Science Foundation, the Environmental Protection Agency, and the State Department.

Brooks heads NASA's GLOBE Aerosols Monitoring Project in the United States. The project has developed an instrument called the GLOBE Sun Photometer and some *protocols*, or standard operating procedures, for its use in collecting Aerosol Optical Thickness (AOT) data.



COURTESY OF FRANK NIEPOLD, THE EDMOND BURKE SCHOOL, WASHINGTON, DC

The Burke team traveled to Croatia to present their findings at an international GLOBE conference. Pictured are Chris Hanawalt, Frank Niepold (teacher), Melanie Benatato, and Gianna D'Emilio.

Dr. Brooks explained how the instrument works in "Postcard from the Netherlands", a GLOBE report appearing in the September 2002 issue of *ChemMatters*.

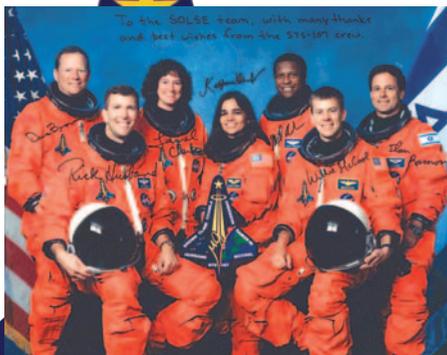
The team, including fellow student Jordan Glist and two recent Burke School grads, Chris Hanawalt and Melanie Benatato, met first to take the daily readings, and later to analyze data and write a report.

In the report "Assessing Satellite-Based Aerosol Retrievals and Ground Truth Validation for Terra's MODIS Sensor Over Urban Areas using the GLOBE Program's Handheld Sun Photometers", they explained that although the aerosol-measuring instruments on the EOS Terra satellite were able to make accurate readings over homogenous surfaces like oceans, they were less successful in making readings over variable terrain like urban areas. Thus, the nine months of simultaneous ground readings over Washington, while important, varied in their agreement with Terra's. The team sees their greatest accomplishment as successfully testing the instrument and establishing effective protocols. Another Burke team is being formed to continue the project when NASA's EOS Aura satellite launches in early 2004. With instruments on board designed to measure the vertical profile of aerosols using different wavelengths of light, Aura will add new and valuable data about global aerosol distribution.

Burke students hope to enlist the help of students whom they met at the recent 2003 GLOBE conference. A school in Bremen, Germany, is planning to take similar data this summer, and several other GLOBE participants are exploring partnership opportunities in the future.

You can read more about GLOBE and its many international research opportunities at the website www.globe.gov. ▲

D E D I C A T I O N



NASA shuttle mission STS 107 launched into a cloudless Florida sky on the morning of January 16, 2003. On board was a flight crew of seven shuttle astronauts ready to deploy more than 80 science experiments, many designed in part by students in the STARS program, a hands-on program involving students ages 11–21 in the adventure of space exploration. In fact, many STARS students were in the viewing stands, cheering as the clock ticked away the seconds before liftoff.

Less than two weeks later, the mission ended tragically with the loss of seven lives and much of the science that the crew worked so hard to bring back for sharing. A portion of the science was sent to ground in midflight. These valuable data are now part of the legacy of STS 107.

Among the many instruments on board, Columbia carried the Shuttle Ozone Limb Sounding Experiment-2 (SOLSE-2). The plan was to use this imaging spectrometer to test a new strategy for monitoring ozone change.

Currently, spectrometers flying on NOAA and NASA satellites look directly downward toward the Earth, which limits their ability to accurately measure ozone in the lower layers of the stratosphere. The new technology called “limb viewing” allows observation of the atmosphere from the side rather than straight down. From this perspective, the layers of the atmosphere appear like layers in a cake, giving instruments an especially good view of the lower stratosphere—the thin layer of

atmosphere containing Earth’s fragile supply of protective ozone.

The measurements made by the SOLSE-2 mission on the Space Shuttle Columbia demonstrated that the limb-sounding technique will work very well for monitoring ozone in next-generation satellites.

Although much of the data was destroyed, the crew did send data to Earth for about 15 minutes during each orbit of the mission. About 40% of the SOLSE-2 data is available—enough to demonstrate that the limb viewing technique was successful.

President George W. Bush honored the Columbia crew at a memorial service in Houston on February 4, 2003. His speech contained these words: “This cause of exploration and discovery is not an option we choose; it is a desire written in the human heart. We are part of the creation which seeks to understand all creation. We find the best amongst us, send them forth into unmapped darkness and pray they will return. They go in peace for all mankind, and mankind is in their debt”.

The October 2003 issue of *ChemMatters* is dedicated to the memory and the legacy of the Columbia crew:

Rick D. Husband, William C. McCool, Michael P. Anderson, David M. Brown, Kalpana Chawla, Laurel Blair, Salton Clark, and Ilan Ramon

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