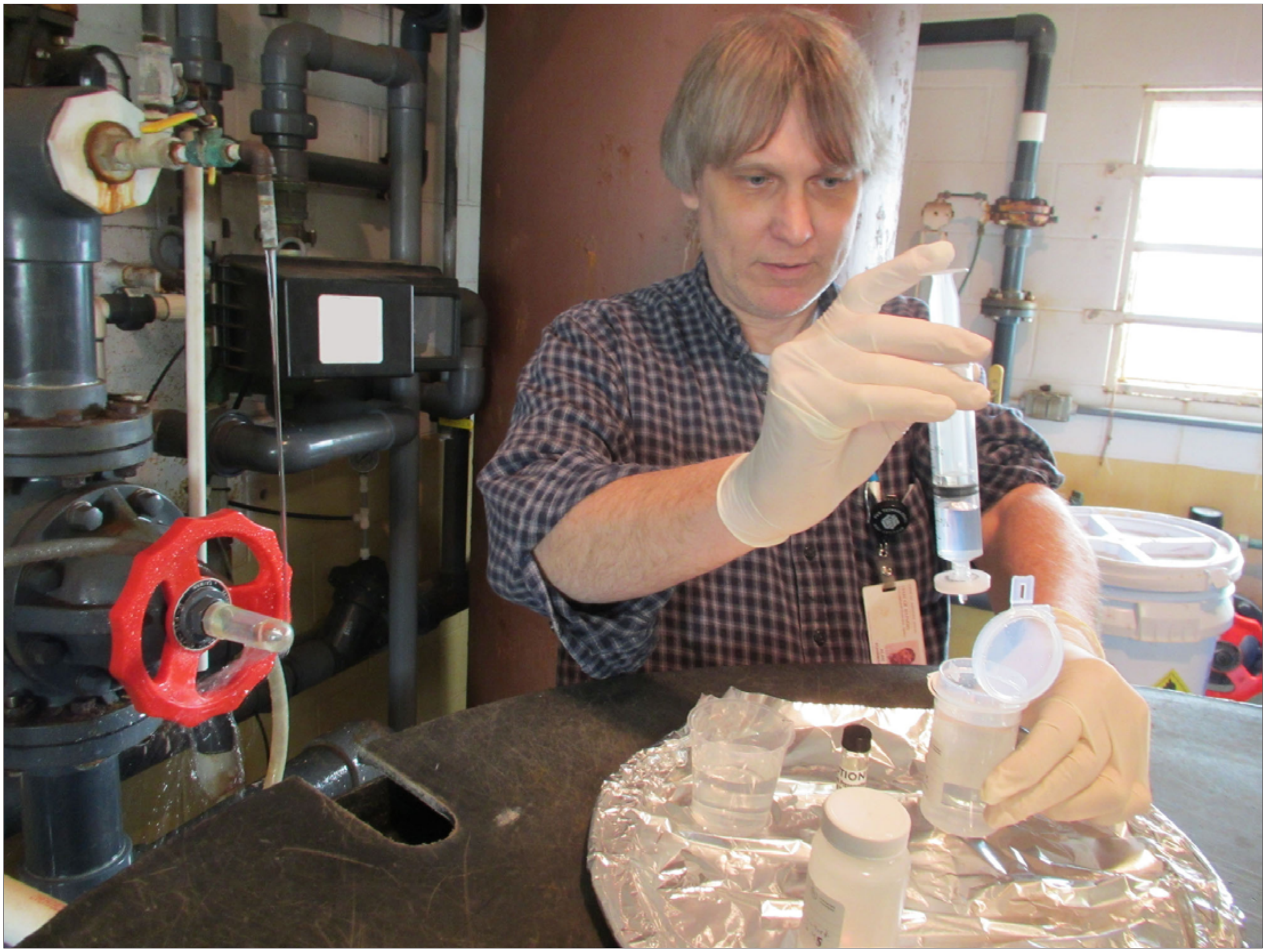
Prepared in cooperation with the Illinois Environmental Protection Agency

Hexavalent and Total Chromium at Low Reporting Concentrations in Source-Water Aquifers and Surface Waters Used for Public Supply in Illinois, 2013



Scientific Investigations Report 2015–5020

U.S. Department of the Interior
U.S. Geological Survey

Front cover and other images: Front cover shows collection of groundwater samples, Union-York Water District (intake 00251). This and other photography by Patrick Mills, U.S. Geological Survey.

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By Patrick C. Mills and Richard P. Cobb

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SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2015

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Conversion Factors and Abbreviations

Inch-Pound to International System Units

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
gallon per minute (gal/min)	0.06309	liter per second (L/s)
	Yield	
gallon per day per square mile ($gal/d/mi^2$)	0.00144	cubic meter per day per square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F = (1.8 × °C) + 32

Abbreviated water-quality units used in this report: Concentrations of chemical constituents in water are given in micrograms per liter (µg/L) and milligrams per liter (mg/L). Micrograms per liter are considered equivalent to parts per billion at the reported concentrations. Milligrams per liter are considered equivalent to parts per million at the reported concentrations.

Concentrations of chemical buffers are given in millimole (mM), a unit of metric measurement that is equal to one thousandth (10^{-3}) of a mole (the amount of a substance that corresponds to its formula mass in milligrams or one thousandth of a gram-molecule).

Specific conductance (SC) of water is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

pH of water is given in standard units.

Abbreviated concentrations of solids used in this report: Concentrations of chemical constituents in solids are given in milligrams per kilogram (mg/kg).

Additional abbreviations: micrometer (µm), millivolt (mv), milliliter (mL), millimeter (mm).

Hexavalent and Total Chromium at Low Reporting Concentrations in Source-Water Aquifers and Surface Waters Used for Public Supply in Illinois, 2013

By Patrick C. Mills[1] and Richard P. Cobb[2]

Abstract

On the basis of their recent review of the human health effects of hexavalent chromium [Cr(VI)] in public drinking water, the U.S. Environmental Protection Agency is considering the need for Federal regulation of Cr(VI). Presently, only total chromium is regulated, at a Maximum Contaminant Level (MCL) of 100 micrograms per liter (µg/L). The occurrence of Cr(VI) in groundwater and surface waters generally is attributed to industrial sources, but can be of natural origin. California's recently established MCL for Cr(VI) of 10 µg/L illustrates the drinking-water concerns associated with Cr(VI). To improve understanding of the possible impact of a Cr(VI)-specific standard that approximates the California level on the management of Illinois' public drinking water, the U.S. Geological Survey, in cooperation with the Illinois Environmental Protection Agency, assessed the occurrence and distribution of Cr(VI) in the State's public-water supplies.

During 2013, untreated water samples were collected to be analyzed for Cr(VI) and total chromium [Cr(T)] at 119 water-supply wells and 32 surface-water intakes; also, 32 treated surface-water samples were collected near the point of treatment and 32 near the furthest point of distribution. Public-supply sample sites were selected by a stratified random method. Samples typically were analyzed within 24 hours of collection at reporting limits of 0.02 µg/L for Cr(VI) and 0.1 µg/L for Cr(T). The occurrence of Cr(VI) was compared with selected geophysical, physical, and sampling factors that might more fully explain its distribution and magnitude of concentrations.

The maximum concentration of Cr(VI) in groundwater was 2.1 µg/L. Maximum concentrations in untreated and treated surface water were 0.29 µg/L and 2.4 µg/L, respectively. All sample concentrations were below the California MCL; only 35 percent were below that State's non-enforceable public health goal of 0.02 of µg/L. Cr(VI) was undetected in 43 percent of untreated groundwater samples, with a median of 0.06 µg/L when detected. All but two (94 percent) of untreated surface-water samples had detections. In untreated surface water, the median concentration was 0.09 µg/L, whereas in treated (tap and distributed) water the median was 0.20 µg/L. Surface waters treated with lime for softening typically had the greatest Cr(VI) concentrations (maximum, 2.4 µg/L; median, 1.2 µg/L).

The maximum concentration of Cr(T) in groundwater was 1.8 µg/L. Maximum concentrations in untreated and treated surface water were 1.8 µg/L and 2.5 µg/L, respectively. All sample concentrations were below the Federal MCL. Total chromium was detected in 65 percent of untreated groundwater samples, with a median of 0.40 µg/L, when detected. All but one (97 percent) of untreated surface-water samples had detections. In untreated surface water, the median concentration was 0.40 µg/L, whereas in treated (tap and distributed) water the median was 0.30 µg/L. As with Cr(VI), surface waters treated with lime typically had the greatest Cr(T) concentrations.

Examination of factors that might account for or be associated with the occurrence of Cr(VI) in public-supply source waters found few clearly evident factors. Associations in frequencies of occurrence and range of concentrations indicate that surface waters and groundwaters of shallow, unconsolidated, unconfined aquifers, particularly alluvial aquifers, are possibly most commonly affected by anthropogenic sources of Cr(VI). Groundwaters of deep (greater than 500 feet) bedrock aquifers, particularly the Cambrian-Ordovician aquifer system, are possibly most commonly affected by geologic sources of Cr(VI). Additional study, with supporting geologic and geochemical data that were not collected in this study, would be necessary to verify these associations.

There was a weak positive relation ($\rho = 0.23$) between concentrations of Cr(VI) and Cr(T) in untreated water samples, with a much stronger positive relation ($\rho = 0.86$ and $\rho = 0.90$, respectively) in samples collected soon after treatment and near the endpoint of distribution. The stronger relation and greater similarity between Cr(VI) and Cr(T) concentrations in treated water samples indicate that Cr(VI) represents a greater proportion of the measured concentrations of Cr(T) in

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[1] U.S. Geological Survey

[2] Illinois Environmental Protection Agency

treated waters than in untreated waters. The analysis of spikes and other quality-assurance samples indicate uncertainties associated with obtaining or confirming consistently accurate analytical results for Cr(VI) at near the applied reporting limit of 0.02 µg/L.

Introduction

The U.S. Environmental Protection Agency (USEPA) regularly reevaluates public drinking-water standards. Following the release of toxicity studies by the U.S. Department of Health and Human Services' National Toxicology Program in 2008 (U.S. Environmental Protection Agency, 2013a), the USEPA launched a comprehensive review of the health effects of hexavalent chromium [Cr(VI)] in public drinking waters. On the basis of this review and consideration of recently available toxicity studies pertaining to ingestion of Cr(VI), the USEPA has proposed to classify Cr(VI) as likely to cause cancer in humans when ingested over a lifetime (U.S. Environmental Protection Agency, 2010a). In 2010, a draft of this human-health assessment (U.S. Environmental Protection Agency, 2012a) was released for public comment and external peer review. Upon finalization of the assessment, its conclusions and other relevant information will be considered to determine the necessity of establishing a specific regulatory standard for Cr(VI) in public drinking waters.

The USEPA has regulated Cr(VI) as part of the total chromium [Cr(T)] standard under the Federal Safe Drinking Water Act (SDWA) (U.S. Environmental Protection Agency, 2012b) since 1992. This standard addresses all forms of chromium, including Cr(VI) and trivalent chromium [Cr(III)]. The trivalent form occurs most commonly in waters used for public supply (Frey and others, 2004) and is generally nontoxic at levels typically found in public drinking water. The present (2014) Maximum Contaminant Level (MCL) for Cr(T) is 100 micrograms per liter (µg/L) (U.S. Environmental Protection Agency, 2013b). In 2014, California established an MCL of 10 µg/L for Cr(VI) (National Ground Water Association, 2014) and, in 2011, established a nonenforceable public health goal of 0.02 µg/L (California Department of Public Health, 2014). New Jersey reportedly is considering a regulatory standard of about 0.07 µg/L (New Jersey Drinking Water Quality Institute, 2010). Additionally, the Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services has a nonenforceable children's drinking water health guideline of 10 µg/L and an adult water health guideline of 40 µg/L (Illinois Environmental Protection Agency, 2011a). These state and Federal guidelines illustrate the drinking-water concerns associated with Cr(VI) and suggest that, if established, the Federal drinking water standard for Cr(VI) might fall within the range of 0.02–40 µg/L and possibly close to 10 µg/L.

The occurrence of Cr(VI) in groundwater and surface waters generally is attributed to industrial sources, but it can be of natural origin (McNeill and others, 2011). Water geochemistry, principally oxic and alkaline pH conditions, enhances the transformation of chromium from the generally nontoxic form Cr(III) to more soluble and toxic Cr(VI). This transformation process has important implications regarding changes in the occurrence and concentration of Cr(VI) during water treatment and distribution. Additionally, there are indications that drinking water might be inadvertently affected by trace amounts of Cr(VI) included in water-treatment additives (Anthony Dulka, Illinois Environmental Protection Agency, written commun., 2011). Accurate representation of in situ concentrations can be difficult because of the time-related instability of the oxidation-reduction (redox) species of chromium (Ball, 2003) and the potential for cross contamination when analyzing at the extremely low concentrations required for present and possible future water-quality regulation. Many of the sampling and processing methods can be quite intricate, requiring strict attention to procedural guidelines. Under the influence of these factors, there may be bias for underestimation or overestimation of dissolved concentrations.

Although the reasonable likelihood of Cr(VI) occurrence in many of the Nation's public-supply waters is well documented (as will be subsequently discussed), none of the available studies specifically address the potential for statewide occurrence of Cr(VI) in the source and drinking waters for public supply in Illinois. Additionally, there remains an incomplete understanding of the factors that affect Cr(VI) distribution in source waters and detection in drinking-water samples, including the potential contributions to Cr(VI) detection of sampling methodology and chromium-species transformation during water treatment and distribution.

The U.S. Geological Survey (USGS), in cooperation with the Illinois Environmental Protection Agency (IEPA), conducted a comprehensive assessment of the occurrence of Cr(VI) in the source and treated public-supply waters of Illinois in an attempt to improve understanding of

1. the occurrence of Cr(VI) in Illinois' waters used for public supply,
2. selected factors that affect its occurrence, and
3. the impact of a specific regulatory standard for Cr(VI) at a level of 10 µg/L or less on management of Illinois' public drinking waters.

During 2013, untreated water samples were collected to be analyzed for Cr(VI) and Cr(T) at 119 water-supply wells and 32 surface-water intakes distributed throughout the State; also, 32 treated surface-water samples were collected near the point of treatment and 32 near the endpoint of distribution (the furthest point, approximating the longest insystem residence time). A reporting limit at the lower end (0.02 µg/L) of those that might be expected for Federal regulation of Cr(VI) was applied in the assessment; a similarly low reporting limit (0.1 µg/L) was applied for assessment of Cr(T). Quality-assurance samples were evaluated along with laboratory analytical results to consider the accuracy of the results and related uncertainty associated with sample collection and analysis at the relatively low reporting limits of this study. The occurrence of Cr(VI) was examined along with selected geochemical, physical, and sampling factors that might more fully explain the distribution and magnitude of concentrations. Data particularly relevant to improved understanding of the occurrence of Cr(VI) with respect to aqueous geochemistry , including dissolved-oxygen (DO) concentrations and redox potentials, were either not available or of insufficient accuracy in this study. Also, other redox-sensitive chemical constituents were not routinely analyzed in all samples; assessment of redox conditions on the basis of those constituent data that were sufficiently available was beyond the scope of the study.

Purpose and Scope

This report presents the analytical results for Cr(VI) and Cr(T) from 215 samples collected by the IEPA at public water facilities in Illinois during January–December 2013. The samples represent untreated source water from water-supply wells and surface-water intakes, as well as treated water at the location of treatment and near the endpoint of distribution. Limited analysis is provided of the (1) geochemical factor pH and selected physical factors that may account for or be associated with the occurrence and distribution of Cr(VI) in the State's source and treated waters used for public supply, (2) selected sampling factors that may be associated with the analytical results of Cr(VI), and (3) the effect of lime as a treatment additive on Cr(VI) concentrations in drinking water. Physical factors that were evaluated included aspects of land use, geohydrology, well construction, and water treatment. Sampling factors included aspects of the sample processing prior to analysis and of the material composition of the water-supply delivery system. Additionally, quality-assurance factors were examined that address the accuracy of the analytical results and the uncertainty associated with sample collection and analysis at the reporting limits of 0.02 µg/L for Cr(VI) and 0.1 µg/L for Cr(T). Results are summarized statistically and presented in figures and tables.

Previous Studies

Hexavalent chromium has been detected in drinking water or groundwater at concentrations above the 100 µg/L MCL for Cr(T) at a number of geographically restricted locations within the United States, including Hinkley, California (Zimmerman, 2014) and Midland, Texas (Texas Commission on Environmental Quality (2013); in large part those elevated concentrations are attributed to industrial contamination. Several reconnaissance studies on a larger scale have documented the occurrence of Cr(VI) in groundwaters and surface waters used as sources for public supply. In samples from Lake Michigan, Cr(VI) concentrations consistently have been detected in the range of 0.2–0.3 µg/L (Central Lake County Joint Action Water Agency, 2011); the lake is a public-water source for over 7,000,000 people in and near Chicago, Illinois and Milwaukee, Wisconsin (Mills and Sharpe, 2010). In a study of chromium occurrence in the western Mojave Desert, Calif., Cr(VI) was detected in about 94 percent of the samples from 133 public-supply, domestic, and observation wells, with maximum and median concentrations of 60 µg/L and 5.5 µg/L, respectively (Ball and Izbicki, 2004). The samples were analyzed by a field-speciation method with a reporting limit of 0.1 µg/L. The concentration of 25 percent of the samples was greater than 10 µg/L. A statewide assessment of Cr(VI) in drinking water obtained from about 6,500 public-supply wells in California found detectable concentrations above 1 µg/L in about 55 percent of well-water samples and above 10 µg/L in 4.5 percent of samples (California State Water Resources Control Board, 2011). In a study of the drinking-water supply facilities of 35 U.S. cities, the Environmental Working Group (Sutton, 2010) found Cr(VI) at concentrations above 0.06 µg/L in the tapwater samples from 25 cities; the greatest concentration was 12.9 µg/L. More than 26 million people are served by the 31 facilities with detected concentrations of Cr(VI). The largest areal reconnaissance study for Cr(VI) in drinking water of the United States, the National Chromium and Boron Occurrence Survey (NCBOS), consisted of the collection of almost 350 public-supply tap samples from groundwater and surface-water sources (Frey and others, 2004). The samples, most of which were chlorinated or otherwise treated, were collected from about 40 states. Cr(VI) was detected above the method detection[3] or reporting limit of 0.2 µg/L in 42 percent of these samples, with a maximum concentration of about 53 µg/L. The study included almost 20 supply facilities and about 30 source water bodies in Illinois. The mean of the sample population was 1.1 µg/L, and the median was less than the reporting limit. Concentrations in groundwater samples, representing 67 percent of the source-water samples, typically were greater than those in surface-water samples; respective 95th- and 75th-percentile concentrations were about 6 µg/L and 1 µg/L in groundwater and 0.5 µg/L and 0.25 µg/L in surface water. Untreated tapwaters (typically from groundwater) had notably greater concentrations than treated waters.

The IEPA indirectly has considered the statewide potential for elevated concentrations of Cr(VI) in Illinois' public drinking waters. Although IEPA has not previously sampled and analyzed for Cr(VI), the agency has reviewed untreated source water (ambient) and treated (finished) water sample results for Cr(T) from the State's 1,750 or so public-supply facilities (Illinois Environmental Protection Agency, 2011a). Cr(T) was detected in only 4 percent of treated water samples collected during the 1993–2010 review period, with no concentrations exceeding the MCL of 100 µg/L for Cr(T). The

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[3] Hereafter the reference to level of detection will be uniformly described as "above the reporting level." The method detection limit (MDL), as defined by USEPA (1986), is the lowest concentration of an analyte reportable with 99 percent confidence that the value is greater than zero. The reporting level, or minimum reporting level (MRL), is the minimum concentration that can be reported by a laboratory as a quantified value (U.S. Environmental Protection Agency, 2010b).

maximum reporting limit for Cr(T) applied in the analysis of these treated drinking water samples from groundwater and surface-water sources was 7 µg/L. The median detectable concentration in treated drinking water was 11 µg/L, with a 75th-percentile concentration of 22 µg/L. The median detectable concentration in treated water from groundwater sources was about 10 µg/L and from surface-water sources was about 14 µg/L. Median detectable concentrations in untreated groundwaters and surface waters were less than those in treated waters (about 8 µg/L and 1 µg/L, respectively).

Chemistry of Hexavalent Chromium

Chromium is a metallic element which is odorless and tasteless and can be present in various oxidation states. The most common forms of chromium in the environment are Cr(III), Cr(VI), and the metal form Cr(0). Chromium is found naturally in rocks, plants, soil and volcanic dust, and humans and other animals. Naturally occurring Cr(III) that can generate Cr(VI) is prevalent in ultramafic igneous rocks near convergent plate boundaries (Stowe, 2006). Reportedly, Cr(VI) also may be found in certain limestone deposits (Frias and others, 1994; Scientific Analytical Institute, 2014). Manganese minerals, including manganese oxide (MnO_2), that are commonly found in association with chromium-bearing rocks have been indicated as a potential oxidant for the transformation of geochemically inert and immobile Cr(III) to Cr(VI), the more soluble and mobile form in aqueous settings (Chung and others, 2001; Oze and others, 2006). Phosphate additions to soils for nutrient amendment are identified as a geochemical mechanism for release of Cr(VI) from enriched soils (Becquer and others, 2003). Ultramafic, chromium-rich rock units or soils generally are not found in Illinois, except to a limited extent in the unglaciated southeastern part as peridotite associated with dikes and sills near structural features (Nelson, 1995). It is possible that eroded chromium-bearing materials from the Canadian shield region could be distributed among the Illinois and Wisconsin Episode glacial deposits that blanket most of the State (fig. 1). However, brief review of readily available scientific literature found no indication of elevated or widespread concentrations of chromium-bearing minerals in these glacial deposits. A survey of near-surface soils (depth less than about 3 feet [ft]) found chromium concentrations in Illinois typically in the range of about 35 to 55 milligrams per kilogram (mg/kg), with the national median about 30 mg/kg; concentrations were as great as about 3,060 mg/kg in the eastern United States (Maryland) and 4,620 mg/kg in the western United States (California) (Smith and others, 2014). To what extent these near-surface samples represent concentrations at depth in aquifers used for supply of drinking water is uncertain. Tourmaline, which in some forms can include chromium as a trace constituent, is a minor component (1–5 percent) of till deposits that are older than the Illinois Episode and either exposed in a small area of western Illinois or buried in parts of western and southern Illinois (Willmann and others, 1963; Kolata and Nimz, 2010). These older till deposits do not serve as groundwater or surface-water source deposits for the State's public water supply. Limestones are prevalent throughout the State, but brief review of readily available scientific literature found no discussion or data regarding Cr(VI) or other forms of chromium associated with Illinois limestones. Manganese is commonly found in Illinois groundwaters, particularly where concentrations are elevated in the glacial drift aquifers[4] (Voelker and Clarke, 1987).

Trivalent chromium occurs naturally in many vegetables, fruits, meats, grains, and yeast. Cr(VI) and Cr(0) generally are associated with industrial processes. Major industrial uses of Cr(VI) are associated with steel and pulp mills, metal plating, leather tanning, wood preservation, and production of dyes and pigments. Occurrences of Cr(VI) in drinking water from these uses are attributed to leakage, poor storage, and (or) improper discharge or disposal (U.S. Environmental Protection Agency, 2010a). Erosion of natural deposits of Cr(III) also can contribute to Cr(VI) in drinking water. At least 60 industrial and landfill sites in Illinois have been identified as locations of operational use or disposal of chromium (Agency for Toxic Substances and Disease Registry, 2011), although to what extent this represents the use or disposal of the Cr(VI) form is uncertain.

Chromium is complex in its behavior in drinking-water systems because of its possible occurrence in various oxidation states. The most common states are the cationic Cr(III) form and the anionic Cr(VI) form. The anionic Cr(VI) species are chromate ($HCrO_4^-$ or CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$). At the low chromium concentrations typical of drinking waters (substantially below 1,000 milligrams per liter [mg/L]), the Cr(VI) chromate species occurs as monovalent $HCrO_4^-$ below pH 6.5 and divalent CrO_4^{-2} between pH 6.5 and pH 10 (Tong and King, 1953; Rai and others, 1987) (fig. 2). The dichromate species would only be present in drinking water under the atypical condition of Cr(VI) concentrations greater than 1,000 mg/L. Such conditions might possibly result from an unexpected industrial discharge. Cr(III) forms a series of hydroxide complexes as pH increases above 4.0 (that is, becomes less acidic and then increasingly alkaline above pH 7.0). Its most predominant anionic species in waters within the pH range common to drinking water (pH 6.5–8.5; U.S. Environmental Protection Agency, 2013c) is $Cr(OH)_3^0$ (Frey and others, 2004).

Cr(VI) becomes increasingly prevalent in waters with DO concentrations greater than about 1–2 mg/L (Ball and Izbicki, 2004; Hawley and others, 2004). In highly oxygenated waters, or in the presence of oxidant additives such as chlorine or chloramine, Cr(VI) is expected to predominate. Cr(III) is

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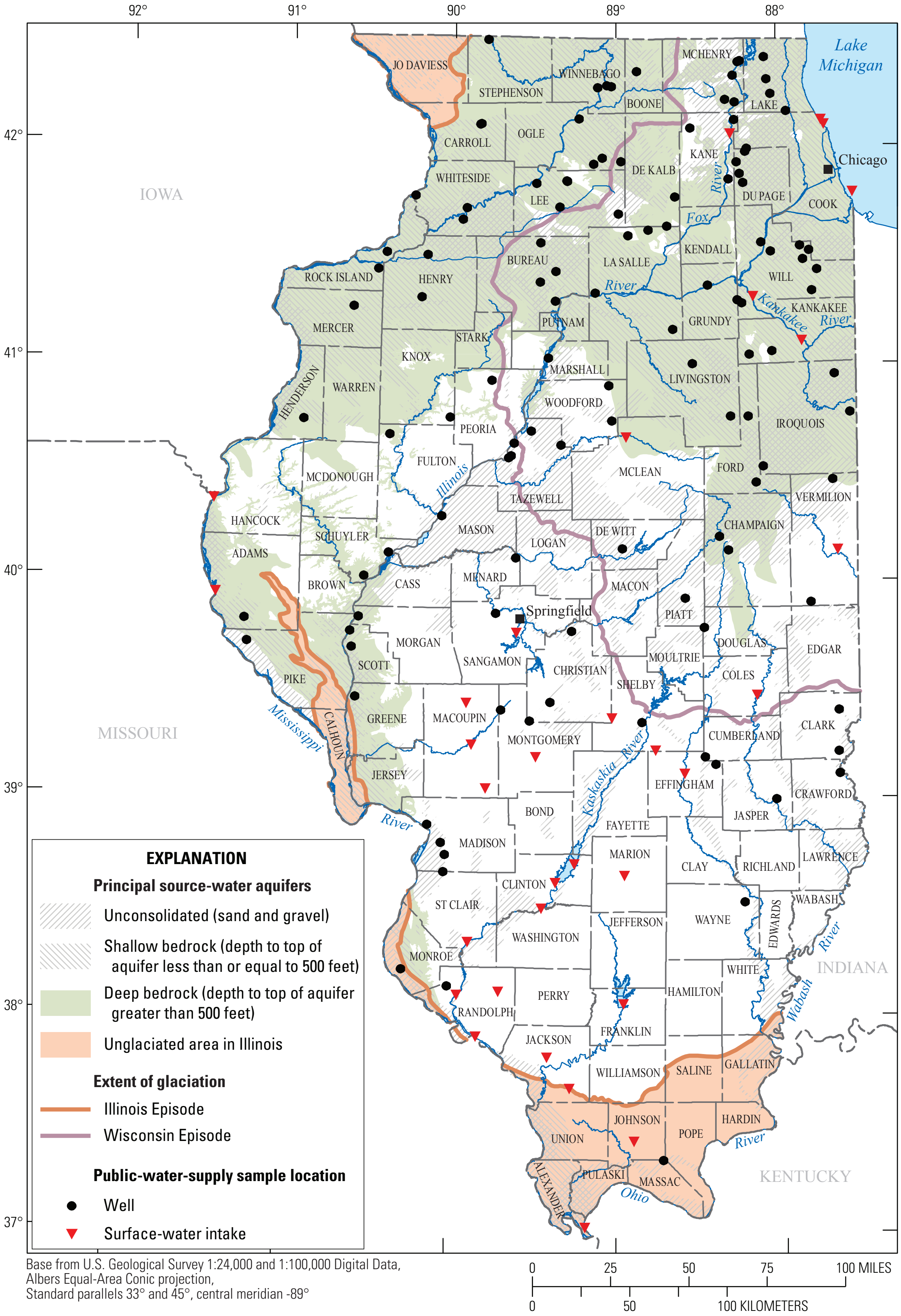
[4] Hydrostratigraphic classifications in this report follow the use of the U.S. Geological Survey (2014), which in most cases conform to the usage of the Illinois State Geological Survey (ISGS) (Visocky, 1997). Lithostratigraphic classifications and references to periods of glaciation follow the use of the ISGS (Visocky, 1997; Kolata and Nimz, 2010).



Base from U.S. Geological Survey 1:24,000 and 1:100,000 Digital Data,
Albers Equal-Area Conic projection,
Standard parallels 33° and 45°, central meridian -89°

Figure 1. Principal source-water aquifers and surface waters used for public supply, selected wells and intakes, and extent of episodic glaciation in Illinois (modified from O'Hearn and Schock, 1984, fig. 1, and Joseph Konczyk, Illinois Environmental Protection Agency, written commun., 2003).

