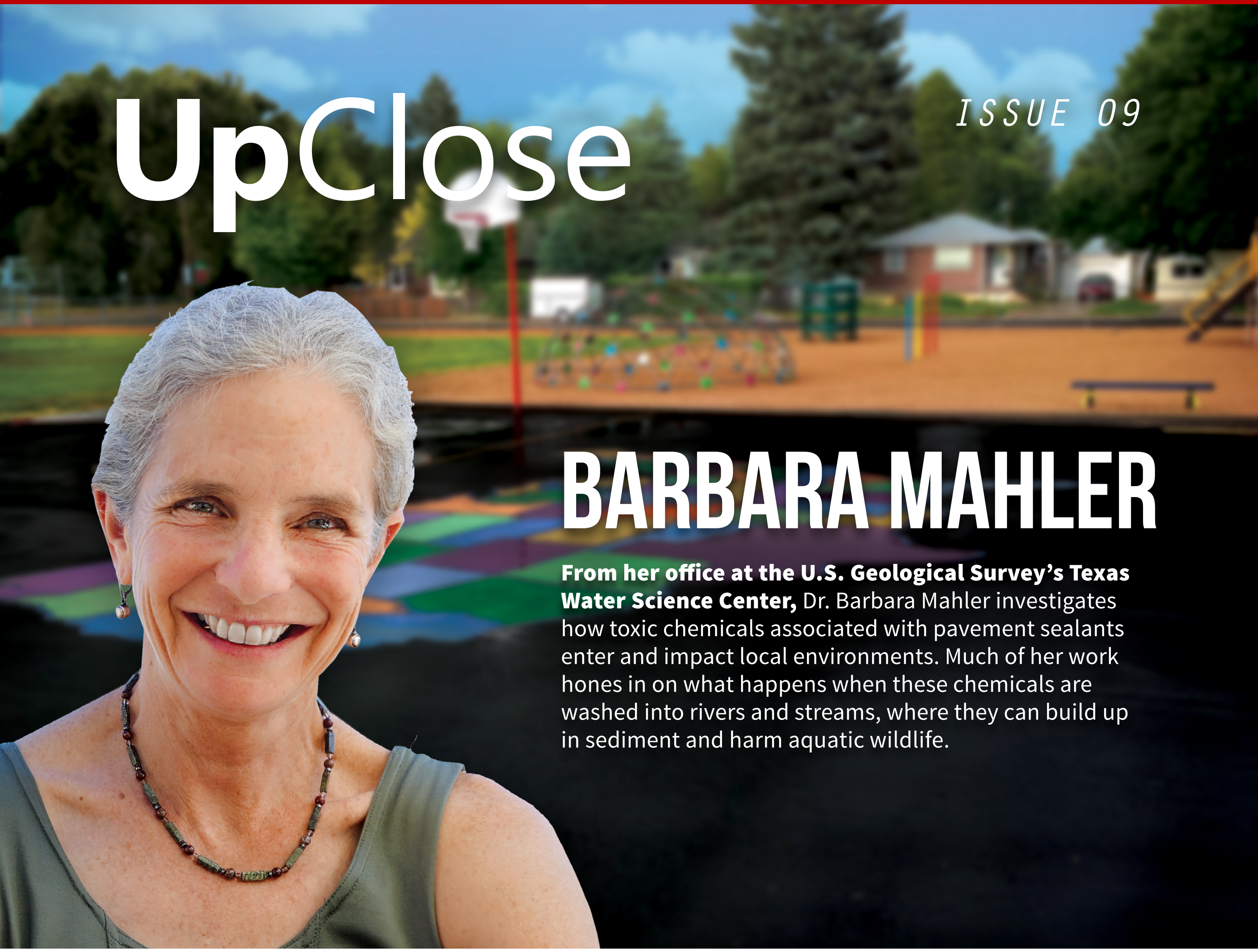
UpClose

ISSUE 09



BARBARA MAHLER

From her office at the U.S. Geological Survey's Texas Water Science Center, Dr. Barbara Mahler investigates how toxic chemicals associated with pavement sealants enter and impact local environments. Much of her work hones in on what happens when these chemicals are washed into rivers and streams, where they can build up in sediment and harm aquatic wildlife.

How did you first become interested in coal tar sealcoat?

