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Where did all the oil go?

CIRES scientists investigate impact of Gulf Oil Spill on air quality

Acid discovered in smoke could pose serious health risks

City air ends up in pristine mountains, neighboring states

Bright city lights affect daytime air pollution

This issue

Background: The aurora borealis and a lidar create a fantastic lightshow in Sondrestrom, Greenland, at the SRI observatory. CIRES graduate student Ryan Neely installed a new channel on the lidar to enable it to make tropospheric water vapor profile measurements. The lidar also measures aerosols in the troposphere and stratosphere. Photo courtesy Ryan Neely

On the cover: Dark clouds of smoke and fire emerge as oil burns during a controlled fire in the Gulf of Mexico following the April 20, 2010, Deepwater Horizon oil rig explosion. Photo courtesy U.S. Navy/Justin Stumberg

1,000 ft.

Height of the Boulder Atmospheric Observatory in Erie, Colorado. In March and February 2011, CIRES and NOAA scientists gathered at the tower to study the chemistry of wintertime nighttime atmosphere. **Page 14**

"There is this molecule in smoke that we can now measure, and it is there in very significant quantities. There are also good reasons to believe that it can have serious health impacts."

—CIRES Fellow Joost de Gouw on the discovery of isocyanic acid in smoke. Read more about this hazardous chemical on **Page 8.**

Know your spheres

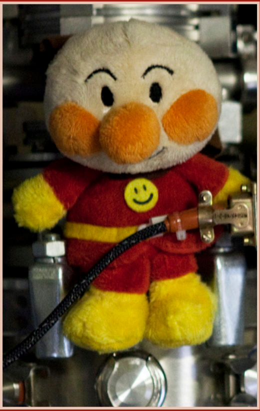
In which level of Earth's atmosphere does the ozone layer reside?

A. Mesosphere
B. Troposphere
C. Thermosphere
D. Stratosphere
E. Exosphere

Answer on page 12

In-flight snack

Anpanman is a popular Japanese anime cartoon character who possesses typical superhero traits, such as mega strength and the ability to fly. But Anpanman also has a head made out of anpan—bread filled with a sweet bean paste—and he allows anyone who is hungry to eat pieces of his face, which he then regenerates. So what does any of this have to do with atmospheric research? **Turn to page 20 to find out.**



New center advances study of aerosols

The new CIRES Center for Atmospheric Chemistry on the University of Colorado at Boulder campus will enable researchers to investigate another important issue pertaining to aerosols: their impact on the environment. "We know this is something important," said CIRES Fellow Jose-Luis Jimenez, interim director of the new facility. "The tools in this new lab will allow us to study these processes in greater detail."

While organic aerosols are linked to health issues, they can also have an impact on climate. The tiny particles scatter or reflect the sun's incoming rays and have a cooling influence on the Earth's surface. While scientists have built models to simulate this cooling influence, the differences between model results and measurements make it difficult to trust the predictions, Jimenez said.

"Resolving this uncertainty is critical to accurate predictions of future climate," Jimenez said. "We want to try to understand the sources and impacts of organic aerosols at the level of detail that allows us to confidently predict their amounts and effects 100 years from now."

The new center is based on a collaboration between CIRES and the Department of Chemistry and Biochemistry, and two new faculty hires are planned. It will house two 25m^3 chambers—large Teflon bags that will act as models of the atmosphere. Scientists will be able to place different chemical mixtures into the bags, shine light of different intensities onto the chambers and observe what takes place with a suite of advanced instrumentation, Jimenez said.

"There are very few similar facilities worldwide at that scale," Jimenez said. "The new CIRES lab will likely become one of the top three in the U.S."

What's in the mix?

Analyzing gases in the air provides valuable information for curbing pollution

Aerosols—those microscopic particles suspended in the air—might measure a mere fraction of the width of a human hair, but their consequences can be dire, according to CIRES Fellow and associate professor Jose-Luis Jimenez. "They affect health in so many ways," he said. "When people breathe in these particles, they can lead to heart disease, asthma or lung cancer."

In a quest to understand the origins and behavior of a particular type of aerosols—organic aerosols—Jimenez and his team used advanced instrumentation such as aerosol mass spectrometry to tell them about the mix of chemicals in the air at a site in Pasadena, Calif. Their month-long study was part of CalNex 2010 (California Research at the Nexus of Air Quality and Climate Change).

"In Los Angeles the air quality has improved a lot over the years, and the steps which have led to the improvement have been strongly guided by the results of these once-a-decade studies," Jimenez said. As scientists and policy makers have gained a better understanding of the causes of air pollution, they've initiated regulations such as requiring truck emissions to be cleaner and banning the use of certain solvents, he said. "But most of the low-hanging fruit has been taken, and although the air quality has improved substantially, it is still bad for you."

"Aerosols affect health in so many ways. When people breathe in these particles, they can lead to heart disease, asthma or lung cancer."

—CIRES Fellow Jose-Luis Jimenez

An important part of the mission of Jimenez' work, and of the larger CalNex study, is to shed light on the causes of air pollution, opening the way to further solutions, Jimenez said. And, even though it typically takes scientists a few years to analyze and interpret the data they collect in such studies, Jimenez and his team have already observed a surprising trend. "It is different from what we expected," he said. "We thought that since we were going to Pasadena, which is not far from downtown L.A., it was going to look nearly the same as when we are in the middle of a city, like in downtown Mexico City."

Instead of a replica of city air pollution, however, the scientists found the atmosphere was already "aged"—chemical reactions had majorly changed the mix of gases and particles, said Jimenez. Scientists typically thought that the mix of pollutants was relatively static and that, although it aged eventually, the process took a long time, he said. "But since the air only takes two or three hours to come from downtown L.A., the results suggest pollution ages very quickly in the atmosphere."

If the current observations are backed up by a full analysis of the data, it could influence the way that both scientists and policy makers address poor air quality, Jimenez said. They would no longer be able to think of the air people breathe in Pasadena as the same as being dominated by the direct emissions from cars, trucks and industry, he said. "So now it is different chemicals and effects that you need to worry about."

The lowdown on CalNex

CalNex 2010 is a major climate and air-quality study carried out in California by NOAA, the California Air Resources Board and numerous academic researchers including several CIRES scientists. "This was the biggest study looking at the intersection of air quality and climate so far," said CIRES Fellow Jose-Luis Jimenez. "For that reason, it was able to pull together a very large coalition of people who wanted to collaborate and a lot of resources."

In spring 2010, the researchers scrutinized the air over and around California by air, by ship and on ground sites at Bakersfield and Pasadena. Scientists will analyze and interpret this data over the next few years. Their scientific goals include understanding the origins of pollutants and greenhouse gases and the transport, reactions and eventual fates of those particles and gases.