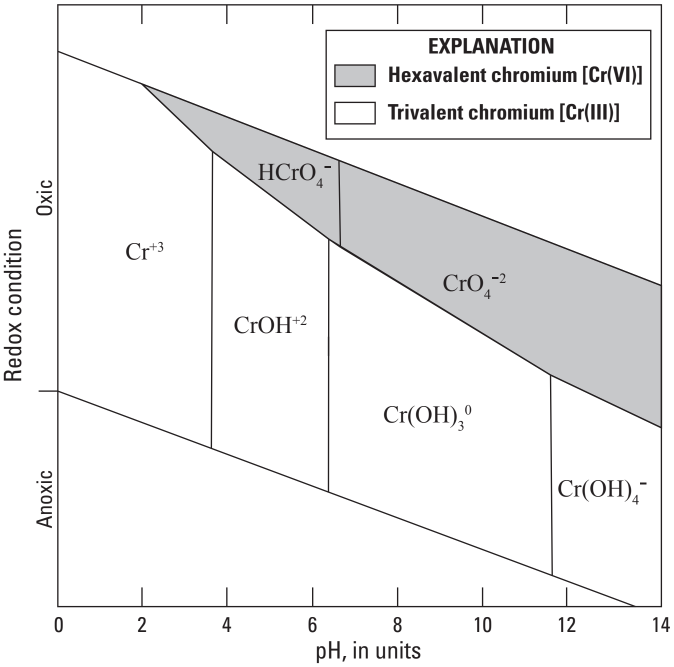


Figure 2. Relation of chromium speciation in water to oxidation-reduction (redox) conditions and pH (modified from McNeill and others, 2013, fig. 2.2).

expected to predominate in waters with very limited oxygen, as characterized by DO concentrations less than about 2 mg/L and (or) redox potential below 0 millivolt (mv) in the pH range common to drinking waters (McNeill and others, 2011).

Findings of the NCBOS study (Frey and others, 2004) indicate that Cr(III) typically is the principal source of chromium concentrations in the Nation’s drinking waters. Cr(III) was found to be the predominant chromium form in samples from surface-water sources but less prevalent in samples from groundwater sources. Often, Cr(VI) was the principal source of chromium concentrations in groundwater samples. Alkaline pH, which can be common to carbonate aquifers (Lindsey and others, 2008), possibly contributes to the more frequent occurrence of Cr(VI) in drinking waters from groundwater sources than surface-water sources. In Illinois, carbonate aquifers are the source of about 10–20 percent of the public water supply from aquifers and for tens of thousands of private well owners (U.S. Geological Survey, 2014a). These aquifers are predominantly in the northern part of the State (fig. 1).

The following discussion summarizes the detailed description of the chemistry of chromium by McNeill and others (2011), particularly in regards to its transformable behavior in treated-water distribution systems. Under changing conditions of water chemistry, Cr(III) can transform to the more soluble and toxic Cr(VI) form, as well as back to the Cr(III) form. The water chemistry, in part, can be affected by treatment additives and the material composition of the distribution infrastructure. Conventional treatment processes, such as filtering and chlorination, may be effective in removing Cr(III) from drinking water, but not Cr(VI) (U.S. Environmental Protection Agency, 2011).

Trivalent chromium can be nearly insoluble between pH 6–10, with minimum solubility at about pH 8. This near insolubility of Cr(III) within the range of pH that encompasses that representative of drinking water largely accounts for the predominance of Cr(VI) in many untreated (raw[5]) and treated (finished) drinking waters. Dissolved or soluble Cr(III) in water can sorb to oxide surfaces, complex with natural organic matter, form precipitate solids, and (or) be fixed in solids. Although with its great tendency toward insolubility, the soluble fraction of Cr(III) can range up to 100 percent, depending on various factors including levels of organic matter, oxides such as $Fe(OH)^3$, and pH, among others. Although Cr(VI) can undergo reactions similar to those for Cr(III), such as sorption or precipitation, there is a much greater tendency for it to remain soluble. Cr(VI) typically does not form precipitates at levels found in drinking water and does not bond strongly to natural organic matter. Therefore, generally present in drinking water as a soluble anion, its potential as a human toxin is much greater than that of Cr(III).

Virtually all transformations between Cr(III) and Cr(VI) associated with the collection, treatment, and distribution of drinking water are influenced by constituents that are either naturally present or purposefully added to the water. The various reactions that might occur and the rates of those reactions are well described in table 1. Upon entry to water-treatment and distribution systems, naturally present concentrations of Cr(VI) can be boosted rapidly (within a few minutes or more) with the transformation of any soluble Cr(III) after treatment, primarily from the addition of oxidants for disinfection. This transformation is problematic to facility operators, because even if Cr(VI) is fully removed from the incoming raw source water, it might reoccur. After treatment, Cr(VI) concentrations could be further boosted during distribution upon oxidant contact with plumbing fixtures that contain chromium. Studies have documented increases in chromium concentrations, including Cr(VI), from incoming untreated water or point of treatment to the endpoint of distribution; a 17-percent increase in chromium concentrations was documented in one study (Craun and McCabe, 1975) and as much as 10 µg/L in at least one sample in another (Frey and others, 2004). A reduction in concentration of 20 µg/L also was documented in the latter study (Frey and others, 2004).

As indicated from the study by Frey and others (2004), reduction reactions that transform Cr(VI) to Cr(III) also can be of great importance to the treatment and distribution process, because they can effectively limit Cr(VI) in drinking water. Such reactions often are manipulated intentionally, as the initial component of the treatment process. By this reaction, dissolved Cr(VI) that might be present can be converted to particulate or sorbed solids that can be settled or filtered for removal

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[5] In this study, all untreated water is considered raw water from an aquifer or surface-water source. Few, if any, potable waters for public consumption from facilities in Illinois, and particularly from the facilities included in this study, distribute untreated water.

Table 1. Potential reactions resulting in transformations of trivalent and hexavalent chromium.

[µg/L, microgram per liter. Modified from McNeill and others, 2011, table 1; p. 18–19 provides references to the various reaction dynamics]

Reaction	Occurs in the presence of—	Typical location or condition
Trivalent chromium [Cr(III)] oxidation to hexavalent chromium [Cr(VI)]		
Fast (minutes to hours)	Manganese dioxide (MnO_2 solids)	Oxygenated high pH groundwater
	Chlorine, hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$)	Water treatment, distribution system
Slower (days to years)	Oxygen	Groundwater, distribution system
	Chloramine	Distribution system
Cr(VI) reduction to Cr(III)		
Fast (minutes to hours)	Ferrous iron (Fe^{+2}), stannous chloride ($SnCl_2$), sulfites	Lower-dissolved-oxygen groundwater; water treatment, distribution system
Slower (days to years)	Absence of dissolved oxygen, sulfides, numerous bacteria	Groundwater; potentially in iron mains and dead ends
Conversion of soluble Cr to particulate Cr		
Fast (seconds to hours)	Water pH greater than 5	Possible whenever soluble Cr(III) is above about 1 µg/L
	Iron or aluminum oxides	Addition of coagulant

from the water. Ferrous iron is commonly used to induce the reduction. Beyond intentional treatment, iron solids that might be present in distribution lines also can induce Cr(VI) reduction; such sources of iron can include, among others, hematite, magnetite, ilmenite, and green rust. Other potential reductants that might be included naturally in the untreated source water or as additives are certain reduced sulfur compounds, organic compounds, microbes, and stannous chloride.

Several other factors further contribute to the complexity associated with Cr(VI) occurrence and transformation in drinking waters and with meaningful characterization of Cr(VI) occurrence and transformation for scientific and compliance-monitoring purposes. Chromium may be a trace contaminant in treatment additives including alum coagulants (Eyring and others, 2002) and possibly lime used for water softening (Missouri Department of Natural Resources, 2010). Other potential sources of chromium include leaching from materials used in treatment-plant and distribution components, such as cast iron, cement, stainless steel, and chrome-plated pipes and sample taps.

Finally, a number of studies have documented that the results of inductively coupled plasma–mass spectrometry (ICP–MS) analysis for Cr(T) may not always relate well to those of ion chromatographic (IC) analysis for Cr(VI), with reported Cr(VI) concentrations sometimes greater than those of Cr(T) in the same water samples. For example, a study of more than 1,500 drinking-water samples found that for samples with concentrations of Cr(T) greater than 1 µg/L, more than half of the samples had greater concentrations of Cr(VI) than Cr(T). From that study, Eaton and others (2001) surmised that there might be differences in the behavior of Cr(III) and Cr(VI) in ICP–MS analysis or possibly problems with sample preservation. Other studies indicate iron may play a role in Cr(T) analysis, limiting full accounting of dissolved chromium in drinking-water samples (Parks and others, 2004). For full review of the chemistry of chromium, including Cr(VI), and its possible geochemical response in natural and treated-water distribution systems under varying conditions of pH, oxygenation, and other factors, the reader is referred to McNeill and others (2011) and Frey and others (2004).

Study Methods

The methods used for well, surface-water intake, and sample-tap selection; land-use determination; sample collection; laboratory analysis; quality assurance; and data analysis are described in the following sections of the report. Quality-assurance methods include onsite (sampling) and laboratory methods.

Well, Intake, and Treated-Sample Site Selection

Untreated (raw) water samples in this study were collected from water-supply wells and surface-water intakes selected by stratified random methods. Separate methods were used for selection of groundwater and surface-water sample sites.

The initial 119 wells selected for sampling in this study represented a collection of wells which previously composed the IEPA Radon Network (Dave McMillan, Illinois Environmental Protection Agency, oral commun., 2001) and was used similarly in an assessment of herbicides and their transformation products in source aquifers for public water supply in Illinois (Mills and McMillan, 2004). The wells in the Radon Network were randomly selected from the larger IEPA Ambient Network of 362 wells compiled by a stratified random method (Illinois Environmental Protection Agency, 2011b). Criteria used for the stratification included aquifer type, geologic-based vulnerability to contamination, and well depth. The selected wells represent principal aquifers, as classified by O'Hearn and Schock (1984) (fig. 1); that is, the aquifers have a potential yield of 100,000 gallons per day per square mile (gal/d/mi^2) or more and an area of at least 50 square miles (mi^2). The wells tap the major types of source-water aquifers in Illinois, including unconsolidated glacial drift and alluvial aquifers and Cambrian- to Pennsylvanian-age bedrock aquifers (generally classified as the Pennsylvanian, Mississippian, Silurian or Silurian-Devonian aquifers and Cambrian-Ordovician aquifer system[6]) (fig. 3).

Among the wells in the Radon and Herbicide Network initially selected prior to 2001, 53 (45 percent) were no longer available for use in the present Cr(VI) study (well abandoned; well for emergency use only; facility no longer a public supplier) or were inappropriate for purposes of this study (pump cycle time insufficiently short; sample tap difficult to access or exposed to possible atmospheric contamination). Typically, replacement wells were selected from the pool of IEPA Ambient Network wells and matched as closely as possible the stratified-selection characteristics and location of the well being replaced. All replacement wells were selected by IEPA personnel. Given the large number of wells requiring replacement and the periodic necessity to select a replacement within a short timeframe, the wells were considered to reasonably match those they replaced. No replacement wells were selected with consideration of expected potential for detection of Cr(VI).

Fifty-six of the selected wells tap unconsolidated aquifers (well depths 28–404 ft), of which 22 are considered alluvial aquifers (well depths 36–145 ft) and the remainder glacial drift aquifers. Sixty three wells tap bedrock aquifers (well depths 45–2,665 ft), of which 3 are open to the Pennsylvanian aquifer (well depths 215–280 ft), 3 are open to the Mississippian aquifer (well depths 70–300 ft), 24 are open to the Silurian-Devonian or Silurian aquifer (45–555 ft), and 33 are open to the Cambrian-Ordovician aquifer (well depths 150–2,665 ft). Alluvial aquifers consist of sand and gravel deposits of streams and rivers; these deposits in glacial drift aquifers result from glacial meltwater. The bedrock aquifers principally consist of carbonates (dolomite and limestone) and (or) sandstone. The 119 wells selected for sampling are listed in appendix 1, and their locations shown in figures 1 and 4.

The network of 32 surface-water intakes selected for sampling was compiled by a stratified random method established for this study. At the time of compilation (around 2010), there were approximately 150 actively used intakes (nonemergency intakes) at about 80 public water-supply facilities in Illinois. A statistically representative network of 32 intakes was selected from a population of about 111 "unique" intakes considered to be routinely used. The following selection guidelines were applied:

1. Multiple intakes of the same supply facility open to the same water body were grouped in a subset population where separated by a distance of less than 4 mi.
2. Multiple intakes of separate supply facilities open to the same water body were grouped in a subset population where separated by a distance of less than 2 mi.
3. Multiple intakes of the same supply facility open to similar, but separate water bodies (a lake and reservoir, for example), were grouped in a subset population where separated by a distance of less than 2 mi.
4. Intakes from the same facility or from separate facilities, and individually open to different types of water bodies (a river and lake, for example), were individually included in the selection population regardless of the distance separating the intakes.
5. Comparatively small side-channel reservoirs adjacent to streams with comparatively small watersheds were considered a river-type water body for application of intake-distance criteria (stream water is presumed to represent the bulk of the water contained in the reservoir).
6. Comparatively large side-channel reservoirs adjacent to streams or rivers with comparatively large watersheds were considered a lake-type water body for application of intake-distance criteria (spring discharge, surface runoff, and direct precipitation are presumed to represent an appreciable percentage of the water contained in the reservoir, in addition to the stream water).

Regardless of satisfying applicable intake-distance criteria, not all Lake Michigan supply facilities were included in the selection population. There are a disproportionately large number of facilities (16) that withdraw from the lake, many with multiple intakes as necessary to serve nearly 3.5 million area residents (Timothy Bryant, Illinois State Water Survey, Illinois Water Inventory Program, written commun., 2010). To provide reasonable representation of the Lake Michigan facilities and the large population they serve, 10 spatially distributed facilities with 11 intakes (2 from the City of Chicago facility) were included in the selection population.

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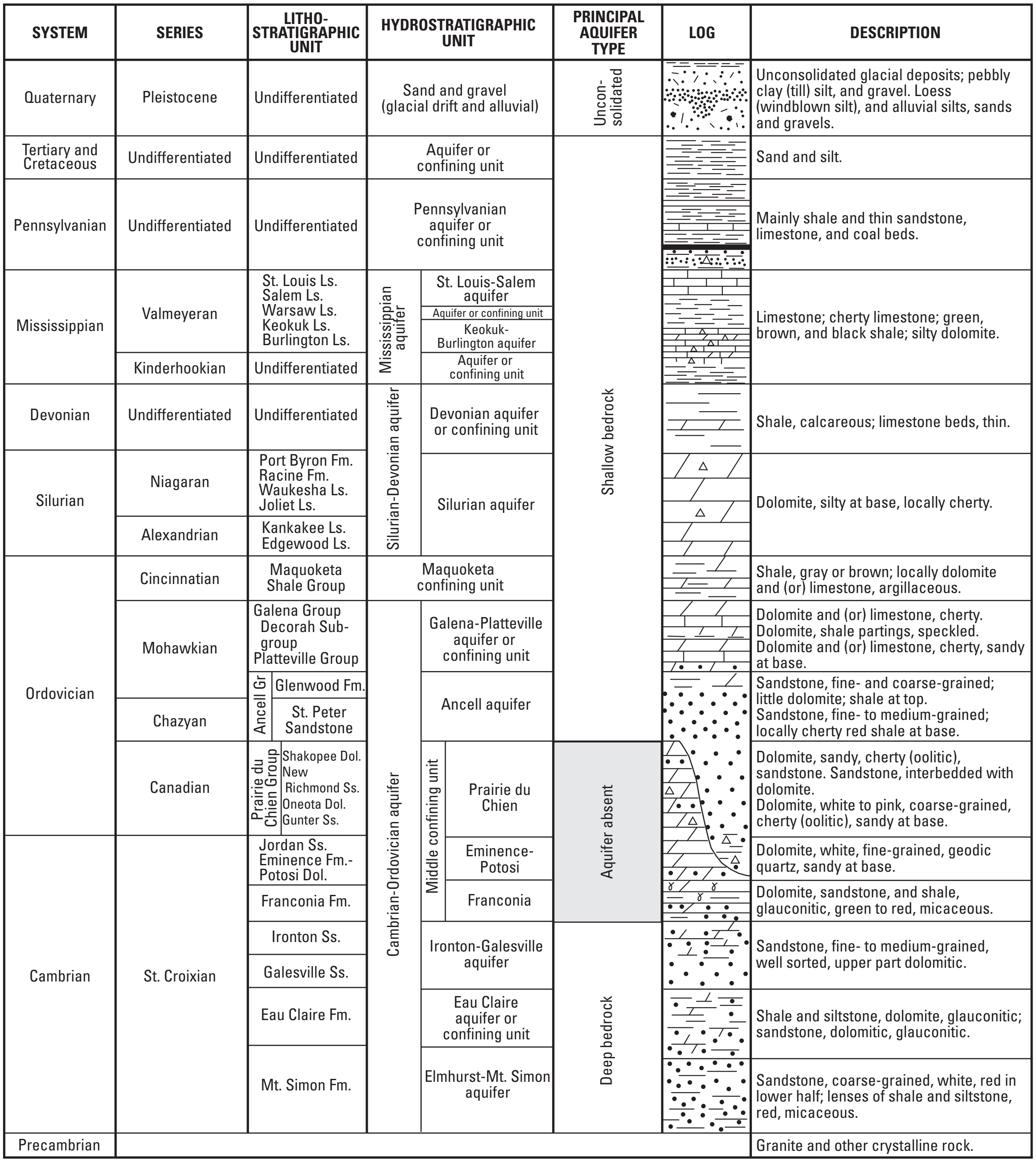
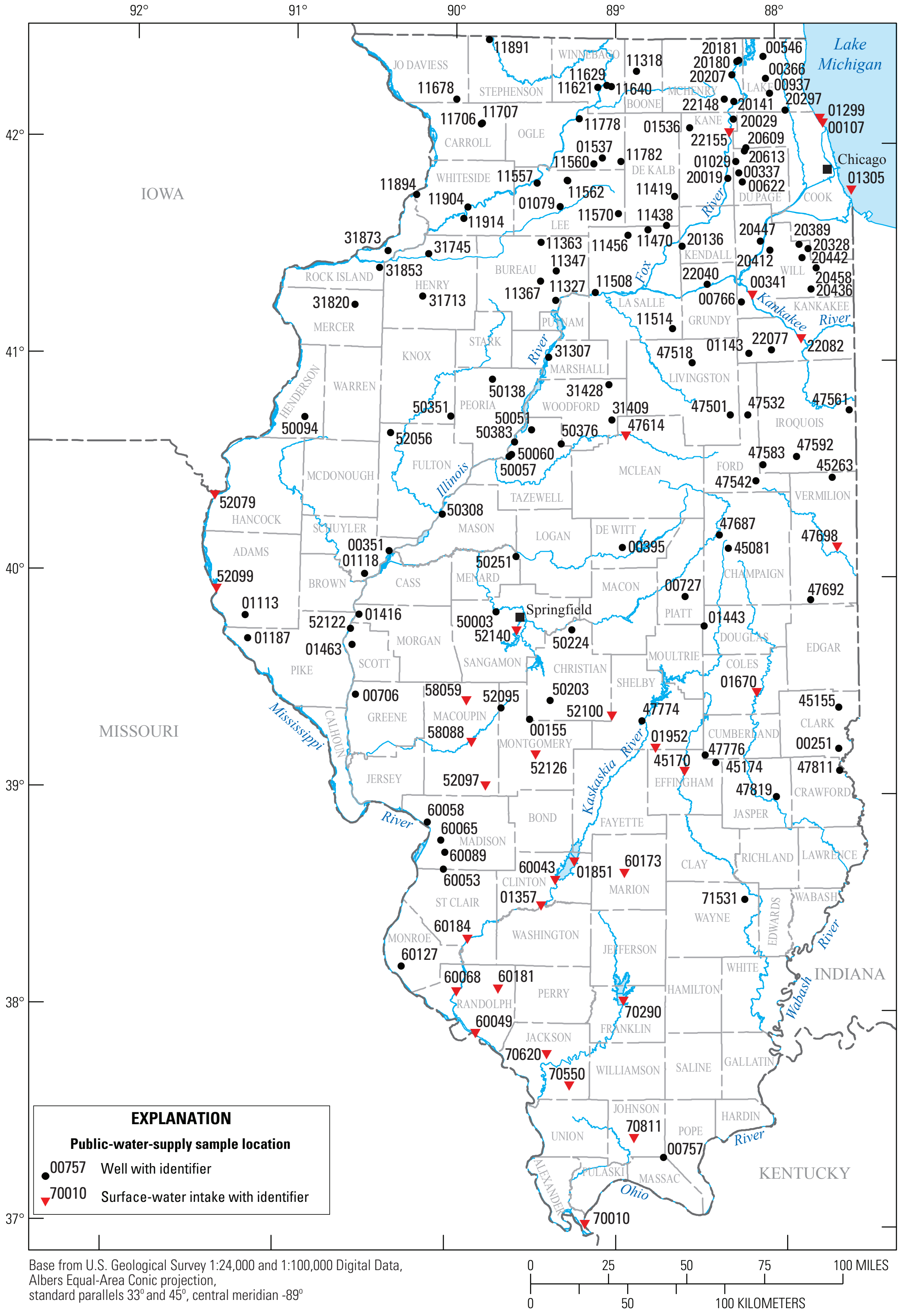
[6] Hereafter referred to as the Cambrian-Ordovician aquifer.



SYSTEM	SERIES	LITHOSTRATIGRAPHIC UNIT		HYDROSTRATIGRAPHIC UNIT			PRINCIPAL AQUIFER TYPE	LOG	DESCRIPTION
Quaternary	Pleistocene	Undifferentiated		Sand and gravel (glacial drift and alluvial)			Uncon-solidated		Unconsolidated glacial deposits; pebbly clay (till) silt, and gravel. Loess (windblown silt), and alluvial silts, sands and gravels.
Tertiary and Cretaceous	Undifferentiated	Undifferentiated		Aquifer or confining unit			Shallow bedrock		Sand and silt.
Pennsylvanian	Undifferentiated	Undifferentiated		Pennsylvanian aquifer or confining unit					Mainly shale and thin sandstone, limestone, and coal beds.
Mississippian	Valmeyeran	St. Louis Ls. Salem Ls.		Mississippian aquifer		St. Louis-Salem aquifer			Limestone; cherty limestone; green, brown, and black shale; silty dolomite.
		Warsaw Ls.				Aquifer or confining unit			
		Keokuk Ls. Burlington Ls.				Keokuk-Burlington aquifer			
	Kinderhookian	Undifferentiated				Aquifer or confining unit			
Devonian	Undifferentiated	Undifferentiated		Silurian-Devonian aquifer		Devonian aquifer or confining unit			Shale, calcareous; limestone beds, thin.
Silurian	Niagaran	Port Byron Fm. Racine Fm. Waukesha Ls. Joliet Ls.				Silurian aquifer			Dolomite, silty at base, locally cherty.
	Alexandrian	Kankakee Ls. Edgewood Ls.							
Ordovician	Cincinnatian	Maquoketa Shale Group		Maquoketa confining unit					Shale, gray or brown; locally dolomite and (or) limestone, argillaceous.
	Mohawkian	Galena Group Decorah Subgroup Platteville Group		Cambrian-Ordovician aquifer		Galena-Platteville aquifer or confining unit			Dolomite and (or) limestone, cherty. Dolomite, shale partings, speckled. Dolomite and (or) limestone, cherty, sandy at base.
		Ancell Gr	Glenwood Fm.			Ancell aquifer			Sandstone, fine- and coarse-grained; little dolomite; shale at top. Sandstone, fine- to medium-grained; locally cherty red shale at base.
	Chazyan		St. Peter Sandstone						
	Canadian	Prairie du Chien Group	Shakopee Dol. New Richmond Ss. Oneota Dol. Gunter Ss.		Middle confining unit	Prairie du Chien	Aquifer absent		Dolomite, sandy, cherty (oolitic), sandstone. Sandstone, interbedded with dolomite. Dolomite, white to pink, coarse-grained, cherty (oolitic), sandy at base.
Cambrian	St. Croixian	Jordan Ss. Eminence Fm.-Potosi Dol.				Eminence-Potosi			Dolomite, white, fine-grained, geodic quartz, sandy at base.
		Franconia Fm.				Franconia			Dolomite, sandstone, and shale, glauconitic, green to red, micaceous.
		Ironton Ss.				Ironton-Galesville aquifer	Deep bedrock		Sandstone, fine- to medium-grained, well sorted, upper part dolomitic.
		Galesville Ss.							
		Eau Claire Fm.				Eau Claire aquifer or confining unit			Shale and siltstone, dolomite, glauconitic; sandstone, dolomitic, glauconitic.
		Mt. Simon Fm.				Elmhurst-Mt. Simon aquifer			Sandstone, coarse-grained, white, red in lower half; lenses of shale and siltstone, red, micaceous.
Precambrian									Granite and other crystalline rock.

Dol. = Dolomite
Fm. = Formation
Gr. = Group
Ls. = Limestone
Ss. = Sandstone

Figure 3. General classification of lithostratigraphic and hydrostratigraphic units that compose source-water aquifers in Illinois. (Lithostratigraphic classifications follow the usage of the Illinois State Geological Survey (ISGS) (Visocky, 1997); hydrostratigraphic classifications follow the usage of the U.S. Geological Survey (2014), which in most cases conform to the usage of the ISGS; figure modified from Visocky, 1997, fig. 2.)



Base from U.S. Geological Survey 1:24,000 and 1:100,000 Digital Data,
Albers Equal-Area Conic projection,
standard parallels 33° and 45°, central meridian -89°

Figure 4. Locations and designations of selected public-supply wells and intakes that tap source-water aquifers and surface waters in Illinois.

A single representative intake was selected randomly from the grouped subset populations for inclusion in the larger selection population of unique intakes. For this subset selection, a random number generator was used (Random.org, 2012a). The population of unique intakes was stratified on the primary basis of region and age of glaciation (glacial provenance) and type of water body in which the intake was located. Glacial provenances were regions of Illinois Episode glaciation, Wisconsin Episode glaciation, and unglaciated regions (fig. 1). Types of water bodies were lakes, rivers, Lake Michigan, and the Mississippi River. These criteria were selected on the basis of the possible influence of terrestrial geology, spatial scale of contributions to the water-body chemistry, and water-body residence time. Subsequently, eight categories were selected for stratified random selection. These categories and the number of included intakes in each category are given in table 2. The number of intakes selected for sampling from each category was based on the percentage of the total selection population of intakes represented by the category, with this percentage applied to a total of 32 intakes to be sampled. One adjustment was made to accommodate the single river facility operated in an unglaciated region of the State (Ohio River; intake 70010) (fig. 1). This facility or category represents less than 1 percent of all intakes and thus was not statistically represented in the proportionalized accounting of 32 intakes for sampling. To include this facility or category, the number of intakes to be selected for the largest category listing (14 intakes; Illinois Episode glaciation–lake) was reduced by one intake. A random sequence generator then was used to select the representative intakes for sampling from an ordered listing of intakes (Random.org, 2012b). Each intake in a category was assigned a rank number up to the total number of intakes in the category. The final selection of intakes for sampling was determined by the sequential order of the randomly shuffled rankings.

Periodically a selected intake was determined to be unavailable or inappropriate for sampling. In such instances, the next available sequentially ordered intake in the same stratification category served as a replacement for sampling. The 32 intakes selected for sampling are listed in appendix 1, and their locations shown in figures 1 and 4.

Inspection of the spatial distribution of the randomly selected wells and surface-water intakes (fig. 1) indicates that some parts of the State are not well represented in this assessment of Cr(VI) in the source waters for public supply. Of particular note, there is a relative absence of wells in the southern half of the State and intakes in the northwestern part. In actuality, the random selection provided a reasonable distribution of wells and intakes in the parts of the State in which groundwater and surface-water supplies presently are developed. In the southern half of the State, relatively few bedrock and unconsolidated aquifers (particularly glacial drift aquifers) are present. In the northern half, both bedrock and unconsolidated aquifers are generally prevalent and serve as the predominant source for public supply. In future years, should increasing demand for public water lead to development of the available but underused, surface-water sources, additional assessment of Cr(VI) in these surface-water sources might be warranted.

Treated water samples were collected from (1) a tap close to the point of treatment and (2) a tap at or near the endpoint of distribution for the public-supply facility. The untreated water and near-treatment tap locations were dictated by facility design. The distribution tap location was one at which regulatory samples routinely are collected under the USEPA Disinfectants and Disinfection Byproducts Rule (Stage 1 and 2) (U.S. Environmental Protection Agency, 2014). At a few locations, the sampling conditions were not conducive to the

Table 2. Criteria and related data used for the stratified random selection of public-supply intakes for sampling and analysis of chromium in Illinois surface waters, 2013.

