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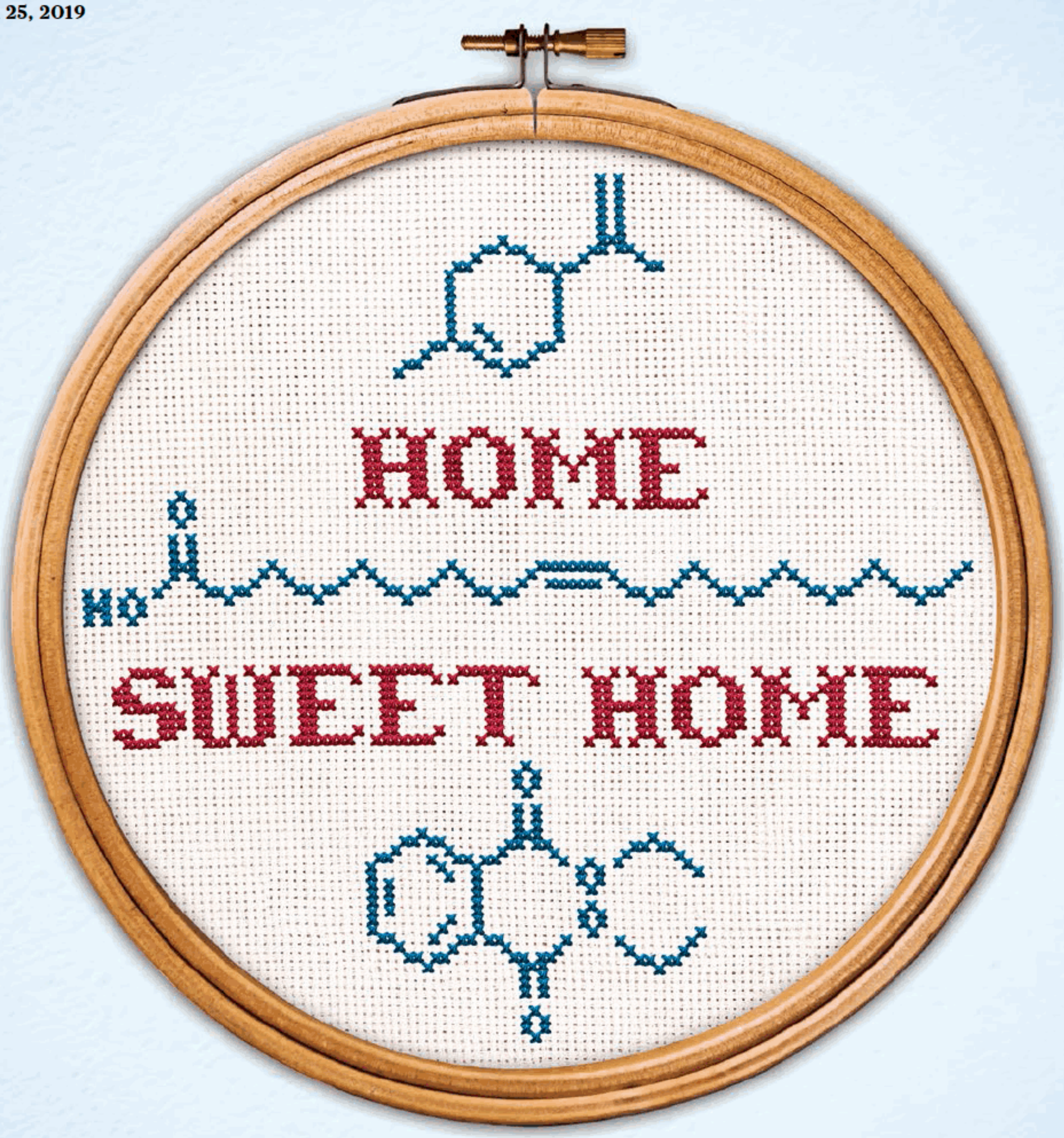

Chemists sample the indoor air we breathe

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Cover story

WHAT'S IN THE AIR IN OUR HOMES?

Outdoor emissions have long been scrutinized. Now atmospheric chemists are moving indoors to analyze chemicals in the air we breathe

CELIA HENRY ARNAUD, C&EN WASHINGTON

Most people spend as much as 90% of their time indoors. And about 70% of that time is spent at home (*J. Exposure Sci. Environ. Epidemiol.* 2001, DOI: 10.1038/sj.jea.7500165). Yet we know little about the air that we breathe indoors, especially in our own dwellings.

