

Clearing the Air about CO₂

California is writing carbon laws that may be difficult to enforce. The problem is nobody knows exactly who is emitting what or how much. Now Irvine researchers say they have a way to fingerprint the very air around us.



The most time-intensive aspect of Pataki's work is analyzing the samples in the laboratory because the carbon must first be separated from the other gases.

Everybody is saying it: We need to limit carbon dioxide (CO₂) emissions.

In 2006, California mandated a rollback to 1990 levels of greenhouse gas emissions by 2020. Over 50 colleges and universities (including the entire University of California system) and 100 cities from California have signed agreements to reduce carbon emissions.

But once the promises are signed and the photos taken, we're left with a couple questions:

Where is the carbon dioxide spigot that seems to have been left on?

And how do we turn it off?

Strange as it may seem, almost 50 years after variations in atmospheric CO₂ were first measured by UC San Diego legend Charles Keeling, scientists are still struggling to quantify where it comes from and which sources are the biggest.

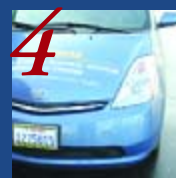
Scientists know that burning fossil fuels like coal, natural gas, and gasoline releases carbon dioxide into the air. From monthly records of fuels sold and fuels burned in power plants, they can calculate the amount of CO₂ released in each state in that month. But that doesn't tell us how much CO₂ is emitted in a given location, or what type of source it is coming from.

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Miracle fuel or the next big environmental headache?



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Over 90 miles to the gallon in a customised hybrid.

HYDROGEN:

Miracle Fuel or the Next Big Environmental Headache?

In the race to find clean energy sources, the White House has made a big bet on hydrogen fuel cells. But has anyone thought about whether hydrogen could damage the environment?

Kristie Boering's lab is in a building not many people on UC Berkeley's campus even know exists. That's probably because there are no windows, most of it is underground, and the roof doubles as a quad for the chemical engineering library.

Walking into a bunker-like lab room she proudly points to a series of racks along the walls holding glass bottles that appear to be empty. Crisscrossing the room are tall panels decorated with networks of glass flasks and clear winding tubes where researchers carefully tweak valves and scribble on notepads.

"These represent thousands of dollars of research," she says. "Go ahead, pick one up. But be careful."

It turns out the bottles and flasks aren't actually empty. Each one contains air carefully collected via plane or balloon from up to 100,000 feet in the stratosphere. Boering is a tenured professor but, with her affable nature and exuberance when discussing atmospheric chemistry, one might mistake her for one of her students. Within minutes of sitting down in her office, she pops up again and starts marking up the whiteboard behind her with chemical equations and diagrams.

As scientists cast about for substitutes for fossil fuels, they keep coming back to hydrogen. But before conducting a global experiment by switching to hydrogen-based energy, Boering says we should learn from previous environmental mistakes like chlorofluorocarbons—which, it turned out, damage the ozone layer—or the fuel additive MTBE—which improved air quality but polluted the water. And, of course, fossil fuels, which turned out to be, well, problematic.

So Boering is asking: if humans switched to a hydrogen economy tomorrow, could we be blindsided by some new environmental show-stopper?



Kristie Boering and colleague Kathleen Mar peer into a network of glass containers of hydrogen. Their work looks at how a hydrogen economy might affect the atmosphere.

The answer, it seems, would require a much bigger whiteboard. To start with, Boering explains that studying the gases in the atmosphere is like balancing a checkbook, and that until now the hydrogen budget has resembled her husband's accounting style.

"If he balances it to within a few hundred dollars, he's happy," she says, shaking her head. "To me, that's a signal that something could be wrong. Maybe there are two huge errors and they happen to cancel out to about \$200. Maybe there were two thousand-dollar mistakes and they cancelled to give you a few hundred."

It's a risk she accepts reluctantly with her finances, but is trying to avoid when it comes to our atmosphere. For hydrogen, the amount of gas currently entering the system and leaving is about the same. Any difference between "income" (sources of hydrogen) and "spending" (sinks of hydrogen) should show up as an increase or decrease in the "balance" (the atmospheric inventory).