CalNex will help decision makers understand the complicated interactions of air quality and climate—because policies to address one are likely to influence the other, as well. And the information gleaned should also prove useful for understanding air quality and climate in other cities and similar regions.

MySphere: A look inside NOAA's WP-3D aircraft. **Page 20**

Investigating the link between dairy cows and aerosols

It doesn't take a scientist to tell residents of California's Los Angeles Basin that cows cause air pollution—their noses can do that.

But CIRES scientist John Nowak might be able to tell them whether, along with the unpleasant smell, the ammonia gas coming from the dairy farms leads to more pollution down the line: pollution in the form of aerosols.

Scientists have often found one particular kind of aerosol—ammonium nitrate—in the L.A. Basin at levels more than 10 times higher than in Houston, another city suffering from air quality issues, Nowak said. This result is due to dairy farms in the region, which provide a large source of ammonia to an already polluted area, he said. But there are still many unknowns in the processes that cause ammonia from the dairy farms to increase aerosols, he said. "There is little information on the transport of ammonia and the effects on aerosols," he said.

To investigate this uncharted territory further, Nowak and his colleagues didn't just sit around dairy farms but took to the skies in NOAA's WP-3D airplane as part of CalNex 2010 (see page 2). "To my knowledge, we are the only ones who fly an ammonia instrument in the U.S.," Nowak said.

Surfing high above and downwind from the unsuspecting cows, they measured the concentrations of ammonia and nitric acid, which together can react to form ammonium nitrate aerosol. They also measured aerosol concentrations and composition. We need all four measurements to understand aerosol formation processes, Nowak said.

"That gives us a lot of unique data," Nowak said. "Now we have field data to test how aerosols are made in the atmosphere."

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Bright city lights exacerbate air pollution

The bright city lights of Los Angeles might attract aspiring movie stars, but according to CIRES scientist Harald Stark, they also contribute to one of the area's less favorable claims to infamy: air pollution.

"It turns out the light reduces the amount of air-cleansing agents at night," said Stark, who made this discovery on several nighttime research flights over the city in 2010 to measure air pollution levels and light intensities.

Each day, pollution from car tailpipes and factory towers pours into the air surrounding cities. Then each night a process in the atmosphere cleans up some of this murky mess: A chemical called a nitrate radical breaks down the chemicals that would otherwise have formed smog and ozone. But this wonder chemical only works in the dark because sunlight destroys it. And so, it turns out, does the glare from bright city lights.

"The lights may be 10,000 times dimmer than the sun, but the effect is still significant," Stark said. "And it

is important because it has the potential of influencing daytime pollution levels."

Stark's measurements indicated the energy of the nighttime lights slowed down nighttime cleansing by up to 7 percent and also increased the starting chemicals for ozone pollution the next day by up to 5 percent.

Fortunately, alternatives to turning the lights out to prevent their damaging effects do exist, Stark said. If more urban lights were pointed to the ground instead of toward the stars, less light would permeate the atmosphere, he said. "It is more efficient for cities to do that because they don't want to illuminate the sky," he said. "They want to illuminate the cities themselves."

One other, less practical, alternative also exists. Red lights don't destroy the radical to the same extent as the high-pressure sodium lights and metal halide lights that dominate city lighting. If cities replaced their current lights with red lights, they could mitigate the damage to the nitrate radical, Stark said. "But turning our cities red doesn't sound like a good idea," he said.

The phenomenon of urban lighting destroying the nocturnal cleaning agent is in no way unique to the bright lights of Los Angeles, Stark said. "L.A. is not the brightest spot in the U.S.," he said. "Las Vegas is brighter, and some of the East Coast cities are brighter too." The next goal of this research would be to investigate the effects of nighttime lights on cities in both the U.S. and worldwide, he said. "Many cities are close to their regulatory limits in terms of ozone levels," he said. "So even a small effect such as this could be important."

TheScience

The atmosphere's nighttime janitors—nitrate radicals—scrub the air clean of pollutants emitted during the day. But city lights can destroy these chemical cleansers, resulting in higher daytime ozone levels.

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Drifting dirty air

City air ends up in pristine mountains, neighboring states

What happens in Los Angeles doesn't stay in Los Angeles—at least when it comes to air pollution. When CIRES Fellow and NOAA scientist Mike Hardesty and his team flew the Twin Otter research aircraft over the mountain ranges east of the Los Angeles Basin, they found the city's ozone, a product of industrial emissions and vehicle exhaust, lifted up into the tree-decked hillsides.

"One might think the pollution is going to be all on the Basin floor down below," said Hardesty, one of the five-member flight team that included CIRES scientist Christoph Senff and NOAA scientists Andy Langford, Raul Alvarez and Robert Banta. "But you can also have high ozone in those nice forest parks on the slopes around L.A."

Surrounding forests and mountains are not the only regions tainted by L.A.'s poor air quality, Hardesty said. Based on their measurements and calculations, the scientists believe the elevated plume could have been responsible for high ozone levels at Canyonlands and Mesa Verde nearly 1,000km to the east. "So we are actually seeing the influence of the L.A. region in Utah and Colorado," Hardesty said.

The team travelled to Los Angeles during summer 2009 to look at the flow patterns of air from the L.A. Basin and to prepare for CalNex 2010 (see page 2). On several four-hour flights above the boundary layer—the layer of air immediately above the Earth's surface—the scientists used an array of cutting-edge instruments to map out the ozone and aerosol structure within the Basin.

Lidar measurements (see page 7) over the San Gabriel Mountains revealed some ozone funneled out of the boundary layer into the free troposphere—a phenomenon known as the mountain chimney effect. As the sun heats the mountain ridges, the air around them becomes warmer than the typical air temperature at the same elevation. This heated air then rises, pulling up air from below and some of the ozone with it.

As this pollution funnels into the free troposphere, winds can carry it to other states, Hardesty said. "In terms

