UpClose

with Timothy Strathmann

Dr. Timothy Strathmann, an environmental engineer at University of Illinois Urbana-Champaign, has dedicated more than a decade to understanding the chemical principles at work behind environmental challenges such as ensuring long-term water quality and developing renewable energy. In more recent years, he and his students have been working to develop processes that could be used to treat wastewater contaminated with pharmaceuticals and other consumer products. The Strathmann Research Group has also conducted studies that investigate processes that degrade aquatic contaminants in natural environments.

IISG sat down with Dr. Strathmann to talk in detail about what happens to pharmaceuticals at a chemical level when water is treated, the risk these chemicals pose after they are broken down, and how his research is helping to develop new, more efficient treatment technologies needed to ensure sustainable water quality.

What connections are there between your work with pharmaceutical contaminants and your larger research portfolio?

My overall research specialty, as time has gone on, is in in the area of redox transformations of organic chemicals. That is the central theme. We have done work on trying to understand the environmental fate and treatment of pharmaceuticals and other emerging classes of contaminants that include a lot of things that I would describe as wastewater-derived contaminants. That is, their major source in natural waters is derived from wastewater treatment plant outfalls. So, this includes most chemicals that we flush down the toilet and dump down our drains. Of course, that is going to include pharmaceuticals, personal care products, in addition to other consumer products. Many of those chemicals are not adequately treated in wastewater treatment plants using existing technologies, and so some portion of them end up released into the receiving waters.

One of the questions we have is what happens to those chemicals that are released into the environment, which is important for not only drinking water treatment plants that are downstream of that wastewater treatment plant release point, but also the effluent-impacted aquatic ecosystems. We are interested in the chemistry that happens to contaminants once released into the natural environment: how redox transformations contribute to contaminant degradation in soil and ground water. There are a lot of minerals and other components of ground water systems that contribute to the transformation degradation of these chemicals. In drinking water treatment plants, we are also interested in how redox processes like chlorine disinfection contribute to the breakdown of pharmaceuticals and other organic pollutants. Finally, for pollutants that are not treatable by existing processes, can we develop new technologies to promote degradation of these chemicals or transformation into products that exhibit much less pharmaceutical potency than the parent drugs?

Recently, we have also been working on processes for producing renewable bioenergy, an outgrowth of new students that have interest in this area. In this work, we are building on the new catalyst technology that we are developing with water treatment—can we develop similar catalyst technologies to make alternative or renewable energy from biomass and waste materials?

How did you decide which pharmaceuticals to study in the simulations of treatment plant purification processes your group has done?

Originally we conducted a survey of a large number of pharmaceuticals. We had a study that was funded by the American Water Works Association Research Foundation—I think now it is known as the Water Research Foundation—to examine the fate of pharmaceuticals in drinking water treatment plants where they use a chemical oxidant called potassium permanganate. Many treatment plants use permanganate to control manganese and chemicals that cause taste and odor problems. There is always the question: if plants use this chemical, are they also getting any benefit in terms of pharmaceutical removal? We did a survey of around 25 pharmaceuticals that were representative of some of the major classes of pharmaceuticals that have been detected in occurrence surveys conducted by organizations like the USGS [the U.S. Geological Survey]. Based upon that survey, we then focused our efforts on a smaller number of pharmaceuticals that exhibited reactivity with permanganate.

They were also selected in part based upon previous studies conducted with other drinking water oxidants, because we wanted to be able to compare the results that we observed to other drinking water oxidants, like chlorine and ozone disinfectants. By using the same model pharmaceuticals, we are able to make those comparisons and be able to say 'for this class of pharmaceuticals, permanganate is less reactive than chlorine versus for this class, where maybe a different trend was observed.' That is in part why we selected individual compounds. There is maybe a group of 20-30 pharmaceuticals that are very widely studied in the environmental chemistry community, in part because of these occurrence surveys, but also because there is a prior literature that we can compare results from studying.

How generalizable are the results of the 20-30 that are commonly studied?

The model compounds are selected in part to represent important classes. There are certainly important chemicals in those classes, including things like ibuprofen, acetaminophen, some of the chemicals used for birth control medications, in heart and blood pressure medications, etc. One of the things we are hoping to be able to accomplish from the studies is to draw some conclusions about the role their chemical structure plays in reactivity. So, what we would say based on our own results is that there are certain chemical structural features that are susceptible to reaction with, let's say, permanganate. Then we can look at other pharmaceuticals and say 'look, if we know the pharmaceutical over here has the same structural feature we can make predictions about its expected reactivity within some measure of uncertainty.'

