ISSUE 08

UpClose

DANA KOLPIN

As the head of the U.S. Geological Survey's Emerging Contaminants Project, Dana Kolpin has dedicated decades to understanding how pharmaceuticals and other contaminants move through the environment. His work gained popular attention in 2002 with the first-ever nationwide study that discovered trace amounts of emerging contaminants in streams across the country.

What first sparked your interest in pharmaceuticals and other emerging contaminants?

Back in the late 1990s, we were seeing papers coming out of Europe documenting that there were compounds like clofibric acid [a degradate of a cholesterol-lowering drug] in European water resources. About the same time, the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program held a meeting of about 30 USGS scientists from across the country to discuss what research was going to take us into the next century. A number of us had seen the European papers, and we just had a light bulb moment—"We don't have a clue what's going on here in the U.S. in terms of pharmaceuticals and other similar types of environmental contaminants."

One of the defining outcomes of this meeting was the divide-and-conquer approach we took to develop the tools needed to measure emerging contaminants in water. The research chemists in the room would say, "I am interested in pharmaceuticals" or, "I am interested in hormones." So, we were able to divvy up the methods development work based on broad classes of chemicals.

As a research hydrologist, I tapped into the national presence of the USGS by going through our network of offices across the country to find appropriate streams where we were already collecting samples in order to keep the overall costs low. We intentionally biased ourselves to streams where we thought we would find these compounds. We looked for sites with potential sources of emerging contaminants, such as downstream of wastewater treatment plants or in areas where there was intense livestock production. We also included a small subset of minimally-impacted sites just to get samples from the other end of the spectrum. Basically, we thought, “Let’s try the new analytical methods being developed for emerging contaminants, and if we don’t find these chemicals here, it’s not going to be a big issue in the U.S.”

That was our national stream reconnaissance published in 2002. It was our first big foray into determining if pharmaceuticals and other emerging contaminants were in U.S. water resources.

Is that level of collaboration and planning common in work like this?

This is probably one of the first where all the pieces quickly fell into place like it did in terms of people and resources.

Fortunately, the funding climate back then was much different than it is today. Herb Buxton was the head of the USGS Toxic Substances Hydrology Program. He thought this was an interesting line of research worth pursuing and gave us some seed money to see what we could find in terms of environmental occurrence. We moved quickly on this. Over the next two years, we sampled 139 streams across the U.S. looking for almost 100 emerging contaminants. Once we started seeing the early results, we knew we had to publish them quickly. We made a concerted effort to get this study into the literature as soon as possible.

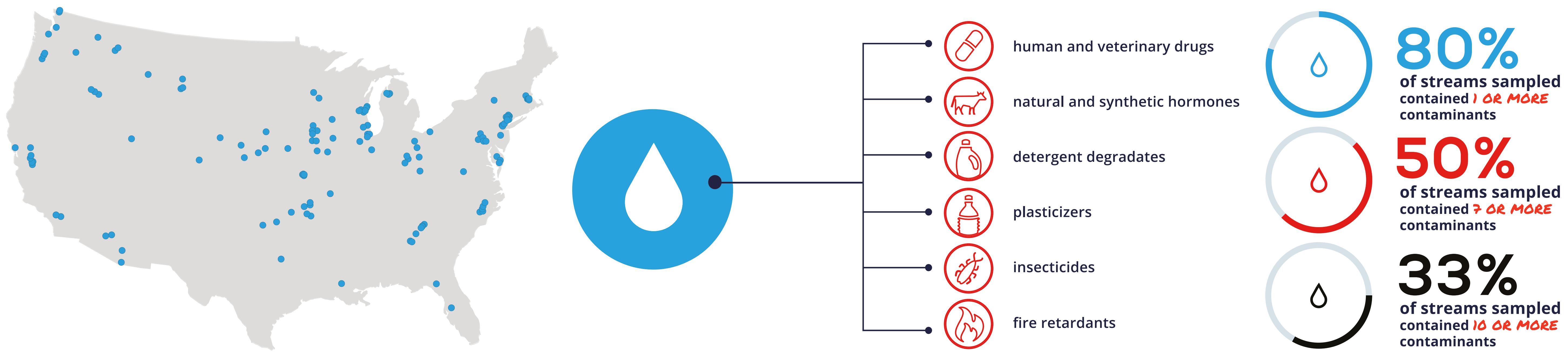
What were the results?

