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Testing And Treating For Chromium

As regulators consider tightening limits on Cr (VI) in drinking water, analysis and treatment technology may limit how low they can go

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Glendale Water & Power

PURIFICATION Water being cleansed of Cr⁶⁺ in Glendale's anion-exchange tests first gets filtered to remove particulates (blue tanks) and adjusted to pH 6.0 using CO₂ (white tank). Then it is passed through the resin (beige tanks).

Amid concerns about the prevalence of carcinogenic chromium(VI) in drinking water, California and federal regulators are considering tightening regulatory standards. The toxic metal can enter the water supply through natural deposits as well as from industrial sources such as steel and pulp mills.

Regulatory calculations will consider not just the toxicology and health effects of the substance but also the economic impact and technical feasibility of regulating it more stringently. Current water analysis and purification technologies are unlikely to be able to detect Cr⁶⁺ and remove enough of it from water to reach the public health goal proposed in December by the [California Office of Environmental Health Hazard Assessment](#): to maintain levels at 0.02 ppb or less.

Currently, California limits the total amount of chromium in drinking water to 50 ppb, whereas federal regulations limit total chromium to 100 ppb. Those regulations don't differentiate between chromium oxidation states. But in typical drinking water with an oxidizing environment at pH 6 to 10, most dissolved chromium would be Cr⁶⁺, says Andrew Eaton, vice president and technical director of [MWH Laboratories](#), a water- and wastewater-testing company located in Monrovia, Calif.

U.S. Environmental Protection Agency data show that 18% of samples tested from across the country contain more than 10 ppb total chromium. A report released in December by the [Environmental Working Group](#) documented Cr⁶⁺ concentrations of 0.03 ppb or more in the drinking water of 31 of 35 cities tested—with 12.90 ppb in Norman, Okla.; 2.00 ppb in Honolulu; and 1.69 ppb in Riverside, Calif. The Riverside amount roughly agrees with what the city has reported to the state. California has monitored some drinking water sources for Cr⁶⁺ since 2001; the results show that about 30% have 1 ppb or more Cr⁶⁺.

Water analysis labs use inductively coupled plasma mass spectrometry to measure total chromium; they use ion chromatography to measure Cr^{6+} . The Cr^{6+} method, known as [U.S. EPA Method 218.6](#), requires filtering a sample through a 0.45- μm membrane and then adjusting its pH to 9 to 9.5. Samples can then be stored at 4 °C for no more than 24 hours before analysis. This analysis time creates “a huge burden” to get samples to the lab quickly, Eaton says. Plus the lab has to be ready to run samples as soon as they arrive. However, on Jan. 11, U.S. EPA advised water agencies voluntarily monitoring Cr^{6+} that they could extend the hold time to five days after sample collection.

Work is under way in multiple labs to determine exactly what conditions promote reliable sample storage and analysis, Eaton says. So far, data from his company as well as from the California [Department of Public Health](#) and U.S. [EPA](#) show that samples are stable for four weeks at pH levels greater than 8, he says.

The sensitivity of detection methods is also a concern. The Cr^{6+} method as it stands now should allow for quantitation down to about 0.05 ppb, say Eaton and Mike Wehner, assistant general manager and director of water quality for the [Orange County Water District](#), which runs its own water analysis lab in Fountain Valley, Calif. Whether and how labs will be able to precisely and accurately go below that threshold is an open question. Using existing protocols it would be difficult to pick out peaks from the noise, Eaton says. But increasing the sample size runs the risk of exceeding column capacity.

Testing capability aside, another issue is what to do with water that exceeds the level set for Cr^{6+} . A decade ago, the city council of Glendale, Calif., directed its water utility to limit Cr^{6+} to 5 ppb in drinking water. But [Glendale Water & Power](#) found no known treatment for reducing chromium levels—the most utilities could do was to blend high- and low-chromium water to dilute the contaminant, says Dan Askenaizer, Glendale’s water quality manager.

With financial support from other nearby cities, the state, and U.S. EPA, Glendale started looking into treatment technologies. After testing different approaches at bench and pilot scales, the city is now conducting demonstration-scale studies of two Cr^{6+} reduction technologies. One uses an anion-exchange resin, which Glendale is testing at 400 gal/minute on well water that starts out at 35 ppb Cr^{6+} . The other uses ferrous sulfate to reduce Cr^{6+} to Cr^{3+} , coagulates the metal with polyacrylamide, and then filters out the resulting particles. Glendale is running that treatment at 100 gal/minute on water that starts out at 70–75 ppb Cr^{6+} .

The two systems have been operating for nearly a year and “both have performed really well,” Askenaizer says. The resin treatment reduces Cr^{6+} concentrations to less than 2 ppb. The reduction/coagulation approach reduces Cr^{6+} levels to less than 1 ppb but has been more challenging to operate. Right now Glendale uses gravel, sand, and anthracite to filter out the coagulated material; the city plans to see if membrane microfiltration can reduce Cr^{6+} to levels below 1 ppb. As successful as the tests have been so far, however, Askenaizer thinks that neither of the two treatment approaches—nor any other he knows of—could get water down to 0.02 ppb Cr^{6+} .

California’s proposed public health goal to limit Cr^{6+} levels to 0.02 ppb is based solely on health considerations and is just the first step toward setting a regulatory level for the metal in the state’s drinking water. The public comment period on the proposal closed on Feb. 15. Many of the comments focused on uncertainties inherent in the use of high-dose studies in animals to extrapolate the risk of cancer from low doses. A key point in Cr^{6+} toxicology is that Cr^{6+} can be reduced in the digestive tract to Cr^{3+} , which is less soluble and much less toxic, says Joseph A. Cotruvo, a water quality consultant and former director of U.S. EPA’s drinking water standards division. Although high concentrations of Cr^{6+} may overwhelm that reduction capability, low concentrations of Cr^{6+} , such as those in drinking water, may be completely converted to Cr^{3+} .

The [American Chemistry Council](#) is currently funding studies both to evaluate the risk of cancer at lower doses and to determine the biological mechanism behind Cr^{6+} carcinogenicity. Senior Director Ann Mason of the industry trade group expects the studies’ results to be released this summer.

Once the public health goal for a protective level of Cr^{6+} is final, the Department of Public Health will also have to set the regulatory maximum contaminant level, which will consider factors other than health. “The state’s health and safety code requires the department to establish a contaminant maximum safety level that’s as close to its public health goal as is technically and economically feasible, placing primary emphasis on protecting public health,” department spokesman Ken August says. For comparison, the California public health goal for arsenic is 0.004 ppb, while the California and federal maximum contaminant levels are 10 ppb.

All told, finalizing the public health goal and setting the maximum contaminant level could take more than two years. Separately, a bill pending in the state legislature would match the maximum contaminant level to the public health goal if a separate level is not set by Jan. 1, 2013.

Federally, EPA currently seeks voluntary monitoring of Cr^{6+} by utilities. It is reviewing the health effects of Cr^{6+} , with a final assessment due later this year. At a Feb. 2 Senate committee hearing, EPA Administrator Lisa P. Jackson said that the agency is likely to regulate Cr^{6+} and that the process will take at least four years ([C&EN, Feb. 7, page 6](#)). As in California, the federal agency needs to consider technical feasibility and cost along with human health protection.