For example, a lot of the endocrine disrupting chemicals of concern, like bisphenol A (BPA) and some of the steroid hormones, contain what is called a phenolic functional group. Although these are the most potent chemicals that I would be scared about in terms of pharmaceuticals, luckily they have these phenolic groups that are very amenable to oxidative destruction. So, now when I see a pharmaceutical that has a phenolic group, I am pretty confident that we can remove the chemical by oxidative treatment technologies.

Do you look any further at those chemicals that are being effectively treated now, or are you focused on the ones not being treated?

Well there is still interest there [in the chemicals effectively treated with existing technologies]. We need to understand these processes because there are a lot of other things in the water—these pharmaceuticals are trace constituents compared to other things in the water that are naturally occurring. The natural organic materials that are in the water are much higher in concentration, so there is a competition for available oxidants that need to be considered.

But, it is true that in many cases we do focus on those contaminants that are more difficult to treat. These might include chemicals that react with conventional oxidants, but maybe the time it takes for the reaction to be completed would be much longer than the amount of time the water spends in the treatment plant. For these, we may want to develop more effective technologies. One of the things we are interested in, are the technologies that are more selective for the contaminants of interest. That is, our hope is to try and treat the so-called 'drop of poison in the ocean of water'. With non-selective technologies, if I want to treat water to remove 90 percent of a trace contaminant, I might need to apply enough oxidant to remove 90 percent of all organic chemicals, even naturally occurring ones that pose no harm. This is very inefficient and potentially costly. Preferably, we want to be able to remove 90 percent of the target pollutant while having little effect on the other naturally occurring chemicals in the natural background matrix.

How much success have you had trying to make more selective treatment processes?

We have learned that permanganate in comparison to something like ozone—ozone is a stronger oxidant than permanganate, but I can probably oxidize larger fraction of a sensitive pharmaceutical in the water using the same dose of permanganate because of its higher selectivity. Even though ozone is more reactive, ozone is also more reactive with all the background matrix components, so it's what we would say is scavenged by the matrix more effectively. If I were to put permanganate in that water and watch its concentration, it doesn't decay as fast, so it is available to react with the contaminants we are targeting.

One of the other things we have been studying is catalysts that transform chemicals by reduction processes rather than oxidation processes. Those reductive processes are much more chemically selective than oxidative processes, in general. What we have found is that chemicals that have reducible structures are going to be more selectively treated with these reductive processes than oxidative processes.

How much fidelity is there between what you are working on in your lab and the purification plants?

For the study funded by the Water Research Foundation, we worked with half a dozen facilities around the country that shipped us their source water, which had varying characteristics. What we did then was run treatments at more realistic conditions—what a real plant would dose and use for treatment contact times—and we monitored the removal of the target pharmaceuticals that we added to the water in really low concentrations—close to what would appear in real water. We then compared the measured results with predictions we made using a model that we developed from the results of our lab experiments. Generally, we observed a good match between measurements and model predictions, and our final project report included a software tool that water utility managers could use to predict pharmaceutical removal that can be achieved at their specific treatment plant.

But we were still doing what I would say are laboratory simulations in the sense that we are still doing it in a laboratory beaker. We weren't doing them

in a treatment plant that has flow conditions and mixing issues. There is a lot more complexity in a real treatment plant. And a real treatment plant has many processes, so ultimately what would be needed to predict the fate of pharmaceuticals for a whole treatment plant would be models maybe for each of the different processes in the treatment plant. The model we developed was just for one process in a plant where, for many plants, it was a big question mark.

So a director of a plant couldn't take your model on its own and make changes in processes?

A director of a plant could say 'well, we have been measuring our treated water, and we have actually found that we still have this particular pharmaceutical in the treated water. But based upon the results that came from this group [Strathmann Research Group], we could predict that if we installed a permanganate treatment process in our plant at roughly this kind of dosing, we could expect that we would remove the chemical.' That would be if it is not being removed by the existing processes. That is maybe how they could use these findings. Or, if they already are using permanganate for control of taste and odor chemicals, they might be able to use the model we developed to tweak the process so that they could also remove some pharmaceuticals. Still, results of the model predictions will need to be validated at the individual water utility.

In your research on iron-redox treatment processes, were the concentrations you were working with naturally occurring?

Well, there are a couple of things. There are studies where we were just trying to understand what might happen if some of the pharmaceuticals are in the natural environment. Iron is one of the most abundant elements in soils. Also, in some soils, the redox state of the soil varies a lot. There are surface soils that are very oxidized. There are also flooded fields where the conditions might become more anaerobic. If, for example, there are antibiotics or hormones used in livestock production and the livestock manure is land-applied on the fields that later become flooded, resulting in a change in the iron redox chemistry, this will lead to iron redox changes that may affect the fate of trace chemicals like pharmaceuticals. Our experiments were designed to better understand the fate of antibiotic chemicals in this dynamic environment. We weren't necessarily developing a treatment process. We were just trying to understand the processes, chemical reactions, and mechanisms by which iron that is in soils can contribute to the breakdown of these chemicals.