Since we are sitting here today still talking about emerging contaminants, we obviously did find these compounds in the streams we sampled. In fact, we found them at almost every site we went to. We even found traces of chemicals like caffeine at some of the minimally-impacted sites. We did find fewer chemicals at the minimally-impacted sites, but we still found traces because there is no such thing as a pristine setting anymore. There may not have been a city with a wastewater treatment plant in these minimally-impacted watersheds, but there were still septic systems and other potential contaminant sources. At the more heavily-impacted sites, we found as many as 38 chemicals in a single water sample.

Overall, we discovered that emerging contaminants were prevalent in the streams we looked at, that they were originating from both urban and agricultural sources, and that what was present was actually a complex mixture of chemicals—pharmaceuticals, hormones, personal care products.

What we have since come to realize is that anything we use in our society has the potential to become an environmental contaminant. I think that point was really underappreciated back then. Sometimes it is easy to forget that even simple things like drinking a cup of coffee can come back around to contaminate our water resources.

Understanding the 1999-2000 EMERGING CONTAMINANTS SURVEY



How did you decide which chemicals to test for?

The chemists focused on broad classes of compounds. Each chemist would figure out which potential compounds to measure by looking at information like how heavily they are used and their chemical structures to get an idea of their environmental persistence. Back then, there just wasn't a lot of other information that we could use to guide our selection of chemicals to test for and to help us determine how many could realistically be included in a single method. Keep in mind that it's just not feasible to have an individual method for every single chemical you want to measure. Instead, you bundle a suite of compounds into the analytical method being developed. The chemists tried to balance including as many compounds as possible without sacrificing overall method performance using the analytical tools they had available at the time.

Analytical tools have changed dramatically since our original stream recon. For example, the pharmaceutical method Ed Furlong developed for measuring about 20 pharmaceuticals required the filtration of a 1-liter water sample. The filtration equipment had to be thoroughly cleaned after every use to prevent potential cross-contamination between sampling sites—which ended up being a very time consuming endeavor. With today's technology, we have a new pharmaceutical method that simultaneously measures 110 chemicals with much better sensitivity than our original method. And now we only need to collect a 20-milliliter sample that's filtered with a disposable hand-syringe filtration unit. These technological improvements are making life much easier in terms of sample collection, shipping, and analysis. The analytical tools and technology are just getting better and better.

The study used five methods to test for these compounds. Were these created just for the study?

Almost. Four of the five methods we used were created from scratch for this study.

How do you do that?

I am not a chemist, but I know it can be quite a laborious process. Basically, you have to find the right match between the analytical tools available and the set of compounds you are hoping to measure. One of the most difficult challenges is being able to process the water samples in a way that you can extract and isolate specific chemicals from the myriad of other chemicals and potential interferences present. In many cases, it's trial and error to figure out which combinations of factors like solvents and types of extracts give you the best overall performance. One way to check how well the method works is to add a known amount of a chemical—a standard—to a sample. If your results are not reasonably close to the amount you put in, you know you have issues.

So methods are created specifically for a class of compounds?

Sometimes a method may be for a certain class of compounds, such as antidepressants. Other times, a method can be for a set of compounds of interest that span multiple classes. Regardless, a chemist will generally start with a laundry list of target chemicals that they would like to develop a method for. The list gets whittled down for various reasons throughout the development process. For example, a compound may be dropped because the performance is below acceptable standards.