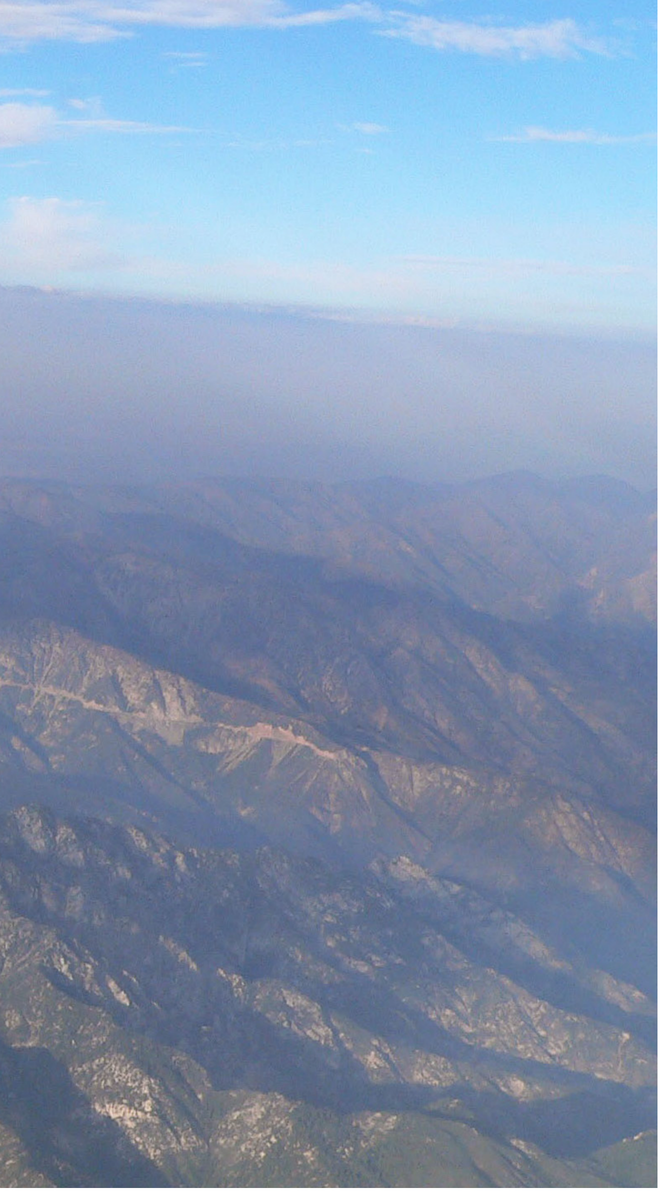


Photo courtesy Raul Alvarez, NOAA

CIRES Fellow Mike Hardesty and colleagues studied ozone levels in the Los Angeles Basin.

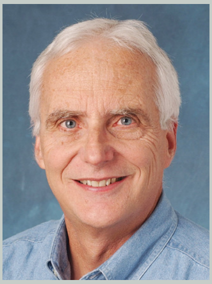
of the states having to conform to EPA regulations, some are very anxious to know how much of the air pollution is imported," he said. "You can't do much about the stuff that comes in."

The team followed up their study with further experiments as part of CalNex 2010. During both the 2009 and 2010 studies, the Twin Otter also boasted a new instrument to measure a variety of pollutants, including nitrogen dioxide, a key contributor to ozone formation. "By looking at the precursors as well as the ozone, we have a nice synergistic experiment that lets us look at some of the sources," Hardesty said.

In 2010, the team also added a small Doppler lidar to measure the winds in the boundary layer below the aircraft. Specifically, the team hopes to put some hard numbers on the movement of air pollutants flowing both up the sides of mountains and through the passes. "We have demonstrated that lofting happens," Hardesty said. "What we want to do next is quantify how much pollution lofts up into the free atmosphere during air pollution episodes."

How does a lidar measure wind and detect air pollution?

Scientists use LIDARs—LIght Detection and Ranging instruments—to detect aerosols and ozone and measure winds in the atmosphere. Lidars are similar to radars, but instead of using radio waves to make their measurements, they use laser light: They emit laser pulses into the atmosphere that are then scattered by air molecules and aerosols. Some of this scattered light returns to the lidars, where it is analyzed to determine wind velocity, detect aerosol layers and measure ozone concentration at several ranges along the lidar line-of-sight.



Lidars make use of the Doppler effect to determine average velocity of particles from which the light is scattered. Because of the Doppler effect, the wavelength of light scattered from particles moving toward or away from the lidar is slightly changed. By measuring the shift in wavelength of the scattered light collected at the lidar, the velocity of the particles can be estimated. Because the particles are very small and move with the mean wind, measuring the average particle velocity is equivalent to measuring the average wind velocity.

To measure ozone, the differential absorption lidar (known as DIAL) method is used. In the DIAL technique, laser pulses at two or more wavelengths are transmitted into the atmosphere, with the wavelengths chosen so that different portions of the energy from each wavelength are absorbed by the ozone along the paths. By looking at the difference in the amount of light at each wavelength, or color, that comes back to the lidar, scientists can calculate the quantities of ozone present in the atmosphere.

"Our ozone instrument is cutting-edge because it incorporates a solid-state laser that directly produces ultraviolet light," Hardesty said. The ultraviolet source has the advantage of being rapidly tunable so as to produce at a very high rate the different wavelengths needed for ozone measurements.

"Our ozone instrument is cutting-edge because it incorporates a solid-state laser that directly produces ultraviolet light."

—CIRES Fellow Mike Hardesty

Smoke hazards

New acid discovered in biomass burning

Burning cigarettes, blazing forests and cooking fires can fill the air with smoke, but with acid? CIRES scientists have found when biomass—trees or other plants—burns, it releases an acidic chemical, isocyanic acid (HNCO), not previously known to exist in smoke.

"There is this molecule in smoke that we can now measure, and it is there in very significant quantities," CIRES Fellow and research scientist Joost de Gouw said. "There are also good reasons to believe that it can have serious health impacts."

De Gouw and his colleagues were first able to detect isocyanic acid when they developed a new instrument, a mass spectrometer designed to measure gaseous acids in the air. In the laboratory, they found biomass burning produced levels of this molecule approaching 600 parts per billion by volume (ppbv).

In the human body, isocyanic acid dissolves to form cyanate ions, and the researchers found that the acid was very soluble at the pH level of human blood. This means it could potentially enter the bloodstream, de Gouw said. At exposure levels of isocyanic acid greater than 1ppbv, the cyanate ion is expected to be present in blood at levels that can contribute to a variety of health problems, such as cardiovascular disease, cataracts and rheumatoid arthritis.

The researchers discovered in controlled burns at the U.S. Forest Service Fire Sciences Laboratory in Missoula, Mont., that all biofuel types produced the gas. But does a real fire, not a laboratory one, give off the acid?

The team didn't have to wait long to find out. Starting on Labor Day 2010, the Fourmile Canyon wildfire raged in the foothills above Boulder, Colo., burning more than 6,000 acres and destroying 169 homes. Scientists at the Boulder NOAA research facility wasted no time in learning what they could about the tragedy.

Photo courtesy Joost de Gouw

CIRES Fellow Joost de Gouw and colleagues discovered the presence of isocyanic acid in smoke during controlled burns at the U.S. Forest Service Fire Sciences Laboratory in Missoula, Mont.

"Boulder has a world-class atmospheric chemistry building, but rarely does it have a full-on hit from a wildfire," de Gouw said. "So just about everyone in that building turned on their instruments."

The team's mass spectrometer detected levels of the acid up to 200ppbv in the air at the site, which was downwind from the fire. "So in Boulder we found that not only is it formed in a laboratory burn, but it also comes out of a real wildfire," de Gouw said.