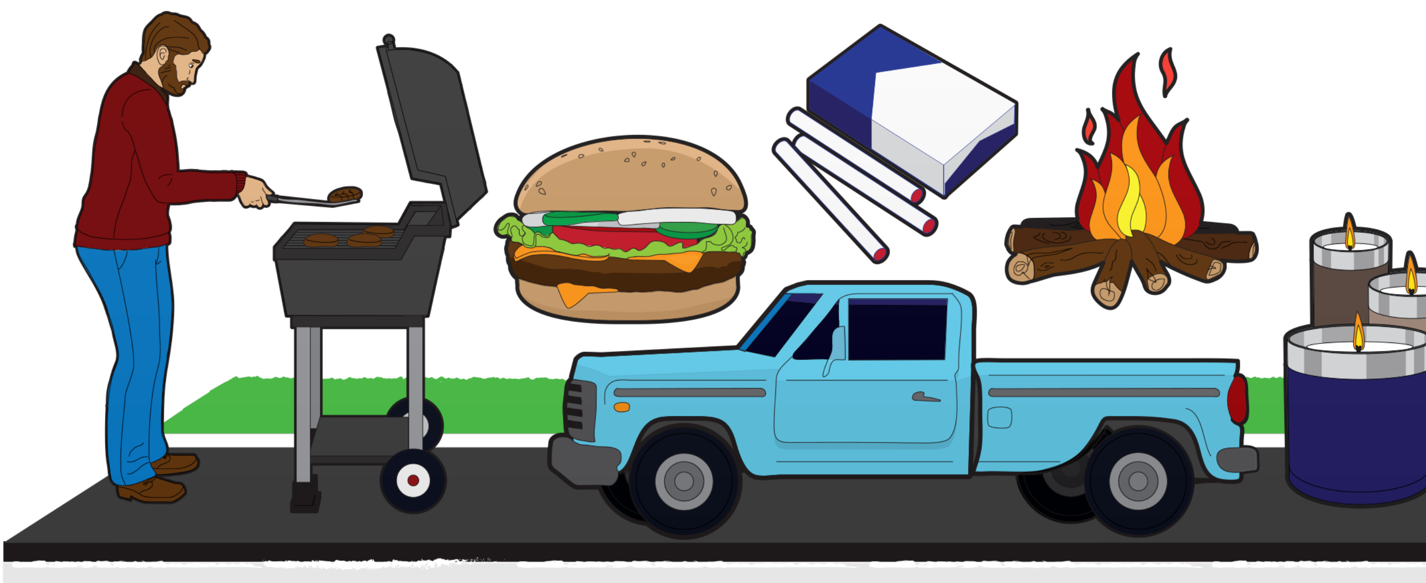
Our team became interested very peripherally. We didn't just wake up one morning and decide this was something that we wanted to investigate. I had been interested in polycyclic aromatic hydrocarbons (PAHs) for a long time. It is a very interesting group of chemicals—they are ubiquitous in the environment, have known health effects, and have been very well studied. This was one of the groups of contaminants we were investigating associated with sediment contamination.

I work for a small group that is part of the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) program. One of the main objectives of the NAWQA program is to evaluate or identify trends in contaminants in water and sediment and then try to understand the causes of those trends—what is making concentrations increase or decrease? Our group was going to lakes and reservoirs across the U.S. collecting sediment cores and looking for how concentrations of contaminants associated with sediment change as you move from older to more recent sediment. What we found was that concentrations of contaminants like DDT, PCBs, chlordane, and some metals were decreasing in the more recent sediment. For example, we saw high concentrations of lead, which is now banned in gasoline, in sediment deposited in the mid-1960s and then started to see concentrations decrease at an exponential rate in the more recent sediment.

We were also looking for whether there were contaminants that were increasing in more recent sediments, and why. That is where PAHs came in because their concentrations were increasing in sediment cores in many parts of the country, largely in urban lakes. This was a surprise to us because there had been quite a bit of documentation in earlier decades that PAH concentrations were decreasing due to improvements in industrial emission controls, home heating, and coal use. But those had been in rural areas where most of the contamination comes from atmospheric deposition. The lakes we were sampling were mostly getting contamination from urban runoff. So, we saw downward trends in rural lakes with atmospheric deposition but upward trends in urban lakes with stormwater runoff. That is when we started asking, “What are we seeing in urban stormwater runoff that is leading to increased concentrations of PAHs?”

But that still didn’t immediately lead us to coal tar sealcoat. The clue for that was first brought up by personnel from the City of Austin Watershed Protection Department. They were also investigating sediment-associated contaminants, and I was doing a cooperative study for them. They had found some extremely high concentrations of PAHs in small urban drainages for residential and light commercial areas. The concentrations were so high that at first we didn’t believe them. They were as high as what you would find at a Superfund site [an area contaminated by large amounts of hazardous waste]. They traced the PAHs to parking lots upstream of these little tiny drainages that had sealcoat on them, investigated what was in sealcoat, and discovered that one major formulation has coal tar, which has very high concentrations of PAHs. That is what led us to investigate urban contamination from PAHs associated with coal tar sealcoat.

EVERYWHERE YOU LOOK
SOURCES



PAHs are created during the combustion of any carbon-based material—from wood to gasoline to meat. These ubiquitous chemical compounds are also found in automobile tires, motor oil, and coal tar pitch.

