Chromium VI Occurrence Analyses and Estimated Treatment Costs

This article is a compilation of recently published information in the Journal of the American Water Works Association examining occurrence of hexavalent chromium in drinking water, comparing potential treatment strategies, and estimating national costs of regulation.

INTRODUCTION

Regulation of hexavalent chromium in drinking waters is proceeding in California and is a priority for the current US Environmental Protection Agency administration (USEPA, 2011). To regulate at the national level, occurrence, health effects, and treatability must be quantified so that a cost–benefit analysis can be used to determine whether there is a meaningful opportunity for health risk reduction (SDWA, 1996). Hexavalent chromium is not currently regulated in drinking waters, but total chromium has a National Primary Drinking Water Regulation maximum contaminant level (MCL) of 100 µg/L, based on a health effects endpoint of allergic dermatitis. The MCL for total chromium in California is 50 µg/L.

Dissolved chromium typically occurs in two oxidation states—trivalent or hexavalent. Total chromium is the sum of the trivalent and hexavalent species. When chromium occurs in the presence of oxidants such as chlorine or chloramines, the trivalent species may be oxidized to the hexavalent species (Saputro et al, 2011; Lai & McNeill, 2006; Brandhuber et al, 2004; Bartlett, 1997; Clifford & Chau, 1988; Ulmer, 1986; Sorg, 1979). Thus, regulating hexavalent chromium at the entry point of the distribution system without regard to total chromium concentration may not be sufficiently protective of public health. This article summarizes occurrence trends of both total and hexavalent chromium based on currently available data. Additional information can be found elsewhere (Seidel et al, 2012). Frey et al (2004) provided the most comprehensive study of chromium occurrence to date in the National Chromium and Boron Occurrence Survey. Other studies of chromium occurrence have primarily consisted of reporting naturally occurring chromium concentrations. For instance, Motzer (2005) cited naturally occurring total chromium concentrations of between 0 and 40 µg/L in groundwater and surface water from several sources.

DATA SOURCES

Chromium occurrence data were obtained from available sources to guide the development of the national occurrence survey. Three primary datasets are used in this analysis: the National Chromium and Boron Occurrence Survey (NCBOS), USEPA's Second Six-Year Review (6YR2), and the California Department of Public Health (CDPH) Water Quality Analysis Database (WQAD).

ANALYSIS OF TOTAL AND HEXAVALENT CHROMIUM OCCURRENCE

Figure 6 shows the cumulative probability distributions for CDPH hexavalent chromium by groundwater and surface water. Hexavalent chromium occurrence in groundwater is shifted toward higher concentrations than for surface water. Frey et al (2004) found similar results. Figure 6 also shows data with the raw waters separated from the treated waters. The distributions of total and hexavalent chromium are similar in surface water. The low level of occurrence is consistent, with surface water speciation being dominated by trivalent chromium (shown in the following section) and the low solubility of trivalent chromium. The groundwater data, however, indicate higher occurrences in the treated waters < 6 µg/L and higher occurrences in raw waters > 6 µg/L. An increase in hexavalent chromium could result from oxidation of trivalent chromium during disinfection. A decrease in hexavalent chromium could be due to treatment or blending provided at some sites. However, the explanation for the crossover shown in Figure 6 cannot be determined with any certainty and could be due to the disparity in the number of samples (1,242 treated samples versus 14,448 raw samples).

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FIGURE 6 Cumulative probability distributions of CDPH hexavalent chromium data in GW and SW separated into raw and treated samples (75th percentile concentration per sample location; nondetects are set to zero)

CDPH—California Department of Public Health, GW—groundwater, SW—surface water

Figure 10 shows the CDPH occurrence of hexavalent chromium in California. Because of the lower detection limit for hexavalent chromium concentration, ranges of 1–5, 5–10, 10–20, and > 20 µg/L are shown. Hexavalent chromium appears to be distributed across California and corresponds closely with both population density and use of groundwaters.