The team continues to use their spectrometer to discover other origins of the chemical. "We know so little about isocyanic acid's behavior in the atmosphere that we want to do a number of follow-up studies," de Gouw said. "This is just the beginning—we need to do a lot more work."

Learn more

CIRES Fellow Joost de Gouw discusses the discovery, significance and potential health impacts of isocyanic acid. Watch the video at **http://cires/news/multimedia**

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CIRES scientist Gabrielle Petron uses a specially equipped Toyota Prius to study air pollution. Photo courtesy Adam Hirsch

Pollution hunters

Tracking down the sources of polluted air

A multi-pronged Prius, decked with a recycling-container chapeau and sprouting tubes from its windows, might look like an artifact from an old science fiction movie, but it is just CIRES scientist Gabrielle Petron's way of taking her research on the road.

From their mobile laboratory, Petron and her colleagues from NOAA's Earth System Research Laboratory are tracking down the origins of the air pollution in the Colorado Northern Front Range region. "It's invaluable being able to drive around and work like a detective," Petron said. "That way, you can try to directly link the air pollution you observe to its source."

The incentive for Petron's grass-roots investigation came from some unexplained observations recorded at the NOAA Boulder Atmospheric Observatory (BAO), an instrumented, 1,000-foot-high tower located in Erie, Colo. (see story, page 14). Air pollution measurements at the tower revealed high levels of a class of pollutants called alkanes, especially relative to long-term measurements from eight similar towers located in other areas of the nation. "We thought, 'Hmm, BAO is not the same—what is going on there?'" Petron said.

The chemical and meteorological measurements, which indicate both the type of the air pollution and the wind direction it comes from, further surprised the scientists. "With the tower being so close to Denver, we thought we would mostly come across urban pollution," Petron said. "But Denver was not a big piece in what we saw."

Instead the scientists found that a lot of the air pollution came from the northeast part of the state, Petron said. This region, Weld County, houses more than 12,000 oil and gas wells and also numerous tanks that store the liquid hydrocarbons or condensate separated from the natural gas at the wells or processing plants. Could these wells and tanks be the major cause of the air pollution observed in the Northern Front Range?

To find out, the team equipped the car with cutting-edge air pollution detection instrumentation and hit the roads. The instruments measured all the common greenhouse gases and air pollutants, including carbon dioxide, ozone, methane and carbon monoxide. The scientists drove around Weld County with a map and their monitoring system to see what they could find.

"We could see the real-time data," Petron said. "Every so often, I'd say to my colleague: 'Wait a second, something is happening. We have to stop and take a sample.'" After the scientists had spent a couple of hours driving, stopping and taking air samples, they would return to their base where the contents of the flasks could be analyzed at two labs.

The team's research will give valuable information about emissions from the oil and gas industry, Petron said. Currently, a large portion of the Northern Front Range of Colorado is noncompliant for summertime ozone. The state and the Environmental Protection Agency are working hard to derive bottom-up inventories in the region, she said.

Petron hopes the study will encourage collaboration between the scientists and regulators with the goal of mitigating air pollution. "The power of doing something locally is that you can have a big impact," she said. "You have direct access to people who have a strong interest in your measurements."

Deepwater hits the air

U.S. Coast Guard

Scientists used NOAA 's WP-3D aircraft to measure the effect of the Deepwater Horizon oil spill on air quality. NOAA

Findings at the catastrophic oil spill site have implications beyond the Gulf

When a team of researchers from CIRES and NOAA raced to the scene of the BP Deepwater Horizon oil spill to assess the disaster's impact on air quality, they found more than they expected.

A significant fraction of the oil that surfaced had evaporated. Also, measurements taken onboard the NOAA WP-3D aircraft revealed that organic aerosols—a form of air pollution—formed from the oil vapors. Aside from the common culprits that create organic aerosols, the researchers discovered a new set of chemicals that contributes to diminished air quality—chemicals that also exist in urban environments.

TheScience

At the spill site, researchers discovered a new set of chemicals that contributes to diminished air quality—chemicals that also exist in urban environments.

"It was very clear that the aerosols were formed from compounds not currently measured," said CIRES Fellow and research scientist Joost de Gouw. Discovering these previously unknown sources of aerosols could improve scientists' understanding of air pollution, said de Gouw. "This really shows that we need to start paying more attention to these compounds," he said.

Aerosols are microscopic particles suspended in the air—in polluted U.S. cities about half of the air pollution particles consists of organic material. Organic aerosols are linked to asthma, cardiovascular disease and even premature death. But scientists only know the origin of a small fraction of the organic aerosols. "The problem has been that we know there are more organic aerosols than we can account for," de Gouw said. "So there is a lot of discussion in the literature on where this organic material comes from."

The team's research on the air quality impacts of the oil spill shed new light on this mystery. In early June, a team of scientists from NOAA and CIRES arrived at the scene of the spill to assess how much of the oil was evaporating into the atmosphere, and whether this oil was a concern for air quality. The team flew for about 14 hours directly over and downwind of the oil spill, and instruments aboard the research aircraft measured many types of air pollution particles, including organic aerosols, and the chemicals that make them.

Based on the current scientific understanding, de Gouw and his colleagues knew where they expected to see the aerosols: exactly where they saw the most volatile components of the oil evaporate, in a narrow plume downwind from the spill site.

But this is not what the scientists observed. "We detected particles being formed, but over a much wider area," said de Gouw. "So that was a big surprise."

The scientists realized that other compounds, aside from the highly volatile components of the oil, had to be contributing to the air pollution. Because they recorded organic aerosols over a broad area, they concluded the heavier, less-volatile compounds that are slower to evaporate were also forming aerosols.

These chemical instigators of air pollution exist elsewhere—not just in catastrophic oil spills, de Gouw said. The oil was not a thick sludge but more similar to the highly refined oil that is used in cars or factories, he said. That means the same heavier compounds that contributed to air pollution over the Gulf Oil Spill also contribute to air pollution in urban environments.

But these compounds are not measured in most air-quality monitoring programs designed to capture the conventional contributors to poor air quality. "This chemistry could be a very important source of aerosols in the urban United States and elsewhere," de Gouw said. "What we learned from this study will help us to improve air quality understanding and prediction."

How the Earth's atmosphere stacks up

Although the Earth's atmosphere extends 10,000km above the planet's surface, the mix and density of the gases change as the distance from the Earth increases. The temperature also changes with altitude, and scientists use these changes to classify the atmosphere into five main layers. From the lowest to the highest, these layers are:

Troposphere

This layer begins at the surface of the Earth and extends out to between 9km at the poles and 17km at the equator. The lowest layer of the troposphere consists of the planetary boundary layer (PBL), which extends from the Earth's surface to a height that ranges anywhere from 100 to 3,000m. The PBL contains much of the pollutants emitted from the ground.