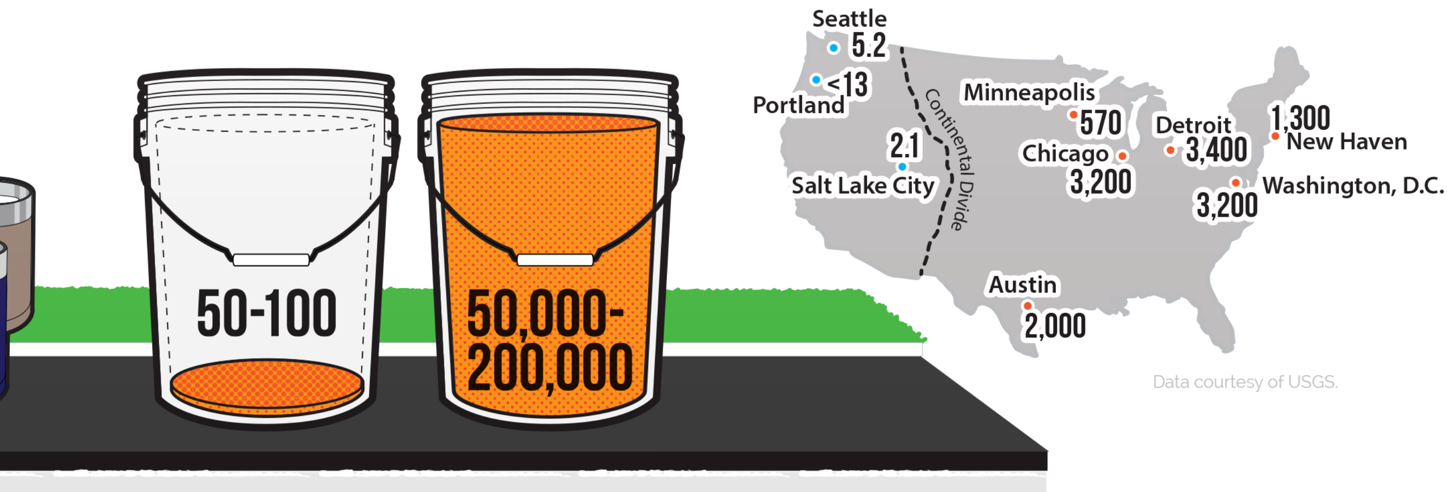
What is coal tar sealcoat, and how is it used?

Sealcoat generically is a black shiny liquid sprayed or painted on the asphalt of parking lots, driveways, and even some playgrounds. It is very rarely used on roadways. It's an optional product that you can apply yourself or have applied after the paving process. It is marketed as increasing the longevity of the underlying asphalt and improving the appearance—it makes the pavement look black and shiny, and the lines show up really well. But sealcoat eventually wears off. The abrasive action of car tires and snow plows abrades the sealcoat into tiny dust particles that wash off, are blown off, or are removed by tires, shoes, etc. Sealcoat typically is reapplied every 3-5 years. Some homeowners even reapply every year.

There are two major formulations of sealcoat used in the U.S. There is an asphalt-based sealcoat, which is primarily used west of the Continental Divide. And there is a coal tar-based sealcoat that is primarily used east of the Continental Divide. This divide isn't hard and fast. There has been coal tar used in the West and asphalt used in the East. But by and large, there is a pretty strong geographic distribution.

These two formulations look very similar, but they are very different chemically. The asphalt-based product has very low concentrations of PAHs because asphalt itself has low concentrations. There are typically around 50-100 parts per million (ppm) of PAHs in an asphalt sealcoat off the shelf. The coal tar-based sealcoat is typically 20-35 percent coal tar pitch or crude coal tar, both of which are known human carcinogens. And the PAH concentration in a coal tar seal-coat-based product off the shelf can range anywhere from 50,000 to 200,000 ppm.

NOT ALL SEALCOATS ARE CREATED EQUAL
EAST VS. WEST



Although they look similar, coal tar sealcoats have drastically higher parts per million concentrations of PAHs than the asphalt-based alternative. In the West, where asphalt-based sealcoats are more commonly used, PAH concentrations in dust swept from sealed parking lots are roughly 1,000 times lower than in the rest of the country, where coal tarsealcoat dominates.

How do PAHs from coal tar sealcoat enter the environment, and why is that concerning?

This is a large group of contaminants formed whenever we burn any type of organic matter. Burning paper, heating motor oil in your car, automobile emissions, cooking a hamburger, used tire particles—all of these create PAHs. So, PAHs are pretty much everywhere in the urban environment.

