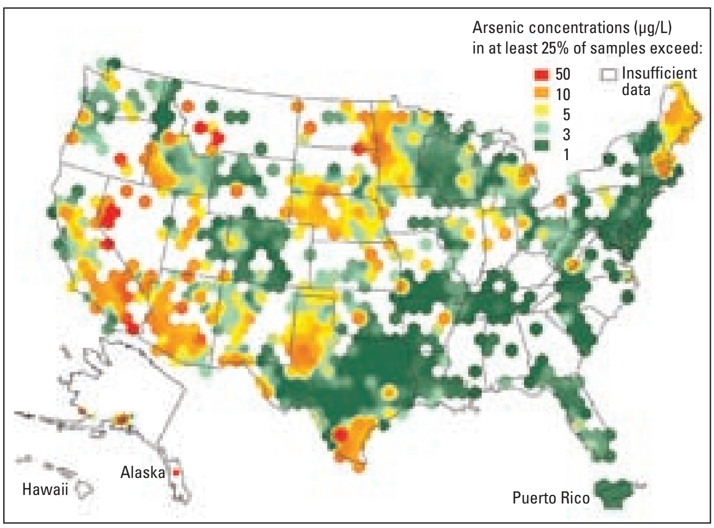
Tiny filters fix big water problems

The city of Brownsville, Texas, gets its drinking water from an aquifer that contains naturally elevated concentrations of arsenic—about 40 parts per billion (ppb). After the U.S. EPA restricted arsenic loads in drinking water to 10 ppb in January 2001, the city was in a bind: how best to remove the toxic metal from its water?

Naturally occurring arsenic is a worldwide phenomenon, and scientists and public-health managers from Bangladesh to Nicaragua to New Hampshire have been working on ways to filter out this toxic metal from drinking water. Many filters use iron because it binds arsenic relatively efficiently. The recently inaugurated Grainger Award honored Abul Hussam of George Mason University for his sand filtration method that incorporates an iron matrix to trap arsenic. This relatively cheap household technology, well tailored to the needs of developing countries with arsenic problems, is already in use in Bangladesh. Larger-scale filtration plants in developed parts of the world, which process thousands of gallons of water a day, use bits of iron to filter arsenic. But the iron flakes can foul filtering membranes, and getting rid of them is difficult.

If the amount of iron used in large filtration plants can be scaled down without decreasing their efficiency, places like Brownsville would have a solution to their arsenic problem. And nanomaterials could be that next-step tool in the arsenal against arsenic.

Researchers from Rice University have been tinkering with tiny, magnetic iron nanoparticles for just such a treatment process. They have created a filtering system that uses nanoscale magnetite (Fe_3O_4) to bind both As(III) and As(V), which can then be removed with a magnet. Preliminary tests with Brownsville groundwater and Houston tap water have been encouraging, and now the team is working to scale up its filter.



Arsenic contamination in water samples in different parts of the U.S.

Nanomagnetite at work

"The first and most enthusiastic response may be right here in America," says Mason Tomson, a principal investigator who is part of the team led by Vicky Colvin and others at Rice University's Center for Biological and Environmental Nanotechnology. New England, New Mexico, Texas, and California, among other places, have naturally occurring arsenic in regional groundwater. After 6 years of testing in Bangladesh, Tomson says, "some of the things we thought might be a concern", such as interfering ions or natural organic material, might not be "as difficult to overcome as we thought they might be."

The team's early experiments tested magnetite nanoparticles of various sizes: 12, 16, and 20 nanometers (nm) in diameter. Protocols on manufacturing such materials, established by Colvin's group, could ensure consistency in size.

The higher surface-to-volume ratio allows for more efficient capture of arsenic by smaller particles. Experiments in Brownsville, conducted by team member Heather Shipley, showed that 20-nm magnetite nanoparticles could treat 20 liters of water a day for a year, yielding 3.65 kilograms (kg) of magnetite bound with arsenic—the waste that would have to be removed or recycled. Only 1.8 kg of waste would be produced with 12-nm magnetite particles.

The move from larger iron-particle flocculants, which require expensive, high-energy magnets, to magnetite nanoparticles allowed the team to use lower-energy magnets successfully. Reporting in *Science* (**2006**, *314*, 964–967) last November, the researchers showed that 16-nm magnetite particles ended up as "a black deposit formed on the back wall [of a separator] where the field gradient was the highest." That cheaper option also makes this technology attractive to smaller treatment facilities and households.

Tomson envisions users "treating groundwater from a well that will not need to be filtered. [They would] add a fraction of a teaspoon of black powder—magnetite—shake it for a few minutes, and put on a magnet and pull the arsenic and iron down to the bottom." Shipley has examined whether a secondary filter could work. "Even with some-thing as trivial as a coffee filter," she says, plus a small amount of diatomaceous earth to aid filtration, the process is still "very fast, very easy". Although initial tests show that a handheld magnet can do the work, field tests are necessary because some components, such as phosphate, can interfere with iron oxides' adsorption of arsenic.