Now imagine the entire world switched over to a hydrogen economy. The hydrogen that actually went into fuel cells would come out as harmless water. But if the natural gas industry is any indication, a hydrogen industry would

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Hydrogen: Miracle Fuel *Continued from page 2*

also leak a fair amount into the air from filling stations, storage tanks, and pipes. Hydrogen is actually more difficult to contain than natural gas. For example, in liquid form, one method of storage, it tends to evaporate.

So what then? Maybe nothing, judging by today's global inventory of hydrogen, which constitutes just 0.00005% of all atmospheric gases. It was long thought that hydrogen emitted into the atmosphere would just escape into space, because the earth's gravity is too weak to hold the lightest of all molecules. (By contrast, the giant planets Jupiter and Saturn, with their larger gravitational pull, consist mainly of hydrogen.) Although that idea would partly explain the scarcity of free hydrogen (that is, hydrogen not combined with oxygen to form water) in the atmosphere, it turns out to be far from the whole story. In 2001 Boering and her team, studying her little bottles of stratosphere, confirmed that more than half of the hydrogen that disappears from the atmosphere every year feeds soil microbes. Perhaps the vast majority of hydrogen input to the atmosphere gets eaten by soil microbes, and the extra that humans might add would just fatten them up a bit more.

Or perhaps not.

“The nature and magnitude of some sinks could solve our problems so that we'd never have a problem with a hydrogen-based energy economy. Or some currently unknown source or unknown feedback could make it potentially worse,” Boering says. “You don't want to invest billions of dollars in technology and then decide that that was the wrong thing to do.”

Other researchers, like Yuk Yung at the California Institute of Technology, have warned that, presuming we someday leak as much hydrogen as we currently do natural gas, the extra hydrogen could ultimately damage the stratospheric ozone layer or deplete hydroxyl radicals. These rare components of the atmosphere act as air-cleaners; the loss of hydroxyl radicals might allow some greenhouse gases, as well as ordinary pollutants, to increase.

But currently, scientists are stuck with “could” and “might,” because some pieces in the puzzle of atmospheric inputs and outputs might still be missing. After careful study, scientists know a little more about the budget of hydrogen in the stratosphere, where interactions are relatively simple. But in the troposphere (the earth's atmosphere below an altitude of 5 to 9 miles), where oceans, power plants, and forest fires complicate the picture, scientists are less certain of the hydrogen balance.



Boering used air samples collected in a number of ways, including by balloon.

One sign that there are still potentially large uncertainties in the budget concerns deuterium, the heavy isotope of hydrogen. Boering's team studies deuterium to see how hydrogen molecules are produced in, destroyed, and removed from the atmosphere. But looking at the bottles of stratosphere in her lab, there seems to be more deuterium than predicted.

The inconsistency suggests that scientists don't know as much as they should about hydrogen in the stratosphere and even less about the troposphere, leaving uncertainties about how the amount of hydrogen in the atmosphere might change in a hydrogen economy. There is more to do, Boering says.

“We can't just wave our hands and use chemical intuition,” she says. “Now is the time to study this, not later when we say ‘oops, we hadn't thought of that.’”

Using her own air samples, bulked-up computer models, and laboratory experiments, she has done her own analysis of stratospheric deuterium. In her most recent paper, she says that the jury is still out on the budget of hydrogen into today's atmosphere and that we should know more before doubling, tripling, or quadrupling the current hydrogen input by humans.

Because all measurements have some uncertainty, the analogy to a checkbook is inexact, but the principle of reducing the chance of a serious error is still valid. “I don't want to be alarmist, I just want to understand the hydrogen budget in today's atmosphere,” Boering says. “There's still a \$200 dollar error in our checkbook. We want that to be a nickel.” ■

PLUGGED IN:

Over 90 Miles to the Gallon in a Customised Hybrid



Researchers at UC Davis are studying drivers' reactions to the Toyota Prius plug-in hybrid.

For an extra \$15,000, a few Californians have taken their Prius relationship to the next level. But what are they getting out of this new relationship? A few researchers at Davis decided to investigate.

Kevin Nesbitt starts his new toy with the press of a button.

"I can get at least 90 [miles per gallon] on the freeway," he says, beaming. "Which I did on the way over here."