The big question is, if there are all these different sources of PAHs in the urban environment, which ones are the most important? That is where concentrations start to come into play. Something like tire particles have 50 ppm of PAHs, and coal tar sealcoat has 50,000 ppm. Another good example is used motor oil. This typically has about 500 ppm of PAHs, meaning coal tar sealcoat has about 100 times as many PAHs. One gallon of coal tar sealcoat is equal to 100 gallons of used motor oil in terms of the PAH content.

Why are we concerned about PAHs? Seven have been identified as probable human carcinogens, and there is an enormous amount of scientific literature that has linked PAHs with mutations, birth defects, cancer, and death in just about every organism you can think of—from little worms and snails up through insects, birds, and mammals.

Are some PAHs more carcinogenic than others? Can the PAHs from coal tar sealcoat be compared with other products?

Some PAHs are more carcinogenic than others. Some are more toxic than others. But in general, the combustion sources, such as used motor oil, wood smoke, and coal tar, tend to create more high-molecular weight PAHs. And what we do know is that many of these PAHs are known to cause cancer.

Let's back up a tiny bit. What is a PAH chemically? A PAH is a chemical that has as its base something called the benzene ring. Benzene has six carbons in a ring. If you start putting those rings together, you get PAHs. Two rings is a PAH—naphthalene. And you could add a third ring or a fourth ring. So, you end up with different numbers and geometric arrangements of benzene rings, but each one is a PAH.

When we say something is known to cause cancer, how is that determined?

The U.S. Environmental Protection Agency and the International Agency for Research on Cancer classify PAHs and other chemicals according to their carcinogenicity. They base these decisions on the scientific literature.

Given that there are so many types of PAHs and so many sources, how do you know the PAHs you see in the environment came from coal tar sealcoat?

We used multiple lines of evidence to try and determine the source of PAHs. One of the approaches we have taken—paired studies—is pretty direct. For example, we sweep dust off an unsealed parking lot and compare PAH concentrations in that to concentrations in dust swept from coal tar-sealed parking lots. We have done a lot of paired studies like that. We looked at PAHs in house dust in apartments that had a coal tar sealcoated parking lot vs. apartments that had a parking lot that wasn't sealed or had an asphalt sealcoat.

Another approach that we use is the PAH fingerprint. PAHs are present in different proportions in different sources. And the proportion of different PAHs in a source—you could think of that as its fingerprint. So, car tire particles have a slightly different proportion of different PAHs than, say, coal tar or used motor oil. We can take advantage of those different fingerprints and statistically determine the combination of PAHs sources that would reproduce the fingerprint we measure in sediment collected from a stream or a lake.

Another interesting angle was taken by Robert Pavlowsky at Missouri State University. He measured PAHs in stream sediment and compared that to how much of the upstream area had coal tar-sealed parking lots. He found a statistically significant relationship that showed that the more coal tar sealcoated parking lots there are upstream of where he had collected the sediment, the higher the PAH concentration in the sediment itself. This takes that paired study idea one step further.

And there are others as well, other lines of evidence. For example, there is something called petrography where you look at carbon particles under a microscope and identify the source of those particles from their form and shape. There was a group at the University of Illinois led by Charles Werth that used organic petrography to identify the carbon source of PAHs on parking lots, for example. Interestingly, they found that a lot of the PAHs on an unsealed parking lot were coming from coal tar. The hypothesis there is that the abraded pieces of sealcoat are sticking to car tires and being transported to other surfaces, like unsealed parking lots.

How do PAHs from coal tar sealcoat get into house dust?

I think it is safe to say that we have learned that wherever coal tar sealcoat is used, there are PAHs in pretty much every environmental compartment in close proximity. Whether it's soil, stormwater detention ponds, house dust, or air, there are very high PAH concentrations.