Chemists also have to deal with the added complication of making sure the method is robust enough to work in all kinds of environmental matrices, such as groundwater, surface water, wastewater treatment plant effluent, and landfill leachate. Because we are trying to understand sources and how compounds move through the environment, we have to look at very different matrices, including ones that can be extremely difficult—imagine trying to measure a sample collected from a hog lagoon [a basin designed to manage waste on a pig farm]. Those are difficult not only because they are nasty smelling but because there are so many chemicals and organic materials in them. Trying to isolate and extract a specific compound in those samples without screwing up your equipment can be extremely challenging.

You used a lot of quality control checks like lab and field blanks to confirm results. Is that because this study was the first at this scale?

No, quality assurance and quality control (QA/QC) is extremely important for every water quality study. This should always be standard practice to ensure the results are of the highest quality. You have to make sure that your field protocols are robust and that you aren't contaminating your water samples. It's not just about how you collect the samples but also what materials your samples are exposed to. For example, if you are trying to measure levels of Teflon® in the water, you don't want to collect a sample using Teflon® tubing. Without a proper QA/QC protocol, what you think is in the water sample may actually be from the materials the samples were exposed to or from products the field personnel were using during sample collection and processing.

QA/QC is also an important mechanism for testing your cleaning procedures. Back during our stream recon study, we did a lot of filtering with certain types of equipment. You want to make sure that the cleaning procedures are sufficient to prevent cross-contamination from one site to the next. For example, if you happen to collect a sample from one site that had a large number of detections, you want to make sure that the cleaning procedures are preventing chemical residues from bleeding over to the next water sample collected. The ultimate goal during any water quality study is to ensure that you're collecting a water sample that truly reflects real-world conditions at each site.

This problem is accentuated when you're investigating emerging contaminants because there are so many more potential sources to be concerned about. For example, with a study looking for atrazine [an herbicide], you know that it's unlikely that field personnel are contaminating the water sample because they haven't been using atrazine in their daily routines. If you are looking at things like caffeine, nicotine, or fragrances, however, you have to make sure that people's daily activities aren't contaminating or compromising the water samples. This can be easier said than done. Asking field personnel not to use DEET during the summer, when mosquitos are thick and there is concern about contracting West Nile Virus, does not make you very popular.

The other issue with emerging contaminants is that we need to measure at such a sensitive level. We are pushing our measurements to continually increasing sensitivities—not just because it is scientifically interesting to do so but because some emerging contaminants, such as hormones, actually have ecologic impacts at extremely low levels. The trace levels that could potentially be picked up through poor field protocols could cause false positives in your results. Proper QA/QC ensures that field protocols aren't compromising your samples.

Are the methods you used in this study still in use today?

Since it has been almost 15 years since the study began, all of those methods have been retired, and new-and-improved versions have taken their place—ones that increase the specificity and sensitivity for measuring emerging contaminants. The gold standard for measuring chemicals in environmental samples changes as technology improves. You can't just develop a method and sit on it and think, "I'm good to go for water quality research." If you want to stay on the leading edge and really figure out what's going on in terms of occurrence, fate, and effects, you have to keep pushing the envelope. There is a multitude of chemicals we just didn't capture the first time around—both parent compounds and degradates. Plus, new chemicals are always hitting the market. You just have to keep expanding your analytical capabilities by prioritizing the next set of important chemicals that need to be investigated.

It is important to keep in mind, though, that you will never be able to measure every potential chemical contaminant. So, we're also developing a diagnostics component that will help us look for unknowns in an environmental sample. This will give us another tool in our environmental toolbox. While we examine a sample for the chemicals that we can measure, we can use the diagnostics to help determine what other chemicals are also present. It may not be able to give you an exact measurement of the concentrations, but the diagnostics will give you a much better picture of what is actually present in the sample.

Even though you can't directly measure it?

Exactly. If a compound routinely shows up during the diagnostic step, you can say, "This is obviously an important compound. Let's see what we can do to add this to our analytical capabilities."

We are also complementing our chemistry with various bioassays [a technique that uses live cells to determine the biological activity of a substance]. Sometimes you'll analyze a sample for hormones and not find any. But if you run the bioassay on that same sample, you may see that it has measurable estrogenic activity. This tells you there is an estrogenic compound present in your sample that you just aren't measuring.