Atmospheric chemists have spent decades upon decades focused on understanding the quality of outdoor air. But given the lopsided ratio of time humans spend indoors versus outdoors, some of these researchers are shifting their attention. They want to use the tools they've developed for monitoring outdoor air and start making the same sorts of measurements inside.

They are finding that indoor emissions come from many sources—stoves, cleaning products, furnishings, and even people. And the chemicals they're detecting aren't always inert. Compounds in indoor air can react with one another and with oxidants to form new molecules. These compounds deposit on particles in the air or collect on surfaces such as walls, windows, and carpets that can reemit them later.

There's a long history of studying worrisome chemicals in indoor air, like carbon monoxide or those in secondhand smoke, says William W. Nazaroff, an environmental engineer at the University of California, Berkeley, who has been a pioneer in indoor chemistry. What is not so well understood is whether exposure to "the rich chemical complexity" of an average home's air causes health effects, he says. To figure this out, atmospheric chemists will first need to catalog what's actually in the air where we sleep, eat, and play. Only then will toxicologists and other health experts be able to determine what effect these chemicals have on health.

In brief

Much effort has been expended on understanding the chemistry of outdoor air. But people spend most of their time at home. So atmospheric chemists have become interested in figuring out what's in the air where people eat, sleep, and play. The scientists are bringing their fancy instruments indoors and using them to catalog the compounds in indoor air, learning that many factors affect its composition. They hope their work will help prioritize chemicals for the study of potential health effects.

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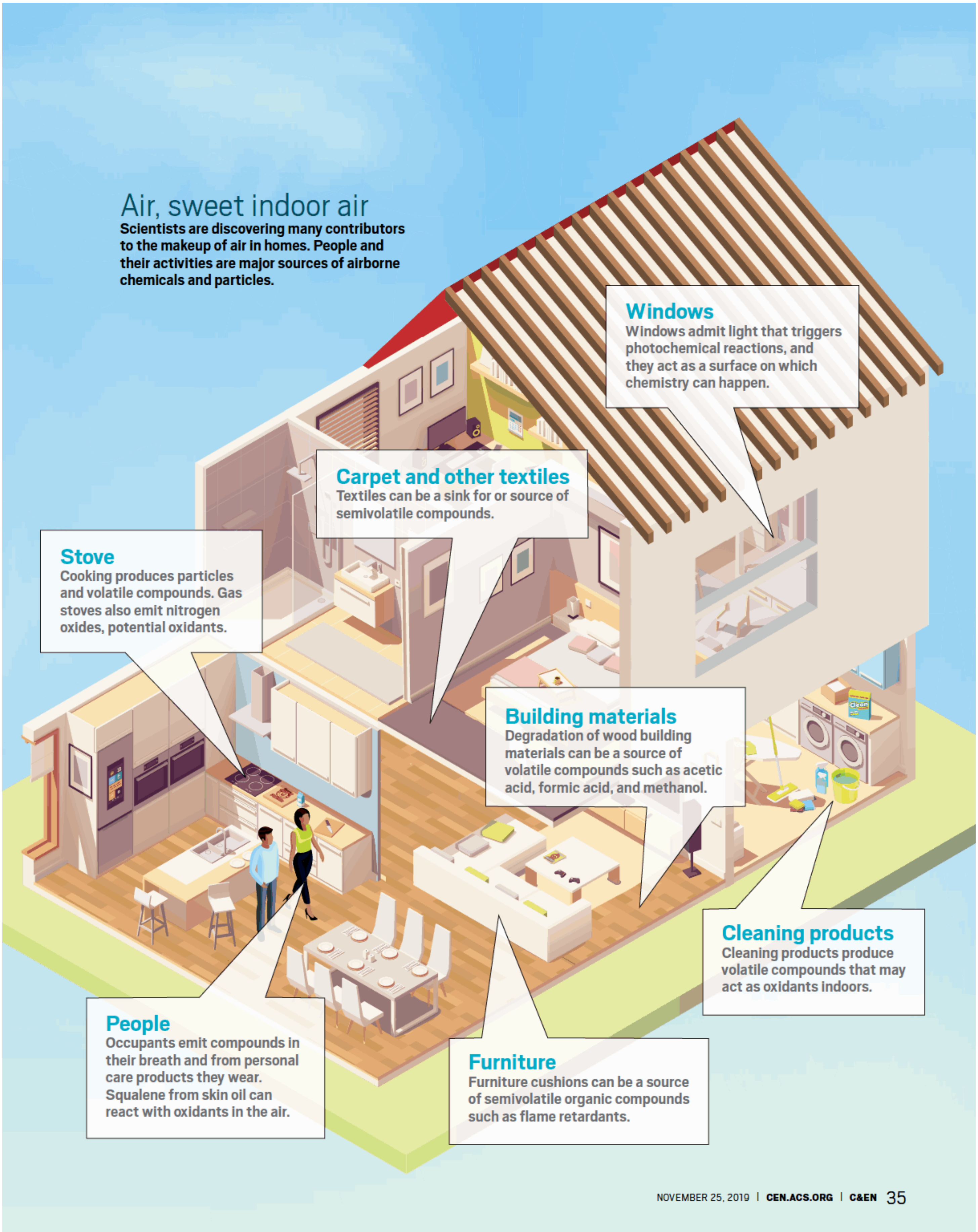
Air, sweet indoor air