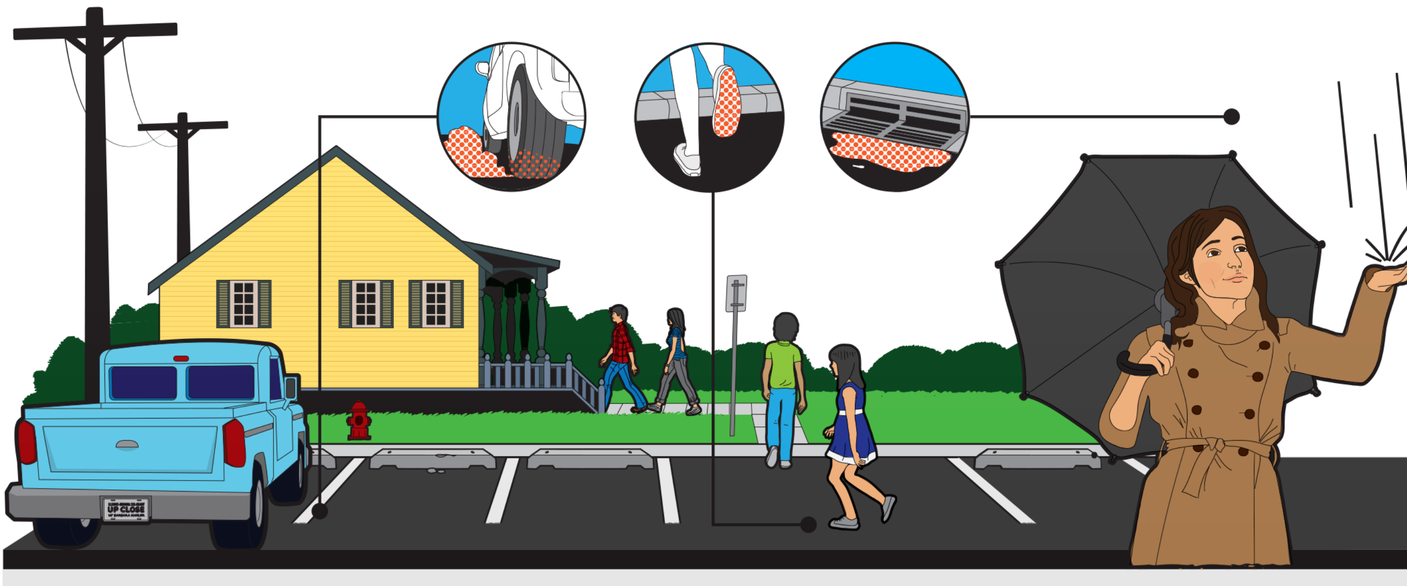
When you walk across a parking lot, bits of dust stick to your shoes, and you carry them indoors with you. In fact, there has been a lot of very interesting work on contaminants in house dust. One of the best known is lead, which was associated with lower IQ in children because children eat dust. It is called non-dietary digestion. Kids spend a lot of time on the floor and then put their hands and toys in their mouths. Anything that is incorporated into the house dust ends up in the kids.

We had read papers on PAHs in house dust, but we were curious to see if the presence or absence of coal tar sealcoat made a difference in those concentrations.

Do children living near coal tar sealcoated areas have an increased cancer risk?

That was the question we asked ourselves, so we worked with a toxicologist at Baylor University, Spencer Williams. We actually had two questions we wanted to answer. The common understanding is that children ingest most of their PAHs from eating grilled meat and even vegetables and beverages. We were curious about the child that lives in an apartment that has a coal tar sealcoated parking lot or driveway. With these higher concentrations of PAHs in the house dust, are they still getting most of their PAHs from their diet, or might they be getting more from non-dietary ingestion?

FROM YOUR DRIVEWAY TO THE ENVIRONMENT
PATHWAYS



Once dry, coal tar sealcoat is abraded into a powder that becomes part of pavement dust. That dust, and the PAHs it contains, is then carried to nearby lakes and rivers in stormwater runoff or tracked into homes and businesses on the bottom of our shoes. Pavement dust can also stick to tires that track the PAHs to new locations.

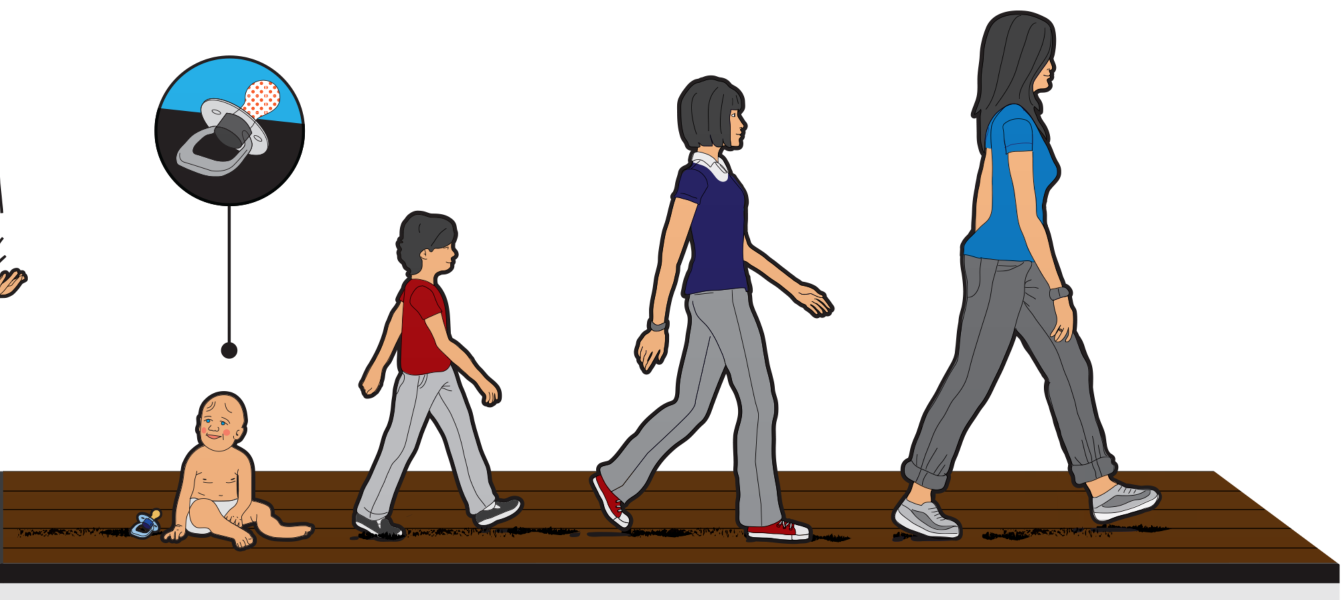
Using our house dust data, the first analysis Spencer did found that the average child living next to coal tar-sealed pavement was actually getting about two times more PAHs through incidental ingestion of house dust than from their diet. And a child living near coal tar sealcoated pavement that consumes, say, 100 milligram of dust per day—about the size of a baby aspirin, so not a huge amount of dust—is getting about 10 times more PAHs through non-dietary ingestion.