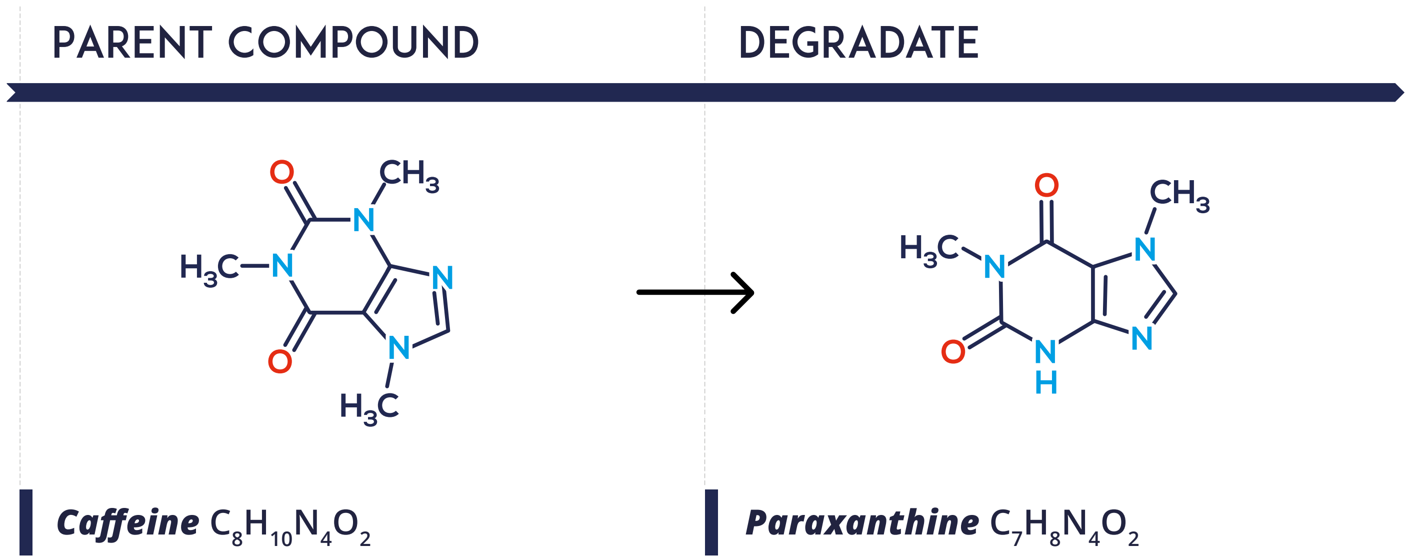
Our ultimate goal is to determine whether the chemicals present in these samples are impacting aquatic and terrestrial organisms. So, we are starting to conduct research like we did at Boulder Creek, where chemistry, bioassays, and exposure experiments were all simultaneously conducted in an integrated study. This approach combines the strength of each technique to better understand the potential connection between chemical exposures and environmental effects.

Are you using environmental diagnostics now?

It's certainly not a new concept. Other scientists from around the world have been conducting research on this topic, but we are just starting to work out the approach that we will use for our diagnostics component. In fact, Jan Christensen talked about this at the EmCon 2014 conference [where IISG interviewed Kolpin]. Others have been blazing the trail, but we're hoping we will be able to add our expertise and enhance it.

I think these new diagnostic methods are extremely important. I was listening to Jerry Schnoor speak at EmCon 2014, and he said that there are 15,000 new chemicals registered every day. There are literally millions of chemicals that could be potential environmental contaminants. And these chemicals can degrade into new compounds, meaning we have even more chemicals to think about in the universe of potential contaminants. This is important because when a chemical degrades, it's toxicity doesn't necessarily decrease. There are plenty of examples of this. The antidepressant venlafaxine degrades to desmethylvenlafaxine, which is also the FDA-approved antidepressant Pristiq®.