Scientists are discovering many contributors to the makeup of air in homes. People and their activities are major sources of airborne chemicals and particles.



Early efforts

A program funded by the Alfred P. Sloan Foundation has paved the way for the recent surge in exploration of the indoor environment. The Sloan Foundation launched its program, the Chemistry of Indoor Environments, in 2013, as an extension of an earlier program, titled the Microbiology of the Built Environment, says Paula J. Olsiewski, a program director at Sloan. Atmospheric chemists were the natural choice to receive grants from the indoor environments program when it launched.

In atmospheric chemistry, "the sophistication of the instrumental techniques and the complexity with which we've been viewing the chemistry has just exploded in the past 10 or 20 years," says Jonathan Abbatt, a chemist at the University of Toronto who was part of the Sloan program's first cohort. "Those techniques are being brought indoors now."

Chemists participating in the Sloan program today aren't starting from scratch. They're building on some indoor chemistry studies that came before the new push to understand the air we breathe in our homes.

One such study was the Relationship of Indoor, Outdoor, and Personal Air (RIOPA) study. Researchers measured the concentrations of a targeted set of volatile and semivolatile organic compounds (VOCs and SVOCs, respectively) and the mass of fine particulate matter outdoors and in a large number of homes in three cities in the US (*J. Exposure Sci. Environ. Epidemiol.* 2004, DOI: 10.1038/sj.jea.7500379). They found that carbonyl compounds such as formaldehyde and acetaldehyde had higher concentrations indoors than outdoors, suggesting that they had strong indoor sources. Other compounds, such as acrolein and crotonaldehyde, came primarily from outdoors into the homes, which were nonsmoking (*Atmos. Environ.* 2006, DOI: 10.1016/j.atmosenv.2005.12.005).

Barbara J. Turpin, now at the University of North Carolina at Chapel Hill, was one of the leaders of RIOPA. "I got involved in indoor chemistry because of outdoor chemistry," Turpin says. "[Indoors is] the main place where people are exposed to outdoor pollution."

That seemingly paradoxical statement is true because people spend most of their time indoors and because there's significant air exchange between the indoor and outdoor environment. Such exchange is driven by mechanical ventilation systems and natural ventilation, which includes doors and windows.

For RIOPA, Turpin and her collaborators collected and stored air samples for later laboratory analysis. They measured indoor concentrations, outdoor concentrations, and concentrations immediately around people. Such data, derived from stored samples, can provide a time-averaged glimpse of what's in the air, but they can't provide information about how certain activities cause real-time changes in the chemistry.

Digging deeper

To get that real-time picture, researchers are now conducting more extensive field studies. In these studies, scientists look at only one or two houses at a time, but they do so thoroughly, with heavy-duty instruments that let them analyze a broader range of compounds throughout the day.

For example, Nazaroff and Allen H. Goldstein, also at UC Berkeley, have done studies in two houses in Northern California. In one house, they measured SVOCs with semivolatile thermal-desorption aerosol gas chromatography (*Indoor Air* 2019, DOI: 10.1111/ina.12561). They made measurements hourly throughout a multiweek campaign.