The troposphere contains approximately 80 percent of the atmosphere's mass and is known as the lower atmosphere.

Stratosphere

The layer above the troposphere, this layer extends to about 51km above the Earth's surface. The temperature increases with height due to increased absorption of ultraviolet radiation by the ozone layer.

Mesosphere

The mesosphere reaches about 80 to 85km above the surface of the Earth. The temperature decreases with height, and the top of the mesosphere is the coldest place on Earth, with an average temperature of about -85°C (-120°F). The stratosphere and mesosphere constitute the middle atmosphere.

Thermosphere

The top of the thermosphere extends up to about 350 to 800km above the Earth's surface. This layer is known as the upper atmosphere.

Exosphere

This layer extends from the top of the thermosphere to thousands of kilometers above the surface of the Earth. It has very few atmospheric molecules in it, and these molecules can escape into space.

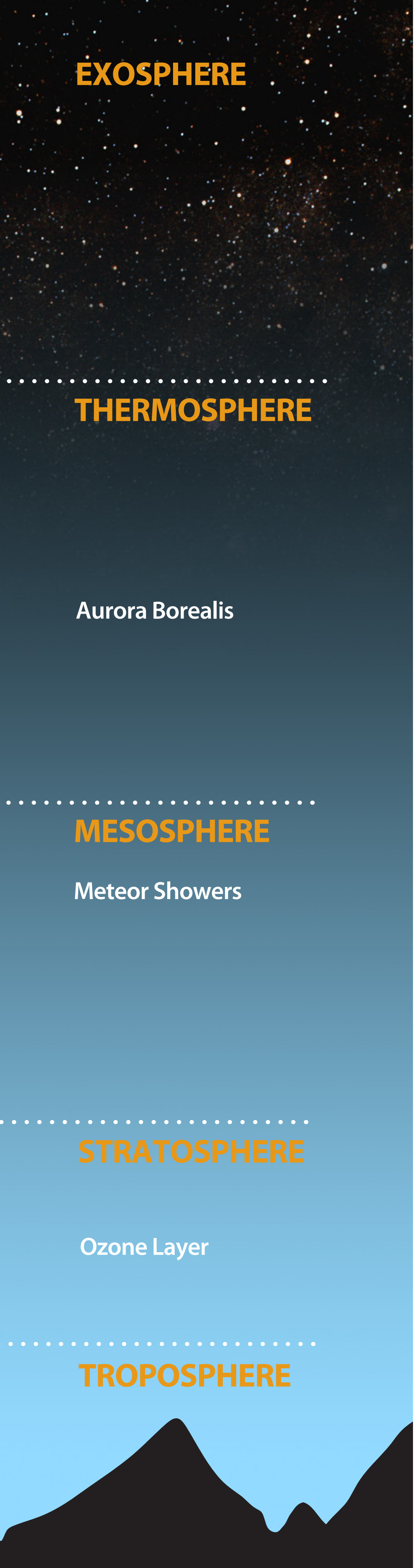
10,000+km

350km–800km

85km

51km

9–17km



The ABC's of air pollution

PRIMARY AIR POLLUTANTS

These pollutants are emitted directly into the air from various sources. They include:

NITROGEN OXIDES (NOx)

When oxygen and nitrogen react at high temperatures, they form nitrogen oxides.

In the northern midlatitudes, fossil fuel combustion dominates the emission of nitrogen oxides, and in the tropics, biomass burning produces the majority of the nitrogen oxides.

In the atmosphere, these nitrogen oxides can react with other chemicals to form ground-level ozone, and nitric acid can contribute to aerosol formation.

CARBON MONOXIDE (CO)

Incomplete combustion of the carbon in fuel produces this colorless and odorless gas. Even low exposures can aggravate cardiac ailments—high exposures can cause nervous system problems.

VOLATILE ORGANIC COMPOUNDS (VOCs)

Fossil fuel combustion, industrial activities, fires and even plants can emit these compounds.

Long-lived VOCs can contribute to aerosols, and short-lived VOCs can react with other chemicals to produce ground-level ozone.

AEROSOLS

The atmosphere contains gases and solid and liquid particles suspended in the air. These particles—typically only a fraction of the width of a human hair—are known as aerosols or particulate matter.

Aerosols are both primary and secondary air pollutants. Winds blowing sea salt, dust and other debris into the atmosphere contribute to the larger aerosols—which are primary air pollutants.

High concentrations of aerosols can cause cardiovascular disease, and the finer particles can be absorbed into the lungs and even sometimes into the bloodstream. Aerosols also contribute to the haze that impairs visibility.

SECONDARY AIR POLLUTANTS

These chemicals are formed through reactions in the atmosphere. They include:

GROUND-LEVEL OZONE

When the sun shines on the mix of VOCs and nitrogen oxides, a photochemical cycle forms ozone—a pernicious air pollutant, toxic to both humans and plants.

ORGANIC AEROSOLS

Inefficient combustion in cars, wood stoves, agricultural fires and wildfires causes organic aerosols to spew into the air. These organic particles account for one-third of the aerosol mass in the atmosphere.

Location, Location

While ozone at ground level is a pernicious air pollutant, ozone higher up in the atmosphere—in the stratosphere—helps make life on Earth possible for humans. Stratospheric ozone absorbs 99 percent of the sun's ultraviolet (UV) radiation before it reaches the planet. The remaining UV radiation that reaches the Earth's surface can damage cells and cause skin cancer and immune-system suppression.

Taking science to new heights

Erie Tall Tower study gives fresh insights on wintertime air pollution

Teetering atop a 1,000-foot, needle-shaped tower in Erie, Colo., might seem like an extreme approach to exploring air pollution, but CIRES scientist Carsten Warneke says this novel approach is ideal.

"It is like a pollution crossroads," Warneke said, speaking of Erie. The tower sits downwind of Denver, very close to natural gas production sites and gets the not-so-subtle smells and gases from Greeley, Colo., dairy farms. The three sources combine to give the researchers plenty to investigate, and the location also occasionally gets a break in the form of clean air funneling in from the Rockies. "Basically it provides a baseline," Warneke said. "It is as clean as you can get."

The tower itself also gives the researchers a unique perspective on air pollution. What's in the air and the chemical interactions that take place in it vary with height, and therefore cannot be fully understood by making measurements only at ground level, Warneke said.

In March and February 2011, CIRES and NOAA scientists conducted a study on the chemistry of wintertime nighttime atmosphere at the tower—dubbed the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) study. The experiment was one of the first of its kind: "Nighttime and winter air pollution have been studied very little," Warneke said.

The wintertime atmosphere is made up of "layers" that don't mix well, Warneke said. During the NACHTT study, a mobile "Tower Laboratory" platform carried more than one ton of instrumentation up and down the 1,000-foot tower, characterizing the chemistry at different heights. "Going *through* those layers tells you more about the chemistry and air pollution," he said.