Stratification category	Number of intakes in category	Percentage of total intakes	Proportional number of intakes per category for 32 total intakes	Final number of intakes per category for sampling
Illinois Episode glaciation–lake	47	42.3	14	13
Illinois Episode glaciation–river	18	16.2	5	5
Illinois Episode glaciation–Mississippi River	10	9.0	3	3
Wisconsin Episode glaciation–lake	10	9.0	3	3
Wisconsin Episode glaciation–river	9	8.1	3	3
Wisconsin Episode glaciation–Lake Michigan	11	9.9	3	3
Unglaciated–lake	5	4.5	1	1
Unglaciated–Ohio River	1	0.9	0	1

study's sampling method. For these infrequent instances, a nearby alternative sample location was selected. Final selection of sample taps for treated water samples was made jointly by personnel of the IEPA and water-treatment facilities.

Sample Collection and Laboratory Analyses

Untreated (raw), treated tap, and distribution water samples were collected by IEPA personnel in accordance with standard presampling protocol of the Illinois IEPA and prescribed methods of analysis for Cr(VI) (USEPA Method 218.6) and Cr(T) (USEPA Method 200.8) (appendix 2). The IEPA protocol, which generally conforms to that of the USGS (U.S. Geological Survey, variously dated), is detailed in the IEPA Quality Assurance Project Plan (QAPP). For inspection of the QAPP, contact the IEPA, Bureau of Water, Division of Public Water Supplies.

IEPA personnel also collected quality-assurance duplicate samples and equipment blanks. USGS personnel prepared and collected quality-assurance spike samples. Details of collection protocols for quality-assurance samples are discussed in the following report section, "Quality Assurance."

Prior to collection of each sample, water was purged from the wells and intakes in a manner to ensure that the samples of untreated source water (groundwater and surface water) would be representative of source-water quality. Wells and intakes typically were operated for 30 minutes or longer prior to site arrival by a sampler for collection of untreated water samples. Upon arrival, wells and intakes were purged through a raw-water tap (before chlorination and other treatment) for an additional 15 minutes or longer to further remove water stored in the well casing and (or) delivery piping and to condition (flush) the sample tap. By use of a calibrated water-quality meter with a flowthrough cell attached to the sample tap, the values of pH, water temperature, and specific conductance were monitored for stabilization of these field-based characteristics of water-quality (hereafter referred to as "field parameters") (fig. 5*A*). The stabilized field-parameter values ensure the collection of samples representative of source-water quality. Concentrations of DO were not monitored because the water-quality meters used by the IEPA personnel responsible for public-water-supply data collection do not contain DO sensors. A sensor for measurement of redox potential (or Eh, in millivolts) is included in the water-quality meters used by IEPA to determine if conditions are stabilized prior to sampling; however, the sensor is not calibrated prior to use, as its restricted use limited to monitoring relative field-parameter values for stability satisfies the agency's programmatic objectives. These redox potential data, which are not archived in the IEPA water-quality database, were of insufficient accuracy for the evaluation of Cr(VI) occurrence in this study.

For collection of treated water samples, water was purged from the delivery piping for a minimum of 10 minutes, primarily to condition the sample tap. In many cases, delivery piping to the tap located soon after treatment was purged for a minimum of 15 minutes because these taps were generally close to the raw-water taps. Field parameters were not monitored for stabilization prior to collection of treated water samples; however, for about 60 percent of these samples a synoptic assessment of field values was made after a few minutes of purging to ensure instrument acclimation to the purged-water stream. These field values along with those obtained during purging for collection of untreated water samples, allowed limited consideration of possible relations between water chemistry and Cr(VI) concentrations in untreated, treated, and distributed waters.

Observations regarding site conditions that might affect the sample results and data recorded prior to sampling to ensure the collection of representative samples are documented by sampling personnel in an IEPA field sheet and UL company (formerly known as Underwriters Laboratories) chain-of-custody form. Examples of an IEPA field sheet and UL form are presented in appendixes 3 and 4. Among other observations, recorded information and data include pump run time prior to sampling, location of raw-water tap relative to the well or intake, sample-tap material composition, and the sequential listing of field parameters during purging.

Samples for Cr(VI) and Cr(T) analysis were collected by using equipment included in sampling kits provided by UL. The kits consisted of a collection beaker, sample bottles, a syringe and 45-µm syringe filter, buffer solution, and blue refrigerant (ice) blocks. The kits were contained in a foam-insulated shipping box. Sampling protocols were developed and provided by UL, but slightly modified by the USGS. The UL protocols were developed to conform to the sampling and analysis requirements of USEPA Method 218.6 for Cr(VI) and USEPA Method 208.6 for Cr(T). These USEPA requirements are described in some detail at the conclusion of this section of the report. Specific details regarding sample collection are given in appendixes 2*A* [Cr(VI)] and 2*B* [Cr(T)]. The modified protocols consisted of adding additional progressive prerinsing of each sampling-equipment component with native sample water (untreated or treated, depending on the sample type) (fig. 5*B*). The repeated prerinsing used only water in contact with a previously prerinsed component in the sequence of its use, with the starting and endpoints a prerinsed sample-collection beaker and sample bottle, respectively.

At all sample sites, efforts were made to limit the potential of sample contamination, including use of protective gloves and placement of all sample-collection equipment on an unused sheet of aluminum foil during sampling. Where possible, and necessary, an effort was made to prevent atmospheric contamination during sampling. Efforts included sampling indoors and closing outside doors if they connected to the sampling space.

Sampling equipment was disposable (single use) and constructed of polypropylene. Samples were collected from sample taps at a flow rate of about 0.25–0.5 gallon per minute (gal/min). Untreated source waters for Cr(VI) analysis were collected in a nominal 100 milliliter (mL) beaker, passed through a 0.45-micrometer (µm) glass-microfiber syringe filter, and discharged into a prerinsed 125-mL sample container (fig. 5*C*). Samples of untreated water to be analyzed for Cr(T) and treated water to be analyzed for Cr(VI) and Cr(T) were collected directly from the sample tap into a 125-mL sample container. An ammonium sulfate and ammonium hydroxide buffering solution (1 mL) was then added to the untreated and treated water samples for Cr(VI) analysis. The sample volume for Cr(VI) analysis was 100 mL, with the sample volume for Cr(T) 100–125 mL.

About 95 percent of the wells and sample taps were enclosed in a well house, thus reducing the possibility of atmospheric contamination of samples and technical issues with sampling. Those samples collected outside were collected when weather conditions should not have affected collection of representative samples. The samples were shipped chilled (4 degrees Celsius [ºC] or less) to UL the evening of the collection. Sample analysis was targeted for completion within 24 hours of collection.

Figure 5. Photos showing typical quality-assurance measures and collection of samples for chromium at selected public-water-supply facilities in Illinois, 2013: *A*, Monitoring of field water-quality characteristics (pH, temperature, specific conductance) for stabilization of values prior to collection of surface-water samples, City of Springfield (intake 52140), water-treatment laboratory.
B, Rinsing sample equipment prior to collection of surface-water samples, City of Springfield, water-treatment laboratory.
C, Collection of groundwater samples, Union-York Water District (intake 00251), water-treatment facility (garage).
D, Preparation of a spike sample at a known concentration of hexavalent chromium [Cr(VI)], U.S. Geological Survey laboratory (See fig. 1 for location of facilities).

The following descriptions of USEPA Method 218.6 for Cr(VI) analysis and USEPA Method 200.8 for Cr(T) analysis are summarized from more detailed descriptions by McNeill and others (2011). The specific collection and analysis methods for Cr(VI) and Cr(T) used in this study are then discussed within the context of the evolving requirements, recommendations, and analytical capabilities of the described USEPA methods.

Method 218.6 combines a colorimetric (C) method used for decades with an IC method. By this enhanced C–IC method, Cr(VI) is separated from the sample matrix to minimize analytic interference and is concentrated to reduce the detection level. In its original development, filtering of water samples (at 0.45 µm) was required, as was the dropwise addition of a buffer solution of ammonium sulfate (250 millimoles [mM]) and ammonium hydroxide (100 mM) to bring the sampled to pH of 9–9.5. Within this pH range, Cr(VI) occurs as chromate (CrO_4^{-2}), which is separated on an analytical column from other anions. The separation minimizes interferences with other anions that might affect the detection and assessed concentration of Cr(VI). With the addition of diphenylcarbazide (eluent) by use of a postcolumn mixing coil, a complex is formed which is measured with a flowthrough spectrometer. As listed, the reporting level of this method was 0.4 µg/L in drinking water and groundwater. This method is described in detail in U.S. Environmental Protection Agency (1994) and Dionex (1998).

The above-described method subsequently was modified to further lower the detection level. Method improvements included lowering the flow rates for the eluent and the postcolumn reagent, increasing the volume of sample injection and the size of the reaction coil, and lowering the concentration of the ammonium sulfate buffer solution by a factor of 10. The resulting reporting limit of this modified method was 0.06 µg/L. The modifications are described in full detail in Dionex (2003). The method was once again modified, with adjustments in flow rates and column configuration. As a result, the reporting limit was further reduced to 0.019 µg/L (Dionex, 2011). It is this modification and reporting limit that is the basis for the analytical method and reporting (0.02 µg/L) used by UL for this study. This and former versions of the method are not presently approved for compliance with the SDWA, because Cr(VI) is unregulated as a specific chemical constituent of drinking water under the guidelines of the SWDA (however, it is regulated as a component of Cr(T), at an MCL of 100 µg/L).

In Method 218.6, contamination, matrix interferences, and redox reactions of chromium are included as potential interferences to analysis. Contamination may be associated with reagents and glassware. Specific requirements are included for the cleaning of glassware and monitoring for reagent contamination. Because of the redox sensitivity of Cr(VI), it is essential to preserve the oxidation state of the chromium in a water sample at the time of its collection. It is also critical to properly buffer the samples to isolate Cr(VI) as chromate, thus limiting the potential of chemical interference during analysis from other anionic species of chromium. At pH 9, the oxidizing potential of Cr(VI) is too low to react with any reductants in the sample, and the ammonium in the buffer inhibits the oxidizing potential of chlorine. Although all versions of Method 218.6 require dropwise addition of buffer to obtain a pH of 9–9.5, a recent drinking-water specific update of the method—USEPA Method 218.7 (U.S. Environmental Protection Agency, 2011)—recommends adjustment to greater than pH 8 by using 1 mL of the buffer added to 100 mL of sample. The UL sampling protocol used in this study incorporates this approach to buffering.

In Method 218.6, 0.45-µm filtration of samples is required prior to preservation; however, current manufacturer protocol (Dionex, 2011) and guidelines of Method 218.7 do not require field or preinjection filtering of samples. The UL sampling protocol used in this study incorporates the Method 218.6 approach to filtering. There are various conflicting requirements for sample holding time prior to analysis. Method 218.6 limits holding time to 24 hours; Federal guidelines (40 CFR 136) allow samples to be held up to 28 days, if preserved; near the start of planning for this study, USEPA allowed a holding time of 5 days (U.S. Environmental Protection Agency, 2011) for voluntary Cr(VI) monitoring; and Method 218.7, whereas recommending samples be analyzed as soon as possible, cites a holding time of 14 days for properly collected, preserved, shipped, and stored samples (U.S. Environmental Protection Agency, 2011). For this study, the most restrictive holding time of 24 hours was applied.

Method 200.8 for Cr(T) analysis using ICP–MS is approved for monitoring drinking-water quality under the SDWA, with an MDL of 0.08 µg/L (McNeill and others, 2011). The MDLs of other approved methods for SDWA monitoring range up to 4 µg/L. For this study, a reporting level of 0.1 µg/L was applied. Although the USEPA method designates a holding time of 6 months with preservation to below a pH 2 with HNO_3 acidification (Federal guidelines 40 CFR 136), the UL sampling protocol followed in this study differed, and samples were preserved only by chilling and typically were analyzed within 24 hours of collection.

Quality Assurance

The quality-assurance program for the data collected during this study focused on three components: training, sample collection and processing procedures, and laboratory analytical methods. The requirements of each of these components are described below. The results of the quality-assurance testing are presented in the following section “Accuracy of Chromium Data.”

Two measures were taken to ensure samplers were fully aware of the sample-collection and handling and shipping requirements of the study: training held prior to the sampling effort and observation of the in-field performance of samplers. For the presampling training, the sample-collection methods detailed in appendix 2 were discussed as were the methods for collecting quality-assurance samples and packaging the chilled samples for overnight shipment and following-day analysis. Additionally, the IEPA QAPP, which summarizes all sample-collection and analysis aspects of the effort, was discussed. Each participating IEPA sampler then demonstrated the collection procedures for Cr(VI) and Cr(T) samples. After the sampling effort began, the USGS project chief observed each sampler in collection of samples at one or more sampling sites, offering or accepting and incorporating any necessary suggestions for representative data collection and handling.

Quality-assurance methods used during sample collection are described in the previous section "Sample Collection and Laboratory Analysis" and in the "National Field Manual for the Collection of Water-Quality Data" (U.S. Geological Survey, variously dated). Other onsite methods consisted of collecting equipment (or field) blanks and sample duplicates for analysis. A constraining factor in the selection of quality-assurance sample number and specific sites was the laboratory's limit on accepting no more than 10 samples per day for analysis in order to satisfy the 24-hour criterion for their completed analysis.

Five equipment blanks were collected (2 percent of field samples). A deliberative process was used to select blank-sample sites to ensure the following considerations:

1. a blank sample was collected by each of the five samplers participating in the study,
2. sample sites generally were distributed evenly throughout the 1-year time frame of the study,
3. sample sites did not overlap those with other quality-assurance samples collected, and
4. sample sites represented the proportionally greater number of groundwater sites than surface-water sites.

Additionally, the temporal distribution of sites allowed for at least two samples to be collected near the beginning of the study to provide early documentation of effective sampling methods (or recognition of any problems).

Each equipment blank was collected after prerinsing the disposable sampling and filtering equipment with laboratory-certified inorganic blank water. The blank water was not certified as free of Cr(VI); heavy metals (unspecified) were certified as below a concentration of 10 µg/L. The blanks were collected as if routine field samples with the inorganic blank water used for the samples. Analytical results of equipment-blank samples are used to evaluate the chromium-free nature of the disposable sampling equipment, effectiveness of routine equipment prerinse methods, and possibility of atmospheric contamination of the sampling equipment.

Ten duplicates were collected (5 percent of field samples). Similar considerations as those for equipment-blank sample sites were applied for selection of the duplicate sample sites. Additionally, each of the sample types (untreated groundwater, untreated surface water, treated surface water, distributed surface water) was represented in approximate proportion to its number of sample sites. Each duplicate sample was collected after its associated routinely scheduled field sample was collected, and a new set of disposable sampling equipment was used for the duplicate. Thus, the duplicate-sample site was treated as if it had not been visited previously. Analytical results of duplicates are used to evaluate the random variation of sampling. Differences in paired quality-assurance samples (duplicates) were evaluated by the relative percent difference (RPD) method (U.S. Environmental Protection Agency, 1989). For this method,

$$RPD = \frac{\left(C1 - C2\right) \text{x} \, 100 \, \text{percent}}{\left(C1 + C2\right)/2} \qquad (1)$$

where

C1 is the concentration of the quality-assurance sample, and

C2 is the concentration of the field sample.

Elevated RPDs may be indicative of inconsistent precision in analytical analysis of concentrations (Duwelius and others, 1996); however, laboratory spike samples provide a more definitive indicator of issues of laboratory precision. The RPD method also was used to quantify differences between Cr(VI) and Cr(T) results in a sample for those samples in which the reported concentration of Cr(T) was less than that of Cr(VI). For this application, C1 represented the Cr(T) concentration and C2 represented the Cr(VI) concentration.

Laboratory quality-assurance samples are used for evaluation of laboratory analytical methods, which include, among others, guidelines for sample holding times, quantitation reporting limits, instrument calibration, sample preparation, and sample analysis. Laboratory quality-assurance methods consisted of spikes prepared in the field and the laboratory and duplicates. Spikes are samples prepared to a known concentration and with minimal change to the matrix of the original sample. Specific methods for selecting and preparing laboratory quality-assurance samples can be obtained from the UL laboratory, on request.

Field spikes were prepared by using a commercially provided Cr(VI) reagent with a concentration of 1,000 µg/L. A reagent at a lower, more appropriate concentration for expected sample concentrations of about 0.02–10 µg/L was not readily available. The USGS National Water Quality Laboratory, which generally prepares spikes of various analytes for USGS projects, could not do so for this project because of concerns about laboratory contamination by the elevated reagent concentration that was available. Spikes were prepared in the USGS Illinois Water Science Center laboratory in various ranges representing the expected sample concentrations. Accurate reagent dilution of 3–5 orders of magnitude to obtain representative sample concentrations was difficult with the available laboratory equipment. As such, the spikes prepared for the study are considered more as qualitative than quantitative indicators of the accuracy of sample analysis by the laboratory. The laboratory quality-assurance checks, including their internally used spikes, are considered the primary indicator of the accuracy of their analytical results.

Spike samples were prepared by USGS staff, with five samples (2 percent of field samples) analyzed for Cr(VI) and four samples (2 percent of field samples) analyzed for Cr(T). The preparations were made within 24 hours of their analysis on the following day. The samples included two at a presumed concentration of 0.0 µg/L and one each at 0.03, 0.98, and 3.90 µg/L (with no 0.03-µg/L spike for Cr(T) analysis). Laboratory-certified inorganic blank water was used for the 0.0-µg/L spikes and in the preparation of spikes of greater concentration. The certified commercially provided reagent was used for Cr(VI) spikes with concentrations greater than 0.0 µg/L. As previously noted in the discussion of equipment blanks, the inorganic blank water was not specifically certified to be free of Cr(VI) below the concentration certification limit. Therefore, the remote possibility remains that Cr(VI) was present in the blank water at concentrations in the range of 0.02–10 µg/L.

Data Analysis

The relational geochemical, physical, and sampling factors were analyzed by inspection of the analytical results for Cr(VI) and Cr(T) and associated data. Inspection included graphical and statistical measures. Analysis of geochemical factors was limited to consideration of pH. As previously noted, other geochemical data either were not available or appropriate for analysis or their analysis was beyond the scope of this study. Physical factors that were evaluated include aspects of land use, geohydrology, well construction, and water treatment. Sampling factors include aspects of sample shipment and processing and the material composition of water-distribution components.

The nonparametric Spearman's rank correlation test (Helsel and Hirsch, 1992) was used to determine the strength of association or covariance between Cr(VI) and Cr(T) concentrations; that is, for example, do Cr(T) concentrations tend to increase or decrease as Cr(VI) concentrations increase, or are their patterns of variation unrelated? This relational test also was used to determine, among others, the correlation between (1) Cr(VI) concentrations and pH, and (2) frequency of detection (representing occurrence) of Cr(VI) and depth-related factors, including depths to the top of aquifer and to the base of the well casing.

The Spearman's rank test method uses ranks of data to determine a monotonic relation (a relation in one direction, but not necessarily linear nor causal) between two continuous variables. The statistics produced are the Spearman's rho (ρ) and the p-value. The values of Spearman's rho range from –1 to +1, where larger absolute values indicate a stronger relation between the variables and $\rho = 0$ is indicative of no association (correlation) between the variables. A positive value of Spearman's rho indicates a direct relation, where the value of one variable tends to increase as the value of the other increases. A negative value indicates an inverse relation, where the value of one variable tends to decrease as the value of the other increases. For statistical testing of the depth-related factors associated with frequency of detection, rank values were assigned to represent selected depth ranges. Ranks of 1 to 6 were used to represent the following intervals of increasing depth: 0–50, 51–100, 101–200, 201–300, 301–500, and greater than 500 ft. For those correlations determined to be statistically significant, the corresponding p-values are included with the results.

The difference in concentration of Cr(VI) between selected sample populations were evaluated by using the Kolmogorov-Smirnov test (Chakravarti and others, 1967; College of St. Benedict and St. John's University, 2014). This is a nonparametric test for the equality of continuous, one-dimensional probability distributions that can be used to determine the degree of similarity or difference between two variables (datasets). Cumulative distribution functions showing the distribution of a variable as a function of the rank order or exceedance probability are developed. The statistics produced are the maximum vertical difference between the cumulative distributions (plotted curves), reported as "D," and the p-value. For those compared populations determined to be significantly different, the corresponding p-values are included with the results.

A confidence criterion (or significance level) of $\alpha = 0.05$ was used to determine the significance of statistical tests reported in this study. The significance level is the probability (p-value) of incorrectly rejecting the null hypothesis. The null hypothesis of a statistical test (for example, there is no difference between two groups of data) is rejected if the p-value is less than or equal to the α value of 0.05. A p-value less than or equal to 0.05 means there is a 1 in 20 or less chance of getting the observed results (that the two groups of data are different) if the null hypothesis is true. The smaller the p-value, the less likely the observed test statistic may have occurred by random chance when the null hypothesis is true, and the stronger the evidence for rejection of the null hypothesis (Helsel and Hirsch, 1992). Unless where indicated otherwise, p-values were greater than 0.05 for applied tests.

In this report, concentrations of Cr(VI) and Cr(T) determined to be less than their reporting limit are censored to (assigned) 0.0 µg/L. A null concentration was assigned to nondetections in this report to readily indicate the general proportion of nondetections in sample populations, particularly where summarized results that represent all concentrations and detected concentrations are compared (table 3) or are presented in figures such as box-and-whisker plots. All concentrations represent those which are equal to or greater than the analytical reporting limit, as well as those which are less than the reporting limit. Detected concentrations represent those which are equal to or greater than the reporting limit. Data summaries in this report that represent detected concentrations are specifically identified.

Presenting statistically summarized results on the basis of detected concentrations is considered useful because the study was conducted to addresses concerns about the possible

Table 3. Summary statistics for detections of hexavalent chromium and total chromium in samples from source-water aquifers and surface waters used for public supply in Illinois, 2013.

[µg/L, microgram per liter; detected (all), samples with detected concentrations (all samples in category, concentrations designated as below the reporting limit censored to 0.0 µg/L); do., ditto. Reporting limit for hexavalent chromium, 0.02 µg/L; for total chromium, 0.1 µg/L. Maximum Contaminant Level for total chromium, 100 µg/L (U.S. Environmental Protection Agency, 2013b)]

Chromium analyte, untreated (raw) water samples	Total number of samples in category	Detection frequency, in percent	Median concentration, in µg/L [detected (all)]	Mean concentration, in µg/L [detected (all)]	Maxiumum detected concentration, in µg/L
Hexavalent chromium: all	151	64.9	0.07 (0.04)	0.14 (0.09)	2.1
Total chromium: all	do.	71.5	0.40 (0.30)	0.51 (0.36)	1.8
Hexavalent chromium: groundwater	119	57.1	0.06 (0.02)	0.16 (0.09)	2.1
Total chromium: groundwater	do.	64.7	0.40 (0.20)	0.51 (0.33)	1.8
Hexavalent chromium: surface water	32	93.8	0.09 (0.09)	0.11 (0.10)	0.29
Total chromium: surface water	do.	96.9	0.40 (0.40)	0.49 (0.48)	1.8
Hexavalent chromium: unconsolidated aquifer	56	42.9	0.14 (0.00)	0.27 (0.11)	2.1
Hexavalent chromium: bedrock aquifer	63	69.8	0.04 (0.03)	0.10 (0.07)	1.1
Hexavalent chromium: surface water (tap[1]); no lime treatment	17	94.1	0.06 (0.06)	0.09 (0.08)	0.25
Hexavalent chromium: surface water (tap[1]); lime treatment	15	100	1.2 (1.2)	1.2 (1.2)	2.4

[1] Treated water samples.

impact of elevated concentrations of Cr(VI) on public health and management of public drinking-water operations in Illinois. Use of the reporting limit of 0.02 µg/L for detected concentrations as a reference level represents the level presumed to be the lowest possible regulatory level (MCL) that might be established for Cr(VI). Estimation of the concentrations that might be less than the reporting limit and their distribution did not address the objectives of this study and was beyond its scope. For estimation of these left-censored data, statistical methods are considered most appropriate (Helsel, 2005) and could be applied by others.

Accuracy of Chromium Data

The quality-assurance tests of this study reflect the accuracy and representativeness of the obtained chromium data. These data could potentially have been adversely affected during sample collection and processing and laboratory analysis; these tests address the uncertainties associated with collection of samples and their analysis at the comparatively low detection and reporting levels of this study.

Cr(T) was not detected in any of the equipment blanks, a result that might be partly attributable to its comparatively greater analytical reporting limit of 0.1 µg/L. Cr(VI) was detected at concentrations of 0.02, 0.03, 0.05, and 0.21 µg/L in four of the blank samples and was undetected in the fifth sample. Water from the same preparation lot was used for the samples with concentrations of 0.02 µg/L and 0.05 µg/L; water from a separate lot was used for the remaining blank samples. It is uncertain whether the source of the Cr(VI) was the disposable sampling equipment, the blank water, or atmospheric contamination or whether the detections are an indication of the accuracy or difficulty of analyzing for this constituent at the low reporting level of 0.02 µg/L. The elevated concentration of 0.21 µg/L in one sample appears not to be related to the Cr contamination of the blank source water, because the concentrations of other blank samples using the same source lot were substantially lower (less than

0.02–0.03 µg/L). Laboratory analytical issues likely account for the elevated concentration, given that the lab-reported Cr(VI) recoveries in the matrix spike (113 percent) and matrix duplicate spike (112 percent) samples were outside the acceptable limits of 90–110 percent.

Blank-water samples that were collected as 0.0-µg/L Cr(VI) spike samples, in which there was no water contact with the sampling equipment other than the sample bottle, indicate possible difficulty in analyzing for this constituent at the low reporting level might account for the low-concentration detections in the various blank-water samples. The two 0.0-µg/L spike samples, prepared from the same source lot, had reported concentrations of less than 0.02 µg/L and 0.04 µg/L, respectively. In general, the method used to prerinse the disposable sampling equipment and use of the equipment itself were determined to contribute only minimally, at most, to the analytical results of the study. Most likely, prerinsing of sample equipment with the untreated sample water effectively conditioned the equipment for collection of representative samples.

Of 10 paired field and duplicate samples, 6 had detectable concentrations of Cr(VI); all 10 paired samples had detectable concentrations of Cr(T) in one (2 pairs) or both (8 pairs) of the paired samples. RPDs for the detectable concentrations of Cr(VI) in the paired samples ranged from –22 to +22; RPDs for the detectable concentrations of Cr(T) ranged from –155 to +857. The RPDs are exaggerated by the low detectable concentrations of Cr(VI) (0.04–0.41 µg/L) and Cr(T) (0.1–1.0 µg/L). When detected, the difference in Cr(VI) concentrations between paired samples was 0.01 µg/L or less for all pairs but one (+0.03 µg/L, duplicate); the difference in Cr(T) concentrations between paired samples was 0.1 µg/L or less for all pairs but two (–0.03, +0.04 µg/L, duplicates). The concentration discrepancy in these two samples is unexplained. For the most part, the measured differences in concentrations of paired samples were at or near the apparent variance of the analytical methods, as indicated by review of the laboratory quality assurance test reports (appendix 4). With minimal random variation associated with sample collection, the analytical results were determined to accurately represent the groundwater quality at the sample sites.

RPDs for the detectable concentrations of Cr(VI) in spikes ranged from –55 to +200; RPDs for the detectable concentrations of Cr(T) in spikes ranged from –12 to +5. The RPDs are exaggerated by the low Cr(VI) and Cr(T) concentrations [0.03–3.90 µg/L, Cr(VI); 0.98–3.90 µg/L, Cr(T)]. The analytical results of the two 0.0-µg/L Cr(VI) spikes indicated one at a concentration less than 0.02 µg/L and one at 0.04 µg/L; respective results of the spikes at higher Cr(VI) concentration were less than 0.02, 1.0, and 4.0 µg/L. The analytical results of the two 0.0-µg/L Cr(T) spikes indicated both at a concentration less than 0.1 µg/L; respective results of the spikes at higher Cr(T) concentration were 1.1 µg/L and 4.1 µg/L. The minor difference between the intended concentration of the 0.03-µg/L Cr(VI) spike and its analytical result of less than 0.02 µg/L is best explained by inaccuracies associated with spike preparation. The resulting Cr(VI) concentration of 0.04 µg/L is unexplained, but it does not seem to be associated with low concentrations of Cr(VI) in the inorganic blank water. Two other spikes and one equipment blank prepared from the same source lot of blank water at intended concentrations of 0.0–0.03 µg/L tested with a concentration less than 0.02 µg/L. The elevated concentration of the spike could be related to atmospheric contamination or analytical inaccuracy. Sample contamination seems unlikely, given the clean condition of the well-facility laboratory where the sample was collected. For the most part, the measured differences in concentrations of paired samples were at or near the apparent variance of the analytical methods, as indicated by review of the laboratory quality-assurance test reports (appendix 4).

The results of the spike analyses, along with those of the equipment blanks and duplicates, indicate possible difficulties in obtaining or confirming consistently accurate analytical results for Cr(VI) at near the applied reporting limit of 0.02 µg/L. Interferences might be associated with contamination introduced atmospherically or during sample collection and processing, but they might also perhaps be associated with laboratory analytical capability.