That was question number one, which led us to your question. Spencer did a human health risk analysis. This is not an epidemiological study. It is based on PAH concentrations in dust, ingestion rates, and what has been published in the literature about ingestion rates, doses, and cancer rates. What he found was that there was a statistically significant increase in cancer rates for people living next to coal tar-sealed pavement. The lifetime estimated cancer rate was 36 times greater for people who spent their lives living in an environment that was adjacent to a coal tar sealcoated parking lot or driveway. And most of that increased risk was incurred during childhood years.

You have also studied PAHs from coal tar sealcoat in lake sediment, like in Texas's Lady Bird Lake. Why that lake?

There are several reasons. It's not just that that the USGS Texas Water Science Center is in Austin. One of the things that made Lady Bird Lake really uniquely situated for that study is that Austin was the first municipality to ban the use of coal tar sealcoat. They banned its use in 2006. So, the obvious question is, what has happened 6-8 years after the ban? Have PAH concentrations gone down in response to the ban? Because this was the first municipality to ban the use of coal tar sealcoat, it represents the longest amount of time that had passed since

PAHS AND HOUSE DUST
IMPACTS ON HUMAN HEALTH



An analysis of PAH concentrations, human ingestion, and cancer rates suggests that the lifetime cancer rate is 36 times greater for those living next to coal tar-sealed pavement. This increased risk is primarily due to ingestion of PAH-contaminated house dust a ban. There is enough of what we call noise in environmental data that you want to make sure that enough time has passed to let you really see a trend. Concentrations bounce up and down. If you look at a very short time period, you might not see anything significant. So we wanted a long enough period of time to have gone by that we could see any trends there may be.

The second reason is that Lady Bird Lake has a pretty good sized watershed, and about 50 percent of the watershed is part of the city of Austin or its extra territorial jurisdiction—the area where the ban was enacted. The other half is not very developed. It's pretty rural. So, we have a good sized lake and a good sized watershed. That made it another good place to try and do this analysis because the sediment in the lake represents the effects of what is going on in the whole city, not just in one neighborhood.

And there is actually one more reason now that I think about it. We had collected a core in the lake in 1998 before the ban was enacted and had seen a strong upward trend in PAHs. Between when the lake was built in 1959 and 1998, we saw about a 20-fold increase in PAH concentrations.

Was coal tar sealcoat used frequently in Austin before the ban?

Yes. Prior to the ban, coal tar sealcoat was used pretty much uniformly. The city estimated that there was about 660,000 gallons of coal tar sealcoat applied every year.

Why did you collect the 1998 core?

It was part of a national study for the NAWQA program looking at contaminant trends in sediment cores across the U.S. In fact, we were really interested in DDT in Austin because there was a very well publicized DDT contamination event that occurred in the early 1960s, which was written up in *Silent Spring*. We were curious to see how that DDT release, and the ultimate restriction on the use of DDT, was reflected in the sediment core.

For all of our sediment cores, we analyze a wide range of constituents—metals, DDT, PCBs, chlordane, and PAHs. So PAHs were just one of the many different contaminants that we had analyzed in the earlier Lady Bird Lake core.

How do you know how much sediment corresponds to a month or a year?

We call that age dating the sediment, and we employ a couple of different markers. If it is a reservoir, one very good marker is the date the reservoir was built. When a wetland area or river is converted into a reservoir, there is a real change in the sediment texture. You know when you walk out in a lake and get all that squishy sediment in your toes? That is a very different type of texture than you get in a river or wetland. What we call the reservoir/pre-reservoir interface is always a strong marker in our sediment cores. And, of course, we know when we collected our cores, so we know the date at the top is when we collected it.