Observing the atmosphere at nighttime also allowed the researchers to understand how a compound called nitryl chloride is made—a chemical that contributes indirectly to smog formation and also influences the chemical cycles that destroy or produce various greenhouse gases. During the night, chloride compounds in the atmosphere interact with nitrogen oxide pollution, produced by fossil fuel combustion, to form nitryl chloride. But exactly where the atmospheric chloride comes from in a region so far from the oceans, and how the nighttime chemistry unfolds to produce nitryl chloride, are not fully understood.

The NACHTT study is sure to advance the understanding of what goes on in the air in the dead of winter, and at night, Warneke said, and the bird's-eye view of the Erie Tower makes the experiment possible.

Early in the morning, from the top of the tower, the researchers can see the "mixing layer" where a lot of the pollution is trapped, Warneke said. "This is the layer that most of us live in," he said. "And that is why it is so important to understand its emissions, chemistry and dynamics."

NOAA (above); David Oonk /CIRES (left)

A sophisticated chemistry laboratory, packed into a room-sized container, travels up and down the Boulder Atmospheric Observatory (BAO) in Erie, Colo., to sample the atmosphere from the ground up to nearly 1,000 feet.

TheScience

The 1,000-foot-tall tower in Erie, Colo., allows scientists to investigate the air—and the reactions that take place in it—at a variety of heights.

Ozone levels can still soar in rural areas

Wyoming's Green River winds its way through the Basin against the backdrop of the sharp-edged Wind River Mountains. A tranquil scene exemplifying a pristine rural environment: clean water, clean land and clean air.

Or maybe not.

TheScience

An unusual combination of raw ingredients, weather and geology produces levels of ozone typically seen only in urban environments.

When a nearby oil company left on its air-monitoring instruments one recent winter, they were in for a real surprise: Their instruments recorded levels of ozone typically seen in only urban environments. "In a rural area, especially in the wintertime, you would never see ozone like this," said CIRES graduate student and ESRL-CIRES Fellowship recipient Ryan Neely. "People would just think it was an instrument error."

Further checks by the Environmental Protection Agency (EPA) confirmed the readings weren't due to faulty diagnostics. Puzzled as to the origins of these high levels of ozone, the EPA passed the mystery on to CIRES scientists.

"We basically went in to discover: What is causing this elevated ozone? Is this a weather-driven event, or is this an emissions-driven event?" said Neely, who collaborated with NOAA researchers Russell Schnell and Samuel Oltmans.

The scientists found the nearby Jonah-Pinedale Anticline natural gas field churned out high levels of all the ingredients necessary to make ozone. But these ozone levels only soared under a unique set of conditions. When a high-pressure weather system moves into the snow-covered region, bringing with it cold temperatures, low wind speeds and clear skies, it creates a shallow temperature inversion, trapping high concentrations of the chemical precursors to ozone. "It basically turns the region into this big fishbowl," he said. "Then the air just sits there and cooks, and the levels of ozone just rise and rise and rise."

While the Green River Basin isn't home to the hundreds of thousands of people found in a typical city, the consequences of high ozone levels are no less severe. "There are still a significant number of people and livestock out there," Neely said.

The observation of high ozone levels in Wyoming's rural environment is not an anomaly, Neely said. "This would happen wherever you have a similar snow-covered Basin, a source of ozone-forming ingredients and the right type of weather systems," he said.

Since the original discovery in Wyoming, the team has observed a similar phenomenon in Utah's Unita Basin. A high mountain range encircles the Basin, which houses both oil and gas extraction wells. Once snow covers the ground in the winter months, the conditions ideal for creating ozone in this Basin perpetuate until the spring thaw, Neely said.

Both the scientists and the oil companies are interested in understanding just how and why ozone can soar in rural areas, Neely said. Oil companies, in particular, want to know how to mitigate air pollution and avoid severe regulations, he said.

"When they have to shut down sites, everybody loses—the taxpayers because they don't get their revenue and the oil companies because they lose millions of dollars," Neely said. "Everybody is interested in understanding the science."

The secret life of a molecule

Using spectroscopy, Veronica Vaida, CIRES Fellow and Professor of Chemistry and Biochemistry at the University of Colorado at Boulder, has discovered several reactions in the atmosphere that influence climate, air pollution and the workings of the atmosphere. This year, the American Chemical Society honored her for her contributions with the E. Bright Wilson Award in Spectroscopy.

How would you define optical spectroscopy for a layperson?

It is the interaction of radiation with molecules that lets you glimpse their properties. Basically, you shine light on a molecule and monitor which wavelengths of light are affected. Knowing what wavelengths it absorbs gives the investigator a window into the molecule's structure and the chemistry of the molecule.

What draws you to this field?

I like the challenge of looking at a molecule 10^{24} times smaller than our world and unraveling its fundamental properties and how these play out on the bigger, atmospheric scale.

What were some unexpected discoveries?

We found that red light, such as is available at dusk and dawn, can initiate reactions in many compounds, including sulfuric, nitric and organic acids, which are important in air pollution. Field measurements were seeing a spike in reactive species when the Sun was at the horizon, but models did not contain the chemistry needed to explain these observations. The chemistry we proposed brought a new paradigm for how light can affect the atmosphere.

Another problem we investigated using spectroscopy involved small aggregates of water—two, three, four waters forming a complex—which absorb light differently than a single water molecule. Atmospheric observations highlighted the possibility that some hidden agent was absorbing solar radiation, but they didn't know what. This discrepancy between models and observations was termed anomalous cloud absorption, and our work contributed to understanding these effects. An increase in the Earth's temperature would increase evaporation of water, and the concentration of these water clusters would go up exponentially. As a result, their effect could be even more important in a global warming scenario, providing a nonlinear amplifier to anthropogenically induced climate change.

In 1979, you became Harvard's first woman assistant professor in chemistry. While there, you were colleagues with E. Bright Wilson, the pioneer of molecular spectroscopy. What was that like?

My office was next door to his, and he was a very good friend and mentor. He advised me on how to think about science, how to go about it, and the right reasons to do it. He remains one of my heroes, which made it especially meaningful for me to get this award.

Student Focus: Amber Ortega

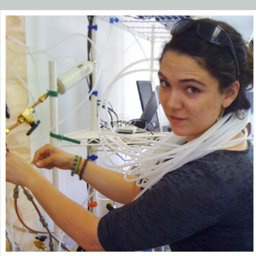


Photo courtesy Delphine Farmer

Of the thousands of different organic particles floating through the air, researchers have only identified 10 to 30 percent of them, and the atmospheric roles of many remain unknown. Amber Ortega, a graduate student with CIRES Fellow Jose-Luis Jimenez' group, is working to change that. During fall 2009, at the U.S. Forest Service Rocky Mountain Research Station's Fire Sciences Laboratory in Missoula, Mont., she investigated the types of organic aerosols (airborne carbon-based particulates) that result during fires.