Comparison of the analytical results for Cr(VI) and Cr(T) found that for 5 percent of the untreated and treated samples, the concentration of Cr(VI) was greater than the concentration of Cr(T). Cr(VI) concentrations greater than those of Cr(T) should not be expected; however, this kind of result is not uncommon to such chromium studies, as was previously discussed in the section “Sample Collection and Laboratory Analysis.” Comparisons were made between results falling beyond the rounding limits of the separate and dissimilar reporting for Cr(VI) results (two decimal places) and Cr(T) results (one decimal place). RPDs for these proportionally unexpected Cr(VI)-Cr(T) pairs ranged from +11 to +135. The RPDs are exaggerated by the low concentrations [0.15–2.1 µg/L, Cr(VI); less than 0.1–1.8 µg/L, Cr(T)]. The difference in concentrations between paired samples was less than was 0.1 µg/L in three pairs, 0.1–0.3 µg/L in eight pairs.

The discrepancy likely results because the sample concentrations approached the reporting limits of the separate analyses [0.02 µg/L, Cr(VI); 0.1 µg/L, Cr(T)] and at or near the expected variance of the analytical methods. Additionally, the laboratory analytical methods differ for the two analytes, and interferences may affect the analyses, as previously discussed.

Occurrence and Distribution of Chromium

The analytical results of Cr(VI) and Cr(T) in untreated source-water aquifers and surface waters tapped for public supply in Illinois are herein presented. Included are findings regarding their frequencies of detection and spatial distribution, along with a statistical summary of the concentration data. Findings from this study are considered with respect to current and proposed regulatory standards and the results of other large-scale studies of Cr(VI) in public-supply waters.

Frequency of Detection and Concentration

The occurrence of Cr(VI) and Cr(T) in the untreated source-water aquifers and surface waters of Illinois, as well as in treated waters, is represented by their frequency of detection and distribution of concentrations. Findings regarding the occurrence of Cr(VI) and Cr(T) are presented in the following discussions. The relation of between concentrations of Cr(VI) and Cr(T) is briefly explored. The summarized analytical results for the samples collected during 2013 are given in table 3. Additionally, these data are given in full in appendix 1, along with their associated field parameters, location, and selected well-construction information.

Hexavalent Chromium

Hexavalent chromium was prevalent in the State's untreated source-water aquifers and surface waters, as indicated by the frequency (table 3; fig. 6) and spatial distribution of detections (fig. 7). Cr(VI) was detected in 65 percent of untreated water samples, with detection frequencies of 57 percent in 119 groundwater samples and 94 percent in 32 surface-water samples (fig. 8*A*). Maximum and median detected concentrations for all untreated samples were 2.1 µg/L and 0.07 µg/L, respectively. In groundwater samples these respective concentrations were 2.1 µg/L and 0.06 µg/L, and in surface-water samples, 0.29 µg/L and 0.09 µg/L. Median concentrations represented by all groundwater and surface-water samples were 0.02 µg/L and 0.09 µg/L, respectively. As evident, detections were substantially more prevalent in surface waters than groundwater and, as a population, concentrations in surface water were greater ($p < 0.001$). The greatest concentrations were found in groundwater, with six detections exceeding the maximum concentration recorded in surface water (fig. 9*A*). It might be speculated that surface-water bodies are more vulnerable to direct natural and anthropogenic contributions of Cr(VI) than groundwater, and because of their typically greater oxygenation, they provide more favorable geochemical conditions for supporting its transformation from Cr(III) and its retention in the hexavalent form. Natural contributions can be from erosion and deposition from adjacent land deposits. Anthropogenic contributions of Cr(VI) can be from direct discharge, overland flow, shallow groundwater discharge, and airborne deposition. The comparatively lower maximum concentrations detected in some surface-water samples might be attributed to the greater capacity for advective dispersal and dilution in surface waters because of their greater flow rates and meteoric interaction than groundwater. Occurrence of Cr(VI) in groundwater presumably more greatly represents contributions from natural sources than anthropogenic sources, particularly as depth to groundwater increases. It is speculated that, in many cases, elevated concentrations in groundwater are associated with and in close proximity to spatially isolated source deposits. As previously noted, the geologic setting of Illinois is not one readily predisposed to widely distributed and (or) elevated occurrences of Cr(VI).

Hexavalent chromium was also prevalent in the State's treated drinking waters, as indicated by their frequency of detection (table 3). Cr(VI) was detected in 97 percent of tap samples collected soon after treatment and in 100 percent of samples collected near the endpoint of their distribution (appendix 1). Maximum and median concentrations for all tap samples were 2.4 µg/L and 0.21 µg/L, respectively. Similarly, maximum and median concentrations for all distribution samples were 2.4 µg/L and 0.19 µg/L. There was a strong positive relation ($\rho = 0.99$) between Cr(VI) concentrations in tap samples and distribution samples. As is evident, Cr(VI) concentrations were significantly greater in treated water samples than untreated water samples ($p = 0.007$).

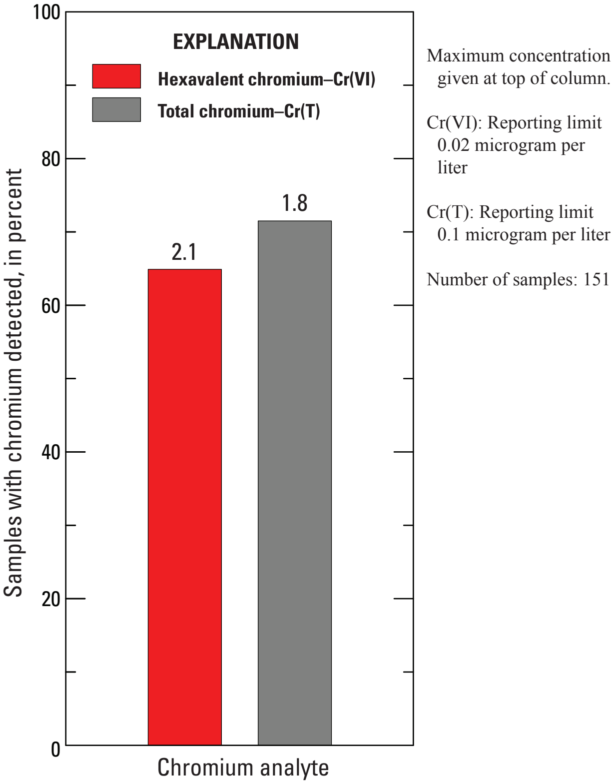
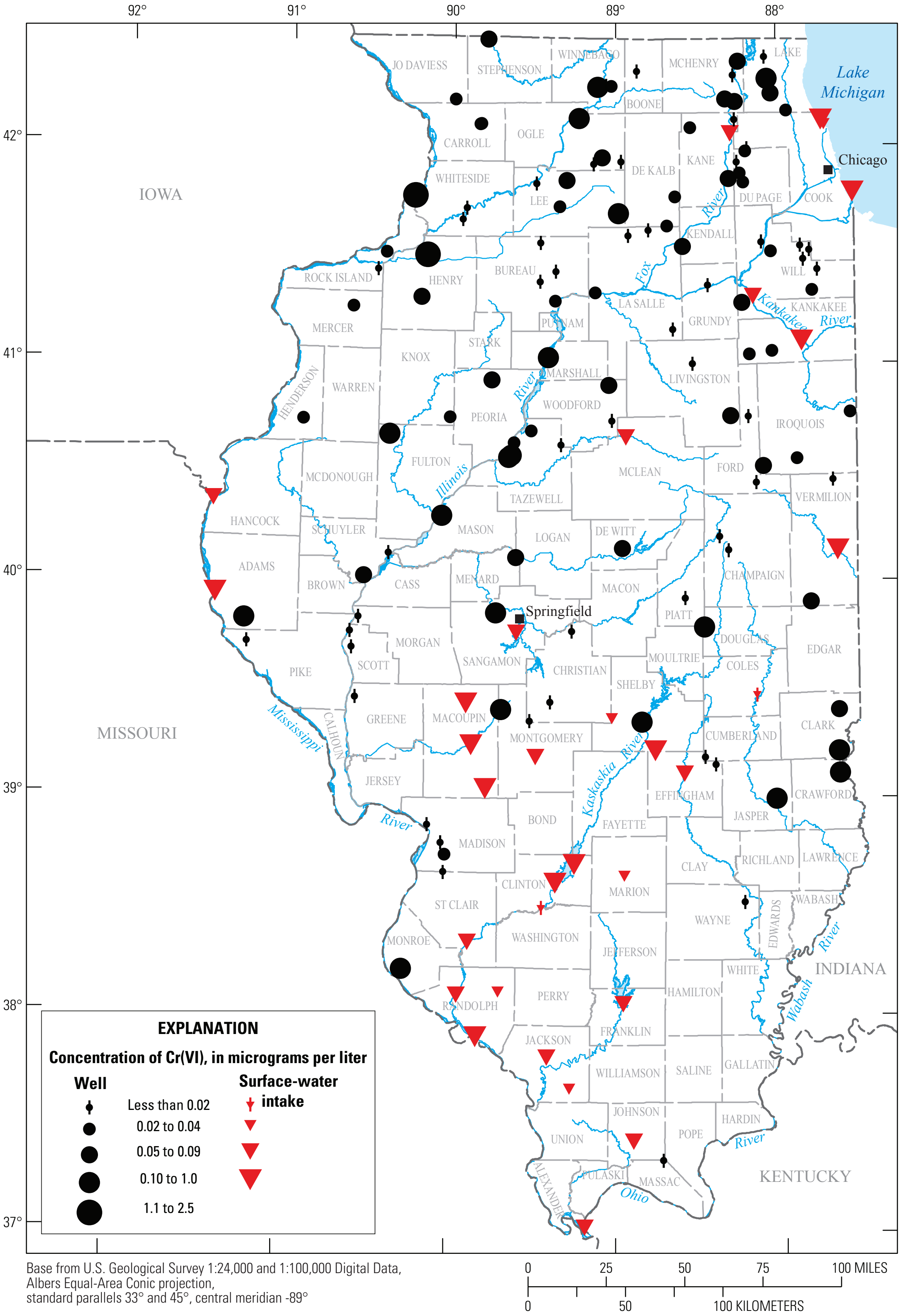
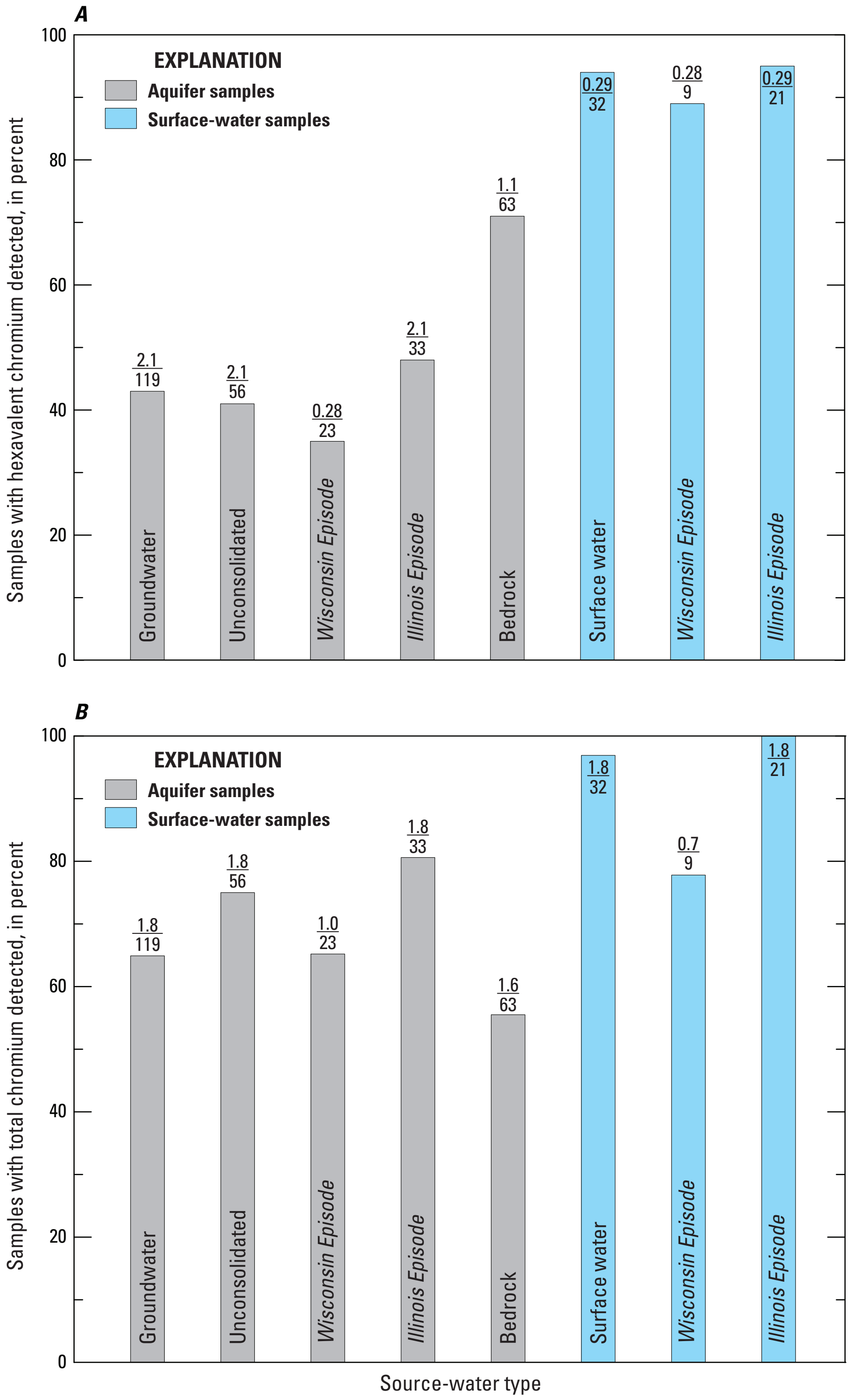


Figure 6. Frequency of detection and maximum concentrations of hexavalent chromium and total chromium in public-supply source waters in Illinois, 2013.



Base from U.S. Geological Survey 1:24,000 and 1:100,000 Digital Data,
Albers Equal-Area Conic projection,
standard parallels 33° and 45°, central meridian -89°

Figure 7. Locations of selected wells and intakes that tap public-supply source-water aquifers and surface waters in Illinois, and the occurrence and relative concentrations of hexavalent chromium [Cr(VI)] in untreated water samples, 2013.



Numbers at top of column are maximum concentration/number of samples

Cr(VI): Reporting limit 0.02 microgram per liter
Cr(T): Reporting limit 0.1 microgram per liter

Figure 8. Frequency of detection and maximum concentrations of *A*, hexavalent chromium, and *B*, total chromium, in public-supply source-water aquifers and surface waters in Illinois, by source type, 2013.

Total Chromium and Relation to Hexavalent Chromium

As indicated by the Cr(VI) findings, Cr(T) also was frequently detected in the source-water aquifers and surface waters of Illinois (table 3; figs. 5 and 8). Cr(T) was detected in 72 percent of untreated water samples, with detection frequencies of 65 percent in groundwater samples and 97 percent in surface-water samples (fig. 8*B*). Where detected, respective maximum and median concentrations were 1.8 µg/L and 0.40 µg/L in all samples, groundwater samples, and surface-water samples.

Cr(T) also was frequently detected in the State's treated drinking waters (table 3). Cr(T) was detected in 81 percent of tap samples and 91 percent of distribution samples (appendix 1). Maximum and median concentrations for both tap and distribution samples were 2.5 µg/L and 0.30 µg/L. There was a strong positive relation ($\rho = 0.93$) between Cr(T) concentrations in tap samples and distribution samples. Cr(T) concentrations were significantly greater in treated (tap) samples than untreated samples ($p = 0.003$).

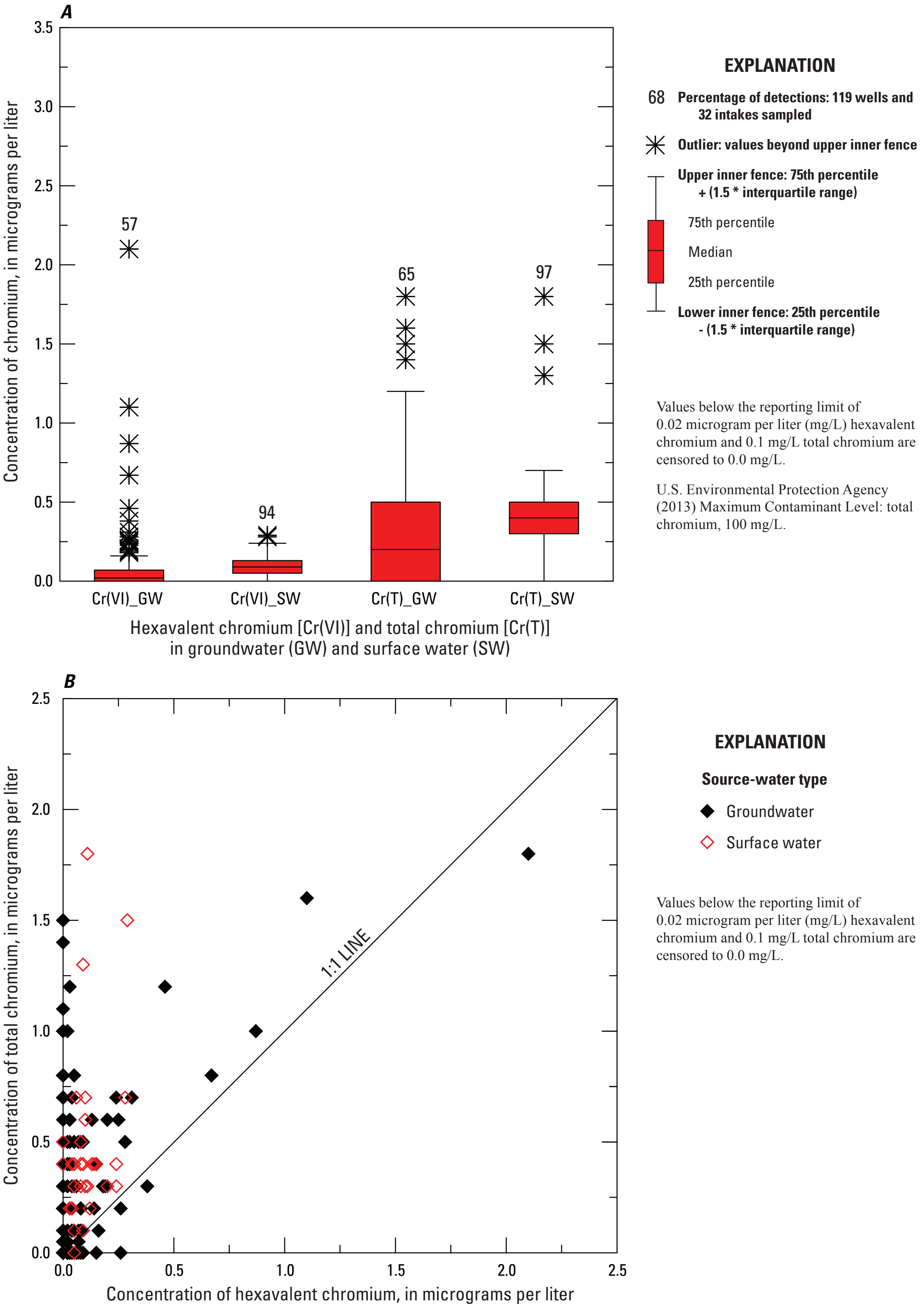
There was a weak positive relation ($\rho = 0.23$) between Cr(VI) and Cr(T) concentrations in untreated waters. This weak relation might be explained by differences in the proportion of Cr(III) in samples from groundwater and surface water. In 52 percent of groundwater samples, concentrations of Cr(T) were two times or greater than those of Cr(VI), whereas in 81 percent of surface-water samples, concentrations of Cr(T) were two times or greater. The relation between concentrations of Cr(VI) and Cr(T) in groundwater and surface-water samples was determined not to be statistically significant, as was the difference between these concentrations within each source-water type. Yet, concentrations of Cr(T) were determined to be significantly higher in surface waters than groundwaters ($p = 0.002$). The observed relations between concentrations of Cr(T) and Cr(VI) in groundwater and surface-water samples are exemplified in figure 9*B*. The typically greater concentrations of Cr(T) in these samples suggest that Cr(III) is the predominant chromium form in most source surface waters and that Cr(VI) and Cr(III) are more equally distributed in source groundwaters. One might expect Cr(VI) to be more prevalent than Cr(III) in surface waters, because these waters typically are more oxygenated than groundwater.

In an attempt to improve understanding of the relation between water oxygenation and the occurrence of chromium forms in untreated source waters, the concentration ratios of Cr(VI) to Cr(T) (hereafter referred to as "VITR") were considered. As has been illustrated in studies of herbicides and their transformation products (Adams and Thurman, 1991), concentration ratios of related constituents that are differently affected by oxygenation can be useful in discerning the conditions or environments that might explain their occurrence and magnitude. In the consideration of chromium forms and their contribution to Cr(T), one might expect a greater VITR for samples from typically more greatly oxygenated surface waters than from typically more poorly oxygenated groundwaters. For this study, VITRs were determined from the 70 sample pairs in which the concentration of each pair member was above its respective reporting limit and the Cr(VI) concentration did not exceed that of Cr(T). The calculated VITRs for untreated groundwater samples (minimum, 0.02; maximum, 0.87) did not differ significantly from those of surface-water samples (minimum, 0.06; maximum, 0.90); thus, this evaluation approach provided no additional understanding of the relation between oxygenation and chromium forms in various source waters.

Comparison to Regulatory Standards and Results of Other Studies

No concentrations of Cr(VI) or Cr(T) in untreated or treated waters exceeded the Federal MCL of 100 µg/L for Cr(T), and no concentrations of Cr(VI) exceeded California's drinking water MCL of 10 µg/L for Cr(VI). Concentrations of Cr(VI) were equal to or greater than California's nonenforceable public health goal of 0.02 µg/L in 65 percent of untreated water samples and 97 percent of drinking-water (tap and distribution) samples from surface-water sources. Cr(VI) concentrations of 23 percent of groundwater samples exceeded the standard of 0.07 µg/L reportedly under consideration in New Jersey; 62 percent of surface-water samples exceeded this standard. Concentrations of 19 percent of untreated surface-water samples that were less than the potential New Jersey standard were greater than that standard after treatment for distribution. The relation between chromium concentrations in untreated and treated water samples will be discussed in further detail in the section "Effects of Treatment and Distribution on Sample Concentrations."

Where studies can be reasonably compared on the basis of somewhat similar spatial scales and reporting limits, the findings of the present study indicate that Cr(VI) in untreated source waters and treated drinking waters is present at lower concentrations in Illinois than in many other parts of the Nation. In nationwide studies (Frey and others, 2004; Sutton, 2010), maximum concentrations were found in the range of 13–53 µg/L, as compared to 2.1 µg/L in the present Illinois study. Concentrations exceeded 0.06 µg/L in 71 percent of samples in one of the studies (Sutton, 2010), and the mean concentration was 1.1 µg/L in the other (Frey and others, 2004). In the Illinois study, the mean concentration for samples with Cr(VI) detected was 0.14 µg/L and for all samples was as low as 0.09 µg/L. Cr(VI) concentrations exceeded 0.06 µg/L in 63 percent of the Illinois samples. Frequency of detection cannot easily be compared between the studies, given the data available from the nationwide studies; however, it appears that the detection frequency in the Illinois study (65 percent) might be less that in the other studies. In one of those studies (Sutton, 2010), the frequency seemingly was 89 percent; in the other (Frey and others, 2004), the reported frequency was 42 percent, but the concentration reporting limit was an order of



Values below the reporting limit of 0.02 microgram per liter (mg/L) hexavalent chromium and 0.1 mg/L total chromium are censored to 0.0 mg/L.

U.S. Environmental Protection Agency (2013) Maximum Contaminant Level: total chromium, 100 mg/L.

Values below the reporting limit of 0.02 microgram per liter (mg/L) hexavalent chromium and 0.1 mg/L total chromium are censored to 0.0 mg/L.

Figure 9. Hexavalent chromium and total chromium in samples from public-supply source-water aquifers and surface waters in Illinois, by source type, 2013. *A*, Box-and-whisker plots of concentrations. *B*, Relation between concentrations.

magnitude greater than that used in the Illinois study (0.2 µg/L compared to 0.02 µg/L).

Detected concentrations in the more regional studies conducted in California were substantially greater than those in Illinois. In one study (Ball and Izbicki, 2004), maximum and median concentrations were 60 µg/L and 5.5 µg/L, respectively; in the other (California State Water Resources Control Board, 2011), detectable concentrations above 1 µg/L were found in 55 percent of the samples and above 10 µg/L in 4.5 percent of the samples. The detection frequency of 94 percent in the study by Ball and Izbicki (2004) was substantially greater than the frequency of 65 percent in the Illinois study. Although Cr(VI) was detected in only 25 percent of the samples in the study by the California State Water Resources Control Board (2011), the reporting limit in that study was greater (0.2 µg/L). The greater Cr(VI) concentrations in nationwide locations outside of Illinois, in part, can be attributed to geologic settings that include natural source deposits of chromium, such as the mafic deposits prevalent in parts of California (Ball and Izbicki, 2004). The geochemistry and hydrology associated with the samples sites, including favorable conditions of pH, redox, and the contact time of water with aquifer materials, also might contribute to the differences in the concentrations between studies. Additionally, sample sites in the other studies may have been closer to industrial source areas for chromium.

At least one nationwide study with substantial data from both groundwater and surface-water sources (Frey and others, 2004) confirmed the findings of the Illinois study, indicating that the greatest Cr(VI) concentrations in untreated water samples were from groundwater sources. Seemingly, unlike the Illinois study, untreated waters (typically groundwater) were found to have notably greater concentrations than treated waters. Although the Illinois study was limited to analysis of surface-water samples, treated waters were found to have notably greater concentrations than untreated waters. This finding is discussed in detail in the section “Effects of Treatment and Distribution on Sample Concentrations.”

From the perspective of an Illinois-based assessment, the findings of this study for Lake Michigan samples matched those of other assessments of Lake Michigan water used for public supply (Central Lake County Joint Action Water Agency, 2011). Untreated, treated, and finished-water samples collected from the three facilities in the present study indicated concentrations close to (0.19 µg/L) or within the consistently determined range of 0.2–0.3 µg/L indicated by others. Furthermore, both assessments used principally the same sampling method, analytical lab, and reporting limits.

Geochemical and Physical Factors Associated With Occurrence of Chromium

Awareness of geochemical and physical factors that could be associated directly or indirectly with the occurrence of Cr(VI) might be useful in identifying aquifers and surface-water bodies that are vulnerable to elevated concentrations of Cr(VI) and require its reduction for public distribution of drinking water. Additionally, this information could allow subsequent monitoring efforts to be focused on locations where the potential for elevated Cr(VI) concentrations appears to be greatest. Focused monitoring should reduce the time and costs associated with the regulatory management of this constituent of concern. Factors examined in this study that may relate to the occurrence and detection of Cr(VI) in Illinois’ public-supply source waters include (1) the pH of untreated and treated water; (2) land use, with a focus on urbanization; and (3) several aspects of geohydrology and well construction.

pH Conditions

The occurrence of dissolved Cr(III) and Cr(VI) in untreated source water or drinking water is, in part, affected by aqueous pH. As previously discussed in the section “Chemistry of Hexavalent Chromium,” pH greatly influences the solubility of these chromium forms. Cr(III) generally is insoluble between pH 6–10. Cr(VI) is increasingly soluble above pH 6 to virtually 100 percent soluble above pH 8 (Eaton and others, 2011). In consideration of the role of pH in chromium speciation, its relation to the occurrence of Cr(VI) in the untreated and treated drinking-water samples of this study was explored.

In untreated water samples, values of pH ranged from 6.3 to 8.6, with a median of 7.0. Fourteen percent of the values were less than pH 6.5–the typical lower value for public drinking water–and less than 1 percent were greater than pH 8.5–the typical upper value for public drinking water. This range of 2 pH represents the guidance for protection of public drinking water against nuisance chemicals under the Secondary Drinking Water Regulations of the U.S. Environmental Protection Agency (2013c). The values for treated water samples available from 19 supply facilities ranged from pH 6.7 to pH 9.6, with a median of pH 8.0. Twenty-one percent of the values were greater than pH 8.5 in both the tap and distribution samples of treated water; 37 percent were greater than pH 8.5 in at least one of the paired samples.

With a range of pH 6.3 to pH 9.6 for the untreated and treated water samples of the study, conditions appear favorable for the occurrence of dissolved Cr(VI) in the drinking waters of Illinois. Yet, on closer examination, there was only a weak positive relation ($\rho = 0.32$) between pH and Cr(VI) concentrations in untreated waters (groundwater and surface water considered collectively) (fig. 10*A*). The concentration of these samples ranged from less than 0.02 µg/L to 2.1 µg/L, respectively. When considered separately, there was no statistically significant relation between pH and Cr(VI) concentrations in either untreated groundwater or surface waters.

The pH values of the nine surface-water samples that were subsequently treated with lime were compared to those values after treatment to determine whether the pH of the water was notably affected as the result of the lime treatment. The small sample size for the pretreatment source-water samples and postreatment tap samples precluded statistical examination of the differences in these sample populations. The median value of pH increased from pH 7.8 in untreated samples to pH 8.3 in lime-treated samples. Also, the pH values of seven of nine samples increased and the maximum value increased from pH 8.6 to pH 9.6 after treatment. This general increase in pH as the possible direct result of lime treatment might contribute to the increase in Cr(VI) noted in treated water samples. Again, the small number of samples available for this evaluation precludes drawing firm conclusions about its results.