The whole degradate issue is extremely important as we try to get a more complete understanding of environmental fate and the potential effects of chemical exposure. If a chemical goes into a wastewater treatment plant but doesn't come out, some people will jump to the conclusion that it was removed during the treatment process. In reality, while the parent compound may no longer be measureable, it may have been transformed to a new chemical. In many cases, chemicals aren't being mineralized to their elemental state during the wastewater treatment process. Or alternatively, the chemical may have just been removed from the liquid waste and concentrated into the sludge, which then becomes a potential terrestrial pathway into the environment.



We saw this in your original study when you found degradates of nicotine and erythromycin but not the parent compounds.

Those are a couple of unusual examples of where we actually had degradates in our analytical methods but not the corresponding parent compounds. My recollection is that there was some sort of issue with getting the parent compounds to work in the analytical methods we were using at that time.

Nicotine is in our new pharmaceutical method. In fact, we are finding both nicotine and cotinine, a degradate of nicotine, in our landfill leachate study. Having both the parent compound and at least one of its principal degradates can be a big help because it opens up the things you can do with the data to help understand a chemical's fate. For example, you can calculate the ratio of the degradate to the parent compound, and you can calculate total concentrations by adding up the parent and its degradates.

There were also a few compounds that you looked for but didn't find. Is that because they weren't there or because they weren't detectable?

That is a good question. I suspect it's some of both. My guess is that if we repeated the study today using the more sensitive analytical methods available, we would find at least some of the chemicals we didn't originally detect. Others may just be degrading somewhere along the way—in our bodies or within a wastewater treatment plant. So, instead of the parent compound, it's one of the degradates that's in the environment. The general rule of thumb is that if a chemical is heavily used but you aren't finding the parent compound in your environmental samples, there is a good chance that there's a degradate you should be looking for.

So, it isn't as simple as detected vs. not detected?

Exactly. There is a range where you are confident that the method is giving you a reasonable concentration. And there's a range where you are confident that the chemical is present, but its concentration is too low to be able to put a firm number on it.

There were sites where you didn't find any contaminates. Was that surprising given that you targeted locations with inputs?

Given the level of knowledge back then regarding emerging contaminants, the number of sites where we did find these contaminants was actually more surprising. Even with our bias towards sites where we would be more likely to find these compounds, we still were not sure how frequently they'd be in our network of streams. And this study was a one-time sampling of the sites, so contaminants that are only episodically present, such as during rain events, could easily have been missed. I suspect that if we repeated the study today with our more comprehensive and sensitive analytical methods, there would be even fewer sites where no contaminants were found.

This study got a lot of media and public attention. Were you expecting that?

No, I wasn't expecting that level of exposure and attention. We always planned to brief our sister federal agencies on our findings and put out a basic press release, but nothing beyond that. Once Environmental Science and Technology (ES&T) informed us they also wanted to also have a press release, we thought, "Okay, this could be something bigger than we had realized." As part of our modified release effort, we made sure that our corresponding USGS data report containing all the concentration data was released the exact same day as the journal article.

Regardless, I still wasn't expecting to have so many downloads and so many citations for this stream recon study. Even 12 years later, this paper is still the most cited paper in ES&T history with over 3,000 citations, and it has become a seminal paper on the topic. The Europeans certainly blazed the trail. We just happened be in the right place at the right time with our national study looking at a broad suite of emerging contaminants.

The popular media honed in on pharmaceuticals even though those weren't the most abundant chemicals or the ones with the highest concentrations. Is there a disconnect between what the public talks about and what the science showed?

Back then, we didn't know a whole lot about the potential environmental effects from emerging contaminants, so it is hard to say if there was a real disconnect. But we do know that not all chemicals are equal in terms of their toxicity. The ones present in the highest concentrations are not always the ones with the greatest toxicity.