When forests, grass and other vegetation burn, the smoke carries different aerosols and gases into the air. Some of these gases then react with sunlight—a process called photochemical processing—or other airborne compounds to form additional aerosol species. Aerosols can harm human health (aggravating allergies, asthma and cardiovascular problems), lower visibility and affect climate.

While at the laboratory, in a $3,000 m^3$ room, Ortega and her team set ablaze 16 types of fuel, such as ponderosa pine, saw and wheat grass, turkey oak and black spruce. Using a potential aerosol mass (PAM) oxidation reactor, she exposed smoke to ultraviolet light to simulate the sun's effects—but at a much faster rate. The device can replicate two weeks of atmospheric aging in about five minutes. An aerosol mass spectrometer then analyzed what organic aerosols were produced between zero to two weeks of effective aging. They discovered that different fuels, such as grasses, generate more organic aerosols after aging than ponderosa pine. "So where a fire breaks out and what species burn greatly affect how much aerosol ends up downwind," Ortega said.

CIRES offers graduate student fellowships. Learn more at cires.colorado.edu/education.

Clearing the air

Discovery of volatile organic compounds (VOCs) leads to new regulations, positive changes in Houston's ozone levels

A thick blanket of yellow haze hovering over Houston is a bit thinner thanks in part to research done by CIRES scientists.

"Houston has shown small but steady improvements in ozone levels since 2000," said CIRES scientist Rebecca Washenfelder, one of the researchers who measured levels of air pollutants over the city in 2006.

As well as being home to more than five million people, Houston is base to the largest group of petrochemical factories in the United States. Every day these factories pump toxic fumes into the atmosphere to form ozone—the major culprit of air pollution.

Ozone is a form of air pollution that can damage the respiratory system. In areas with high ozone levels, rubber bands and bike tires get brittle and crack, Washenfelder said. "Ozone is attacking the rubber," she said. "It's also attacking your lungs."

To address the issue, the Texas Commission on Environmental Quality (TCEQ) planned to place stringent controls on the emissions of nitrogen oxides—one of the key ingredients needed to make ozone.

But a study by CIRES and NOAA scientists in 2000 showed that nitrogen oxides weren't the only culprits in producing ozone. When the crew flew the NOAA WP-3D research aircraft through plumes billowing from the factories below, they discovered another class of compounds—volatile organic compounds (VOCs)— was important for Houston's high ozone levels.

"This was a big surprise—VOC concentrations were much higher in Houston than in any other U.S. city we'd studied," Washenfelder said. "It turns out that the petrochemical industries in Houston are big emitters."

The results inspired TCEQ to regulate VOC emissions from the petrochemical industry, and when the scientists measured the levels of both nitrogen oxides and VOCs in 2006, the news was good.

TheScience

CIRES scientists discovered the petrochemical industry pumped a particular class of chemicals—volatile organic compounds—into the atmosphere that contributes to high ozone levels. Identification and regulation of these chemical culprits may have played a role in Houston's improved air quality.

"When we returned in 2006, we saw that nitrogen oxide and VOC emissions from many of the industrial complexes near Houston had decreased," Washenfelder said. "It was great to see that there had been a measurable change."

Washenfelder believes stricter emissions regulations on combustion sources have led to the decrease in nitrogen oxides. It is less clear, however, whether the reduction in VOCs was due to the new regulations or due to economic changes, she said.

Although whether the entirety of the lower emissions can be attributed to the scientists' discovery is still unclear, the fact that their earlier study had helped and will continue to help reduce VOC emissions is not.

"There are good indications that air quality has improved as a result of our work," Washenfelder said. "That's about as exciting as it gets."

In hot pur-soot

Researchers monitor black carbon levels

Soot from coal burned in China ends up as haze over Hawaii—in concentrations that rival urban centers. “These are some of the highest levels of black carbon that we’ve seen in remote areas like the middle of the Pacific Ocean,” CIRES Fellow and NOAA scientist David Fahey said. “It likely flowed over from Asia.”

The burning of coal, diesel, biofuel, such as firewood, and biomass (for example, agricultural waste, forests and grasslands) releases black carbon, a fine particulate that makes up soot. Because these tiny particles penetrate deep into the lungs, long-term exposure can cause emphysema, chronic bronchitis and asthma, while the organic byproducts that often coat the particles may raise cancer risk. In terms of global climate, black carbon is also an important heat-trapping agent, absorbing solar radiation and affecting cloud formation.

State-of-the-art monitoring of soot is now giving researchers an unprecedented look at its global distribution and behavior. “We’re interested in exactly how much there is, where it came from and what its fate is,” Fahey said. As part of the HIAPER (High-Performance Instrumented Airborne Platform for Environmental Research) Pole-to-Pole Observations of Carbon Cycle and Greenhouse Gases study, Fahey and his team outfitted NCAR’s long-range jet with a soot photometer (see sidebar). On five missions between January 2009 and September 2011, the plane will have flown more than 40,000km on each circuit between latitudes 67°S to 85°N—roller-coastering from 0.5km to 8.5km, continuously sampling the air. “This gives us a wealth of information about the vertical, ‘ground to the top of the atmosphere’ distribution of materials,” Fahey said.

The data are essential for improving model predictions, which currently have black-carbon uncertainty factors of 10 to 100, Fahey said. “A lot of air pollution and climate science hinges on models, so they need to accurately reflect the atmosphere and not some fantasy planet,” he said. “These fundamental observations can feed into the models so the projected values are closer to reality.”

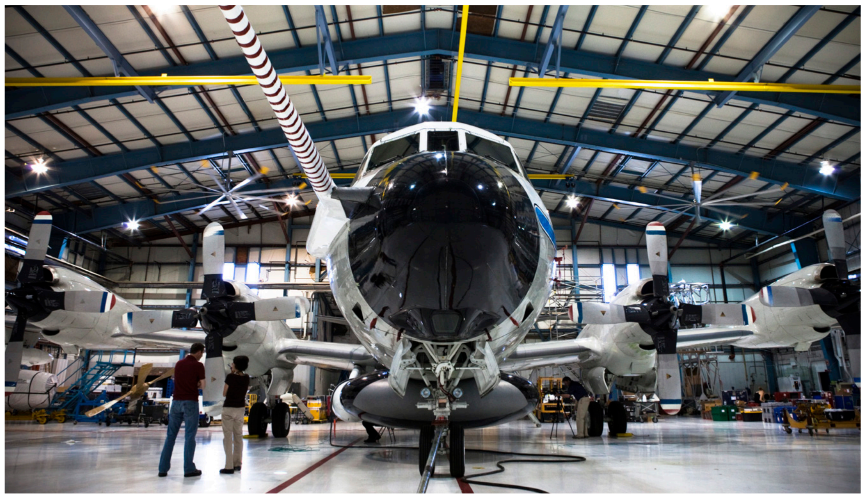
Fahey’s team also took lower-elevation measurements, which are more relevant to the air we breathe, in the Los Angeles region, as part of the CalNex 2010 project (see page 2). These yielded heartening results. Despite a steady increase in the use of diesel in L.A., black carbon concentrations are lower now than in 1965 because of government regulations. “Without such stringent standards, L.A. could have looked more like what you see in the Pearl River Delta in China, where levels are up to 10 times higher,” Fahey said.