A key feature of the magnetite–nanoparticle method is that it removes both As(V) and As(III) with equal efficiency, Tomson emphasizes. "This is very important in the business. . . . As(III) generally is the most difficult [and] requires chlorine to oxidize it to As(V)."

Typical groundwater contains a mix of As(V) and As(III), and Shipley notes that although some wells may contain 70% As(V) and 30% As(III), others have the opposite proportion. Once adsorbed, the arsenic in either form "appears to be bound very tightly and does not easily desorb"; this has implications for disposal of the nanomaterial and whether it can be desorbed for reuse. It would be a "tremendous advantage" to be able to switch "on and off" the adsorption/desorption processes, Tomson says; that capacity remains to be tested.

For an individual household, the team projects that 200–500 milligrams of the magnetite nanoparticles would be necessary to treat a liter of water, at "a fraction of a penny a day and less than a kilogram of waste a year," says Tomson. Larger-scale plants, which treat tens of millions of gallons a day, "would have to do reuse and regeneration recovery [of the nanomaterials]. Otherwise, the mass of magnetite you would have to separate in a commercial water treatment [plant] is too large to be practical."

Sushil Kanel, a postdoctoral researcher at Auburn University and coauthor of the work on nanoscale, zerovalent iron, thinks Tomson's method could still be affordable and practical in many settings, "but more research is needed to apply the techniques using real field groundwater" from the U.S., Bangladesh, and elsewhere. He would like to see those tests in place as well as water-column experiments, noting that the Rice team's technology is ready for implementation only for community-scale pilot tests.

Expanding nanoparticles' reach

Nanofilters such as those developed by the Rice team might also prove to be an able platform for the removal of other metals. Crystal Clear Technologies, a company based in Portland, Ore., has been working on a multilayered, nanostructured filtration method to remove copper, lead, uranium, and other toxic elements in addition to arsenic, and they hope to get a product ready for the developing world as soon as possible, potentially in the next few years. The method relies on a substrate of zeolites (which have nanosized pores) and other minerals that have been functionalized with covalently attached simple organic molecules, says Darren W. Johnson, a chemist at the University of Oregon.


HEATHER SHIPLEY

Arsenic in contaminated water (left) stuck to nanoparticles of iron sulfate, which collected at the bottom of the tube (right) in a magnetic field.

Johnson comments that iron-oxide substrates also potentially can be modified and that the magnetite method from the Rice team provides larger available surface areas and the possibility of further functionalization. Plus, "their point is that down at the smaller nanocrystal size, [nanoscale] properties come into play," contributing to aggregation behavior that allows the magnetic-removal method to work, he emphasizes. NanoMagnetics, Ltd., a U.K.-based company, also plans to develop a magnetic method of removing arsenic. Called MagnetoFerritin, the system uses osmosis to desalinate water, and the company claims it removes other contaminants as well.

MagnetoFerritin and Crystal Clear's methods are only two of many nanotechnology products under development. Johnson notes that the Crystal Clear system has seed money and proof of concept, but further support is necessary to boost it to the next stage. (Some "gap funding" will come from the Oregon Nanoscience and Microtechnologies Institute, or ONAMI.)

Remaining challenges

Some nanofiltration technologies remain too specific for the larger task of water filtration in general, says Glenn Austin of the PATH Safe Water Project. The Seattle-based nonprofit organization recently received a $17 million grant from the Bill & Melinda Gates Foundation to test point-of-use water treatment methods in developing countries.

"One thing we've learned in the past 6 months is that [such products have] a very narrow bandwidth in contaminants they address," Austin says. "They do a great job with arsenic, or with select pathogens, but they need to combine core technologies to do a [complete] job" for the broader purposes of getting clean drinking water. That kind of multicontaminant platform could drive up costs, depending on what it takes to manufacture nanoparticles with specific coatings.

Nevertheless, Austin says, "nanotechnology offers some really interesting possibilities," and its potential "certainly fires up my imagination." Other ideas include an oversized coffee filter made of nanotreated paper, which could change colors once it is no longer working and then be thrown away. "Today, it's not a silver bullet," Austin says, but "nanotechnology could represent a future breakthrough in price and performance, so it is really a matter of timing."

Meanwhile, Shipley and colleagues' filtration method is ready to be tested with both small and large volumes of water. They plan to publish results of further tests on Houston tap water and Brownsville groundwater in the near future. The team has also begun introducing the household method to Nicaragua, where volcanic soils contribute low levels of arsenic to groundwater. Family and community point-of-use sites will serve as a testing ground starting sometime next year.

—NAOMI LUBICK