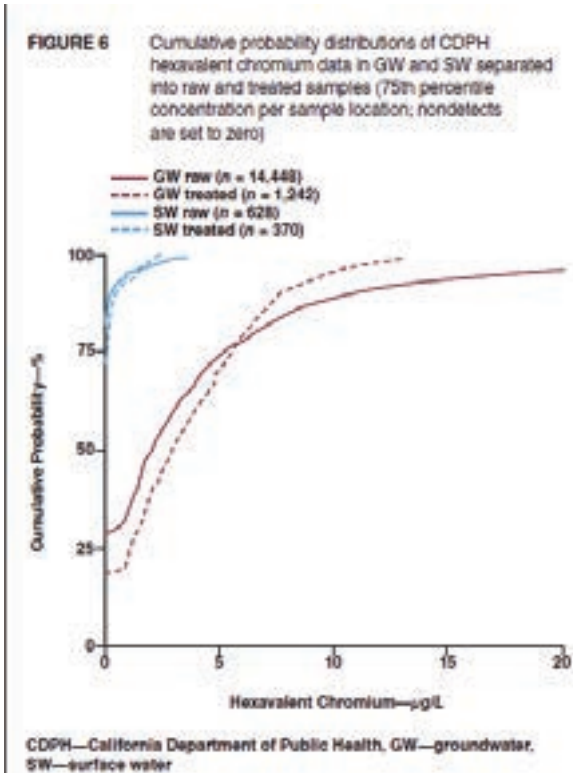FIGURE 10   California map of 75th percentile hexavalent chromium concentration by system

Figure 9 shows that total chromium is distributed across the United States. The greatest number of high chromium concentrations appears to be in the southwestern United States from California to Texas. The region surrounding the Great Lakes also appears to have widespread occurrence.

FIGURE 9   US map of 75th percentile total chromium concentrations from Second Six-Year Review data by system (for systems with more than two samples)

Hexavalent chromium [Cr(VI)] is a topic of substantial public discussion. The US Environmental Protection Agency (USEPA) regulates total chromium, including Cr(VI) and trivalent chromium Cr(III), in drinking water with a maximum contaminant level (MCL) of 100 µg/L. A National Toxicology Program rodent study (NTP, 2008) triggered a reassessment of risk by USEPA and the state of California. Although the USEPA risk assessment is still in progress, the California risk assessment is complete and has set the stage for development of a drinking d smaller systems to monitor for Cr(VI) and total chromium. The USEPA Integrated Risk Information System analysis is scheduled to be complete complete before the end of 2014; the UCMR3 occurrence data collection will be completed in 2015. These two efforts set the stage for consideration of either regulating Cr(VI) per se or changing the total chromium standard should the USEPA find a standard warranted.

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In California, the total chromium MCL is 50 µg/L. Currently, no federal or state regulations for individual chromium species [i.e., Cr(VI) or Cr(III)] exist for drinking water. However, a nonenforceable public health goal for Cr(VI) of 0.020 µg/L was established in July 2011 by the California Office of Environmental Health Hazard Assessment (OEHHA, 2011). With the public health goal now finalized, the California Department of Public Health (CDPH) is required to develop a Cr(VI)-specific MCL (California Health and Safety code §116365.5). CDPH expects to propose a Cr(VI) MCL applicable at entry points (EPs) to the distribution system by July 2013, with a final enforceable MCL established between July 2014 and July 2015. CDPH is collecting treatment feasibility and cost information relevant to a range of MCL conditions down to 1 µg/L. The timing of a final rule will be dependent on technical and administrative requirements.

This article provides estimates of both national and California-specific costs of compliance with a new Cr(VI) drinking water standard. In developing these cost estimates, several key knowledge gaps were identified, and research needs were also delineated.

TREATMENT TECHNOLOGY OVERVIEW

Bench-scale (Brandhuber et al, 2004), pilot-scale (McGuire et al, 2006), and demonstration-scale testing (Blute et al, 2013) of chromium treatment technologies has been performed, mostly by the city of Glendale, Calif., in partnership with the Los Angeles Department of Water and Power, the city of Burbank, and the city of San Fernando as well as other agencies. Testing in these studies identified several effective treatment technologies to achieve Cr(VI) treatment targets < 5 µg/L (i.e., the target of the studies): reduction/coagulation/filtration (RCF), weak-base anion exchange (WBA), strong-base anion exchange (SBA), and reverse osmosis (RO).

In contrast to past cost-of-compliance estimates (Frey et al, 1998), this analysis does not use a treatment technology forecast to identify which treatment would be selected at a given entry point predicted to need Cr(VI) treatment. Instead, because of a lack of sufficient information to substantiate a technology forecast, this analysis considers each of these technologies and presents the range of potential minimum treatent costs.

RCF. The RCF process has been shown at pilot- and demonstration- scale to effectively remove chromium to < 5 µg/L in Glendale. In this process, Cr(VI) is reduced to trivalent chromium [Cr(III)] by ferrous iron, then filtered as particles. Lower treatment goals may be achievable with microfiltration in place of granular filtration; this is being studied at Glendale. The kinetics of the reduction reaction may be site-specific but have been shown to be complete within 15–30 min. After reduction, the excess ferrous iron must be oxidized for removal. If chlorine is used for oxidation, a minimal dose must be used to avoid conversion of Cr(III) back to Cr(VI). Oxidation via aeration does not require minimal dosing. Filtration is then used to remove the co-precipitated iron and chromium. For the RCF process, residuals include the waste backwash water from the filters, which will contain elevated levels of iron and Cr(III) as well as any other constituents that were removed by the coagulation and filtration process. If these constituents are sufficiently removed from the waste backwash water, the remaining water can be returned to the head of the treatment plant and the resulting solids sent to an appropriate facility for disposal.