His pride is obvious as he wheels the Toyota Prius plug-in hybrid around a corner, his colleagues, Rusty Heffner and Ken Kurani seated happily in the back.

"I am almost obsessed with trying to get the highest mileage," he says. "When I get home I almost want to go out and drive the route again and see if I can do better."

It's true. During the ten-minute drive around his campus, Nesbitt is so focused on the dashboard's efficiency readout, he gets momentarily lost at one point.

Nesbitt's fixation on the dashboard is not unusual. In fact, it's the way most people in their latest interview work reacted to this car. Back inside their building at UC Davis, Heffner tells of an interview he did with a woman who was driving a company-provided plug-in for a business trip.

"As she got into the trip, she got more and more interested in watching the fuel economy, maximizing the fuel economy, and getting the battery to regenerate. It became this kind of really intriguing game to her that had nothing to do with saving money," he says.

At first glance, the cars tested were not much different from normal hybrids. They both have an electric motor and an internal combustion engine; they both use batteries to help power the vehicle. But these plug-in conversions have an extra battery in back, where the spare tire would go. And coiled next to it, an extension cord.

Ordinary hybrids are essentially gasoline-powered vehicles with better fuel economy than a standard car. Designs vary, but all hybrids include an electric motor or motors, powered by a battery that can be recharged by the gasoline engine. (The Prius can be powered by the electric motor, directly by the engine, or both simultaneously.) An early concept of a plug-in hybrid electric vehicle (PHEV) was a car that functioned mostly as a battery-powered electric, so long as it was plugged back in before the battery was fully discharged. It charged up in the garage during the night when electricity demand was low. In the morning, the gasoline engine only kicked in after the stored electricity had been all used up. The current batch of plug-in conversions introduces a new idea for plug-in hybrids. Rather than run solely on electricity, they blend more electricity directly into the power of the car, still replacing gasoline but not driving as much on electricity alone. That means lower energy costs, less pollution, and lower greenhouse gas emissions, especially if the power plants that supply the electricity are fueled by renewable sources or nuclear power.

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Kevin Nesbitt demonstrating the Toyota PHEV to students at Kerr Middle School.

Kurani, Heffner, and Nesbitt work for the Plug-in Hybrid Vehicle Research Center, which is directed by Tom Turrentine at UC Davis. Of the 30 or so plug-in conversions on the road when they started their study, they have interviewed 24 of the drivers to learn how they interact with the car. Kurani says this is a crucial time for this kind of work.

Of interest to the team is how often people plug in their cars and whether they will use them for long-distance trips as well as daily travel. The team says it's important to have public studies on how consumers will potentially use a car, rather than depending solely on industry studies. That way, Kurani's team acts as a social counterbalance to company studies that are more focused on marketing. Their results provide an independent evaluation of the benefits of PHEVs and help agencies like the Air Resources Board and the Environmental Protection Agency develop incentives and regulations.

Among their results, the team found that some drivers of the plug-in conversions plugged in their car just about anywhere they could—for instance, at their office or at friends' houses. This suggests that concerns of some policy-makers that companies will invest billions into this technology only to have people ignore its defining feature—the plug—may be unfounded. On the other hand, the experience of a couple drivers whose home location and work schedules meant they could not

recharge at home or work indicates the importance of having at least one “recharging base” for PHEV drivers to maximize the amount of electricity they are able to use.

But do these results predict the behavior of future PHEV drivers? The people interviewed in this study were driving after-market custom conversions that cost an extra \$15,000 and up. Most of the cars were paid for by institutional buyers conducting technical feasibility studies. And, unlike the early concept PHEV, the converted Priuses draw some power from their gasoline engines when driving over 35 mph, thus providing little practical “electric-only” driving. The functional design of future PHEVs is not known, nor is their price—although they are likely to be cheaper than custom conversions, which are themselves coming down in price.

Nevertheless, Kurani feels it is important to learn what we can at this very early stage of experimentation with PHEVs. The team's new study, starting this winter, will loan converted Prius PHEVs (like the one Nesbitt was driving for the Center) to randomly selected people to drive. With an augmented readout screen, the team will then track how much and where people use them.