As it turns out, pharmaceuticals are a very important class of emerging contaminants. There is mounting evidence that at least some have chronic effects on aquatic and terrestrial organisms. For example, when you expose fathead minnows to antidepressants, it slows their reaction to predators. When you are low in the food chain, having a slow reaction to predators is not a good thing. But these chronic, behavioral effects are more difficult to identify and understand than the acute effects, where you just have to count the dead bodies.

I think the public picked up on the pharmaceutical aspect because these are compounds that are easily relatable, and it's easier for the public to understand why there may be potential environmental effects. This reaction was completely different than the reaction to my previous research on pesticides. The public was certainly concerned about these compounds being present in the water, but in terms of the source of these pesticides, their feeling was more like, "That's coming from the farmer, not from me." But when you are saying there are chemicals like caffeine in our drinking water, it seems to bring things to a personal level and makes the public think, "Holy cow, there are traces of pharmaceuticals in my drinking water! How did they get there?" Hopefully that is one of the take-home messages of this research—everything we use has the potential to be an environmental contaminant.

As for sources of emerging contaminants, wastewater treatment plants have certainly gotten the most attention, but I always try to stress that they are not out of compliance. They are doing everything that they're supposed to be doing. It's just that compounds like pharmaceuticals were not part of the equation when these plants were constructed. I suspect that at some point, the U.S. Environmental Protection Agency could very well start regulating some of these emerging contaminants, but that is not the role of the USGS. Our role is to provide the science so others can determine if regulations are needed.

Around this same time, USGS released the results of national studies on groundwater and source water that didn't get quite as much attention. What important results came out of those?

These companion studies documented that emerging contaminants were not just a stream issue. They showed that the compounds are mobile and persistent enough to be transported into groundwater and sources of drinking water. I think documenting pharmaceuticals in sources of drinking water was what helped spur the Associated Press's huge story in 2008 about pharmaceuticals in drinking water.

There has been a lot of work on this topic in the last 12 years. What knowledge gaps do you think still exist?

We have come a long way, but we still really don't have a grasp of the full consequences of exposure to emerging contaminants. We are continuously expanding our knowledge of the chemicals present in the environment, but a majority of the research on effects has focused on exposure to individual chemicals or to a small set of chemicals. In reality, fish and other aquatic organisms are exposed to complex mixtures of chemicals simultaneously—10s to even 100s in number.

Another knowledge gap deals with degradates. We know that few emerging contaminants are being degraded to their elemental state, but we don't always know enough about the primary degradation pathways of these compounds to know what else we should be looking for. And developing the necessary analytical methods for degradates can be problematic since there are not always analytical standards available for that kind of work.

Still, we have come a long way over the last 12 years, and I think the progress is going to be exponential over the next five years. When we were first starting our research on emerging contaminants, there were maybe 20 papers published on this topic in an entire year. Now there are easily over 500 papers relating to emerging contaminants published each year, and that number is still growing. Early on, someone suggested that emerging contaminants would be a hot topic for about five years and then there would be a new topic that would take its place. Well, that has obviously not been the case.

More recently, you have been looking into chemicals in landfill leachate across the country. What is leachate and why study it?

Leachate is basically the water generated in a landfill. As precipitation percolates through a landfill, the water picks up contaminates. This is a pretty nasty matrix to analyze. It doesn't smell as bad as, say, a hog lagoon sample, but the water is really discolored and looks like a glass of tea. In newer landfills, it is common to have systems in place that collect the leachate so it can be piped to a wastewater treatment plant, irrigated onto nearby land, or even discharged into a stream.

We're studying landfills because they're a common disposal mechanism for our nation's solid waste. If medicine take-back programs aren't available, one of the recommendations for disposing of expired and unused pharmaceuticals is to mix them with either kitty litter or coffee grounds and then throw them into the garbage. The objective of this recommendation is not to prevent environmental contamination but to prevent the secondary use of medications. This got us thinking about what types and concentrations of pharmaceuticals are in landfill leachate. While we were in the process of designing this study, we thought, "As long as we're taking samples, let's not just look at the pharmaceuticals. Let's do a comprehensive study and measure as many emerging contaminants as we can to see what we find." So, for our first landfill study, we sampled 19 landfills and tested for 202 different chemicals. This was the first national scale study looking at a broad suite of emerging contaminants in landfill leachate in the U.S.