WBA. WBA has emerged as an attractive, simple-to-operate Cr(VI) treatment technology to achieve treatment goals down to 2 µg/L or less. WBA requires depressed treatment pH conditions (Clifford, 1999). A pH level of 6.0 was effective in testing at Glendale, for the one resin tested (Blute et al, 2013; McGuire et al, 2007). Posttreatment adjustment to a higher, more alkaline pH is then necessary to avoid corrosion of pipe materials in the distribution system. WBA resin is not regenerated on exhaustion but is disposed of as solid waste after dewatering and is replaced with new resin.

In addition to removing Cr(VI), WBA also removes other inorganic elements, including copper, vanadium, and uranium (Blute et al, 2012). Depending on the uranium concentrations in the raw water and the treated water goal, the spent WBA resin residuals may be classified asradioactive or hazardous waste and require processing and more expensive disposal options.

At this point, results for WBA resin testing have only been reported and published for Cr(VI) removal in one drinking

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water quality (i.e., Glendale). Other studies are under way to investigate the effect of water quality on resin capacity for Cr(VI), but knowledge gaps exist around variability in resin capacity over a range of typical water quality condition such as pH and competing anions.

SBA. SBA has been implemented by utilities with nitrate, arsenic, perchlorate, and other groundwater contamination issues and, as such, has been researched extensively. Cr(VI) treatment goals down to 1 µg/L have been documented at both pilot-scale (McGuire et al, 2007) and existing full-scale treatment systems for the removal of other contaminants. Because the functional groups of SBA resins remain ionized over a wide pH range, these resins do not typically require pH depression for operation (Clifford, 1999). After the exchange capacity of SBA is exhausted for the constituent of interest, the resin is regenerated in place with salt solution (i.e., brine). The primary constituent of the brine waste stream is salt, but the brine also contains the Cr(VI) removed from the water onto the resin as well as any other constituents that may adsorb on the resin (e.g., arsenic, nitrate, sulfate). Brine waste can be challenging to dispose of inland and in states that have more stringent restrictions on waste composition, such as California. SBA brine is likely to be classified as a hazardous waste in California because of chromium concentrations, which may necessitate treatment of the brine to separate the hazardous component as a solid waste and the nonhazardous brine as a liquid waste. Other utilities outside of California may find that brine waste can be disposed of to the sewer.

RO. RO has been demonstrated to be able to achieve greater than 90% rejection of chromium in bench-scale testing (Brandhuber et al, 2004). Theoretical understanding of RO membrane operations supports the idea that removal of Cr(VI) to < 1 µg/L should be achievable, although this has not been tested at full scale in a drinking water application to the authors' knowledge. However, the need for restabilization of corrosive RO permeate generally requires the use of treatment chemicals such as lime or calcite, and lime has recently been found to sometimes contain chromium as a trace impurity (McNeill et al, 2012). Disposal of RO concentrate is also a limiting factor in most noncoastal locations, similar to SBA, but at larger proportions of the flow (e.g., 10% for RO). However, the ability of RO to remove co-occurring constituents may

make RO a preferred non–low-cost alternative for some utilities.

In an RO process, > 99% of the divalent ions and > 95% of monovalent ions are removed from the water and retained in the concentrate. In this evaluation, the RO concentrate volume generated is assumed as approximately 10% of the volume of water treated, which is a loss in the amount of water produced for consumption. Assuming 100% rejection of these constituents, their levels in the concentrate will be 10 times those in the raw water.

Other compliance strategies. Other treatment technologies (e.g., biological reduction/filtration, chemical reductive media) were considered but not included in this analysis because their applicability would be too low to affect the overall cost numbers or because their treatment performance and associated costs are not yet proven. Also, blending and source abandonment were not considered as compliance strategies in this analysis because applicability and costs of blending and abandonment are site-specific.

NATIONAL COST ESTIMATE

Residuals management basis for cost approach. For development of the national cost estimate, two scenarios were evaluated that represent the ends of the disposal spectrum. The scenarios differ in their assumptions regarding the need to treat waste and manner of residuals disposal, representing two ends of the spectrum as shown in Table 4. The cost of a Cr(VI) treatment system is highly affected by whether the residual streams generated need to be treated and/or disposed of off-site, which can vary by state and locality. The qualities and quantities of the waste products from the four technologies vary. A description of the assumptions made under each scenario is shown in Table 4 and briefly described in the following section.