In the other house, they measured VOCs using proton-transfer reaction time-of-flight mass spectrometry (*Indoor Air* 2019, DOI: 10.1111/ina.12562). The researchers used tubing to bring air to the instrument from the outdoors as well as five indoor spaces—attic, basement, kitchen, bedroom, and crawl space. They cycled through the spaces every 30 min.

Nazaroff and Goldstein were surprised by what they found. "The vast majority of organic chemicals that we could measure in air were substantially higher indoors than outdoors," Goldstein says. Out of approximately 200 detected chemicals, about half had concentrations about 10 times as high indoors as outdoors, and about 80% had concentrations at least twice as high indoors.

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>
> **—Allen H. Goldstein,** atmospheric chemist, University of California, Berkeley

Some emissions came from cooking and cleaning. "It was clear that cooking with the oven at high heat tended to cause a lot more emissions than other types of cooking. We had a day where the residents broiled some scallops at very high temperatures, and the emissions were impressive," Goldstein says. The emissions were coming not from the scallops but from deposited organic films inside the oven that were baking off.

Some of the most interesting indoor chemicals come from spices used in cooking, Goldstein says. "A lot of flavor compounds in spices are actually terpenoids—monoterpenes and sesquiterpenes and terpene alcohols. It turns out that many of those chemicals are quite reactive in air."

The time-resolved measurements allowed the researchers to see such activities as spikes on top of an already high—and persistent—background.

"If the high background levels are persistent, it means there are continuous emissions indoors. They're from the building itself or from organic films that are on all the surfaces," Goldstein explains. "We could make the concentrations go down by increasing the ventilation rate of the house. But as soon as we turned down the ventilation rate by closing the windows, all the chemicals came back to their baseline, which means that there's a relatively abundant reservoir of most of these chemicals indoors."

So the contents of a house can be a source for chemicals emitted into the air. And so can the house itself. The researchers saw some compounds that they think are degradation products of hemicellulose and lignin from the house's wooden frame.

"The way we did these studies was very intensive," Goldstein says. In addition to the chemical measurements, they asked residents to keep a diary of all their activities in the houses. They installed sensors to keep track of which rooms were occupied, which windows were open, and which appliances were on or off. "The residents had to be extraordinarily willing to cooperate with us."

Photochemical effects

But compounds emitted into the indoor air can be tricky: they can transform into

Researchers can measure emissions from the skin and breath of occupants in this steel chamber.

CREDIT: COURTESY OF JONATHAN WILLIAMS AND GABRIEL BEKO

other molecules, making tracking them difficult. Oxidation reactions are the main pathway for the transformation of chemicals in the air. Outdoors, hydroxyl radicals are the main players in these reactions. The radicals are generated when sunlight breaks down, or photolyzes, ozone and other precursors. The radicals then go on to pluck electrons from nearby compounds and transform them.

Most of the precursors that become hydroxyl radicals outdoors can't be photolyzed indoors because there isn't enough light, says Cora Young, a chemistry professor at York University who studies oxidation chemistry both outdoors and indoors. Indoors, oxidants other than hydroxyl radicals come into play. Young is particularly interested in the role of chlorine as an oxidant. It plays only a minor role outdoors, but it may play a bigger role indoors.

Chlorine is also generated by the photolysis of precursor molecules, but it requires less light for its creation. "Even with the weak light sources indoors, you can still get photolysis," Young says. "We're still in the beginning stages of understanding this, but it seems like there's a potential for chlorine to be a lot more important than previously thought because of the differences in light availability."

In one study, Young used cavity ring-down spectroscopy to measure hydrogen chloride levels generated by cooking, mopping with bleach, and running a dishwasher (*Indoor Air* 2018, DOI: 10.1111/ina.12509). HCl forms when chlorine reacts with organic compounds in the air, so it's essentially a marker—though an ambiguous one—that oxidation chemistry has occurred. The dishwasher emitted HCl only when chlorinated detergent was used, with emissions occurring during both the washing and drying cycles. Both mopping with bleach and cooking increased HCl levels. The dwelling's electric stove had no emissions when it was on without food, so Young presumes that the observed HCl increase during cooking comes from the food itself.