In between there, we have a couple of other markers. One of the things we take advantage of is an isotope of an element called cesium. That isotope was largely produced during the testing of atomic weapons in the 1960s, and it reached its peak in 1963-1964. So we can find the cesium peak in our cores and know that depth corresponds to that date.

And there are some other markers. For example, we uniformly see a peak in lead, and we know that corresponds to just before lead was removed from gasoline. So, we can use some of these known patterns in other contaminants and their restrictions as age markers. In some situations, we can even use large flood events. We can identify flood deposits in a sediment core and say, "We know there was a big flood in 1987, and this sediment was deposited during that flood." In a way, we are detectives, and we use many different clues to try to piece together a core's age.

Do you repeat this analysis with every core taken for a study?

We do it pretty much with every core we take because there is always some spatial variation, even within the same lake or reservoir. When we first started the coring program several decades ago, we were extrapolating from one core to another. But we quickly realized that was not as reliable as we would have liked it to be. So we now do age dating on pretty much every core we collect.

How many cores did you collect in Lady Bird Lake?

We had the core from 1998 and some bed sediment samples that were collected in 2000. And we had a smaller core that was collected in 1999 or 2000. So, we had several data points before the ban. Then we went back in 2012 and collected a couple of long cores. And in 2014 we collected a long core and what we call a box core.

The reason we collect different types of cores is that they tell us different things. The long cores can go further back in time. They go deeper and can get down to that pre-reservoir interface, which is really useful. But they are fairly small in diameter, so to get enough material for the laboratory to analyze, we have to send a very thick sediment interval, which can represent several years. From the long core we collected after the ban, for example, we really only have a couple of samples that represent sediment deposited after the ban. But, we have that pre-reservoir date.

The short box cores are much larger in diameter. They don't go as deep, but we can submit a much thinner sediment interval to the lab, and we can get much finer time differences in the upper part of the core. So, we can get a much better idea of what's going on in the more recently deposited sediments with one of these short, fat cores. We collected some of each so that we had both types of information.

What were the results of the study?

We found that if we compare the peak concentration before the ban to the concentration in the most recently deposited sediments—between 2012 and 2014—we see a decrease in PAH concentrations by almost 60 percent.

Was that surprising?

Frankly, yes. We were surprised because we have done quite a few sediment core investigations as part of the NAWQA program—we have well over 100 cores now—and have calculated how long it takes for the concentration of a contaminant to decrease by half once it's banned. We call that a half time. So, for example, after lead was banned, how long did it take before we saw the concentrations in the most recent sediments fall to half of what they were at its peak?

The half times we have measured typically range from 12 to 15 years. So we didn't expect to see such a large decrease in eight years. We were hopeful that, if there was a change, we would be able to detect it statistically. It was a short time, and there is always noise in the data. But not only were we able to see a statistically significant change, it turned out to be even more than 50 percent, which was larger than we would have expected in this amount of time.

Do you have hypothesis for why?

I don't. It is certainly something we have thought about. I really don't have anything that I can put my finger on that would explain why this was more rapid than we might have expected.

That said, it might be that contaminants like DDT and lead are more associated with soil erosion, which might be a slightly slower process than something that is coming completely from impervious cover, which is well connected to the storm drain system and delivered very rapidly to creeks and streams. That might speed up the change we see. This is just a hypothesis. It hasn't been investigated.

Could we expect similar declines in other lakes if coal tar sealcoat was banned?

We would certainly like the opportunity to analyze this in other lakes. There are a lot of different things that affect the rate at which contaminant concentrations change in a waterbody—everything from sedimentation rate to use to precipitation patterns. So, I wouldn't necessarily say that we would expect to see exactly the same thing in other lakes. But to us, this was pretty strong evidence that restricting the use of coal tar sealcoat would ultimately result in a decrease in PAH concentrations in the receiving waterbody.

Can the full 60 percent decrease be attributed to the ban?

We used the statistical fingerprint approach I mentioned earlier to find out how much of the PAH concentrations at the peak and in 2014 were coming from sealcoat. What we saw was that the majority of the decrease in PAHs was attributable to coal tar sealcoat. At the same time, we also found that quite a bit of the PAHs we are still seeing in the sediment are associated with coal tar sealcoat. So, we can expect that the PAH concentration will decrease over time as legacy sealcoat in the watershed continues to be abraded and removed.

So, the concentration isn't just down. It's trending down?

It is trending down. It has decreased 60 percent, but we believe that it is still continuing to decrease.

Do we know what impacts this could have on wildlife or human health?