The relation of pH to Cr(VI) concentrations, as associated with differing water treatments, also was examined. For the surface-water samples with available data, trends in the relation between pH and Cr(VI) concentrations were compared for samples before treatment, at the tap soon after treatment, and near the endpoint of distribution. Additionally, treated samples that excluded the addition of lime (for example, chlorinated only) were compared to those that included lime. As previously noted, samples collected near the endpoint of distribution might not uniquely represent an initially treated water sample. The distributed waters might include water or waters from multiple sources and (or) released from storage after treatment but before the date of sample collection of this study.

For the raw, untreated surface waters without the subsequent addition of lime, there was a strong positive relation ($\rho = 0.86$) determined between pH and Cr(VI) concentrations. The pH and concentration ranges of these samples were pH 7.3–8.2 and 0.04–0.24 µg/L, respectively. However, for the raw, untreated waters that were subsequently treated with lime, there was no significant relation between pH and Cr(VI) concentrations. The pH and concentration ranges of these samples were pH 7.2–8.6 and 0.08–0.24 µg/L, respectively. Their median values of pH and concentration were virtually the same (pH 7.7–7.8; 0.10–0.09 µg/L). It is uncertain why the relation between pH and Cr(VI) concentrations differed so for the two sample sets. Both sets represent raw surface waters prior to undergoing any treatment.

For tapwaters, there was no significant relation between pH and Cr(VI) concentrations, regardless of the type of treatment. The pH and concentration ranges of waters not treated with lime were pH 7.2–9.0 and 0.04 –0.23 µg/L, respectively. For waters treated with lime, the pH and concentration ranges were pH 7.7–9.6 and 0.09–2.2 µg/L, respectively. There was an increase in the median concentration of Cr(VI) from 0.09 µg/L to 1.2 µg/L and maximum concentration from 0.24 µg/L to 2.2 µg/L after treatment.

For waters near the endpoint of distribution, there also was no significant relation between pH and Cr(VI) concentrations, regardless of the type of treatment. The pH and concentration ranges of waters that were not treated with lime were pH 6.7–9.0 and 0.03–0.22 µg/L, respectively. For waters with the addition of lime, the pH and concentration ranges were pH 7.5–9.1 and 0.14–2.2 µg/L, respectively.

A moderate positive relation ($\rho = 0.53$) between pH and Cr(VI) concentrations was indicated when samples representing water prior to treatment (raw) and soon after treatment that included lime were examined as a collective dataset. This relation is evident when viewed graphically (fig. 10*B*). As indicated by the 14 available samples, concentrations of Cr(VI) were significantly higher ($p < 0.001$) in tapwaters soon after treatment with lime than in untreated source waters. It is uncertain whether added lime contains Cr(VI) as a trace constituent and accounts for the apparent increase in concentrations of Cr(VI) in the treated waters or whether the increased pH seemingly associated with the addition of lime establishes geochemical conditions favorable to the conversion of Cr(III) to Cr(VI). Additional consideration of the relation between lime additions in treated water to Cr(VI) concentrations is included in section “Effect of Treatment and Distribution on Sample Concentrations.”

Land Use

Land use was evaluated to determine a possible relation to the frequency of detection and concentration of Cr(VI) in public-supply source waters of Illinois. Frequencies and concentrations were considered with respect to extent of urbanization; that is, source waters were classified as either principally urban or principally rural. Industrial sources are often cited as a principal basis for Cr(VI) contributions to the environment. For the present evaluation, the assumption was made that industrial sources of chromium are more likely to be associated with urban settings than rural settings. Historically, industrial production and disposal facilities have tended to be most densely located in or near urban settings. Regardless of setting, contamination of natural waters from industrial use of chromium can, in part, result from direct discharge of wastes to surface and groundwaters, improper disposal in landfills with discharge to groundwater, indirect discharge to surface waters from shallow groundwater discharge, and direct deposition in surface waters as airborne discharge from

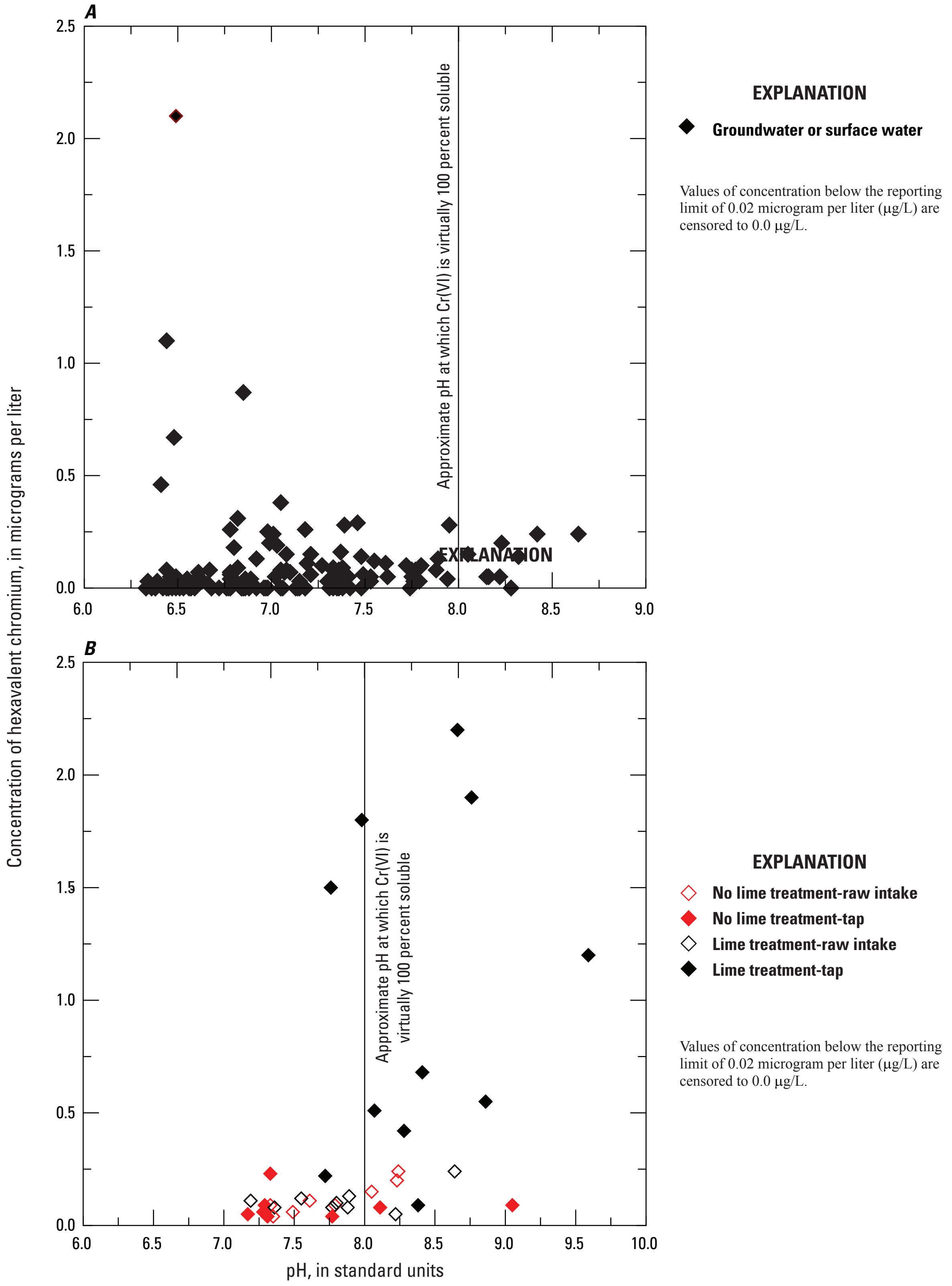


Figure 10. Relation of concentrations of hexavalent chromium to pH in source waters used for public supply in Illinois, 2013. *A*, Samples from groundwater and surface-water sources of untreated (raw) water. *B*, Samples from surface-water sources of untreated water and tapwater treated with lime.

exhaust stacks. Urbanization status was determined for the 119 groundwater-sample sites and 32 surface-water sites. By their closer positioning to industrial sources and potential for multiple routes of chromium exposure, it was expected that surface waters in industrial urban settings would be more vulnerable to Cr(VI) contributions than groundwaters in these settings.

For the urban-rural designations, a state-scale land-use map was prepared from the National Land Cover Database at a 30-meter resolution (U.S. Geological Survey, 2014b) and the location of each groundwater and surface-water site plotted on the map. Plotted land cover was limited to areas classified as developed, low intensity; developed, medium intensity, and developed, high intensity. Those sample-site areas satisfying all of the following criteria were designated as "urban" for the examination of land use as relational factor for Cr(VI) occurrence. The criteria included the following:

1. Land cover is mapped principally as "developed, medium intensity" or "developed, high Intensity,"
2. metropolitan areas and communities have a minimum nominal population of 10,000, and
3. there is evidence of present or past industrial activity in the area.

Sites falling in smaller-sized urban areas were inspected for evidence of industrial activity by using satellite imagery (Google Earth , 2014). All imagery that was used was from after 2011. Exceptions to this approach for land-use designations included three Lake Michigan sites in the Chicago region (intakes 01299; 00107; 01305) and a Will County site (intake 00341) (fig. 4). The Lake Michigan sites were considered as within the land-based area of Chicago mapped as "developed, medium intensity" or "developed, high intensity." Although the community population of the somewhat rural Will County site is only about 5,000[7], there was evidence of past industrial activity, and the riverside community is about 18 miles (mi) downstream of the more populous (about 27,000) and industrialized city of Kankakee.

On the basis of the designation criteria for land use, 8 surface-water sample sites were designated as urban and 24 as rural. Urban sites included the three Lake Michigan sites, the Kankakee River sites (intakes 22082; 00341, respectively) in Kankakee and Will Counties, a Fox River site (intake 22155) in Kane County, a Mississippi River site (intake 52099) in Adams County, and a lake site (intake 52140) in Sangamon County (fig. 4). Designation of urban surface-water sites was somewhat problematic because most of the sites included rural areas within their watersheds. In this regard, two of the sites designated as rural also were evaluated separately as urban sites. These sites are situated at or near the downstream-most location of the State's two largest rivers and might represent the collective water chemistry associated with industrial activity dispersed throughout the upstream reaches and watersheds of these rivers. The Alexander County site (intake 70010) withdraws water from the Ohio River and the Randolph County site (intake 60049) withdraws from the Mississippi River (figs. 3 and 7). Of the groundwater sample sites, 32 were designated as urban and 87 as rural.

As previously noted, Cr(VI) was detected in all but 2 of the 32 untreated water samples from surface-water sites, which includes 100 percent of the urban sites. Maximum concentrations did not distinctly differ between land-use types, with 0.29 µg/L recorded at a rural Clinton County site (intake 01851) and 0.28 µg/L recorded at an urban Lake Michigan site (intake 01299) (figs. 4, 7, and 11). Median concentrations were nominally greater at the urban sites (0.12 µg/L) than rural sites (0.08 µg/L). A larger sample population for urban surface-water sites would be necessary to more identify any statistically significant relation between Cr(VI) concentrations and land use. Concentrations of Cr(VI) in samples from the two sites that also were separately considered as urban sites were 0.08 µg/L (intake 60049, Ohio River) and 0.11 µg/L (intake 70010, Mississippi River). Thus, concentrations detected at these sites did not notably differ from those considered fully representative of urban sites or rural sites.

For untreated water samples from groundwater sites, detection frequencies for Cr(VI) were similar between urban and rural sites (53 and 59 percent, respectively). Median detected Cr(VI) concentrations in samples from urban and rural sites also were similar (0.04 µg/L and 0.07 µg/L, respectively), as were the median concentrations for all samples (0.02 µg/L and 0.03 µg/L, respectively). The maximum concentration detected at urban sites (0.87 µg/L; Tazewell County, well 50060) was less than that at rural sites (2.1 µg/L; Whiteside County, well 11894) (figs. 4, 7, and 11). Statistically, there was no significant difference ($p > 0.05$) in concentrations between untreated groundwater samples from urban and rural sites.

The Whiteside County site is within a small rural community (population about 900) with no ready evidence of present or past industrial land use or upgradient industrial land use. The site well, about 0.25 mi from the Mississippi River, withdraws water from the unconfined Mississippi River alluvial aquifer and also possibly from the river. It may be that the site water chemistry represents, in part, urban and (or) industrial contributions of Cr(VI) from sources distributed upstream along the river. About 1 mi west, across the river and upstream in the closely located towns of Camanche and Clinton, Iowa, is a riverside industrial complex. Inspection of satellite imagery (Google Earth, 2014) of the various facilities in the complex indicates operations that include surface storage and shipment of coal and scrap metal recycling. Both operations are possible sources of chromium (West Virginia Geological and Economic Survey, 2002; Trustworthy Metal, 2014).

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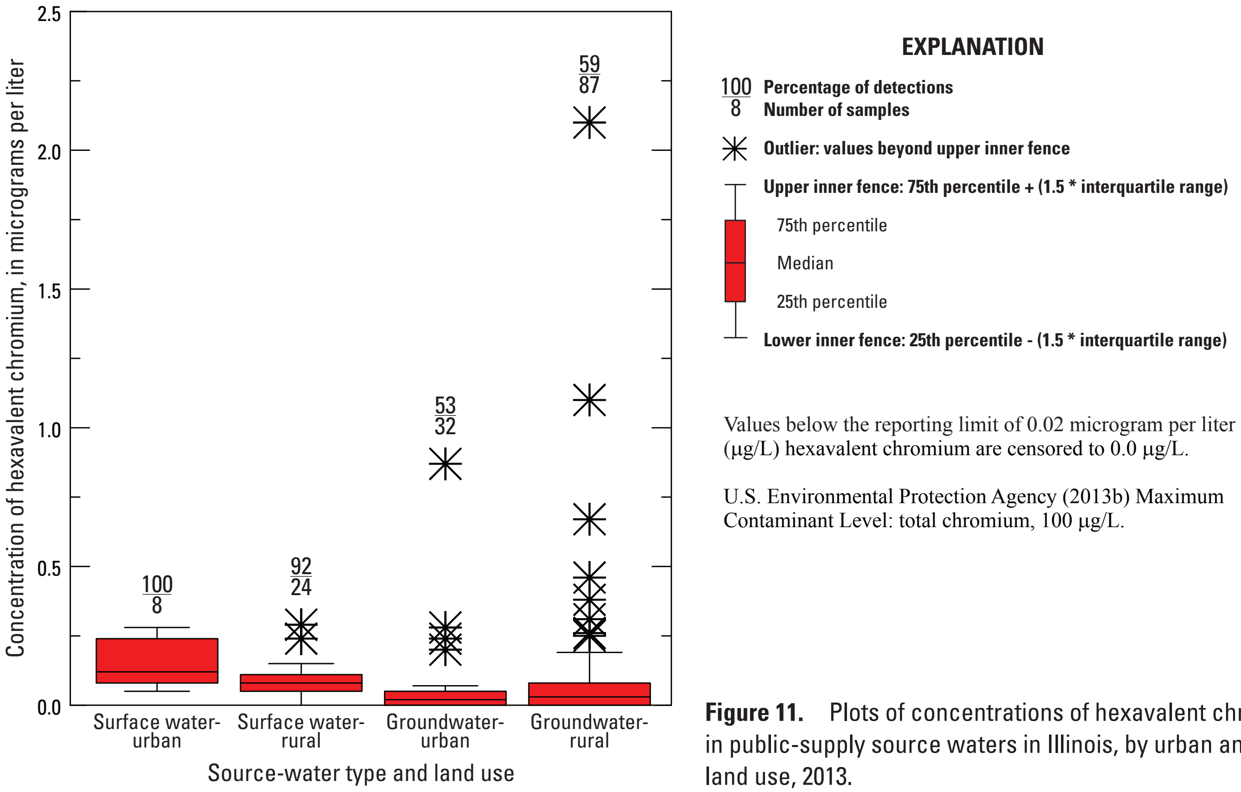
[7] All community population data included this report are from the 2010 Census (U.S. Census Bureau, 2014).



Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium are censored to 0.0 µg/L.

U.S. Environmental Protection Agency (2013b) Maximum Contaminant Level: total chromium, 100 µg/L.

Figure 11. Plots of concentrations of hexavalent chromium in public-supply source waters in Illinois, by urban and rural land use, 2013.

Collectively, urban surface waters may be more vulnerable to anthropogenic sources of chromium than urban groundwater, as suggested by their greater concentrations and frequency of detection of Cr(VI). However, factors other than urbanization seem to account for this apparent difference in vulnerability. Separately, in both urban and rural land-use settings for surface waters and groundwaters, there was minimal evidence of differences in vulnerability attributable to the settings. Evaluation of the relation between land use and Cr(VI) occurrence might have provided more insightful results if additional information was examined, including (1) known or potential industrial sources in proximity to the source-water sample locations and (2) areas contributing recharge or inflow to the supply wells and intakes. Added detail, however, is not always beneficial to such examinations. For example, in considering the relation between land use and occurrence of herbicide compounds in groundwater, Kolpin and others (1997) report that even when land-use patterns are considered in great detail, the relation between land use and occurrence of herbicide compounds in groundwater seems to be strengthened only marginally. Many factors can contribute collectively to the occurrence of chromium in groundwater and surface waters, including historical trends in land use and industrial activity, groundwater age, local flow patterns, geology, and ambient water and chromium chemistry.

Geohydrology and Well Construction

Geohydrologic factors that were examined for association with the occurrence of Cr(VI) included factors related to groundwater systems and to surface-water systems. The groundwater factors were (1) aquifer type (unconsolidated or bedrock), (2) aquifer confinement (unconfined or confined), (3) aquifer depth, and (4) aquifer age and lithology (considered collectively). Well-casing depth also was examined as a groundwater-related factor. The surface water-related factors that were examined for association with the occurrence of Cr(VI) were (1) type of surface-water body (lake or river) and (2) glacial provenance.

The selected factors could be considered, in part, to reflect the interrelation of water age, water source, aquifer type, aquifer depth, and oxygenation with the occurrence of Cr(VI). Surface water is younger than groundwater. Groundwater typically is younger in unconsolidated aquifers than in bedrock aquifers. This is particularly true for most unconsolidated aquifers used for public supply in Illinois (Robert Kay, U.S. Geological Survey, oral commun., 2104). The younger age of groundwater in unconsolidated aquifers can be attributed, in part, to the comparatively shallower depths and more rapid recharge rates of most unconsolidated aquifers (Kolpin and others, 2000). Associated with the comparatively younger age, shallower depths, and more rapid recharge rates is generally greater oxygenation (Holm and others, 1986). Where chromium is present, oxygenated waters are more likely to be enriched in Cr(VI) than Cr(III) (McNeill and others, 2011).

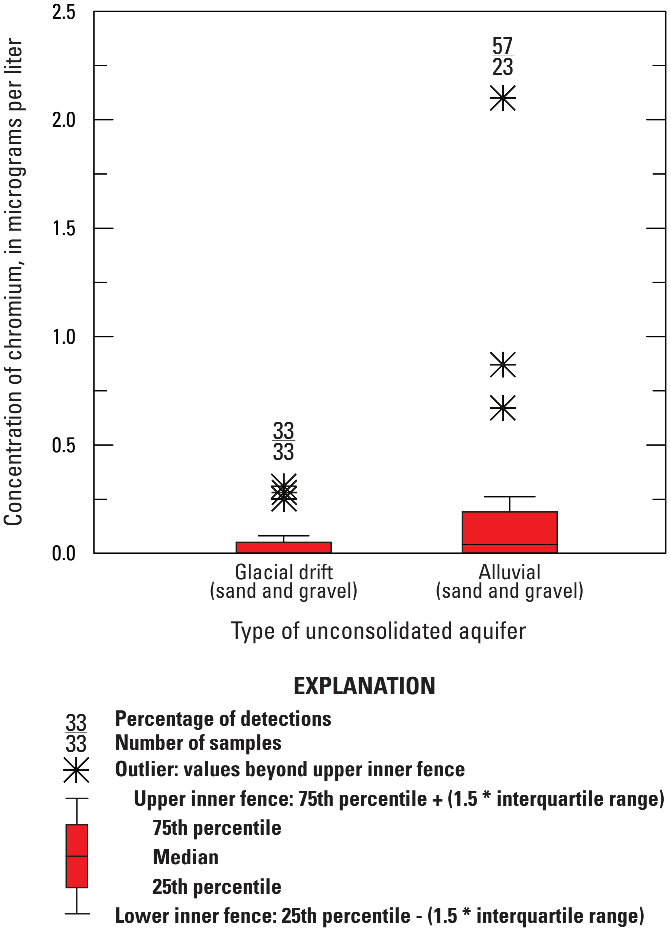
Thus, surface waters might be expected to be more vulnerable to occurrence of Cr(VI) than unconsolidated aquifers and unconsolidated aquifers more vulnerable than bedrock aquifers. These physical factors may be indirectly associated with the occurrence of Cr(VI) in natural water systems; however, with the exception of oxygenation, they should not be considered causative. The geochemistry of water systems including pH and oxygenation, in association with available geologic source materials of chromium, more directly account for the occurrence of dissolved Cr(VI) in water (John Izbicki, U.S. Geological Survey, written commun., 2014).

Groundwater-Related Factors

As previously noted, redox data, including DO, were not available for examination of their role in the occurrence of Cr(VI) in the source waters used for public supply in Illinois. Also, the limited scope of the study precluded analysis of possible alternative indicators of redox conditions (discussed in the following section “Other Factors”). In the absence of these DO and redox data and related analyses, the possible association of various aspects of geohydrology and well construction with Cr(VI) occurrence in the State’s source-water aquifers was briefly examined. These factors might relate indirectly to the geochemical conditions in these aquifers and (or) in other ways be associated with the occurrence of Cr(VI) in these aquifers.

Cr(VI) was detected more frequently in samples from bedrock aquifers (70 percent, representing 53 percent of sample locations) than from unconsolidated aquifers (43 percent, representing 47 percent of sample locations) (fig. 9). Although the concentrations were not greatly different, statistical analysis of the distributions of Cr(VI) concentrations in samples from bedrock and unconsolidated aquifers indicated the concentrations in unconsolidated aquifers are significantly greater than those in bedrock aquifers ($p = 0.02$). Maximum concentrations were 2.1 µg/L in unconsolidated aquifers and 1.1 µg/L in bedrock aquifers; mean concentrations were 0.11 µg/L and 0.07 µg/L, respectively. Median concentrations were marginally greater in bedrock aquifers than unconsolidated aquifers (0.03µg/L and 0.0 µg/L, respectively). Additionally, only 6 percent of concentrations were greater than 0.20 µg/L in bedrock aquifers, whereas 14 percent were greater in unconsolidated aquifers. These findings might, in part, be explained by consideration of the depth of the aquifers. All but 12 of the 63 bedrock aquifers in the sampling are designated as shallow bedrock aquifers (depth to the top of the aquifer is less than or equal to 500 ft below land surface). Depth to the top of shallow bedrock aquifers with detections of Cr(VI) ranged from land surface to 467 ft, with 45 percent of the detections from aquifers with depths of 200 ft or less. These depths did not notably differ from those associated with Cr(VI) detection in unconsolidated aquifers (ranging from land surface to 200 ft). Detection frequency of Cr(VI) in samples from deep bedrock aquifers (depth greater than 500 ft) was 83 percent. This elevated frequency of detection suggests the geologic units that compose these deep aquifers might contain natural chromium source materials for Cr(VI).

The occurrence of Cr(VI) in unconsolidated aquifers appears to be associated with the type of aquifer. Glacial drift aquifers represent 59 percent of the unconsolidated aquifers in the study, and alluvial aquifers represent 41 percent. Cr(VI) was detected in 57 percent of samples from alluvial aquifers and in 33 percent from glacial drift aquifers. Concentrations of Cr(VI) were significantly greater ($p = 0.02$) in samples from alluvial aquifers (fig. 12). Maximum and median concentrations in alluvial aquifer samples were 2.1 µg/L and 0.04 µg/L, respectively; the median for detected concentrations was 0.19 µg/L. In samples from glacial drift aquifers, the maximum and median concentrations were 0.31 µg/L and 0.0 µg/L, respectively; the median concentration for detected concentrations was 0.08 µg/L.



Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium are censored to 0.0 µg/L.

U.S. Environmental Protection Agency (2013b) Maximum Contaminant Level: total chromium, 100 µg/L.

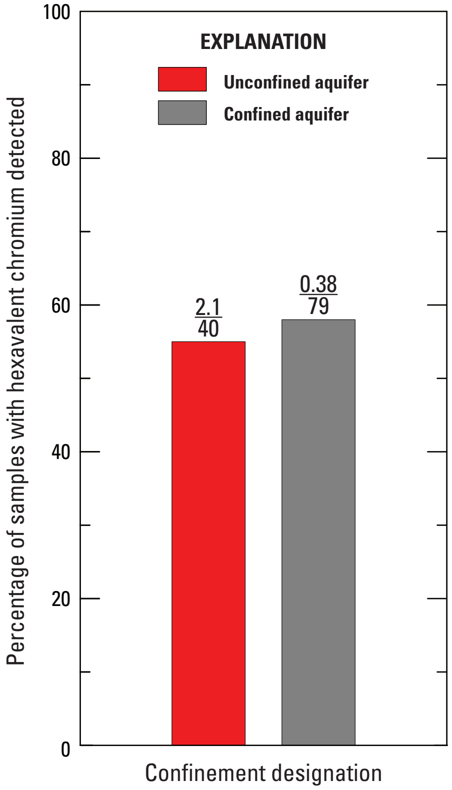
Figure 12. Plots of concentrations of hexavalent chromium in public-supply source-water aquifers in Illinois, by glacial drift aquifer and alluvial aquifer, 2013.

Generally, wells open to alluvial aquifers were shallower than those open to glacial drift aquifers. The maximum and median depths for wells that tapped alluvial aquifers were 145 ft and 78 ft, respectively. For wells that tapped glacial drift aquifers, these respective depths were 118 ft and 404 ft. The elevated concentrations of Cr(VI) in alluvial aquifer samples might reflect anthropogenic sources of chromium, as suggested by their relative proximity to land surface. Other possible contributions of chromium in these aquifers might include mineralogic differences in their composition and (or), in some cases, the contribution of surface waters entrained with the groundwater withdrawals. Most of the wells open to an alluvial aquifer are about a mile or less from a river or stream.

As with unconsolidated aquifers, a greater occurrence of Cr(VI) in unconfined aquifers than confined aquifers might be expected. Unconfined aquifers generally are shallower, the groundwater is of younger age, and the recharge rates are greater than those of confined aquifers; thus, unconfined aquifers more likely to be oxic. Confined aquifers typically are more likely to be anoxic (Yamanaka and others, 2006). Both unconsolidated and bedrock deposits can be unconfined, as are the shallow bedrock aquifers in northern Illinois in particular (fig. 1).

Aquifers are considered confined when the potentiometric surface (water level) in the aquifer is above the top of the aquifer; confined aquifers are bounded above and below by lithologic units of distinctly lower permeability than that of the aquifer (U.S. Geological Survey, 1989). For this study, designation of aquifers as confined or unconfined relied on those of the IEPA. The status of aquifer confinement of wells included in the IEPA Ambient Network have been designated by policy in order to evaluate the vulnerability of Illinois' source-water aquifers to contamination (Illinois Environmental Protection Agency, 1995). The primary approach used for these designations was a weighted-ranking method that includes five hydrogeologic criteria determined from well-construction logs and other data sources. For example, one criterion is, "Does at least one contiguous unit of impermeable geologic materials greater than 10 ft thick overlie the aquifer (excluding the top 10 ft of soil materials)?" If insufficient data are available for the weighted-ranking method, the designations are based on alternative hydrogeologic-related vulnerability criteria (Berg and others, 1984), tritium data (Illinois Environmental Protection Agency, 2003; Mills and others, 2002, p. 9), evidence of human sources of contaminants (such as synthetic organic compounds), and (or) information from detailed hydrogeologic investigations of the aquifer (Wade Boring, Illinois Environmental Protection Agency, oral commun., 2003). Each of these approaches for designating aquifers as confined or unconfined is based on the assumption that groundwater from confined aquifers generally represents old recharge (about 50 years or older) and groundwater in unconfined aquifers generally represents comparatively young recharge (younger than about 50 years).

On initial consideration, aquifer confinement does not appear to be readily associated with the occurrence of Cr(VI) in groundwater (fig. 13). Cr(VI) was detected in samples from 58 percent of wells that tap aquifers designated as confined (representing 66 percent of wells or aquifers) and 55 percent of wells that tap aquifers designated as unconfined (representing 34 percent of wells or aquifers). However, statistical analysis of the distribution of Cr(VI) concentrations in samples from confined and unconfined aquifers found concentrations to be significantly greater in unconfined aquifers ($p = 0.003$). Maximum concentrations of Cr(VI) were 2.1 µg/L in unconfined aquifers and 0.38 µg/L in confined aquifers. Mean concentrations were 0.25 µg/L and 0.07 µg/L, respectively; median concentrations were 0.09 µg/L and 0.04µg/L. Furthermore, the five highest concentrations of Cr(VI) were found in samples from unconfined aquifers, with 35 percent of the detections greater than 0.10 µg/L. The unconfined aquifers included in the study population were predominantly unconsolidated (78 percent). Only 8 percent of detections were above 0.10 µg/L in samples from confined aquifers. The distribution of concentrations suggest that unconfined aquifers, which generally are shallower than confined aquifers, might



Numbers at top of column are maximum concentration/number of samples

Reporting limit 0.02 microgram per liter

Figure 13. Graph showing frequency of detection of hexavalent chromium in public-supply source-water aquifers in Illinois, by designation of aquifer confinement, 2013.

be more directly affected by anthropogenic sources of chromium than confined aquifers. Anthropogenic contaminants are typically the result of discharges at or near land surface. Other sources of the chromium detected in unconfined aquifers, including geologic, also might be possible.