Gas stoves are a major source of indoor oxidants. The combustion produces a lot of nitric oxide, which reacts with ozone. That interaction removes ozone from the indoor environment, eliminating it as a potential oxidant, Young says. But stoves also seem to produce a lot of HONO (nitrous acid), which can photolyze under low-light conditions and form hydroxyl radicals. "I've spent a lot of time measuring NO_x and HONO outdoors," Young says. "When I saw these levels coming from the gas stove, I was tapping the instrument, asking, 'Is this thing OK?' I've never seen anything like it before."

All these oxidants are of interest, not necessarily because they're harmful themselves but because they can lead to the production of new compounds, which may or may not have health effects.

Scratching the surface

When atmospheric chemists move indoors, another big difference they notice, aside from lower light levels, is the ubiquity of surfaces. Outdoors, these scientists often study chemistry that occurs in the upper atmosphere, and the main surface they're concerned with there is the surface of aerosol particles.

"If you're away from the ground in the atmosphere, there's the particle, and there's a lot of air. And the amount of material that's in the condensed phase in the particles is small," the University of Toronto's Abbatt says.

But indoors, surfaces are everywhere. They are places where chemicals can be adsorbed and reemitted, often after undergoing some sort of reaction. And the amount of material on those surfaces is much higher than in the great outdoors.

Vicki H. Grassian, a chemist at the University of California San Diego, is studying indoor surface chemistry. She's also the leader of the SURFace Consortium for Chemistry of Indoor Environments (SURF-CIE), which is part of Sloan's Chemistry of Indoor Environments program. Indoor chemistry is "one of the hardest problems I've ever thought about in terms of chemical complexity," she says. She is studying indoor surfaces to determine what compounds are deposited on which surfaces. She is particularly interested in the molecular mechanisms of processes happening on indoor surfaces. Such data could then be fed into computational models of indoor chemistry.

Grassian's group has started with glass model systems to mimic windows and other glass surfaces. The researchers are studying how organic gases and particles interact with silica surfaces, how these species stick to the surface, and how they get pushed off again (*Chem. Sci.* 2019, DOI: 10.1039/C8SC05560B). They're also studying how the gases react with indoor oxidants. The team uses atomic force microscopy coupled to infrared spectroscopy to study the deposition of organic films on glass surfaces placed in various indoor environments (*Environ. Sci. Technol. Lett.* 2018, DOI: 10.1021/acs.estlett.8b00355).

Glass isn't the only surface in homes. There are also walls and countertops and carpets.

Textiles such as carpets and clothing have a huge capacity to absorb organic compounds, says Glenn Morrison, an environmental engineer at UNC Chapel Hill. "If you put new carpet in a home, it will release VOCs. But it's also going to be absorbing so many SVOCs that you'll see the concentration of SVOCs in the air go down for months."

The human factor

When Jonathan Williams, an atmospheric chemist at the Max Planck Institute for Chemistry, became interested in indoor chemistry, he realized that every home has the potential to be different. People cook different foods. They use different cleaning products, different furnishings, different consumer products. And some people smoke.

"Every house on the street can have a different exposure," Williams says. He wanted to look at factors that apply to all homes. "What is the common thing in any living space? There's only one, and that is the person."

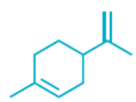
Williams's group had already measured volatiles emitted by people in a cinema to detect their emotional responses to films. So he knew that people emit "a prodigious amount of chemicals." He then extended this cinema work to collaborate with researchers at the Technical University of Denmark measuring volatile chemicals emitted by people.

The researchers ran experiments in room-sized steel chambers with low background emissions. They varied the temperature, humidity, and ozone concentration of the chamber and the age and clothing cover of the participants. "With just those five variables, we were able to see enormous differences in what a person emits," Williams says. They measured how those variables affected VOCs, ammonia, carbon dioxide, methane, particles, total OH reactivity (a measure of the total reactivity of the air, from which they hope to deduce the amount of radicals), and microbes.

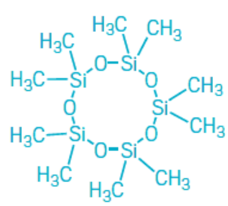
He and his collaborators found that at low temperatures, humans emit less VOCs than at high temperatures. In and of itself, this might not be surprising, but "even 5 degrees makes a big difference," Williams says. And a person's choice of long or short sleeves affected the measurements. "People have to become aware that the decisions they make can really influence the chemicals that they're exposed to because a lot of them are coming from their skin or breath."