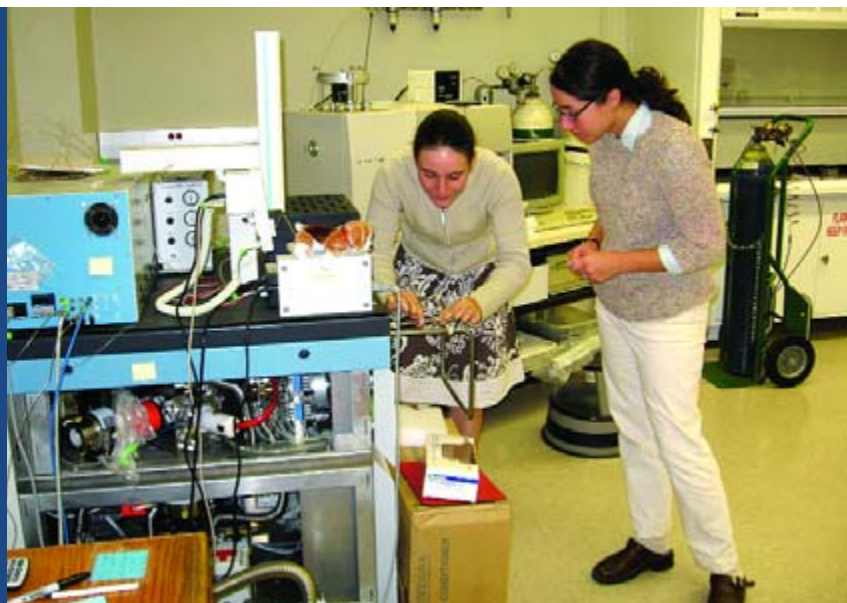
“We wanted to hear what's going on in people's heads in a car where, depending on how they drive it and recharge it, they may be getting well over 100 miles per gallon of gasoline,” says Kurani. “That's a qualitatively different experience than any conventional car on the road.” ■

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Ken Kurani, University of California, Davis

“California is implementing AB 32, which actually regulates CO₂ emissions. And as a part of that regulation, you have to be able to monitor sources and make sure people are complying with the law. And there is actually no good way of doing that right now.”

Diane Pataki, University of California, Irvine



Climate researchers have set up a number of monitoring stations to measure CO₂ in the air directly, but those measurements don't tell us where the CO₂ came from. To these monitoring stations, CO₂ from one source looks just like CO₂ from another.

Enter urban ecologist Diane Pataki and her team at the University of California at Irvine. Pataki has applied sophisticated techniques for exploiting subtle differences in CO₂ from different sources, giving her a way to essentially check the license plates on gases in the air and see where they come from.

“California is implementing AB 32, which actually regulates CO₂ emissions,” Pataki says. “And as a part of that regulation, you have to be able to monitor sources and make sure people are complying with the law. And there is actually no good way of doing that right now.”

The carbon dioxide driving climate change comes from a tapestry of different sources: automobiles, home heating, coal- and natural-gas burning power plants, and industrial burners. Carbon dioxide from these sources mixes with that of forest fires and agricultural burns as well as what is exhaled by animals, microbes, and even plants. (Plants take in carbon dioxide and produce oxygen during the day; at night they breathe out CO₂.)

This creates a problem for scientists studying atmospheric systems: How do you trace a gas that comes from just about everywhere? Pataki has answered this by combining three different techniques to separate out natural gas CO₂ from car exhaust CO₂ from the CO₂ released by plants and animals.

The first technique is to just keep a running tally of carbon dioxide and its sister chemical, carbon monoxide (CO). CO results from incomplete combustion. Although different engines and burners emit different amounts, plants and soils emit very little CO. The ratio of CO₂ to CO gives a general idea of how much CO₂ comes from fuel combustion versus natural sources. That is, the carbon *monoxide* originates from combustion while carbon *dioxide* originates from both combustion and natural sources.