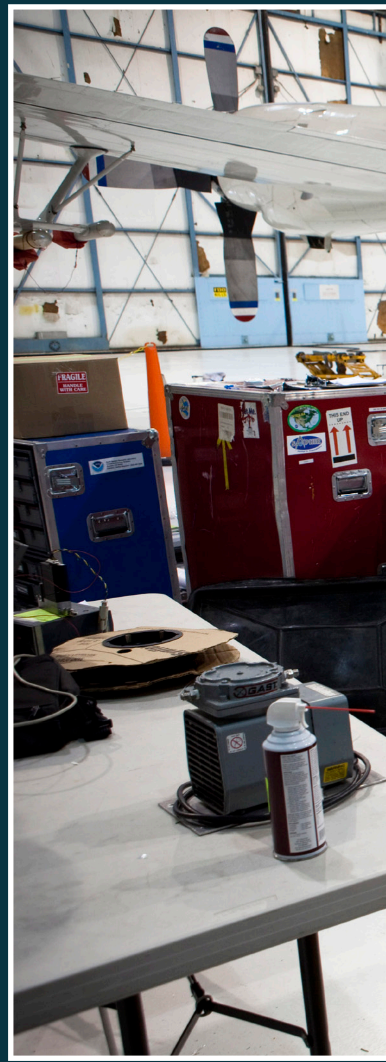
The work being done by Fahey and others will help policy makers decide how to best achieve such reductions. “If we know how much black carbon there is, we can ask, ‘How many people are breathing this? Is that bad for them? How bad? Where are the hot spots?’” Fahey said. “And since this is happening in all the world’s cities, everybody has to act in concert to reverse the systematic effects.”

NASA[1]s WB-57 aircraft in Houston in spring 2011; the Single Particle Soot Photometer is on the lower left in the aircraft pallet in the foreground. Members of the David Fahey team include: Ru-Shan Gao (far left), Anne Perring (third from left), Laurel Watts (fourth from left), Fahey (fifth from left) and Joshua Schwarz and Ryan Spackman (not pictured). Photo courtesy David Fahey

Everything you need to seek out soot

To precisely measure atmospheric soot levels, David Fahey's team custom built an autonomous device—a single particle soot photometer—that selectively measures only black carbon particles and their coatings. They mounted the device into the belly or cabin of three types of planes: NASA's WB-57F high-flier (which cruises above 19km), the NSF NCAR GV long-range jet (16km) and NOAA's WP-3D "Hurricane Hunter" (6km). An inlet outside the aircraft brings air into the photometer where a laser zaps the sample with infrared light. "Black carbon particles absorb the radiation, heat up and emit light, like an electric heater glowing red, until they vaporize at about 4,000 Kelvin," Fahey said. Since black carbon is the only atmospheric aerosol known to absorb infrared wavelengths with high efficiency, measurements of the emitted light reveal the quantity and size of black carbon particles present.





MySphere

How people work, research and relax at CIRES

On board the NOAA WP-3D (P3) Orion N43RF

Since the mid-1970s, scientists have soared the skies in NOAA's WP-3D aircraft to investigate the Earth's atmosphere, hurricanes, severe storms and climate trends.

1 The P3 can accommodate 18 to 20 crew members and up to 12 scientists or media members. Fully loaded with personnel, scientific equipment and fuel, the P3 weighs in at 135,000lbs.

2 Prior to takeoff, cool air is pumped into the P3 to keep the inside of the plane and the scientific equipment cool. Flying at low altitudes (reaching a maximum of 27,000 feet) can be hot work, and the instruments would cut out at high temperatures.

3 CIRES scientist Justin Langridge works on an aerosol extinction cavity-ringdown spectrometer. The P3s participate in a wide variety of environmental research missions in addition to their widely known use in hurricane research and reconnaissance.

4 A stuffed version of Japanese anime character Anpanman (see description of his superpowers on page 1) accompanies the PAN-CIMS (Peroxyacetyl Nitrates Chemical Ionization Mass Spectrometer).

5 The outside of the P3 is equipped with a wide array of air inlets for researchers to gather data.

6 The P3 can remain in the air for up to 11 hours per flight, so having coffee on board is a must. Here, CIRES researchers Harald Stark and Carsten Warneke relax in the plane's galley.

7 N43RF is one of two NOAA WP-3Ds. It features a decal of Miss Piggy with the slogan *"Aero-nautical . . . but nice!"* The other plane, N42RF, features *"Sky-Hopper"* Kermit the Frog.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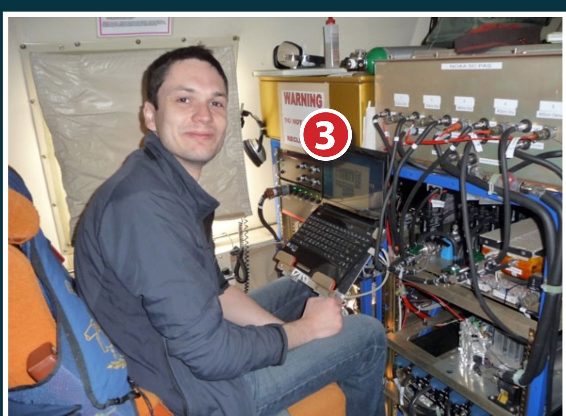
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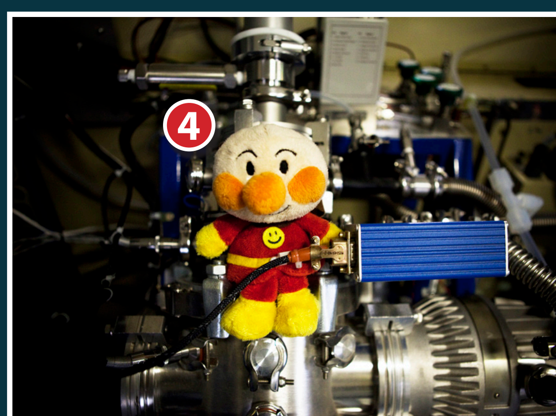
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