Of the detections from aquifers designated as confined, 83 percent were from bedrock aquifers; only 17 percent were from unconsolidated aquifers. Analysis of the distribution of Cr(VI) concentrations in samples from confined bedrock and confined unconsolidated aquifers indicated their concentrations were not significantly different. The small number of samples from unconfined bedrock deposits precluded similar statistical analysis for Cr(VI) concentrations in unconfined bedrock and unconsolidated aquifers. Although the extent of aquifer confinement does not appear to be solely associated with occurrence of Cr(VI), the elevated frequency of Cr(VI) detection in confined bedrock aquifers further suggests that source geology might partly contribute to the occurrence of Cr(VI) in certain source-water aquifers of the State.

It is possible that extent of aquifer confinement is more directly associated with the occurrence of Cr(VI) than indicated, because designations of confinement used in this examination might not always be accurate. It is presumed that the weighted designation method (Illinois Environmental Protection Agency, 1995) relied greatly on lithologic information from the construction log of sampled wells. Designations based on such an approach might not always take into account the lateral extent and continuity of the confining units and the possible contribution of fractures in either bedrock or clay-rich deposits. The presence of fractures could allow preferential movement of water and Cr(VI) into a seemingly confined aquifer.

Depth to top of the aquifer was examined for a possible association with the occurrence of Cr(VI) in the source-water aquifers of the State. Mills and McMillan (2004) conducted a similar examination in their study of the occurrence of herbicides and their transformation products in Illinois aquifers. For the present examination, depth to the top of an aquifer (or aquifer depth) is defined as depth to the top of the aquifer material, regardless of whether the aquifer material is fully saturated. This depth factor might relate to the extent of oxygenation of the aquifer, physical and (or) hydraulic isolation from anthropogenic sources of chromium, as well as other possible factors that could be associated with the occurrence of Cr(VI).

There was no statistically significant relation between frequency of Cr(VI) detection and aquifer depth (from land surface) (fig. 14) or concentrations of Cr(VI) and aquifer depth. Regardless of aquifer depth, as classified in six ranges from 0–50 ft to greater than 500 ft, detection frequencies fell within the relatively narrow range of 50–83 percent. The comparatively elevated frequency of detection (83 percent) of Cr(VI) in samples from the greatest depth interval further suggests geology (aquifer mineralogy) might substantially contribute to the occurrence of Cr(VI) in Illinois' deepest source waters. These deep aquifers generally are composed of sandstone and (or) carbonate strata, with the sandstone units the principal source of water supply (Wilson, 2011).

Examination of concentrations above 0.1 µg/L also found that of the 20 detections of Cr(VI) above this level, 65 percent were of samples from the shallowest aquifers (depth 50 ft or less); 85 percent were of samples from aquifers with depths of 200 ft or less. Additionally, the four greatest concentrations (0.46–2.1 µg/L) were in samples from the shallowest aquifers. From this consideration, anthropogenic sources might plausibly account for much of the Cr(VI) occurrence in Illinois' shallow source waters.

With the geology of the unconsolidated and bedrock aquifers possibly contributing to Cr(VI) occurrence, the related aspects of aquifer age and lithology were examined collectively for association with the frequency of detection and magnitude of Cr(VI) concentrations. For unconsolidated aquifers, the examination considered glacial provenance (Illinois Episode glaciation or Wisconsin Episode glaciation) (fig. 1). As a consequence of the somewhat different source areas within the Canadian Shield for the Illinois and Wisconsin Episode glacial advances, their glacial mineralogy differs (Willmann and others, 1963). For bedrock aquifers, the examination considered the age of an aquifer in conjunction with its principal lithology.

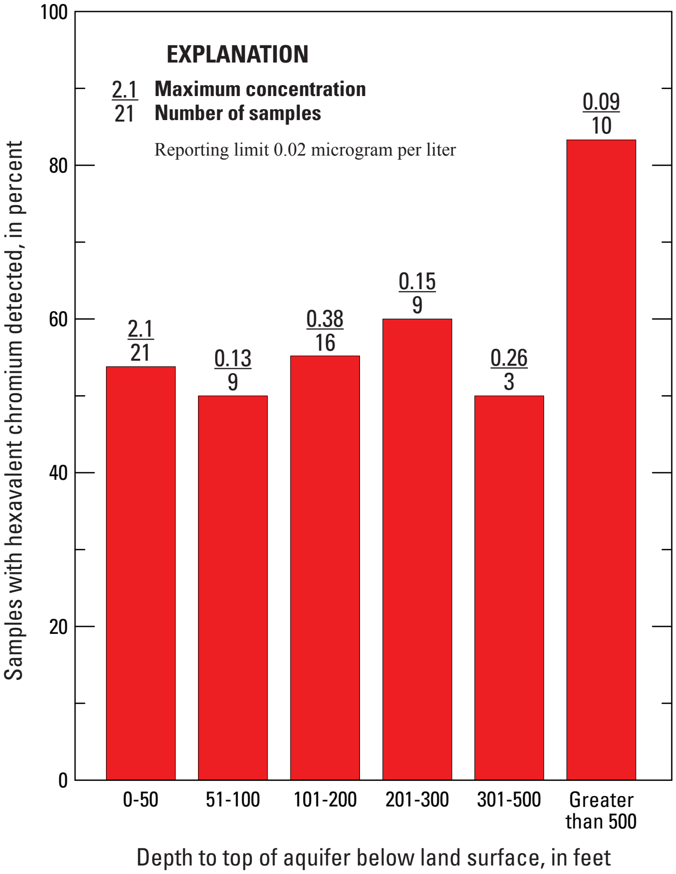


Figure 14. Frequency of detection of hexavalent chromium in public-supply source-water aquifers in Illinois, by aquifer depth, 2013.

The glacial provenances associated with the individual wells in this study may not always accurately represent the age of the glacial deposits that compose the aquifers tapped by the wells. Determining the age of deposits at the depth at which wells tap glacial aquifers was beyond the study scope. In most cases, the provenance designations are expected to be accurate. This is certainly true in areas of the State beyond the southward extent of Wisconsin Episode glaciation (fig. 1). Throughout the east-central to northeastern parts of the State, the Wisconsin Episode deposits overlie older Illinois Episode deposits. Of the 23 wells in this area of multiple glacial advances, the comparatively shallower wells are considered likely to tap only Wisconsin Episode or younger aquifers. The deepest wells (up to 404 ft), might be open in part or full to Illinois Episode aquifers. Also, for this examination, wells open to postglacial alluvial deposits were assigned to the glacial provenance of their mapped location; two alluvial wells in the far southwestern and southern unglaciated areas of the State (wells 61027; 00757, respectively) (figs. 1 and 4) were designated as within the region of Illinois Episode glaciation.

Hexavalent chromium was detected in samples from 48 percent of wells in the area of Illinois Episode glaciation (representing 55 percent of unconsolidated aquifers) and 35 percent of wells in the area of Wisconsin Episode glaciation (representing 41 percent of unconsolidated aquifers) (fig. 8*A*). Included in the calculation of frequency of detection for Illinois Episode glaciation was the detection (0.67 µg/L) from a site (well 00757) in the unglaciated southern part of the State (figs. 1 and 4).

Maximum concentration in the area of Illinois Episode glaciation was 2.1 µg/L (well 11894); this well taps younger Mississippi River alluvial deposits (fig. 1). Excluding the results of this site and those of another well that taps Illinois River alluvial deposits (0.87 µg/L; well 50060), the greatest detected concentration in glacial drift aquifers within the area of Illinois Episode glaciation was 0.31 µg/L (well 52095). Maximum concentration in the area of Wisconsin Episode glaciation was 0.28 mg/L (well 11894). Analysis of the distribution of Cr(VI) concentrations in samples from wells open to unconsolidated aquifers in the areas of Illinois and Wisconsin Episode glaciation indicates their concentrations do not significantly differ.

The relation of geology to occurrence of Cr(VI) also was examined in the context of the age and lithology of the unconsolidated and bedrock aquifers. These aquifers include (1) Quaternary sand and gravel aquifers, which can be classified as typically older glacial drift aquifers and typically younger alluvial aquifers, and (2) Paleozoic bedrock aquifers (fig. 3). The principal bedrock aquifers (or aquifer systems) in increasing age are the following:

1. Pennsylvanian aquifer, with sandstones the principal source of water,
2. Mississippian aquifer, with limestones the principal source of water,
3. Silurian and Silurian-Devonian aquifers, with dolomites and limestones the principal sources of water, and
4. Cambrian-Ordovician aquifer, with sandstones and dolomites the principal sources of water.

A number of wells included in the study are open to specific subunits of the Cambrian-Ordovician aquifer, such as the Ironton-Galesville or Galena-Platteville aquifers. Generally, these subunits are composed principally of either sandstones or dolomites. For this examination of geology, wells open to Silurian and Silurian-Devonian aquifers were considered collectively as open to the Silurian-Devonian aquifer, and wells open to any of the subunits of the Cambrian-Ordovician aquifer were considered collectively as open to this aquifer system.

Hexavalent chromium detections in samples from various unconsolidated and bedrock source-water aquifers ranged from 33 percent for the glacial drift aquifers to 76 percent for the Cambrian-Ordovician aquifer (table 4; fig. 15). Disregarding the limited representation by Mississippian aquifers (about 2 percent of aquifers), the maximum concentration of 2.1 µg/L and the greatest median concentration for detections of 0.18 µg/L (and 0.07 µg/L for all concentrations) were recorded in samples from alluvial aquifers. As previously indicated from the examination of glacial provenance, elevated concentrations of Cr(VI) in alluvial aquifers might, in part, be associated with anthropogenic contributions. Generally, Cr(VI) concentrations were greatest in these aquifers and the detection frequency (59 percent) generally similar to that of the bedrock aquifers. Glacial drift aquifers possibly are somewhat less vulnerable to anthropogenic contributions of Cr(VI) than alluvial aquifers. Glacial drift aquifers generally are more deeply buried than alluvial aquifers and often beneath a sequence or sequences of finer-grained deposits.

The findings regarding geology as a relational factor associated with the occurrence of Cr(VI) also seem to support those of the previously discussed examinations of other possible factors; that is, geology (aquifer mineralogy) might contribute largely to the occurrence of Cr(VI) in Illinois' bedrock aquifers. However, other unstudied factors, such as geochemical conditions, also may contribute in an important way to its occurrence. Geology as a possible factor in the occurrence of Cr(VI) in bedrock aquifers seems to be supported by the comparatively low frequency of detection of Cr(VI) associated with the glacial drift aquifers. Most bedrock aquifers, which have greater frequencies of detection and approximately similar concentrations of Cr(VI) relative to glacial drift aquifers, typically are overlain by glacial drift aquifers or low-permeability unconsolidated deposits. Although Cr(VI) concentrations often seem to be greater in alluvial aquifers than bedrock aquifers, these typically shallower aquifers are considered an unlikely primary source for the comparatively frequent occurrence and elevated concentration of Cr(VI) evidenced in the bedrock aquifers. Alluvial aquifers have a comparatively small spatial footprint, and most groundwater flow associated with them is likely to be as discharge to surficial water bodies rather than as recharge to the underlying bedrock systems.

Table 4. Summary statistics for detections of hexavalent chromium in samples from various unconsolidated and bedrock aquifers used for public water supply in Illinois, 2013.

[µg/L, microgram per liter; detected (all), samples with detected concentrations (all samples in category, concentrations designated as below the reporting limit censored to 0.0 µg/L); do., ditto. Reporting limit for hexavalent chromium, 0.02 µg/L. Maximum Contaminant Level for total chromium, 100 µg/L (U.S. Environmental Protection Agency, 2013b)]

Aquifer designation	Aquifer type	Percentage of aquifers	Detection frequency, in percent	Median detected concentration, in µg/L [detected (all)]	Mean detected concentration, in µg/L [detected (all)]	Maximum detected concentration, in µg/L
Alluvial	Unconsolidated	18.5	59.1	0.18 (0.07)	0.39 (0.23)	2.1
Glacial drift	do.	28.6	32.4	0.07 (0.00)	0.12 (0.04)	0.31
Pennsylvanian	Bedrock	2.5	66.7	0.09 (0.04)	0.09 (0.06)	0.14
Mississippian	do.	2.5	66.7	0.21 (0.03)	0.21 (0.14)	0.38
Silurian-Devonian	do.	20.2	62.5	0.03 (0.02)	0.11 (0.07)	1.1
Cambrian-Ordovician system	do.	27.7	75.8	0.05 (0.03)	0.08 (0.06)	0.46

Additionally, alluvial aquifers in the State are commonly underlain by low-permeability glacial till deposits that blanket most of their distributed area (Illinois State Geological Survey, 2014). It is recognized that at some locations within the State withdrawals from the bedrock aquifer are suspected of inducing flow from streams and alluvial aquifers into the bedrock aquifers (O'Hearn and Gibb, 1980).

Throughout this report, including the following section "Effects of Treatment and Distribution on Sample Concentrations," an apparent association between elevated Cr(VI) concentrations and water-treatment using processed limestone is discussed. The lime treatment, typically referred to as water softening, is used to reduce the natural hardness of the water associated with elevated concentrations of calcium and magnesium. In Illinois, Mississippian-age limestone reportedly is the source for the processed lime (Anthony Dulka, Illinois Environmental Protection Agency, written commun., 2012). However, neither an elevated frequency of Cr(VI) detection nor elevated concentrations were evidenced in untreated water samples collected from the Mississippian aquifer. These findings might easily be explained by the limitation of having collected only three samples collected from this aquifer. Also, it is possible that the limestone deposits near the few sample locations are mineralogically dissimilar to the source limestones used for the water-treatment additive.

Although well construction is not considered a factor that directly contributes to the occurrence of Cr(VI) in groundwater, certain aspects of construction might be indirectly associated with its occurrence. As groundwater systems deepen, the waters are increasingly likely to be anoxic and DO limited, particularly in Illinois groundwaters (Holm and others, 1986; Wilson, 2011). As is documented, geochemical conditions in groundwater systems are a controlling factor in chromium speciation. In consideration of a possible association between depth in groundwater systems and occurrence of Cr(VI), a particular aspect of well construction was examined: the depth below land surface to the base of the well casing. This is the depth to the top of the open or screened interval of a well, and thus, the shallowest depth at which groundwater may enter a well. Total depth of a well is often evaluated as a factor for its possible association with various water chemistries (Mills and McMillan, 2005; Wilson, 2011). For this study, well-casing depth was presumed to provide a more realistic indicator of distance from recharge areas (and thus, of younger, and possibly more oxic waters) than does total well depth. Thus, well-casing depth was examined in relation to the frequency of Cr(VI) detection and concentrations of Cr(VI).

There was a weak positive relation between well-casing depth and frequency of Cr(VI) detection ($\rho = 0.25$) (fig. 16); although, this relation was not statistically significant ($p = 0.09$) given the marginally lower alpha criterion ($\alpha = 0.05$) applied in this study. Also, there was no significant relation between well-casing depth and concentrations of Cr(VI). Regardless of casing depth, as classified in six ranges from 0–50 ft to greater than 500 ft, detection frequencies fell within the relatively narrow range of 47–68 percent. The absence of an apparent association between well-casing depth and occurrence of Cr(VI) possibly can be attributed to unique aspects of well construction. Many of the wells included in the study (53 percent) tap bedrock aquifers and thus are open to the aquifer from the base of the well casing to the base of the well (lengths of open intervals were up to 1,500 ft). Water may

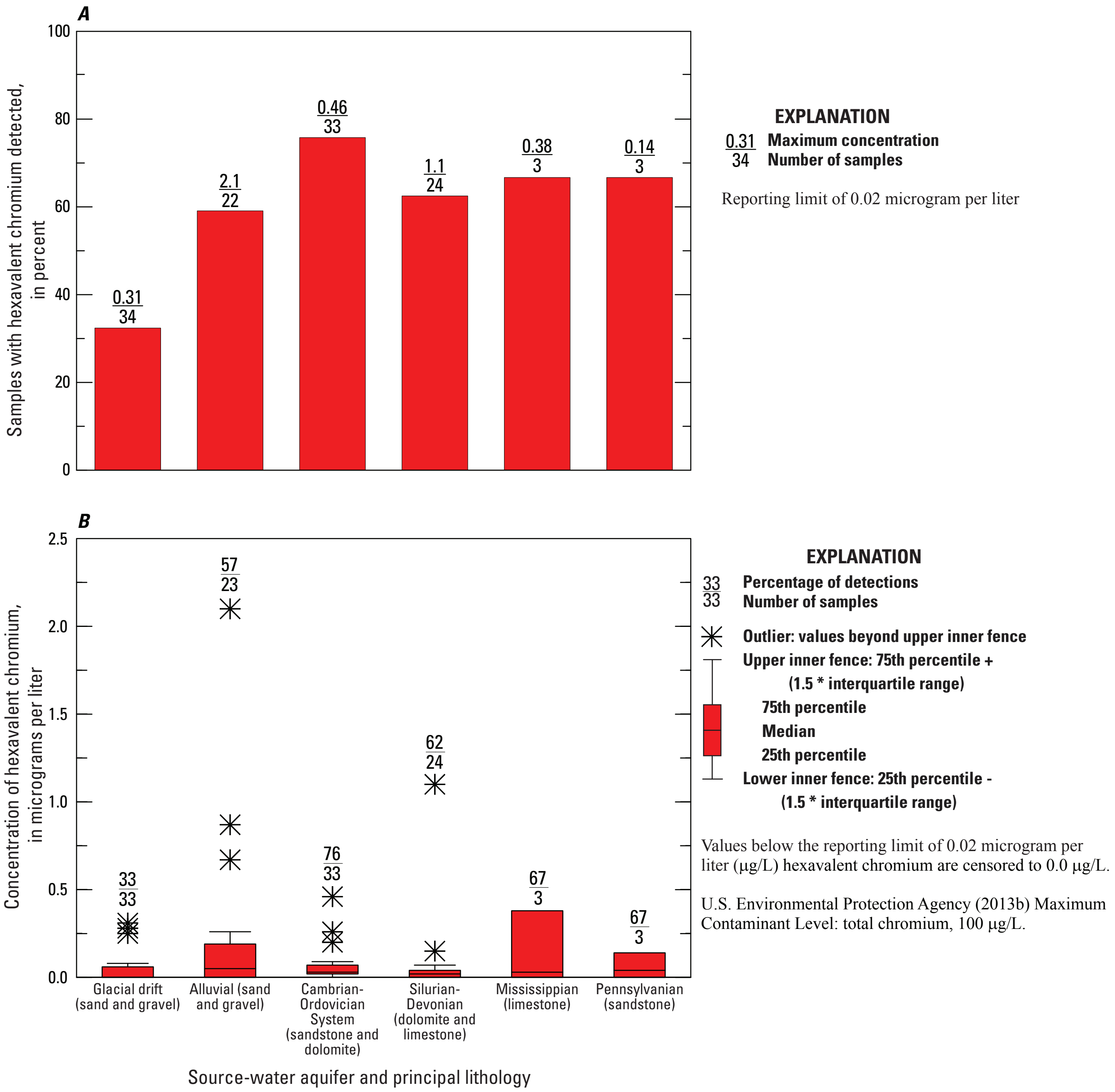


Figure 15. Hexavalent chromium in public-supply source-water aquifers in Illinois, by age and lithology of aquifer, 2013. *A*, Frequency of detection. *B*, Box-and-whisker plots of concentration

enter these wells from various depths in the aquifer. Generally, open (screened) intervals of wells that tap unconsolidated aquifers more closely approximate total well depths than do open intervals of wells that tap bedrock aquifers. On statistical examination, there was no significant relation between well depth and frequency of Cr(VI) detection in unconsolidated aquifers. There was a weak inverse relation between well-casing depth and concentrations of Cr(VI) ($\rho = -0.24$) for wells tapping unconsolidated aquifers; although, this relation was not significant ($p = 0.08$). Neither well-casing depth nor total well depth appear to be associated with or useful indicators of the possible occurrence of Cr(VI) in aquifers.

There may be other possible explanations for the apparent absence of relations between the selected geohydrologic and well-construction factors and the occurrence of Cr(VI). Several explanations, among others, are that (1) any given sample water mass is a composite of waters of multiple ages, so mixing of only a small quantity of recently oxygenated recharge

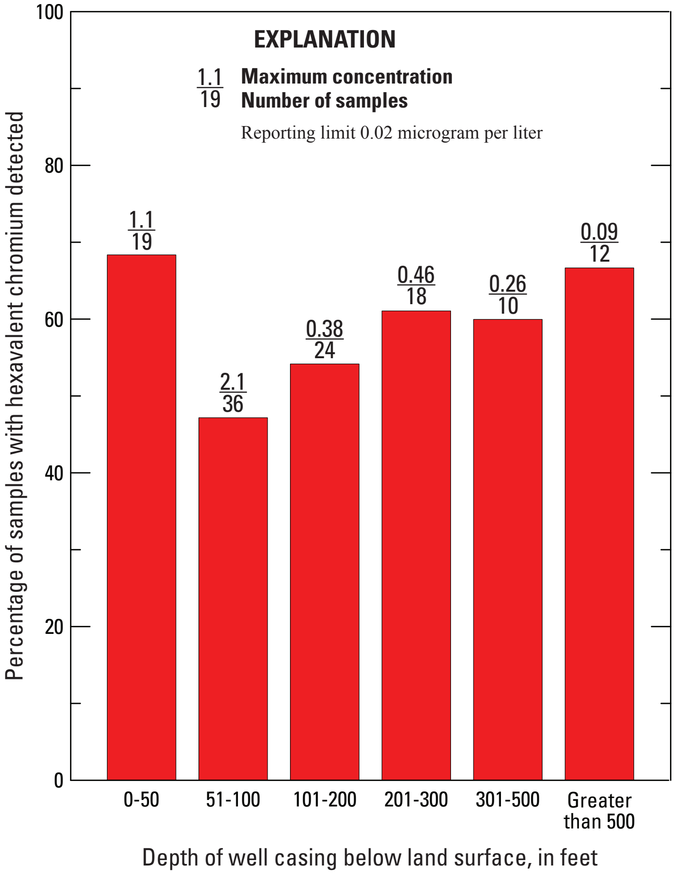


Figure 16. Frequency of detection of hexavalent chromium in public-supply source-water aquifers in Illinois, by well-casing depth, 2013.

in which Cr(VI) might be present with older recharge could result in detection of trace concentrations; (2) recent recharge may circumvent confining units and (or) move rapidly to depth in an aquifer by preferential flow through fractures or improperly constructed (grouted), damaged, or unused wells; and (3) the water chemistry that is intended to be representative of the aquifer might change upon withdrawal and collection as a sample.

Surface-Water-Related Factors

Glacial provenance also was examined as a factor that might be associated with the frequency of detection and magnitude of concentrations of Cr(VI) in surface waters used for public supply. The locations of surface-water intakes were designated as within the region of Illinois Episode glaciation, Wisconsin Episode glaciation, or an unglaciated region (only two intakes in this latter region) (fig. 1). Cr(VI) was detected in all samples from surface-water intakes located in the area of Illinois Episode glaciation (representing 66 percent of surface-water sources); 88 percent of intakes in the area of Wisconsin Episode glaciation (representing 28 percent of surface-water sources) (fig. 8*A*); and in both samples from the unglaciated region in the southernmost part of the State (fig. 1). Maximum concentration in the area of Illinois Episode glaciation was 0.29 µg/L (intake 01851). This intake taps a south-central Illinois lake in Clinton County (fig. 7). The maximum concentration in the area of Wisconsin Episode glaciation was 0.28 µg/L (intake 01299); this intake taps Lake Michigan. Maximum concentration in the unglaciated region was 0.08 µg/L. As with the frequency of detection and maximum concentrations, median detected concentrations (0.09 µg/L and 0.10 µg/L, respectively) were virtually indistinguishable between the regions of episodic glaciation; thus, glacial provenance seems to have limited bearing on the occurrence of Cr(VI) in surface-water sources for public supply. The small number of samples from the region of Wisconsin Episode glaciation precluded statistical comparison of Cr(VI) concentrations in surface waters in regions of Wisconsin and Illinois Episode glaciation.

The similarity in Cr(VI) occurrence in regards to glacial provenance of surface-water sources may, in part, be related to minimal differences in the mineralogic composition of the glacial materials, particularly in what seems to be a paucity of chromium minerals. Additionally, about half of the intake locations are rivers or reservoirs fed by rivers, and several of these rivers—including the Mississippi, Kaskaskia, and Ohio Rivers—traverse both glacial regions; thus, there is notable potential for the mixing and homogenation of the water chemistry in many of these surface-water bodies.

To improve understanding of the relation between the type of source-water body and occurrence of Cr(VI) in surface-water sources used for public supply, sample results were examined with respect to whether the source-water sources were lakes or rivers (fig. 4). Sources designated as lakes varied widely in area and storage capacity and included spring-fed impoundments, riverside reservoirs for water withdrawn from a river, instream reservoirs, and Lake Michigan. Sources designated as rivers varied widely in length and flow capacity and included creeks, rivers that traversed distances representing only a few counties up to a large part of the State, and multistate rivers, such as the Mississippi and Ohio Rivers. Cr(VI) was detected in samples from 91 percent of surface-water intakes withdrawing water from lakes and 92 percent from rivers (representing 63 and 38 percent of surface-water sources, respectively). The maximum concentration in samples from lakes was 0.29 µg/L (intake 01851); this intake taps an instream reservoir on the Kaskaskia River (figs. 3 and 6). The maximum concentration in samples from rivers was 0.15 µg/L (intake 60043). Interestingly, this intake taps the Kaskaskia River just downstream of the aforementioned reservoir. With the frequency of detection, maximum concentrations, and median detected concentrations (0.10 µg/L and 0.09 µg/L, respectively) generally indistinguishable between lakes and rivers, the type of water body appears to have limited bearing on the occurrence of Cr(VI) in surface-water sources for public supply.

On closer examination, there might be some difference in Cr(VI) occurrence associated with these water bodies.

Concentrations vary more widely in the lake samples (range, less than 0.02 µg/L to 0.29 µg/L; standard deviation, 0.09 µg/L) than the river samples (range, 0.05 µg/L to 0.15 µg/L; standard deviation, 0.03 µg/L). Yet, analysis of the distribution of Cr(VI) concentrations in samples from lakes and rivers indicates their apparent difference in concentrations is not significant. Possibly the small number of samples (lake, 22; river, 10) affected the statistical findings. The availability of an additional number of data for analysis could possibly reveal a stronger association between type of water body and Cr(VI) occurrence.

Included in the wider range of CR(VI) concentrations in lake samples were five concentrations (0.20–0.29 µg/L) that exceeded the maximum concentration in river samples. In addition to the sample collected from the reservoir on the Kaskaskia River (intake 01851), elevated concentrations were detected in three samples from Lake Michigan (intakes 00107; 01305; 10299) and one from a small downstate reservoir (intake 01952) (figs. 3 and 6). It can be speculated that this subtle difference in Cr(VI) occurrence might result, in part, from the greater potential for atmospheric contribution of Cr(VI) to lakes and the more stable hydrologic and geochemical environments of lakes for maintaining relatively steady concentrations from whatever the contributing source. Subject to periodic flushing and dilution in response to storm events and climatic trends, rivers might tend toward consistently lower and narrower ranges of Cr(VI) concentrations than lakes, although there might also be a greater potential for short-lived spikes in concentrations at a given location in rivers.

Other Factors

Several other factors are recognized as affecting the occurrence of Cr(VI) and Cr(T) in natural waters and in the laboratory analysis for chromium in water samples. Although redox indicator measurements such as DO were unavailable for this study, redox conditions (including concentrations of DO) have been documented as substantial contributing factors to the occurrence of Cr(VI). In addition to the assessment of these characteristics of water chemistry, future studies could benefit from the assessment of various other redox-sensitive constituents. Redox reactions are generally driven by microbial activity (Wilson, 2011). The microorganisms that drive these reactions obtain energy by transferring electrons from an electron donor to an electron acceptor. The electron acceptor is reduced and the donor is oxidized. Dissolved oxygen (O_2) is the preferred electron acceptor. Under anoxic conditions, naturally available electron acceptors can include, among others, nitrate (NO^{3-}), manganese (Mn^{4+}), and ferric iron (Fe^{3+}). Dissolved and particulate organic carbon generally are the principal electron donors (Thurman, 1985). Reduced forms of nitrogen, iron, and manganese also can be important donors. Future studies could include analyses for these electron acceptors and donors.