The other two methods involve isotopic analysis of the carbon and oxygen in CO₂. Natural carbon is a mixture of three isotopes: carbon-12 (which accounts for about 99.89% of the carbon atoms), carbon-13 (about 1.11%), and carbon-14, a very rare radioactive form of carbon. Pataki says it boils down to the fact that CO₂ from different sources has different proportions of these three isotopes. “It's the mass of the molecule,” says Pataki, “that allows us to measure the different proportions of carbon isotopes in CO₂ from different sources, using an instrument called a mass spectrometer.”

Carbon-14 provides a clear way to discriminate between modern and ancient sources of CO₂. Because living things get their carbon from the atmosphere (plants get it directly, animals from eating plants), the CO₂ emitted from plants and soils contains tiny amounts of carbon-14. Fossil fuels, on the other hand, form underground over millions of years from dead plants. By the time it is burned as fuel, all of the carbon-14 (which only has a half-life of 5730 years or so) has long since disappeared.

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If Pataki and her graduate student Sonja Djuricin find CO₂ with no carbon-14, it's like a neon sign that it came from a tailpipe, a gas-fueled power plant, or a furnace.

Very subtle differences in the chemistry and biochemistry of different carbon isotopes cause the proportions of the stable isotopes carbon-12 and carbon-13 to vary slightly from source to source. Gasoline has slightly more carbon-13 than natural gas. With very precise measurements using their mass spectrometer, Pataki and Djuricin can also measure the proportions of carbon-12 and -13 and deduce how much of the CO₂ came from natural gas and how much from gasoline.

All of this means Pataki can stand on a hilltop, fill a canister with air, and track the various CO₂ inputs. These days, Pataki is in one of the country's best laboratories for gunk of all kinds in the air: the Los Angeles Basin. Raised in Queens, she is at home in urban jungles and doesn't mind sampling in back alleys or dirty culverts if she has to.

Pataki's methods for measuring carbon sources have attracted widespread interest. If the technique is successful and scalable, it may be adopted by researchers monitoring carbon all over the state.

In her previous lab in Salt Lake City, Pataki observed that, unexpectedly, the highest emitters of CO₂ in the summertime were the plants and soils. Measurements in wintertime showed clearly the increase of carbon emissions from building heating on cold days.

Starting this fall, Djuricin will drive to a half dozen spots around the L.A. area and fill canisters with air to see how it differs from Salt Lake City. Pataki says this kind of specific monitoring gives consumers and lawmakers a better idea of where conservation is most necessary in their area.

Pataki is excited to examine the differences between Salt Lake City—which is rapidly growing—and L.A.—which is “grown out.” She expects a higher impact of cars and more diffuse natural gas in L.A. But the big question in her mind is whether city planning changes could someday ultimately cut our energy use.



Post-doctoral researcher Amy Townsend-Small collects animal-based methane emissions at the source - with a few of the producers looking on.

“There's more leverage in urban planning,” she confides, “than people have generally acknowledged. It's people driving long distances to go to work or run errands instead of driving shorter distances, walking more, using public transportation or even working from home. And a lot of that has to do with how and where cities are built.” Her research will improve our ability to know exactly what and where our greenhouse gases are increasing so that policy makers can better direct their attention and regulations to the primary targets.

What's next? Pataki and post-doctoral researcher Amy Townsend-Small are now trying to apply their isotopic analysis techniques to sourcing the other major greenhouse gases: methane (CH₄) and nitrous oxide (N₂O). Their new adventure will take them to more rural locations, where they will be sampling things like cows, farms, sewage treatment plants, and landfills. ■

UCEI REQUEST FOR PROPOSALS

Proposals Due February 4, 2008

The University of California Energy Institute (UCEI) requests proposals for two grant programs: (1) California Energy Studies, and (2) Energy Science and Technology. The range of subjects appropriate for both programs includes energy production (resources and supply systems), efficient energy use, and environmental and health effects of energy production and use. California Energy Studies also includes the economics, politics, and regulation of energy systems. Energy relevance is a key criterion in the review process.

Proposers must be employed by the University of California and qualified to be principal investigators at a University campus. Awards will be announced on or about May 16, 2008 for the period July 1, 2008 through June 30, 2009. Awards typically will be in the range of \$10,000 to \$35,000. Decisions on awards will be made competitively on the basis of a peer review process. Additional encouragement is offered to faculty early in their careers. **U**

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