There haven't been any studies on that. Even at peak concentrations, the PAH levels in Lake Bird Lake were always less than something called the probable effect concentration, or the PEC, which is 23 ppm for PAHs. That is the level at which we would expect to see adverse effects on the ecological community living in the sediment. It was always lower than that at Lady Bird Lake. But that is largely a function of the fact that it is a really big lake and it gets sediment from a very large watershed.

Concentrations of PAHs in Austin's little tiny streams were extremely high. They were at Superfund site levels. Even within Austin, there is a wide range of concentrations—from 8 ppm in Lady Bird Lake to 1,500 ppm in some of the little drainages. And I would expect we would see the same thing in other parts of the country. There is definitely a size effect. The coal tar sealcoat gets diluted as it works its way downstream with more and more clean sediment.

But there are sites where the concentrations in the sediment exceed the PEC. If you lowered those by 60 percent, you would be at concentrations that would be much less likely to cause adverse effects.

There was one site where the concentrations went up, correct?

Yes, there was an anomalous site. This was not where we collected the sediment cores. Lady Bird Lake is, strictly speaking, a reservoir. There are a series of dams on the Colorado River—not the famous one, but the one in Texas. Each one of those reservoirs has a different lake name. Lady Bird Lake is a really long, skinny lake, and there is some sediment removal when we get large floods. There can be some sediment scouring. But we were able to find an area at the very downstream end of the lake in a kind of lagoon that is depositional and doesn't have a lot of sediment removal. That is where we collected our cores.

The site you are talking about is up reservoir. When we collect bed sediments in those areas, sometimes there is just an inch or so of sediment because it gets scoured out. That upstream site had anomalously high PAH concentrations. When we measured the concentrations in 2008, they were even higher than what we had measured in 2000. This is a bit of a mystery. It looks as though it is a point source because the PAHs are not spreading out into the rest of the lake. At the other bed sediment sites, we saw decreases in PAH concentrations. The PAHs at the anomalous site have a slightly different fingerprint too. There is some point source of PAHs there that doesn't appear to be coal tar sealcoat.

Do you plan to look into that more?

We don't, but that is something the City of Austin may be interested in pursuing.

Do we know how the ban has impacted PAHs in house dust?

That is a really interesting question. We have not looked at how that might have affected house dust. I think a lot of it depends on whether a parking lot with coal tar sealcoat had been resealed with an asphalt-based product.

When we did our earlier study, we didn't just choose 23 random apartments. Half had coal tar sealcoated parking lots and half did not. So, while the proportion of parking lots in Austin with coal tar sealcoat has most certainly gone down because of the ban, we would still see high concentrations of PAHs in the dust on parking lots with legacy coal tar. And, therefore, we would likely still see high concentrations in nearby residences.

Coal tar pitch is also used in industrial aluminum and in roofing. Are we concerned about those products as well?

Coal tar pitch is used in the aluminum industry as part of the electrolysis process, but it is not actually in the consumer product. There is a difference there. It is also used in roofing applications. From what I understand, there are asphalt- and coal tar- based products. From an environmental point of view, the difference is that we aren't resealing our roofs every couple of years because we don't drive on our roofs. We don't have that same process of abrasion that we have with parking lots. There is not that constant action of abrasion and reapplication.

What should homeowners be looking for to determine whether coal tar pitch is in the sealcoat they are using?

At this time, every product that contains coal tar or coal tar pitch should be accompanied by something called a material safety data sheet, or MSDS. These are required to list any hazardous materials. Coal tar, and the amount used, should be listed. MSDSs are being replaced by safety data sheets, but SDSs will still contain information on product ingredients.

What new projects are you working on now?

Up until now, a lot of our research has been on the coal tar sealcoat particles on sediment, in soil, and in house dust. Recently we have been doing some research on the effects of the water part of the runoff. In other words, if you seal a parking lot and then it rains, is the runoff from the parking lot toxic? And for how long after the seal coat has been applied? How long does it take until that runoff is no longer toxic?

We have a couple of studies on that particular subject—one looking at the toxicity of runoff and another looking at its genotoxicity. In other words, how the stormwater impacts cellular DNA and the ability of DNA to repair itself if it's damaged. We had a test plot on a parking lot sealed with coal tar-based seal-coat and collected runoff starting just hours after application and continuing out for more than three months after application. We worked with the Columbia Environmental Research Center toxicity lab in Columbia, MO, which is part of USGS. They did our toxicity tests using fathead minnows, which are little fish, and something called *Ceriodaphnia dubia*, a little water flea at the base of the food chain. The genotoxicity and DNA repair capacity work was done by a group of collaborators in France, actually. We froze all our samples and sent them to them. They did the DNA investigation in Lyon. Both of these studies were recently published and are available on the USGS coal tar sealcoat website.

PHOTOS
U.S. Geological Survey

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