Under scenario 1, the liquid waste streams from the RCF, SBA, and RO processes are discharged locally to the sanitary sewer without any treatment and with no hydraulic restrictions. This assumption may be plausible in some locations, particularly if the volume of the residual streams discharged to the sewer is diluted by all the other flows received at the wastewater treatment plant. However, this assumption is not valid in some places in the United States where the discharge of a salt brine or concentrate from an ion exchange plant or RO facility is not allowed

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because of strict limitations on total dissolved solids levels in the effluent of the wastewater treatment plants. In addition, scenario 1 assumes that the wastewater treatment plant can receive the elevated chromium and other constituents removed by the treatment technologies and concentrated in their residuals streams. For the WBA resin, this scenario assumes that the spent resin can be disposed of in a municipal landfill as a nonhazardous waste. Experience suggests that the spent WBA resin will likely be classified as a nonhazardous waste by the federal Toxicity Characteristic Leaching Test (Blute et al, 2012). However, WBA resins have a high capacity for uranium. Even with low uranium levels in the water, if the uranium accumulates on the resin to detectable levels, then the resin cannot be disposed of in a municipal landfill, and scenario 1 does not apply.

Scenario 2 includes more stringent requirements for the handling and disposal of residual waste streams. For example, scenario 2 assumes that the waste backwash water from the RCF process requires treatment to concentrate iron/chromium particles to ~ 20% solids if they cannot be discharged to the sewer untreated. Solids are assumed to be disposed of in a municipal landfill. The recovered water is then returned to the head of the treatment plant. The ability to dispose of the dewatered sludge to the municipal landfill may exist for most states (i.e., sludge passes the Toxicity Characteristic Leaching Test). One exception is California, where the waste fails the California Waste Extraction Test (Blute et al, 2012) and is required to be disposed of in a California hazardous waste facility or transported out of state for disposal in a nonhazardous facility. For SBA and RO under scenario 2, high total dissolved solids concentrate/brine will be treated through ferrous iron addition and solids precipitation, with solids handled as described for the RCF process and liquid waste disposed of offsite as a nonhazardous waste. For WBA under scenario 2, the spent WBA resin is assumed to contain total uranium and thorium at greater than 0.05% by weight (> 500 mg/kg), which would then classify the spent resin as a low-level radioactive waste (LLRW) and require its disposal at one of the three dedicated LLRW facilities in the United States, located in Utah, Washington, and South Carolina.

PUTTING A POTENTIAL Cr(VI) MCL IN PERSPECTIVE
The national cost for a low Cr(VI) limit would likely be

substantially higher than those for previous drinking water regulations. For example, the 10-µg/L Arsenic Rule MCL was estimated to have a total annual cost of $0.5 billion/year and initial capital cost of $4.1 billion (Raucher & Cromwell, 2004 [adjusted to 2012 dollars]). For a corresponding Cr(VI) goal of 10 µg/L, although the lower-end estimates are quite similar (national annualized cost of $0.55 billion/year with corresponding capital costs of $3.4 billion), the upper-end estimates are significantly higher with a national annualized cost of $5.1 billion/year and corresponding capital costs of $28 billion—costs that are almost 10 times as much as those for the Arsenic Rule. Even using the average of the estimated potential range of the minimum national costs, achieving a 10-µg/L Cr(VI) treatment goal would cost four times as much as complying with the Arsenic Rule. Further, this analysis does not take into account land acquisition or additive costs of existing treatment.

These costs increase as the treatment goal decreases. A similar comparison can be made in California between potential costs for a Cr(VI) standard and the revised arsenic standard. The California-specific annual cost range for a Cr(VI) treatment goal of 10 µg/L is projected at $0.3 billion–$0.5 billion/year, with corresponding capital costs projected at $2.1 billion–$3.1 billion. By comparison, CDPH estimated the California- specific total annualized costs (including monitoring, treatment, and residuals disposal; assuming 7% interest and a 20-year period) to comply with a 10-µg/L arsenic MCL to be $200 million/year (adjusted to 2012 dollars; CDPH, 2008). The 10-µg/L Cr(VI) total annual cost estimates are 1.5–2.5 higher than those estimated for the 10-µg/L Arsenic Rule because of both higher occurrence—681 EPs have been estimated to require treatment for a 10-µg/L Cr(VI) MCL, whereas CDPH estimated 493 sources to be affected by arsenic at 10 µg/L—and treatment costs; chromium treatment can be substantially more expensive, particularly when considering residuals disposal.

Please refer to the full article for additional information, such as cost calculation methodology and community-level cost estimates.