What were the results?

We found 129 of the 202 chemicals in at least one landfill, with as many as 82 compounds detected in a single leachate sample. What we found was really a grab bag of chemicals ranging from pharmaceuticals to personal care products to hormones. This really documents that landfills truly are a reflection of what we dispose of.

The most frequently detected compounds were bisphenol A (BPA), cotinine, DEET, lidocaine, and camphor, which were found in almost every landfill sampled. The concentrations we measured were from just a few nanograms per liter to over 7 million nanograms per liter. In fact, we had several samples with concentrations in the millions of nanograms per liter. Interestingly, BPA was one of the chemicals that was not only found in almost every landfill but was also found at the highest concentrations. BPA is in lots of different products—from plastics to receipts. It's been shown to be an estrogenic compound, and there has been a recent push to remove it from at least some of our products. Even though it is a weakly estrogenic compound compared to a natural estrogen like estrone, this is offset by the fact that it was found at a concentration five orders of magnitude higher than the natural estrogens. Overall, we generally found household and industrial chemicals in the highest concentrations, followed by the prescription and non-prescription pharmaceuticals, plant and animal sterols, and biogenic hormones.

This study gave us an idea of what can be present in leachate generated in a landfill, but we did not look at leachate concentrations leaving the landfill. We did that in follow-up research. Those results are currently being examined and interpreted for our next leachate report.

Do we know much about how chemicals degrade in landfill conditions? Would you expect it to be different than in waterways?

I don't think we fully understand this yet. Obviously, we are finding a host of chemicals at some pretty hefty concentrations, so things are not being completely degraded within the landfills. We are working with Bradley Stevenson and his colleagues at the University of Oklahoma, and they are finding some very unique microbial populations in leachate compared to what you find in other environments. This combination of unique microbial populations, chemical conditions, and high organic matter may lead to either faster or slower chemical degradation. This is such a different environment that we just aren't sure how the chemicals are reacting.

Where do you see your work going now?

Our projects look at all aspects of emerging contaminants—from sources to fate and transport to environmental effects. We think livestock is an important source that is particularly under-investigated since livestock production in the U.S. generates over one billion tons of manure each year. Much of this waste is applied to the land as a source of plant nutrients. Our preliminary research found that there are high levels of emerging contaminants, such as hormones and antibiotics, in livestock manure. This certainly raises questions about both aquatic and terrestrial impacts. For example, would livestock manure that contains large concentrations of antibiotics affect soil bacterial populations? Bacteria play an important role in natural soil functions. If you start whacking these natural bacterial populations with large concentrations of antibiotics, will that cause a change in these important natural functions? We have certainly documented effects like that in the laboratory. We are currently conducting a national study to get a better handle on which livestock-derived contaminants are ending up in streams and if they are having environmental effects.

The public wants to know whether they should be concerned about emerging contaminants, so the USGS is putting concerted effort into integrating biological and chemical research and increasing our collaborative efforts. We want to better understand the relationship between exposure to complex chemical mixtures and environmental health. So far, most of the research on effects has focused on fish. Little has been done on other aquatic species and even less on terrestrial organisms, although we have seen chemical uptake into earthworms following exposure via biosolid or livestock manure applications. We are putting particular emphasis on the Chesapeake Bay, where a high prevalence of intersex characteristics in smallmouth bass has been found in various watersheds. When we collected water and sediment in and around smallmouth bass nesting areas, we found 135 different chemicals. I feel very good knowing that taxpayer dollars are being put towards research that has high public interest.

We are also at the stage where we're looking at our research plan for the next five years. We want to take stock of where we are and what we have learned, look at what others are saying about research gaps, and think about what we can and should be contributing scientifically in both the short and long term.

www.unwantedmeds.org

PHOTOS
U.S. Geological Survey

IISG-14-100 E