

A Q&A

Emerging Disinfection Byproducts in Drinking Water



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Disinfection byproducts (DBPs) in drinking water form when disinfectants react with naturally occurring organic matter. DBPs can have effects on human health, but only a small percentage of currently identified DBPs are regulated by the U.S. EPA. Susan Richardson's research focuses on identifying and determining formation mechanisms of DBPs and integrating toxicological characterization with chemical characterization approaches. The goal of her research is to solve human health issues surrounding drinking water DBPs.

LCGC: Tell us about your research involving disinfection byproducts (DBPs) in drinking water.

RICHARDSON: We've been using mass spectrometry to uncover DBPs that are responsible for the human health effects we've seen in human epidemiologic studies — things like bladder cancer, miscarriage, and birth defects. We work with toxicologists, epidemiologists, water treatment engineers, and regulators to try to solve these important human health issues. DBPs can also form in swimming pools. We're looking into both sources.

LCGC: Where do DBPs come from, and how are they formed? Are they persistent in water?

RICHARDSON: DBPs are unattended consequences of using disinfectants to try to kill harmful pathogens in drinking water. DBPs form when these disinfectants react with natural organic matter, bromide and iodide salts that are naturally occurring, and other contaminants in source waters. We think natural organic matter is the primary precursor to the formation of DBPs. Natural organic matter is present from the decay of leaves and other plant matter that fall into the water.

DBPs are not traditional contaminants that are already present in the water. They're formed during drinking water treatment. Many DBPs persist in drinking water; in fact, most will continue to form in the distribution system; in other words, in the pipes after water leaves the treatment plant and travels to your home. Levels can actually increase, so the water coming into your home could have higher levels of particular DBPs than the water as it leaves the water treatment plant.

A few DBPs are less stable and may decrease from the plant to your tap, but most DBPs are stable enough to show up at the part-per-billion (ppb) level in your tap water. These contaminants typically are present at much higher levels than other contaminants such as pharmaceuticals or pesticides. In fact, pharmaceuticals and pesticides may or may not be present in your drinking water, but DBPs are always in the water if it's treated with the disinfectants.

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LCGC: Does your work focus on regulated DBPs, unregulated DBPs, or both?

RICHARDSON: My research involves both regulated and unregulated DBPs, but primarily unregulated DBPs. Most toxicologists believe that the regulated DBPs are not the ones causing the human health effects. Bladder cancer is the primary type of cancer that we see in the epidemiologic studies, but none of the regulated DBPs cause bladder cancer in animals. We suspect that the regulations are missing the important DBPs in our water.

We're focusing on unknown DBPs in drinking water to identify them and determine which ones are causing the human health effects so that, ultimately, we can eliminate them from drinking water.

LCGC: What are government regulatory bodies doing to protect humans from DBP exposure?

RICHARDSON: The U.S. EPA currently regulates 11 DBPs in drinking water; other countries regulate some DBPs as well. Almost 700 DBPs have now been identified; however, none of other 700 are currently being controlled. One concern is that drinking water treatment plants often lower the regulated DBPs by changing their treatment method, and that can actually increase the formation of some of the more-toxic unregulated DBPs.

LCGC: What type of DBPs are you focusing on and why?

RICHARDSON: We're focusing on iodinated DBPs because of their enhanced toxicity. Iodoacetic acid, which we first identified from a nationwide occurrence study in 2004, is the most genotoxic of all DBPs studied to date. We're also focusing on nitrogen-containing DBPs because they have increased toxicity relative to DBPs without nitrogen. And, we continue to identify DBPs that were not previously known. We're investigating other sources of iodine in the formation of these iodo-DBPs and other forms of iodine besides iodide salt, which is naturally present in much of our source waters from salt water intrusion into our cities located along coastlines.

We recently discovered that compounds used in medical imaging, "X-ray contrast media," can be a source of iodine in the formation of iodinated DBPs. X-ray contrast media can be present at high ppb levels in our source waters; in fact, they're present at the highest levels of any pharmaceutical found in rivers and other environmental waters.

LCGC: Can you tell us what the analytical challenges are in analyzing for low levels of DBPs?

RICHARDSON: We have analytical challenges both in the qualitative identification of low levels of DBPs and in quantifying important target DBPs. For example, it can be a challenge to get enough concentration factor to see low levels of DBPs. Because of this, we often use XAD resins for extraction so that we can extract several liters of water on our

large homemade solid-phase extraction columns. It's challenging to identify an unknown DBP if it's present at trace levels. When obtaining good high-resolution data to aid in the identification, some sensitivity is usually sacrificed, and you can miss trace-level DBPs.

You can't apply a single extraction or mass spectrometry method to all DBPs. Some DBPs are degraded by certain quenching agents, such as sulfite, and others by ascorbic acid. We use quenching agents to freeze our sample in time when we take that drinking water sample so that the DBPs we measure later in the lab are at the same levels as when we took the sample.

Some DBPs are more volatile than others such that different liquid-liquid extraction or different solid-phase extraction procedures need to be used to optimize their recoveries. Some DBPs, such as haloacetic acids, require derivatization before they can be analyzed by GC-mass spectrometry. There's not a one-size-fits-all GC-mass spec temperature program. For example, halonitromethane DBPs need to be analyzed at a lower injection port temperature because they'll decompose at the typical hot injection port temperatures used.

As a result of these complexities, it can be difficult to develop new rugged analytical methods for a diverse group of DBPs.

LCGC: How are you using high-resolution accurate mass in your research?

RICHARDSON: High-resolution accurate mass has been one of our most important tools for identifying new unknown DBPs in drinking water. We use high-resolution mass spectrometry because the accurate mass gives you several decimal places. For example, instead of knowing that the mass of your unknown is 200, you know that it's 200.10245. With these extra decimal places, you can generally determine the molecular formula so you'll know the exact number of carbons, hydrogens, oxygens, nitrogens, and iodines in your molecule. We still need to determine how these atoms fit in a chemical structure but knowing what the formula is for the molecule and for the fragment ions helps tremendously in piecing together the structure of the unknown molecule.

LCGC: What are the latest developments in analytical technology relating to high-resolution accurate mass?

RICHARDSON: Previously, we used a magnetic sector mass spectrometer for the high-resolution accurate mass data, but we're currently using the new GC OrbiTrap and a high-resolution time-of-flight mass spectrometer. These instruments give great high-resolution data with much less loss in sensitivity compared to the magnetic sector mass spectrometer.

We're also using LC OrbiTrap to identify new high-molecular-weight DBPs in our X-ray contrast media work. Using these instruments, we recently were able to identify new iodinated DBPs and new nitrogen-containing DBPs that were not known before.