# Between water and rock -- a new science

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The Clark Fork River is not as pristine as it appears. Heavy metals bound to nanoparticles occur in the river sediment and water hundreds of miles from a long-closed mine, now a Super Fund clean-up site. Credit: Nicholas W. Haus

Water chemistry and mineralogy are scientific fields that have been around long enough to develop extensive knowledge and technologies. The boundary of water and rock, however, is not a thin wet line but the huge new field of nanoparticle science.

Scientists are discovering that aquatic nanoparticles, from 1 to 100 nanometers, influence natural and engineered water chemistry and systems differently than similar materials of a larger size. “Nanoparticles are in an awkward intermediate state, between elements dissolved in water and minerals that you can hold in your hand,” said Michael Hochella Jr., University Distinguished Professor of geosciences at

Virginia Tech. “The nanoscale represents a transition zone. For instance, the electronic, magnetic, and optical properties at the atomic, nano, and bulk scales are all different.”

The cover story of the December issue of the Royal Society of Chemistry’s *Journal of Environmental Monitoring* offers a critical review of the emerging field of “Aquatic environmental nanoparticles.” Written by Virginia Tech Ph.D. students Nicholas S. Wigginton of Holt, Mich., and Kelly (Plathe) Haus of Rochester, Minn., and Hochella, the article looks at recent advances in identifying nanoparticles in water and in understanding their properties and reactivity.

The review considers nanoparticles formed by natural processes in water and as unintended consequences of human activity, such as mining or water treatment.

“Because iron is the most abundant transition metal on Earth, and oxygen is the most abundant element in the crust, iron oxides are found in virtually all natural water and soil systems across a wide spectrum of pH, salinity, and geologic settings,” wrote Wigginton. Over billions of years, nature produced iron-oxide nanoparticles that carry elements and compounds great distances in rivers and groundwater, and that are also involved in catalysis and organic transformation. “And these nanoparticles account for a disproportionately large amount of potentially reactive surface area in the environment. As a result, what was once considered to exist in the dissolved fraction of water can no longer be viewed as such,” he said.

Meanwhile, humans are changing the natural nanoparticle distribution with no idea of the consequences. For instance, attempted cleanups can mobilize contamination release downstream or within a contamination plume through nanoparticle transport. And because contaminants are bound to nanoparticles, stability and interaction of contaminants are different than what was once predicted.

Even noninvasive clean-up is problematic, the review reports. Bioremediation of soluble uranium by microorganisms, such as metal-reducing bacteria, is of high interest. But a field study showed a large fraction of unreduced uranium after such an attempt. “The complexities behind the fate of metal and radionuclide contaminants during nanoparticle formation make predicting the final products very difficult,” said Wigginton, who has worked on this question at Pacific Northwest National Laboratory.

And the tools that make the study of nanoparticles possible, which include the scanning tunneling microscope, transmission electron microscope (TEM), atomic force microscope, are not part of any field kit.

The article relates two cases from the authors’ published and yet to be published research.

Due to almost 150 years of copper and silver mining and smelting activities, the Clark Fork River has been contaminated with high levels of toxic metals including arsenic, lead, zinc, and copper. More than 100 million tons of mine waste has been introduced directly into the river and surrounding floodplains.

Toxic metal location, distribution, and transport in the Clark Fork River, the largest EPA Super Fund clean-up site in the U.S., has been Hochella’s research for many years. Transport of heavy metals is now the subject of Kelly Haus’ Ph.D. thesis. Despite remediation, elevated levels of metals occur more than 300 miles downstream from the mining source. Hochella’s group has sampled the riverbed and floodplain sediments and extensively studied them using TEM, discovering toxic heavy metals as structural components of several nanocrystalline phases.

Hochella and Haus have also identified metal-bearing nanoparticles in water samples from the river.

“In Montana, we are finding that nanoparticles are important in transporting toxic heavy metals, such as lead and arsenic, down the river,” said Hochella. “These particles are incredibly small – 5 to 10 nanometers. Historically, we have not even known the nanoparticles were there. Now we know that lead in solution is different than if it is attached to a particle. But finding the particles is not easy. And impact on bioavailability is still unknown.”

He asks, “Are the metals less toxic if they are associated with nanoparticles than if dissolved as atoms in water? If a person, animal, fish, or insect ingests this water, will lead pass harmlessly through if it is associated with a nanoparticle?

“What Kelly learns about the role of nanoparticles in metal transport will be applicable to rivers worldwide,” Hochella said.

Closer to home, the authors asked, can environmental nanoparticles, which both transport and break down contaminants, affect the quality of our drinking water – despite or because of water treatment processes?

As a model system for identifying the mineral phase(s) of nanoparticles extracted from treated waters, Virginia Tech researchers examined tap water from Washington, D.C., which had had a significant problem with dangerously high lead concentrations in drinking water, likely due to leaching from lead-bearing pipes promoted by breakdown products of disinfection agents, according to Marc Edwards, professor of civil engineering at Virginia Tech, who was named a MacArthur Fellow for his work. The Virginia Tech geosciences group’s TEM data showed the presence of many nanoparticles of various compositions, sizes, and morphologies, some of which contain lead.

Wigginton wrote, “Although very few studies have been done to address the origin of nanoparticles in drinking water systems, it is relatively safe to assume one of three mechanisms: 1) the particles themselves (not necessarily the sorbed species that they are carrying) are native to the source water and are resilient enough to withstand chemical processing steps at the treatment facility; 2) nanoparticulate phases precipitate once inside the treatment plant and/or distribution system in response to changing chemical conditions; or 3) corrosion of pipes promoted by disinfectants and/or their degradation byproducts could cause nanoparticles attached to the piping material to detach.” He said that preliminary evidence suggests lead transport is influenced by environmental nanoparticles from the source water that have made it through the treatment facility and into the distribution system.

The researchers concluded that “environmental nanoparticle science will have to advance aggressively along at least two research paths: 1) fundamental research on the physical property and chemical reactivity variability of nanoparticles as a function of their size; and 2) the detailed study and understanding of the influence of nanoparticles on aqueous chemical processes.”

Hochella observed that the Journal of Environmental Monitoring prefers to give engineers and scientists information about processes, “but we are not yet able to tell engineers and scientists in the field where the nanoparticles and metals are and why nanoparticles behave differently. But it certainly is important that they know that recent research is calling assumptions about transport, remediation, and water treatment into question.”

The review concludes that “nanoparticle science goes well beyond the traditional boundaries of aqueous colloid science, but clearly these fields are highly complementary and are already beginning to merge.”

Source: Virginia Tech