And how does it contribute?

We found some unexpected results for sulfamethoxazole, a widely used sulfa drug. Our work found that this drug contained a structural feature that was sensitive to transformation by reactions with reduced iron present in the soil. So, from a basic chemistry perspective, we were able to see that under iron-reducing soil conditions, these chemicals are degraded very rapidly due to this process, which was somewhat unexpected. We would have assumed that if the chemical was degraded by a straight-up biodegradation process that degradation would be much faster under aerobic conditions than it would have been under these anaerobic conditions. Ultimately, the degradation process was driven by the activity of soil microorganisms, but indirectly. The soil microbes were 'breathing iron' in the absence of oxygen, and exhaling reduced iron species that then chemically reacted with sulfa drug.

If iron degrades the pharmaceutical chemicals very rapidly, does that mean that less treatment would be needed for water to be safe?

Let's say there is an agricultural field in a rural area and communities nearby are using ground water for their drinking water source—they just tap a well and use the water without further treatment. We would be less concerned that people drawing upon that ground water source are going to be exposed to these chemicals because there are a lot of biological and chemical processes that are contributing to the breakdown of these chemicals, thereby reducing the risk of exposure. Right now, we don't really understand all the processes by which these chemicals are broken down. That is part of what our study was trying to accomplish—just understand maybe that in this scenario or in this situation the ground waters were more protected than in this other situation with these other chemicals.

Some characteristics of the byproducts of this degradation are unknown, then?

The short answer is that we don't usually know much about the relative potency or the pharmaceutical activity of these byproducts relative to the parent compound. In some studies we have coupled our chemistry studies with bioassays that we conducted with collaborators who were measuring the collective potency of byproducts forms from these reactions. And in all of those cases we found that the collective potency of the byproducts, even if structurally similar to the parent drug, was severely diminished by redox transformation.

This isn't really too surprising for me. When companies develop new drugs, they usually examine a large number of very similar structures and find that very small structural changes can have very large effects on how active the drug is. Therefore, it is not surprising to me that if you work in the reverse direction—that causing very small changes to the parent drug during water treatment dramatically reduces the activity of the resulting product.

Now, that doesn't mean that these products aren't active in some other way. The assays we used were designed to measure a single mode of action, for example the ability to act as an antibiotic toward one strain of microorganism. So, it could be that there is some other mode of toxicity. We don't want to give the impression that our assays are saying these things are completely benign, but they provide a simple measure to say, at least in respect to inhibiting the growth of a particular strain of bacteria, that byproducts have negligible activity relative to the parent drug.

So the byproducts do not have anti-bacterial activity?

They may have activity, but it is significantly depressed. In the studies where we have been able to conduct such assays, most of the evidence would suggest that, for example, if 50 percent of the parent drug has been degraded by redox processes, the remaining solution is roughly 50 percent as potent as the starting solution. In other words, most of the remaining potency can be attributed to how much parent drug is remaining in the treated solution.

What is preventing knowing more about the potency of these byproducts?

We do not know in detail everything about the biochemical activity of the byproducts. You only know if something is toxic in a certain way if you think to look for that toxicity. This is something that is always going to be the case. It is an issue of the number of chemicals. I am not a toxicologist, but let's say that the gold standard in toxicology is some sort of animal test. Those are very expensive studies and many people have serious concerns about large scale animal toxicity testing. Therefore, such tests are often only conducted for chemicals of great concern. If I identified 25 byproducts, and a cancer screening for one of those chemicals costs a million dollars . . . you can see how quickly the costs would add up.

Some of these mixture bioassays are very nice in the sense that even though we don't know about the individual chemicals present in the mixture, it is nice to know that at least the collective mixture of products appears to lose the established activity of the drug. We are currently working with collaborators to go a little bit further and examine the effects of chemical reactions on a broad range of genetic markers to try to understand more specifically how chemical transformation affects different modes of potential toxicity.

Can you predict the potency of a chemical's byproducts based on what is known about chemicals with similar structures?

That is a good question. I think we would say that with a structural unit we might be able to make some predictions about the types of reactions, the types of transformations that occur. It is certainly a very difficult question. We would love to be able to someday in the future look at a structure and make predictions like: it is going to go to these five products, and these five products might go to these five products. And then, yes, maybe we could [predict the potency of byproducts], if we know that this type of group has a certain toxicity. Maybe that is something we should be looking for.