Various anions also have been identified that can interfere in C–IC analysis for Cr(VI) as the chromate anion CrO_4^{2-} and carbon and alkalinity can interfere in ICP–MS analysis for Cr(T) (McNeill and others, 2011). Dionex (2003) conducted bench tests with chloride and sulfate to evaluate their potential for anionic interference in C–IC analysis for Cr(VI). Both of these anions are commonly present in natural waters and are periodically found in elevated concentrations in these source waters and in drinking water (Iowa Department of Natural Resources, 2009; Kelly and others, 2012; U.S. Environmental Protection Agency, 2012c). On the basis of spike recoveries, the Dionex tests found an increasing bias toward underestimation of Cr(VI) concentrations if chloride and sulfate concentrations were greater than about 500 µg/L. However, it was also determined that spike recoveries were greater than 80 percent at anionic concentrations as high as 1,000 mg/L for chloride and 2,000 mg/L for sulfate. This recovery rate for the noted range of anionic concentrations indicates that C–IC analysis for Cr(VI) in the present study probably was not affected in any meaningful way by the possible presence of competing anions in the water samples. The typical chloride and sulfate concentrations in drinking water are less than about 250 µg/L (U.S. Environmental Protection Agency, 2013c; 2012c).

Specific conductance (SC) correlates with the sum of dissolved major-ion concentrations in water and often with a single dissolved-ion concentration (Hem, 1985). SC was examined as a possible indicator of the magnitude of concentrations of dissolved ions, such as chloride and sulfate, that might affect laboratory analyses of chromium. The examination also considered its possible relation with concentrations of Cr(VI). Values of SC in untreated groundwater and surface water ranged from 106 to 4,000 microsiemens per centimeter at 25 °C (µS/cm), with a median value of 647 µS/cm. Of the 147 available values, 16 percent were greater than 1,000 µS/cm. There was a weak inverse relation ($\rho = -0.26$) between SC and Cr(VI) concentrations. Concentrations in waters with a SC greater than 1,000 µS/cm did not differ significantly ($p = 0.07$) from those in waters with lower values of SC. On the basis of this examination, the laboratory results of this study for chromium do not appear significantly affected by ionic interferences during analysis.

The Metropolitan Water District of Southern California (2000) identified the potential for false-positive determinations of Cr(VI) as the result of carbon mass interference in ICP–MS analysis. Further study by Eaton and others (2001) confirmed this potential bias, with the resulting apparent concentration of Cr(T) in at least one sample near the MCL of 100 µg/L. The study identified a strong correlation between alkalinity and false positives for Cr(T) analysis. As reported, the magnitude of error in Cr(T) analysis depends on factors additional to alkalinity; however, in general, waters with elevated alkalinities will be expected to result in a greater occurrence of false positives by ICP–MS if carbon is not removed before analysis or a carbon correction factor is not applied. At the time of its reporting (2001), the authors of that study indicated that this potential for carbon interference was not identified as such in published ICP–MS analytical methods for Cr(T), including USEPA Method 200.8. It is uncertain whether this issue has now been addressed in the USEPA method used for the present study. A brief literature review suggests that current analytical protocols for chromium analysis recognize the potential for carbon interference and apply various procedures to inhibit or account for the interference in analytical results. Carbon and alkalinity data were not collected or analyzed for in the present study. Future studies of Cr(VI) occurrence might benefit from determination of the variously noted constituents of water samples that can interfere with the laboratory analyses for chromium.

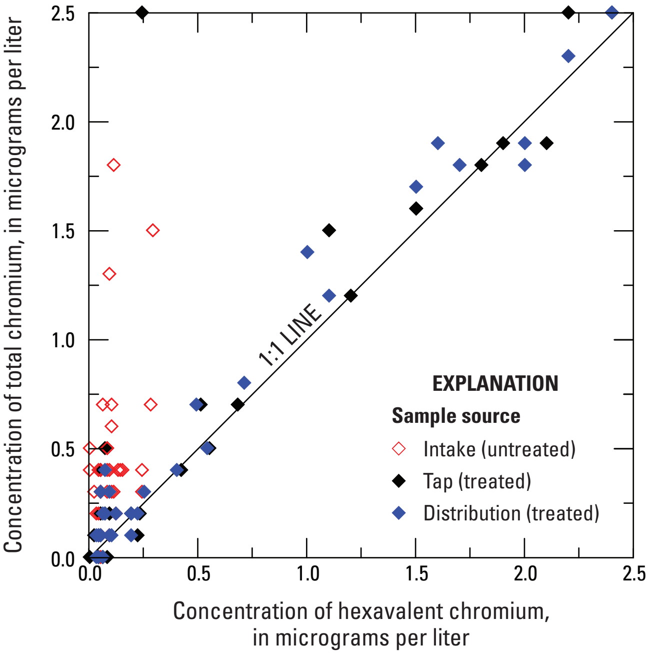
Effects of Treatment and Distribution on Sample Concentrations

After withdrawal of raw waters from source aquifers and surface waters, the waters are typically treated before public distribution as potable water for drinking and other purposes. Treatment is required for various purposes including removal or reduction of undesirable dissolved or suspended constituents, including clay particles, bacteria, iron, manganese, organic compounds, and radionuclides, among others; disinfection; and softening (reducing hardness or the concentration of dissolved calcium and magnesium in water). Treatment procedures can, in part, include the following:

1. coagulation–flocculation and sedimentation by addition of agents such as alum (aluminum sulfate) or iron salts (such as iron(III) chloride);
2. filtration by use of sand and membrane filters, as wells as activated carbon “filters”;
3. processing with ultrafiltration membranes (less than 0.2-millimeter pores), ion-exchange systems, and reverse osmosis using semipermeable membranes;
4. addition of chlorine (as sodium hypochlorite or chloramine, for example), potassium permanganate, or ozone as oxidizing agents for disinfection; and
5. fluoridation (addition of hexafluorosilicic acid) and conditioning with lime and soda ash as precipitating agents for reduction of hardness.

As a result of the various possible treatment processes to which the raw water may be subjected, as well as its subsequent storage and distribution, there is potential for changes in its chromium content (concentration and (or) valence). To evaluate these possible changes, three treated water relations were examined. The examinations considered (1) the relation of concentrations of Cr(VI) to Cr(T) in samples collected upon withdrawal (untreated raw water), soon after treatment, and near the endpoint of distribution; (2) the relation of Cr(VI) in untreated water to Cr(VI) in treated water; and (3) the relation of Cr(VI) in treated water to Cr(VI) in distributed water. Each of these examinations was completed by using the 32 sample sets collected from the surface-water sources selected for this study (figs. 1 and 3). The scope of the study did not allow for examination of the possible effects of the wide variety of likely treatment processes used in Illinois on Cr(VI) occurrence in treated water for public distribution. The examination was restricted to lime treatment for water softening on the basis of reports of lime additions enhancing Cr(VI) concentrations in treated public supply waters of Illinois and Missouri (Missouri Department of Natural Resources, 2010; Anthony Dulka, Illinois Environmental Protection Agency, written commun., 2012; Song and others, 2012).

Comparison of the concentrations of Cr(VI) to Cr(T) in samples collected upon withdrawal (untreated raw water), soon after treatment, and near the endpoint of distribution found notably different trends for each sample type (fig. 17). As previously discussed in the section “Total Chromium and Relation to Hexavalent Chromium,” concentrations of Cr(T) in the untreated water samples typically were greater than those of Cr(VI), indicating that both Cr(III) and Cr(VI) were present in most of the samples. There was a weak positive relation (ρ = 0.23) between Cr(VI) and Cr(T) concentrations, suggesting that this relation might reflect differences in the proportion



Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium and 0.1 µg/L total chromium are censored to 0.0 µg/L.

U.S. Environmental Protection Agency (2013b) Maxiumum Contaminant Level: total chromium, 100 µg/L.

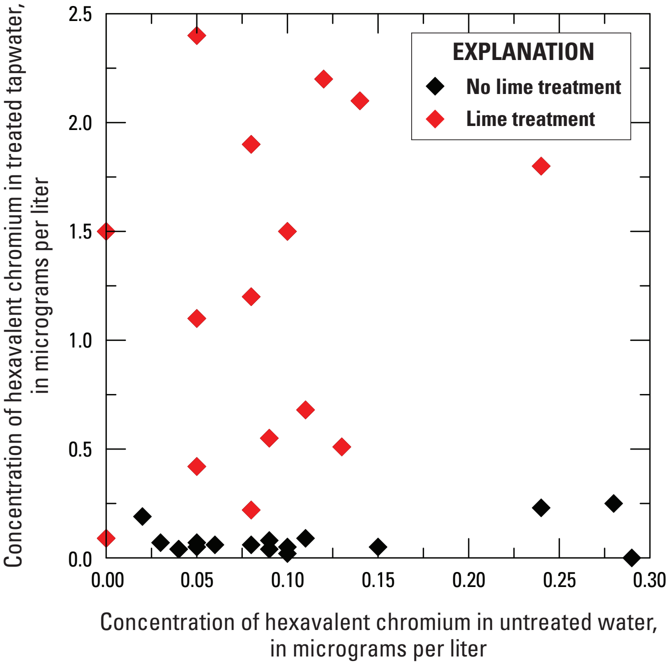
Figure 17. Relation of concentrations of hexavalent chromium to total chromium in intake (untreated), tap (soon after treatment), and distribution (near endpoint) samples from public-supply surface-water sources in Illinois, 2013.

of Cr(III) in samples from groundwater and surface-water sources. The calculated difference between concentrations of Cr(VI) and Cr(T) in these separate source-water types were determined to not be statistically significant.

In contrast to the untreated water samples, there was a strong positive relation between Cr(VI) and Cr(T) concentrations in both the posttreatment (tap) (ρ = 0.86) and distribution (ρ = 0.90) samples from surface-water sources. Similar treatment and distribution samples were not collected from groundwater sources for comparison. The notable change in the correlation between Cr(VI) and Cr(T) following treatment indicates that some aspect or aspects of the various treatment processes that are deployed affect chromium forms and their concentrations in the samples. Other contributing factors should not be discounted, including source histories (routing and storage conditions and sampling times for the untreated and treated waters). Yet, the relatively short distance required for water to be routed from the raw-water tap to the treated-water sample tap at most sites and the small difference in the times samples were collected do not suggest that the samples represent uniquely different water volumes that might contribute substantially to the noted differences in chromium concentrations. This conclusion is supported by the strong similarity of Cr(VI) and Cr(T) concentrations in treated and distribution samples, as will be discussed subsequently in greater detail. Several conflicting trends were noted in the differing Cr(VI) and Cr(T) concentrations after treatment of the raw intake water. Concentrations of Cr(VI) and (or) Cr(T) either increased, decreased, or did not appreciably change after treatment. The most frequent and pronounced change was a substantial increase in both the Cr(VI) and Cr(T) concentrations, as observed in almost one half of the samples.

Examination of the relation of Cr(VI) concentrations in untreated water to those in treated water (fig. 18), along with the strong relation noted between Cr(VI) and Cr(T) in the treated water samples, further indicate that some aspect or aspects of treatment results in a significant increase in Cr(VI) concentrations. In all but two of the treated water samples, the concentrations of Cr(VI) exceeded the maximum concentration (0.25 µg/L) recorded in the samples that were not treated with the lime additive. Further investigation determined that 15 public-supply treatment facilities included in the study soften their water by use of a lime-based additive. These facilities are among the approximate 20 facilities in Illinois that use a lime-based additive to soften surface waters and 25 facilities that use it to soften groundwater. The source location or locations of the limestone were not determined for this study, but limestone deposits of this age are readily present and quarried in southern, southwestern, and western Illinois and adjoining States.

Examination of the relation of Cr(VI) concentrations in treated tapwater to Cr(VI) concentrations in distribution water (fig. 19) indicates little difference in these concentrations between the point of treatment and near the endpoint of distribution. It is uncertain why the relative concentrations of these two chromium forms remain stable after treatment. This stability might relate, in part, to use of the oxidant chloramine, which provides relatively persistent disinfection of treated water. More stable oxygenation of the water may contribute to more stable chromium concentrations and forms. Concentrations of Cr(VI) between treated- and distributed-water samples tended to vary more in samples in the upper range of concentrations (above about 1 µg/L) (fig. 19). There was no consistent trend in the variation however, because concentrations in some samples increased and others decreased after treatment. Factors that might account for the variation are unknown, but possibly include differences in the source histories for the "paired" treated- and distributed-water samples and (or) the precision of the laboratory analytical method.

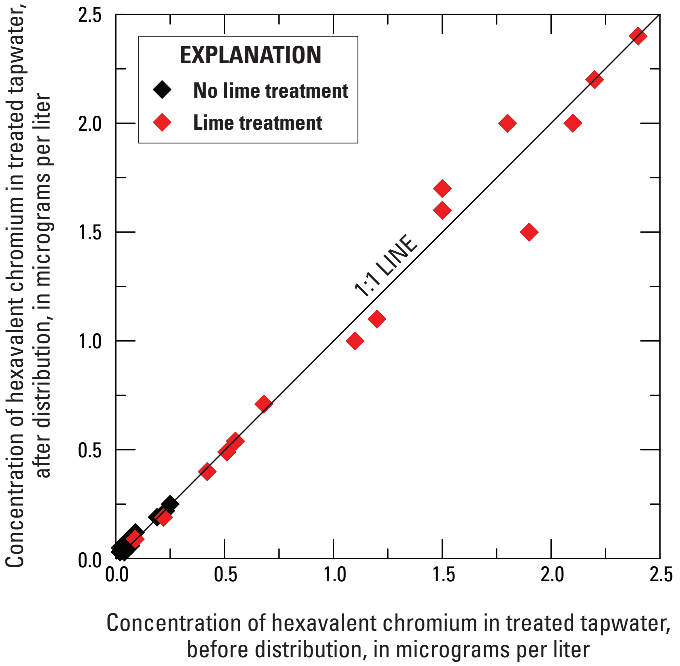


Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium are censored to 0.0 µg/L.

U.S. Environmental Protection Agency (2013b) Maximum Contaminant Level: total chromium, 100 µg/L.

Figure 18. Concentrations of hexavalent chromium in intake (untreated) and tap (soon after treatment) samples from public-supply surface-water sources in Illinois, 2013.

These results were in sharp contrast to those of the NCBOS study (Frey and others, 2004, p. 50–51). In that study, Cr(VI) concentrations were determined for 20 untreated samples and 321 samples individually treated by one of 10 processes. The maximum concentration detected in treated samples conditioned by water softening (addition of lime and (or) soda ash; representing 6 percent of treated samples) was less than about 0.3 µg/L. These results were in very close agreement with the results representing all but one of the various other treatment processes that were evaluated and the results representing no predistribution treatment. Median and



Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium are censored to 0.0 µg/L.

U.S. Environmental Protection Agency (2013b) Maximum Contaminant Level: total chromium, 100 µg/L.

Figure 19. Relation of concentration of hexavalent chromium in tap samples from public-supply surface-water sources in Illinois, soon after treatment and near the endpoint of distribution, 2013.

95th-percentile concentrations in the more affected "disinfected only" samples (representing 44 percent of treated samples) were about 0.5 µg/L and 1 µg/L, respectively, and in the more affected untreated samples (representing about 6 percent of all samples) were about 7.5 µg/L and 17.5 µg/L, respectively. Thus, the water-softening process, with the assumed addition of lime, did not appear to notably affect Cr(VI) concentrations in the treated samples. In that study, the comparatively greater concentrations of Cr(VI) in the "affected" samples generally were associated with samples from groundwater sources. Potable waters from groundwater sources were much more likely to be untreated or only undergo disinfection treatment than potable waters from surface-water sources. As with the treated water samples included in the present Illinois study, those samples in the NCBOS study conditioned by water softening generally were associated with surface-water sources.

The role lime addition plays in the increase in Cr(VI) concentrations in the treated public-supply waters of Illinois is uncertain. The contrasting results regarding lime treatment found in this study and the NCBOS study (Frey and others, 2004) suggest that Cr(VI) may be present as a trace constituent in only certain kinds of lime or other additives used throughout the United States by public-water suppliers. The presence of Cr(VI) seemingly would depend on the source deposits for the additives. Eyring and others (2002) found measureable levels of chromium in alum additives. Possibly, the addition of lime alters the geochemical conditions of the water, particularly pH, thus enhancing conditions conducive to transformation of Cr(III) to Cr(VI) (as previously discussed in the section "pH Conditions"). Questions remain regarding the manner in which lime additions affect Cr(VI) concentrations and why this addition seems to result in an increase in Cr(VI) concentrations in the treated water of only some drinking-water systems.

Sampling Factors Associated with Analytical Results of Chromium

Sampling factors associated with the analytical results of Cr(VI) were evaluated with respect to selected aspects of (1) sample shipment and processing, and (2) material composition of the infrastructure components of water distribution. Factors associated with shipment and processing included sample temperature at the time of arrival at the laboratory for analysis and the holding time between the time of sample collection and sample analysis. Evaluation of the material composition factor was limited to consideration of the composition of the sample tap at the point of sample collection. It is important to better understand the extent to which these sampling factors might affect sample integrity, and thus, influence understanding of laboratory analytics that are intended to solely represent the chemistries of waters intended for public distribution.

Sample Temperature and Holding Time

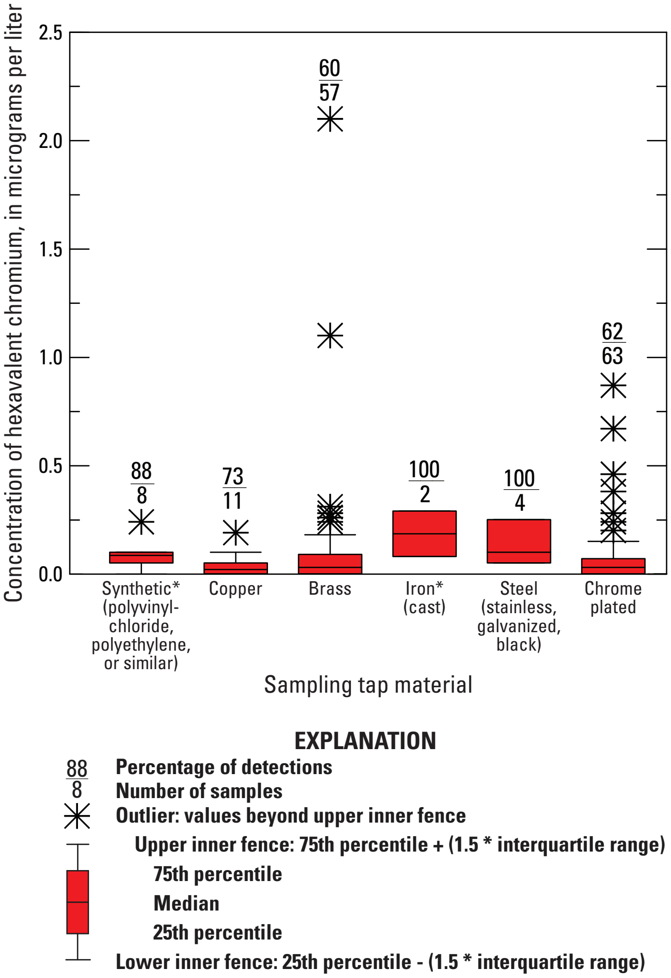
Sample temperature and holding time were considered as possible factors that might affect analytical results. Only six samples (about 3 percent of untreated, treated, and distributed samples) exceeded the target sample-preservation temperature of 4 °C. Of these, all but two were less than 2 °C above the target temperature. The untreated and treated samples from one facility (intake 70010) were at a temperature of about 12 °C upon arrival at the laboratory. Consideration of the Cr(VI) and Cr(T) analytical results of the properly chilled distribution sample (0.09 µg/L and 0.1 µg/L, respectively) indicated the elevated temperatures had no evident effect on the analytical results for Cr(VI) and C(T) of the untreated (0.08 µg/L and 0.5 µg/L, respectively) and treated (0.06 µg/L and less than 0.1 µg/L, respectively) samples. Thus, in this study there was no indication that sample temperature at time of analysis affected Cr(VI) or Cr(T) sample results. A more controlled study, with a range of known concentrations and preservation temperatures would be necessary to improve the evaluation of the relation between sample temperature and analytical results.

Holding times in this study were somewhat more divergent from the target holding time of 24 hours than were temperatures from that target. About 35 percent of samples were analyzed more than 24 hours after their collection. However, of these, only five samples were analyzed beyond 30 hours; four of these samples (intakes 00395, 1 sample; 58059, 3 samples) were analyzed about 31 hours after collection and one (well 20019) about 46 hours after collection. Inspection of the holding-time data, particularly those sample data with holding times of 30 hours or more provided no apparent evidence of a relation between the holding times of this study and analytical results. For those holding times greater than 30 hours, the Cr(VI) concentrations were close to or below 75th-percentile concentrations. Of the four samples with concentrations greater than 0.5 µg/L, the greatest two were analyzed within 24 hours of sample collection and the remaining two within 25 hours. Presently, USEPA Method 218.7, the updated version of Method 218.6, cites a holding time of 14 days (U.S. Environmental Protection Agency, 2011), with no USEPA cited holding time for Method 218.6 lower than 5 days. As with the sample temperature assessment, a more controlled study with a range of known concentrations and holding times would be necessary to improve the evaluation of the relation between holding time and analytical results.

Sample Tap Composition

The potential effect of the composition of sample taps on the analytical results for Cr(VI) was considered to ensure the results were not noticeably biased by a tap-related Cr(VI) contribution or other alteration of the samples. The construction materials of 96 percent of the raw-water sample taps for groundwater and surface-water sources were inspected and recorded on the IEPA field sheet and UL chain-of-custody form (appendixes 3 and 4). In most cases, the inspections were brief and the determined materials not verified with input from the facility operator. Therefore, all identifications of materials are considered presumptive and may differ from the actual composition of the taps. In some cases, sample taps consisted of multiple parts, such as a brass valve with a rubber hose or copper tubing with a chrome-plated valve. It should be recognized that the taps are minor endpoint components of a substantially larger network of distribution lines, which can be composed of a variety of materials that are likely to differ from those of the taps. For these reasons, this assessment of sample-tap materials only is considered exploratory.

Sample-tap materials were found to fall into six general categories: synthetic, copper, brass, steel, iron, and chrome-plated (or similarly appearing metallic plating). The materials are listed here in increasing order of their presumed potential to contribute to or affect the chromium composition of the water samples. Synthetic materials, representing about 6 percent of raw-water taps, included polyvinyl chloride (PVC), polyethylene, rubber, and similar such materials. Although certain plastics can contain chromium in colorants (Garments Tech, 2013), it is unlikely that chromium is used in the white- or beige-colored tap fixtures prevalent in potable-water-treatment systems and is likely to be fixed in the plastic, if present. Copper represented about 8 percent of taps and brass about 39 percent. Brass may contain trace amounts of chromium. Iron material represented about 1 percent of taps, and was principally cast iron; chromium can be present in cast iron in amounts ranging from a trace up to about 28 percent (Acme Alloy, 2001). Steel materials represented about 3 percent of taps, and included stainless, galvanized, and black steel; about 10–20 percent of the metallic composition of stainless steel is chromium (Engineers Edge, 2014). Chrome-plated material represented about 43 percent of taps, and included



Values below the reporting limit of 0.02 microgram per liter (µg/L) hexavalent chromium are censored to 0.0 µg/L.

Synthetic* and Iron*: all samples are from surface-water sources. Source-water samples from 115 wells and 30 intakes.

U.S. Environmental Protection Agency (2013b) Maximum Contaminant Level: total chromium, 100 µg/L.

Figure 20. Box-and-whisker plots of concentrations of hexavalent chromium in public-supply source waters in Illinois, by sample-tap material, 2013.

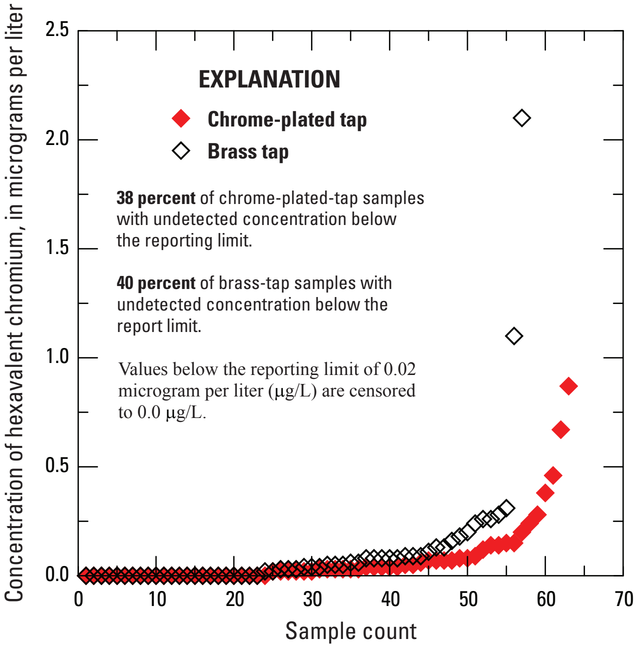


Figure 21. Concentrations of hexavalent chromium in public-supply source waters in Illinois, by chrome-plated and brass sample-tap material, 2013.

chrome-plated material of any base-material composition. For this proportional listing of tap materials and the following described findings, multicomponent taps of more than one composition were represented by the composition of the predominant part of the tap.

Graphical results of the sample-tap assessment are presented in figures 20 and 21. These results provide no apparent evidence of sample-tap composition affecting Cr(VI) occurrence or concentration in water samples. The frequency of greater concentrations of Cr(VI) associated with brass and chrome-plated taps suggests that these materials might more readily affect sample concentrations than the other tap materials. Yet, the median concentrations and frequencies of detection associated with the brass and chrome-plated materials are no more evident of a material effect on Cr(VI) concentrations than those statistics associated with the other materials. The median concentration of samples from potentially leachable chrome-plated taps (0.06 µg/L) was less than that of samples from all tap-material types (0.08–0.18 µg/L) other than copper (0.04 µg/L). Also, the small sample population of taps materials other than brass and chrome-plated limit the significance of this comparative analysis. Brass and chrome-plated sample taps represented about 83 percent of the study population.

Statistical examination of the concentrations of Cr(VI) associated with sample taps constructed primarily of chrome-bearing materials (stainless steel, chrome) and those of taps presumably constructed of non-chrome-bearing materials (synthetics, copper, brass, iron) indicated no significant difference between these concentrations. Although the second greatest maximum concentration of Cr(VI) (0.87 µg/L) was detected in a sample of a potentially leachable chrome tap, the greatest concentration (1.1 µg/L) was detected in a brass tap with presumably little to no leachable source of chromium. Condition (age) of the tap, the natural variability in Cr(VI) and pH of the source waters, or other factors appear to more strongly account for the variability of the sample results than the material composition of the taps.

Some of the variability in sample results might be attributed to the common occurrence of somewhat elevated concentrations of Cr(VI) in surface waters. This is indicated by the comparatively elevated median concentrations and detection frequencies in samples from taps composed of synthetic and iron materials. Although small in number (10), all samples from these taps were from surface-water sources. Although the source history of the water samples was not expected to affect the tap-sample analysis to any notable extent, this history might have been a contributing factor to the variability of results. Source history includes the timespan between withdrawal and collection of the samples and the material composition of the pumps and transmission lines with which the water samples were in contact. Although not documented in this study, it is presumed that pump and transmission lines were not made of chrome-bearing materials and that transmission distances were relatively short (in the range of tens to hundreds of feet). With most well and intake pumps withdrawing water in the range of hundreds to thousands of gallons per minute, it is similarly presumed that the typical transmission times and contact times for the sampled waters were short.

Summary and Conclusions

On the basis of its recent review of the human health effects of Cr(VI) in public drinking water, the USEPA is considering the need for its specific Federal regulation. Presently, only Cr(T) is regulated, at an Maximum Contaminant Level (MCL) of 100 µg/L. The occurrence of Cr(VI) in groundwater and surface waters generally is attributed to industrial sources, but it can be of natural origin. Water geochemistry—principally oxic and elevated (alkaline) pH conditions—enhances the transformation of chromium from the generally nontoxic form Cr(III) to more soluble and toxic Cr(VI). This transformation process has important implications regarding changes in concentration during water treatment and distribution of the water to the public. California's MCL of 10 µg/L Cr(VI) for drinking water established in 2014, and a lower limit of about 0.07 µg/L possibly under consideration in New Jersey, illustrate the drinking-water concerns associated with Cr(VI). To improve understanding of the possible impact of a Cr(VI)-specific standard within the approximate range of the State limits on management of Illinois' public drinking water, the USGS, in cooperation with the IEPA, assessed the occurrence of Cr(VI) in the State's public water supplies.

During 2013, untreated water samples were collected at public-supply facilities from 119 water-supply wells and 32 surface-water intakes; also, 32 treated surface-water samples were collected near the point of treatment and 32 near the endpoint of distribution. Sample sites were selected by a stratified random method. Samples typically were analyzed within 24 hours of collection at a reporting limit of 0.02 µg/L. The occurrence of Cr(VI) was compared with selected physical, geochemical, and sampling factors that might more fully explain its distribution and magnitude of concentrations. Certain geologic and geochemical data (redox potential and DO) of sufficient accuracy were not collected as part of this study; their availability would have contributed to a more complete understanding of the occurrence of Cr(VI) in the groundwater and surface waters of Illinois.