UC Berkeley's Goldstein and his colleagues have also done observational studies of occupants' effects on the air composition in a university classroom (*Environ. Sci. Technol.* 2016, DOI: 10.1021/acs.est.6b04415). The researchers measured the VOCs and ozone in the room for 2 weeks.

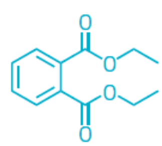
Oleic acid



Limonene



Decamethylcyclopentasiloxane (D5)



Diethyl phthalate

Squalene

Chemicals in indoor environments come from many sources. The ones shown here come from cooking (oleic acid), cleaning products (limonene), personal care products (D5), vinyl flooring (diethyl phthalate), and people themselves (squalene).

"We discovered that when a classroom was normally occupied with more than about 20 students, two-thirds of the volatile organic compounds in the room were coming from the people, a little less than a third was coming from outdoors, and less than 10% was coming from objects in the room itself," Goldstein says. They detected by-products of metabolism such as isoprene and acetone.

The largest emissions by far were from personal care products. The levels were highest in the morning and tapered off later in the day.

"We were very surprised that the dominant volatile organic compound in the room turned out to be a cyclic methylsiloxane," Goldstein says. The main one, decamethylcyclopentasiloxane, known simply as D5, is a common ingredient in antiperspirants, hair conditioners, cosmetics, and lotions and acts as a lubricant or moisturizer in these products. "People were being exposed to these cyclic methylsiloxanes even if they chose not to wear the personal care products," Goldstein explains. "We're all breathing the air in the room."

Group effort

Intense indoor studies in residential settings are limited by what the occupants of a house will endure. It's a not-so-secret secret, Young says, that most indoor air studies in homes are conducted inside the principal investigator's house. That way, she jokes, "occupants' complaints can be managed." But a way around such complaints is to do a study where there are no occupants.

Members of the indoor chemistry community banded together in 2018 to undertake a 4-week field study inside a house specifically set aside for measurements. HOMEChem—House Observations of Microbial and Environmental Chemistry—was the brainchild of Delphine K. Farmer, an atmospheric chemist at Colorado State University, and Marina E. Vance, a mechanical engineering professor at the University of Colorado Boulder.

They wanted to do a large-scale field campaign like the ones the atmospheric chemistry community undertakes. Such a project would create a treasure trove of data, and the process of carrying it out would bring researchers together as a tight-knit community. "After a couple of meetings with a whiteboard, we had the idea for HOMEChem," Farmer says. The Sloan Foundation provided more than $1 million for the project.

Top left: Researchers and visitors pose in front of the test house at the University of Texas at Austin used for the HOMEChem field campaign. Top right: Researchers made measurements while performing various activities. Here, they're measuring the temperature, which affects emissions, while cooking stir-fry. Bottom left: Researchers set up instruments inside the test house before the start of HOMEChem. Bottom right: Delphine Farmer (left) and Allen Goldstein chat during the HOMEChem campaign.

CREDIT: CALLIE RICHMOND (ALL)

And the perfect house was waiting for them at the University of Texas at Austin. A group of professors there had bought the never-lived-in manufactured house with funds from their US National Science Foundation IGERT (Integrative Graduate Education and Research Traineeship) grant, says Richard L. Corsi, one of the original purchasers, who is now dean of the Maseeh College of Engineering and Computer Science at Portland State University.

The house is designated as a piece of laboratory equipment. That means it doesn't have a lived-in history. (And researchers aren't allowed to sleep there.) But it provides a place for running experiments that might be too intrusive to perform in a person's actual house.

HOMEChem builds on the legacy of studies such as RIOPA and the ones carried out by Goldstein and Nazaroff—both of whom also took part in HOMEChem.

"We had a huge amount of advanced online instrumentation," Farmer says. "We were able to look at orders of magnitude more types of molecules in the indoor environment than had previously been seen simultaneously."

In addition to measuring organic compounds, the researchers also measured oxidants such as hydroxyl radicals, ozone, and nitrogen oxides. "They're crucial to understanding what happens in an indoor environment," Farmer says.