These are big picture goals that the whole field is working toward. But it is a very challenging thing. These drugs have very complex structures relative to other pollutants that the environmental chemistry community has been studying. One of the reasons why we have only really studied these chemicals in recent years is because they have pretty complex structures and they usually have multiple structural units that you have to be tracking at the same time.

What additional complexity is added by the fact that the makeup of water is different across regions?

Certainly that could affect the pathways [of transformation]. There may be involvement of the other constituents in the water. And also, yes, even something as simple as the pH of water might affect the ultimate pathway by which a reaction occurs. You may find at one pH condition that one set of products dominate. Or, maybe you get the same type of products, but the ratio varies. These are very difficult questions to answer and that is what keeps us in business.

Does this complexity mean that we will never have a single way to treat the same pharmaceutical pollutant across all regions and treatment processes?

I think we need to consider the site, the water quality. In almost any kind of process, you need to consider the water quality conditions at each site. Also, if you are going to use a particular technology, it is important to do some tests to validate how things are performing at the plant or in the source water that you are dealing with. There is not a one-size-fits-all solution—that is the big picture.

Are the treatment processes that you are developing generally new processes or are they alterations to existing methods?

We are working on both approaches, but I would say most of our research in the past several years is focused on what I would call 'next generation technologies' and trying to think about the future of water treatment. Maybe dealing with something that is 10 years down the road, especially with this ever growing body of pollutants, and some that are untreated by current technologies. We are thinking about those kinds of things. We do do some work where we are trying to better understand and predict pollutant treatment with existing technologies. But particularly our work with catalytic technologies is aimed at the future and transforming the way we treat water in a very fundamental way. And, also trying to think about if we use certain materials like photo-catalysts, can we potentially develop processes that instead of adding a chemical like chlorine to water, you could use sunlight to power the process? There are a lot of technical hurdles that we need to overcome before these technologies are ready for 'prime time', but they of-

fer some significant potential for revolutionizing the way we purify water in possibly much more sustainable ways.

We have been talking about your past work, but is there anything you are working on right now that you are particularly interested in or is showing results you did not anticipate?

Some of the things that we are doing that are most exciting now is that we have some collaborations with researchers in Saudi Arabia at the King Abdullah University of Science and Technology (KAUST). We are working with material scientists there who are experts in developing highly controlled nanostructured materials. We are working with them to develop new materials and catalysts that are potentially more active for degrading problematic pollutants, but also are able to be used in real waters more effectively where there are all of these other constituents that we don't want to target and we want to keep from 'fouling' or 'poisoning' our catalysis. Our hope is that with these controlled nanostructures we can really target the contaminants that we want while minimizing interactions of the active portions of these materials with the non-target, natural organic materials or other metals and cations that are in the natural water.

Where are you in that work?

It is very early on.

How long does work like this usually take to generate usable results?

We work on a timescale where we would hope to have some of our initial results, promising results, within a couple of years. That is a typical time frame.

Is there anything else you would want to say to people interested in pharmaceutical contaminants and your research in that area?

One of the things to keep in mind is that just because we can detect a chemical doesn't mean that there is necessarily a risk posed by that chemical. We need to keep this in mind when you hear stories that pharmaceuticals are being detected in our drinking water sources. Our ability to detect chemicals is racing ahead and waters that we now, today would analyze and say there is nothing in this water, 10 years from now that same water sample we might be able to detect something in it. That is why we also need more research to understand the toxicology of these chemicals. Maybe individually these chemicals are very low in concentrations, and I am not concerned about any one of them, but the fact is that we are being exposed to mixtures of chemicals. We need to have a much better idea of the risks of those mixtures.

Also, I don't think it is realistic that we are going to remove everything. I think we need to understand, again, the relative risks of exposure to different chemicals. Because you detect something doesn't mean it should be a serious concern to us. For example, I am not concerned personally about very low levels of ibuprofen in the water where you would need to drink thousands of gallons of water to get the exposure of one Advil tablet. It might take you your whole life—you will never get enough ibuprofen in that to take one pill. But, at the same time we don't want to say 'well, that means we don't have to be concerned at all.' There are some chemicals, for example some of these very potent steroid hormones, where even at the very trace levels at which we are detecting them it has been documented that it can affect aquatic ecosystems; it can affect particularly those organisms that live near the outfalls of wastewater treatment plants. There I would say we need to be prioritizing chemicals of concern, and need to learn more about them so we can make these priority decisions. We need to be able to focus our resources, focus our potential regulatory pressure on the chemicals that matter. Those are not easy questions, but I think that is what we need to be focused on.