But the biggest difference between HOMEChem and previous studies is that the earlier studies were observational—the scientists didn't tell the occupants what to do. In the case of HOMEChem, "we were able to ask what happens if you do certain activities," Farmer says.

Dozens of researchers descended on the UT Austin test house in June 2018. They carried out a packed schedule of experiments that looked at factors such as occupancy, cooking, cleaning, and ventilation (*Environ. Sci.: Processes Impacts* 2019, DOI: 10.1039/c9em00228f). Some days, a single type of activity was repeated multiple times, such as cooking stir-fry and letting the house air out between batches.

Other days involved sequential activities such as cooking followed by intense cleaning. They used different cleaning regimens on different days to see how various types of cleaning products—pine-oil-based, chlorine-based, ammonia-based, and so-called natural cleaning products—affected the chemistry in the house. Mopping with a pine-scented cleaner raised limonene levels, whereas mopping with bleach raised chloroform levels.

The researchers measured particle concentrations inside and outside the house. They found that concentrations of particles smaller than 2.5 μm were generally lower inside than outside, but not during cooking.

Peter F. DeCarlo of Drexel University measured aerosol particles as part of HOMEChem. "Many indoor particles come from outdoors," he says. "But cooking activities generate huge amounts of particles that dwarf the concentration coming in from outdoors." These particles come from cooking-fuel combustion and from cooking oils and food.

The researchers also found that the order of activities influenced the indoor air chemistry in their experimental home. If they first mopped without having done something else—such as cooking—they got one set of observations. If they cooked dinner and then mopped, they got another set of responses.

"We don't see a changing baseline from day to day, but we do see that what happened immediately before one activity can impact the chemistry that's occurring," Farmer says. The chemicals from different activities were reacting with one another to form new products.

DeCarlo's group also measured ammonia in the test house. Ammonia is a known eye and lung irritant. It's also quite reactive. DeCarlo is interested in ammonia because it's been shown to drive other nitrogen-containing species off surfaces and back into the air. A prime example is nicotine from tobacco smoke that's been deposited on surfaces—so-called thirdhand smoke—being driven back into the air.

But first, DeCarlo needed to determine an ammonia baseline. He and his team found that the background level of ammonia indoors was about 10 times as high as typical outdoor levels (*Environ. Sci. Technol.* 2019, DOI: 10.1021/acs.est.9b02157). All the planned activities—cooking, cleaning, and occupancy—increased ammonia levels, with the biggest boost coming from cleaning.

DeCarlo suspects that the high background level of ammonia is coming from the building itself. "What we're learning more and more is that building materials become a sponge for whatever's happening inside," he says.

Moving toward health

Studies such as HOMEChem still mark the early days of understanding indoor chemistry. HOMEChem and most other field studies at this point are cataloging the organic compounds in homes and trying to establish a baseline of what's in indoor air before asking questions about

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>
> —**Peter F. DeCarlo,** atmospheric scientist, Drexel University

whether those compounds are harmful. Some studies, however, have begun assessing the health effects of specific suites of chemicals.

For instance, Heather M. Stapleton of Duke University is leading the TESIE, or Toddlers' Exposure to SVOCs in Indoor Environments, study. In that experiment, researchers have visited homes in the Durham, North Carolina, area and collected house dust samples, hand wipes from children, and blood and urine samples from kids who were willing to participate (*Environ. Int.* 2019, DOI: 10.1016/j.envint.2019.105061). The scientists were focused on detecting molecules such as flame retardants, plasticizers, and pesticides.

They found that the amount of phthalates in children's urine correlated with the percentage of vinyl flooring in the house. Phthalates are used as plasticizers in vinyl flooring and are known to have endocrine-disrupting effects. In some homes, all the floor was vinyl. Children in those homes had elevated levels of phthalate metabolites.

"Unfortunately, in our study, the homes that had 100% vinyl flooring were public housing," Stapleton says. Public housing authorities renovate such homes infrequently, so residents have little choice when it comes to replacing old flooring.

Despite such studies, understanding exposure and how various compounds affect human health is still a long way off.

"It's very clear that most of our exposure to organic chemicals is happening in indoor air, and most of that is happening in residences," Goldstein says. "It's relevant to try to understand these things, but we certainly aren't trying to make a claim that we know a specific health effect that people should worry about from these chemistries that we're observing." ■