The maximum concentration of Cr(VI) in groundwater was 2.1 µg/L. Maximum concentrations in untreated and treated surface water were 0.29 µg/L and 2.4 µg/L, respectively. All sample concentrations were below the California MCL; only 35 percent were below that State's non-enforceable public health goal of 0.02 of µg/L. Cr(VI) was undetected in 43 percent of untreated groundwater samples, with a median of 0.06 µg/L, when detected. All but two (94 percent) of untreated surface-water samples had detections. In untreated surface water, the median concentration was 0.09 µg/L, whereas in treated water (tap and distributed) the median was 0.20 µg/L. Surface waters treated with lime for softening typically had the highest Cr(VI) concentrations (maximum, 2.4 µg/L; median, 1.2 µg/L). Concentrations of 19 percent of untreated surface-water samples that were less than the potential New Jersey standard were greater than that benchmark after treatment for distribution.

The maximum concentration of Cr(T) in groundwater was 1.8 µg/L. Maximum concentrations in untreated and treated surface water were 1.8 µg/L and 2.5 µg/L, respectively. All sample concentrations were below the Federal MCL. Total chromium was detected in 65 percent of untreated groundwater samples, with a median of 0.40 µg/L when detected. All but one (97 percent) of untreated surface-water samples had detections. In untreated surface water, the median concentration was 0.40 µg/L, whereas in treated water (tap and distributed) the median was 0.30 µg/L. As with Cr(VI), surface waters treated with lime typically had the greatest Cr(T) concentrations (maximum, 2.4 µg/L; median, 1.2 µg/L).

The analysis of spikes and other quality-assurance samples indicate possible difficulties in obtaining or confirming consistently accurate analytical results for Cr(VI) at near the applied reporting limit of 0.02 µg/L. Interferences might be associated with the collection and processing of samples or with laboratory analytical capability. The lack of readily available standards and inorganic blank water of sufficiently low concentrations of Cr(VI) hamper the preparation of field spikes and equipment blanks for quality assurance of environmental water samples. Cr(VI) concentrations of the quality assurance and environmental samples can often approach the relatively low reporting limit applied in this and similar studies.

Examination of factors that might account for or be associated with the occurrence of Cr(VI) in public-supply source waters found few clearly evident factors. Associations in frequencies of occurrence and range of concentrations indicate that surface waters and groundwaters of shallow, unconsolidated, unconfined aquifers, particularly alluvial aquifers, are possibly most commonly affected by anthropogenic sources of Cr(VI). Groundwaters of deep (greater than 500 feet) bedrock aquifers, particularly the Cambrian-Ordovician aquifer, are possibly most commonly affected by geologic sources of Cr(VI). Additional study would be necessary to verify these associations.

There was a weak positive relation ($\rho = 0.23$) between concentrations of Cr(VI) and Cr(T) in untreated water samples, with a much stronger positive relation ($\rho = 0.86$ and $\rho = 0.90$, respectively) in samples collected soon after treatment and near the endpoint of distribution. The stronger relation and greater similarity between Cr(VI) and Cr(T) concentrations in treated water samples indicate that Cr(VI) represents a greater proportion of the measured concentrations of Cr(T) in treated waters than in untreated waters. Examination of such factors as material composition of sample taps and sample temperature and holding time found no evidence that these sampling factors contributed to the occurrence or magnitude of Cr(VI) detections in the collected samples.

Future related studies might consider examining the role of lime and related water softeners on occurrence of Cr(VI) in treated public waters. This examination could include determination of the source and mineralogic content of the carbonates from which the lime additives used in Illinois are produced. Studies that might further explore the factors related to occurrence of Cr(VI) in Illinois groundwater and surface waters could benefit from collection of site-specific data on Eh (redox potential) and DO in conjunction with the collection of water-quality samples. These data, along with an understanding of the mineralogic content of aquifer materials, also could allow the relative vulnerability of various aquifers to Cr(VI) occurrence and the determination of their principal source of Cr(VI) (anthropogenic or geologic) to be more fully addressed.

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Appendixes

Appendix 1. Table of well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.

Appendix 2. Protocols for collecting representative samples of untreated source water and treated water. *A*, Hexavalent chromium. *B*, Total chromium.

Appendix 3. Example Illinois Environmental Protection Agency field sampling record.

Appendix 4. Example analytical result report and quality-assurance documentation provided by UL laboratory.

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

AQUIFER AND PRINCIPAL LITHOLOGY: AL (SG), Alluvial (sand and gravel); GD (SG), Glacial drift (sand and gravel); SD (DL), Silurian-Devonian (dolomite and limestone); SI (DL), Silurian (dolomite and limestone); PV (S), Pennsylvanian (sandstone); MS (L), Mississippian (limestone); CO (SD), Cambrian-Ordovician (sandstone and dolomite)

GLACIAL PROVENANCE AND SURFACE-WATER BODY: IE-L, Illinois Episode glaciation–lake; IE-R, Illinois Episode glaciation–river; IE-MR, Illinois Episode glaciation–Mississippi River WE-L, Wisconsin Episode glaciation–lake; WE-LM, Wisconsin Episode glaciation–Lake Michigan; WE-R, Wisconsin Episode glaciation–river; U-L, Unglaciated–lake; U-OR, Unglaciated–Ohio River

Reporting limit for hexavalent chromium, 0.02 µg/L; for total chromium, 0.1 µg/L.
Maximum Contaminant Level for total chromium: 100 µg/L (U.S. Environmental Protection Agency (2013b).

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
00107	42N13E-22.4c	IE-L	09/05/13	na	Brass/cast iron	na	8.2	21.9	303	0.20[2]	0.3
do.	do.	do.	do.	do.	Chrome	N	7.3	22.0	311	0.19	0.2
do.	do.	do.	do.	do.	Chrome	N	7.3	22.6	311	0.19	0.2
00155	11N 4W-34.2e1	GD (SG)	09/04/13	35	Brass	na	6.8	13.4	811	<0.02	0.7
00251	9N11W-20.6h2	GD (SG)	02/27/13	115	Galv steel	na	7.0	14.3	734	0.25	0.6
00337	39N 9E-8.3d1	SI (DL)	05/13/13	350	Chrome	na	6.6	11.8	1,100	0.02	<0.1
00341	33N 9E-26.1b	WE-R	10/24/13	na	??	na	8.2	9.4	680	0.05	0.1
do.	do.	do.	do.	do.	Copper/brass	Y	8.3	10.0	434	0.42	0.4
do.	do.	do.	do.	do.	Copper/brass	Y	8.7	16.6	435	0.40	0.4
00351	2N 1E-26.8g3	MS (L)	05/08/13	92	Brass	na	6.9	13.9	934	<0.02	1.5
00366	44N10E-10.6g	SI (DL)	11/20/13	250	Chrome	na	7.1	11.1	781	0.15	<0.1
00395	20N 2E-35.8f1	GD (SG)	11/12/13	360	Brass	na	7.2	13.3	900	0.06	0.3
00546	45N10E-4.4g2	GD (SG)	08/28/13	150	Chrome	na	6.9	11.7	685	<0.02	<0.1
00622	39N 9E-28.2e1	SI (DL)	06/25/13	368	Copper/brass	na	6.4	11.6	983	0.02	<0.1

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
00706	12N13W-29.2h1	GD (SG)	04/25/13	90	Brass	na	7.18	10.2	465	<0.02	0.2
00727	17N5E-24.2h1	GD (SG)	08/01/13	143	??	na	7.2	15.6	792	<0.02	1.0
00757	14S 4E-1.5f1	AL (SG)	01/15/13	102	Brass	na	7.4	14.1	435	<0.02	0.1
00766	32N 9E-5.6d	CO (SD)	12/05/13	795	Brass	na	7.0	14.7	1,880	0.08	0.1
00937	44N10E-35.4b	SI (DL)	01/22/13	262	Chrome?	na	7.1	12.0	796	0.07	<0.1
01029	40N 9E-19.3a	CO (SD)	07/15/03	1,425	Chrome	na	6.5	14.6	537	<0.02	<0.1
01079	20N10E-15.8d	CO (SD)	10/30/13	1,115	Chrome	na	6.4	12.2	584	0.03	<0.1
01113	3S 7W-8.8b3	MS (L)	04/04/13	300	Chrome	na	7.0	13.6	572	0.38	0.3
01118	1N 1W-33.6e	AL (SG)	11/20/13	60	Brass	na	6.8	13.0	857	0.09	<0.1
01143	30N 9E-27.3b	SI (DL)	10/03/13	260	Brass	na	7.4	12.3	726	0.03	0.4
01187	4S 7W-20.1g1	AL (SG)	06/12/13	60	Brass	na	6.7	14.3	623	<0.02	<0.1
01299	42N13E-16.4g	WE-LM	01/30/13	na	Chrome	na	8.0	2.9	305	0.28	0.7
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.24	2.53
do.	do.	do.	do.	do.	Chrome	N	do.	do.	do.	0.25	0.3
01305	38N15E-15	WE-LM	10/23/13	na	Chrome	na	8.4	2.7	352	0.24	0.3
do.	do.	do.	do.	do.	Chrome	N	7.3	14.6	296	0.23	0.2
do.	do.	do.	do.	do.	Chrome	N	7.5	15.3	303	0.22	0.2
01357	1N 3W-33.7g	IE-L	09/03/13	na	Brass	na	??	??	??	<0.02	0.5
do.	do.	do.	do.	do.	Chrome	Y?	8.4	28.2	324	0.09	0.2
do.	do.	do.	do.	do.	Brass	Y?	8.0	25.4	321	0.09	0.3
01416	16N13W-22.5g2	AL (SG)	03/14/13	90	Chrome	na	7.1	14.7	771	<0.02	0.4

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
01443	15N 7E-6.4h3	AL (SG)	08/27/13	75	Copper	na	6.6	12.0	817	<0.02	0.2
01463	14N13W-6.6f	AL (SG)	04/11/13	65	Brass/nylon	na	7.0	13.1	735	<0.02	<0.1
01536	42N 6E-28.3c	CO (SD)	03/12/13	1,250	Chrome	na	6.6	14.3	523	0.02	0.4
01537	40N 1E-14.3h	CO (SD)	06/26/13	893	Chrome	na	6.5	12.0	509	0.05	<0.1
01670	12N 9E-24.4f	WE-L	03/27/13	na	PVC	na	8.3	5.4	371	<0.02	0.4
do.	do.	do.	do.	do.	Chrome	Y?	??	??	??	1.5	1.6
do.	do.	do.	do.	do.	Chrome	Y?	do.	do.	do.	1.6	1.9
01851	3N 1W-19.6f	IE-L	02/06/13	na	Cast iron	na	7.5	2.7	249	0.29	1.5
do.	do.	do.	do.	do.	Chrome	N	??	??	??	<0.02	<0.1
do.	do.	do.	do.	do.	Copper	N	do.	do.	do.	0.03	<0.1
01952	9N 4E-16.5a	IE-L	09/26/13	na	PVC	na	8.6	21.9	361	0.24	0.4
do.	do.	do.	do.	do.	Chrome	Y	8.0	21.8	256	1.8	1.8
do.	do.	do.	do.	do.	Brass	Y	8.7	21.0	258	2.0	1.8
11318	45N 3E-27.6b1	GD (SG)	04/29/13	100	Chrome	na	6.4	10.7	740	<0.02	1.0
11327	15N10E-17.7g1	SI (DL)	02/19/13	334	Chrome	na	7.5	13.3	3,330	0.03	0.5
11347	17N10E-29.5c1	GD (SG)	02/27/13	270	Chrome	na	6.5	11.8	660	<0.02	0.5
11363	18N 9E-9.5c2	GD (SG)	04/01/13	404	Brass	na	7.0	12.0	485	<0.02	<0.1
11367	16N 9E-16.6g3	GD (SG)	04/22/13	270	Chrome	na	7.0	11.9	537	<0.02	0.4
11419	38N 5E-14.4d1	CO (SD)	09/16/13	573	Brass	na	6.6	11.2	550	0.04	<0.1
11438	37N 5E-32.1c2	CO (SD)	01/31/13	502	Chrome	na	6.6	12.2	597	0.02	0.5
11456	36N 3E-18.4d1	CO (SD)	09/17/13	150	Brass	na	6.8	12.5	563	<0.02	<0.1

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
11470	36N 4E-8.4h1	SI (DL)	10/29/13	230	Brass	na	6.6	11.7	554	<0.02	<0.1
11508	33N 1E-16.8a2	CO (SD)	12/03/13	2,665	Chrome	na	6.6	23.7	1,550	0.02	<0.1
11514	31N 5E-16.1d1	PV (S)	07/22/13	280	Chrome	na	6.9	12.9	813	0.04	<0.1
11557	21N 9E-5.5a1	CO (SD)	06/17/13	1,870	Chrome	na	6.5	14.5	538	<0.02	0.7
11560	21N10E-1.6f1	SD (DL)	05/14/13	298	Chrome	na	6.3	11.9	831	<0.02	<0.1
11562	21N10E-1.7g1	CO (SD)	01/30/13	769	Brass	na	6.4	11.1	558	0.08	0.2
11570	37N 2E-10.1c1	CO (SD)	07/01/13	1,053	Brass	na	6.8	12.4	424	0.26	<0.1
11621	44N 1E-22.6c1	CO (SD)	02/04/13	1,600	Chrome	na	7.0	11.9	573	0.20	0.6
11629	44N 2E-18.7a2	GD (SG)	06/18/13	295	Chrome	na	6.4	11.3	767	<0.02	1.1
11640	44N 2E-20.4h1	CO (SD)	02/04/13	1,457	Chrome	na	6.6	12.5	489	0.03	<0.1
11678	43N 2E-10.7d2	CO (SD)	11/06/13	530	Chrome	na	6.6	11.0	547	0.04	<0.1
11706	24N 6E-5.5e1	CO (SD)	08/06/13	1,100	Chrome	na	6.4	12.2	523	0.02	0.1
11707	24N 6E-5.6d1	CO (SD)	07/16/13	1,082	Brass	na	6.3	12.6	529	0.03	0.6
11778	25N11E-32.6g1	CO (SD)	08/12/13	740	Chrome	na	6.4	11.6	683	0.46	1.2
11782	40N 2E-23.2f2	CO (SD)	10/08/13	723	Chrome	na	6.9	11.5	489	<0.02	<0.1
11846	40N 1E-20.1a1	CO (SD)	03/26/13	345	Chrome	na	6.4	10.8	481	<0.02	0.2
11891	29N 6E-22.2b1	CO (SD)	12/09/13	355	Stainless steel	na	6.5	11.1	546	0.05	0.2
11894	21N2E-35.5h2	AL (SG)	01/28/13	88	Brass	na	6.5	11.6	591	2.1	1.8
11904	20N 5E-15.8b1	CO (SD)	02/20/13	820	Chrome	na	6.6	13.8	578	<0.02	<0.1
11914	19N 5E-5.2a1	GD (SG)	10/28/13	176	Chrome	na	6.8	11.3	572	<0.02	<0.1

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
20019	39N 8E-23.8f1	CO (SD)	01/29/13	1,297	Brass	na	6.6	11.9	620	0.05	<0.1
20029	42N 8E-14.2h1	GD (SG)	06/24/13	183	Chrome	na	6.4	11.4	937	<0.02	<0.1
20136	35N 6E-6.2f1	CO (SD)	10/01/13	287	Chrome	na	6.6	11.3	720	0.07	<0.1
20141	43N 8E-14.1e1	CO (SD)	12/10/13	1,300	Chrome	na	6.8	15.3	450	0.07	0.1
20180	45N 9E-7.8d1	SI (DL)	05/21/13	294	Copper	na	6.6	11.7	647	0.04	0.3
20181	45N 9E-7.3e1	SI (DL)	09/18/13	255	Brass	na	6.9	12.9	813	0.04	0.1
20207	45N 8E-35.5a1	GD (SG)	04/02/13	60	Chrome	na	6.3	12.5	1,290	<0.02	0.4
20297	43N11E-34.5f1	SD (DL)	04/23/13	280	Chrome	na	7.2	11.3	1,110	0.03	0.2
20328	35N12E-13.6e1	SI (DL)	07/17/13	500	Brass	na	6.6	12.2	1,120	<0.02	0.6
20389	35N12E-9.4h1	SI (DL)	08/22/13	420	Chrome	na	7.0	13.0	1,610	<0.02	0.7
20412	35N 10E-13.8e2	SI (DL)	05/23/13	305	Brass	na	6.8	12.8	1,590	0.02	1.0
20436	33N12E-24.2g1	SI (DL)	08/15/13	300	??	na	6.9	12.2	1,160	0.02[4]	0.4
20442	35N12E-34.6g1	SI (DL)	06/20/13	430	Brass	na	6.8	12.4	1,240	<0.02	<0.1
20447	36N10E-33.7e1	SD (DL)	05/02/13	303	??	na	6.8	12.4	1,700	<0.02	0.3
20458	34N13E-17.5e1	SI (DL)	10/09/13	460	Brass	na	6.8	11.9	1,340	<0.02	<0.1
20609	41N 9E-34.1b1	SI (DL)	08/27/13	200	Chrome	na	6.4	11.3	986?	<0.02	<0.1
20613	40N 9E-3.5b1	SI (DL)	06/03/13	392	Chrome	na	??	??	??	0.04	0.2
22040	33N 7E-4.4c1	CO (SD)	05/30/13	1,462	Chrome	na	7.1	16.4	769	<0.02	<0.1
22077	30N10E-26.1h1	SI (DL)	07/25/13	163	Brass	na	6.8	14.7	990	0.02	<0.1
22082	30N13W-8.3g	WE-R	11/26/13	na	Copper/ chrome	na	7.8	3.5	677	0.10	0.7

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
do.	do.	do.	do.	do.	Chrome	Y	7.8	3.5	479	1.5	1.6
do.	do.	do.	do.	do.	Copper/ chrome	Y	7.9	9.3	460	1.7	1.8
22148	43N 8E-8.2c1	CO (SD)	11/19/13	1,300	Brass	na	6.8	14.5	488	0.06	<0.1
22155	41N 8E-11.2g	WE-R	12/10/13	na	Chrome	na	??	??	??	0.09	0.4
do.	do.	do.	do.	do.	??	Y	8.9	6.3	730	0.55	0.5
do.	do.	do.	do.	do.	Chrome	Y	8.4	11.7	748	0.54	0.5
31307	30N 3W-26.1b3	AL (SG)	02/07/13	50	Brass	na	7.2	13.5	688	0.26	0.2
31409	26N 2E-5.7a1	GD (SG)	10/16/13	120	Brass	na	6.4	12.6	718	<0.02	0.8
31428	28N 2E-7.5c2	CO (SD)	02/07/13	2,005	Chrome	na	7.5	21.3	3,130	0.05	0.8
31713	15N 3E-7.3e1	CO (SD)	08/13/13	1,377	Brass	na	6.7	15.1	845	0.08	0.1
31745	18N 3E-33.7a2	SI (DL)	06/04/13	45	Brass	na	6.4	12.6	1,260	1.1	1.6
31820	15N 2W-27.8c1	SD (DL)	08/05/13	604	Brass	na	6.8	14.3	1,890	0.04	0.1
31853	17N 1W-26.4c1	SI (DL)	04/09/13	555	Brass	na	6.5	12.8	716	<0.02	0.8
31873	18N 1E-32.7G2	SI (DL)	03/11/13	445	Chrome	na	6.7	13.1	462	0.02	0.3
45081	20N 8E-33.8a1	GD (SG)	04/11/13	338	Brass	na	7.4	12.8	646	<0.02	<0.1
45155	11N11W-8.4a1	GD (SG)	03/14/13	68	Copper	na	7.0	12.5	627	0.05	0.5
45170	8N 5E-25.4c	IE-L	07/16/13	na	PVC	na	7.9	27.4	290	0.08	0.4
do.	do.	do.	do.	do.	Steel/nylon	Y	9.6	27.1	234	1.2	1.2
do.	do.	do.	do.	do.	Chrome	Y	9.09	23.0	265	1.1	1.2
45174	8N 7E-11.8e1	AL (SG)	03/13/13	36	Brass	na	7.0	11.8	769	<0.02	0.4

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
45263	23N12W-11.3e3	GD (SG)	08/29/13	104	Chrome	na	7.3	13.8	692	<0.02	0.4
47501	26N 8E-3.8g1	GD (SG)	09/18/13	100	Steel	na	7.4	18.5	1,040	0.05	0.1
47518	29N 6E-10.8e1	CO (SD)	11/25/13	1,940	Brass	na	6.8	21.3	2,300	<0.02	<0.1
47532	26N 9E-4.2f1	GD (SG)	01/16/13	79	Copper	na	7.0	12.6	760	<0.02	0.3
47542	23N 9E-14.2g1	GD (SG)	09/05/13	340	Brass	na	7.4	13.2	672	<0.02	<0.1
47561	26N11W-2.4g1	GD (SG)	12/04/13	116	Brass	na	7.3	13.0	542	0.03	<0.1
47583	24N10E-20.8g1	GD (SG)	10/17/13	226	Brass	na	7.3	12.8	801	0.08	<0.1
47592	24N14W-1.6d2	GD (SG)	10/24/13	176	Copper	na	7.4	13.2	746	0.02	<0.1
47614	25N 2E-1.4f	WE-L	02/20/13	na	Plastic	na	8.2	1.9	610	0.05	<0.1
do.	do.	do.	do.	do.	Copper	Y	??	??	??	2.4	2.5
do.	do.	do.	do.	do.	Chrome	Y	do.	do.	do.	2.4	2.5
47687	20N 7E-2.8c1	GD (SG)	03/14/13	283	Chrome	na	7.4	12.4	726	<0.02	0.8
47692	17N13W-27.6e1	GD (SG)	03/12/13	28	Chrome	na	7.1	13.4	577	0.07	0.5
47698	19N11W-6.5e	WE-L	07/11/13	na	Chrome	na	7.6	23.8	513	0.12	0.2
do.	do.	do.	do.	do.	Chrome	Y	8.7	25.0	279	2.2	2.5
do.	do.	do.	do.	do.	Chrome	Y	8.6	22.7	282	2.2	2.3
47774	11N 3E-35.6a2	AL (SG)	01/22/13	63	Brass	na	7.4	12.9	618	0.16	0.1
47776	9N 6E-14.2f1	GD (SG)	12/17/13	65	Chrome	na	7.5	14.8	697	<0.02	0.2
47811	8N11W-29.4h2	AL (SG)	02/27/13	32	Copper	na	7.0	13.2	631	0.19	0.3
47819	7N11E-31.8a2	PV (S)	12/19/13	269	Chrome	na	8.3	14.3	915	0.14	0.2
50003	16N 6W-12.5g	AL (SG)	07/11/13	55	Brass	na	6.8	12.8	657	0.18	0.3

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
50051	26N 4W-24.5a	GD (SG)	07/25/13	260	Brass	na	7.4	12.4	770	0.28	0.5
50057	24N 5W-3.3h1	AL (SG)	11/14/13	91	Brass	na	7.0	14.0	947	0.24	0.7
50060	25N 5W-35.4d1	AL (SG)	10/10/13	145	Chrome	na	6.8	15.5	1,320	0.87	1.0
50094	9N 5W-25.1c1	MS (L)	12/10/13	70	Chrome	na	6.6	12.3	768	0.03	<0.1
50138	11N 6E-24.1e1	CO (SD)	09/25/13	1,680	Brass	na	7.4	22.3	2,710	0.09	0.5
50203	12N 3W-35.5d2	GD (SG)	05/21/13	85	Chrome	na	6.8	13.2	639	<0.02	0.2
50224	15N2W-12.6g1	GD (SG)	01/29/13	70	Brass?	na	7.3	15.0	806	<0.02	0.8
50251	19N 5W-13.2h2	GD (SG)	12/17/13	145	Chrome	na	7.1	13.1	508	0.08	0.2
50308	21N 8W-6.8e	AL (SG)	11/05/13	96	Chrome	na	7.2	14.2	519	0.15	0.4
50351	9N 5E-7.6d1	CO (SD)	06/11/13	1,572	Copper/ brass?	na	7.8	22.0	4,000	0.03	1.2
50376	25N 2W-16.2g1	GD (SG)	12/09/13	335	Chrome	na	7.2	12.6	583	<0.02	0.3
50383	25N 5W-12.5e	AL (SG)	05/07/13	78	??	na	6.9	13.7	1,270	0.04	0.7
52056	8N 1E-15.a1	AL (SG)	09/24/13	66	Brass	na	6.9	13.0	651	0.13	0.6
52079	4N 9W-4.5a	IE-MR	06/25/13	na	PVC	na	7.8	25.3	417	0.09	1.3
do.	do.	do.	do.	do.	Chrome	N	7.4	24.9	556	0.04	<0.1
do.	do.	do.	do.	do.	Chrome	N	7.3	22.4	428	0.03	0.1
52095	11N 5W-18.4h1	GD (SG)	07/02/13	44	Brass	na	6.8	15.0	636	0.31	0.7
52097	7N 6W-20.3h	IE-L	04/30/13	na	Plastic	na	7.3[5]	14.6[5]	332[5]	0.10	0.6
do.	do.	do.	do.	do.	Plastic	N	??	??	??	0.02	0.1
do.	do.	do.	do.	do.	Plastic	N	do.	do.	do.	0.05	0.1
52099	2S 9W-3.2f	IE-MR	04/04/13	na	Chrome	na	7.5	9.9	469	0.14	0.4

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
do.	do.	do.	do.	do.	Chrome	Y	??	??	??	2.1	1.9
do.	do.	do.	do.	do.	Brass	Y	do.	do.	do.	2.0	1.9
52100	11N 2E30.6c	IE-L	03/21/13	na	Chrome	na	7.8	4.5	294	0.03	0.2
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.07	0.5
do.	do.	do.	do.	do.	Chrome	N	do.	do.	do.	0.07	0.2
52122	15N14W-12.3g2	AL (SG)	01/30/13	85	Brass	na	7.1	13.8	635	<0.02	0.2
52126	9N 4W-36.3h	IE-L	04/03/13	na	Plastic	na	8.2	7.9	310	0.05	0.3
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.07	0.2
do.	do.	do.	do.	do.	Chrome	N	do.	do.	do.	0.06	0.2
52140	15N 5W-13.3h	IE-L	11/26/13		Chrome	na	7.8	8.3	373	0.08	0.5
do.	do.	do.	do.	do.	Chrome	Y	8.8	9.2	248	1.9	1.9
do.	do.	do.	do.	do.	Brass	Y	8.9	16.8	245	1.5	1.7
58059	12N 8W-35.8d1	IE-L	11/05/13	na	Brass/galv steel	na	7.6	12.3	265	0.11	0.3
do.	do.	do.	do.	do.	Chrome	N?	9.0	15.0	321	0.09	0.2
do.	do.	do.	do.	do.	Chrome	N?	9.0	17.0	326	0.12	0.2
58088	9N 7W-10.7g	IE-L	09/24/13	na	Brass	na	7.9	22.8	315	0.13	0.4
do.	do.	do.	do.	do.	Chrome	Y	8.1	23.5	366	0.51	0.7
do.	do.	do.	do.	do.	Chrome	Y	7.8	25.0	388	0.49	0.7
60043	2N 2W-19.5h	IE-R	06/04/13	na	Steel	na	8.0	22.2	329	0.15	0.4
do.	do.	do.	do.	do.	Chrome	N	7.2	22.5	334	0.05	0.4
do.	do.	do.	do.	do.	Chrome	N	6.67	20.9	340	0.07	0.4

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
60049	7S 7W-25.4h	IE-MR	06/05/13	na	??	na	7.2	20.6	304	0.11	1.8
do.	do.	do.	do.	do.	Copper	Y	8.4	20.9	263	0.68	0.7
do.	do.	do.	do.	do.	Chrome	Y	7.9	18.8	285	0.71	0.8
60053	3N 8W-31.2a1	AL (SG)	10/08/13	102	Brass	na	6.7	15.1	947	<0.02	0.1
60058	5N 9W-20.4h2	AL (SG)	06/27/13	92	Copper	na	6.8	14.8	819	<0.02	<0.1
60065	4N 9W13.1c1	GD (SG)	05/16/13	112	Chrome	na	7.0	14.4	631	<0.02	1.4
60068	5S 8W-13.7a	IE-R	08/15/13	na	Chrome	na	7.5	25.1	357	0.06	0.7
do.	do.	do.	do.	do.	Brass	N	7.3	25.0	358	0.06	<0.1
do.	do.	do.	do.	do.	Chrome	N	6.9	27.3	391	0.06	<0.1
60089	3N 8W-5.6d1	AL (SG)	08/13/13	106	Copper/brass	na	6.8	14.1	919	0.02	<0.1
60127	4S11W-1.5a1	AL (SG)	03/06/13	59	Chrome	na	6.5	15.1	872	0.67	0.8
60173	2N 2E-2.3d	IE-L	07/17/13	na	Chrome	na	7.4	28.0	290	0.04	0.2
do.	do.	do.	do.	do.	PVC	N	7.3	28.2	234	0.04	0.1
do.	do.	do.	do.	do.	Chrome	N	7.3	24.1	265	0.04	0.1
60181	5S 5W-7.5b	IE-L	05/21/13	na	PVC	na	7.7	23.4	348	0.10	0.3
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.05	0.2
do.	do.	do.	do.	do.	Chrome	N	do.	do.	do.	0.05	0.3
60184	2S 7W-28.3e	IE-R	12/10/13	na	Cast iron	na	7.4	2.8	478	0.08	0.3
do.	do.	do.	do.	do.	Brass	Y	7.7	3.6	541	0.22	0.1
do.	do.	do.	do.	do.	Chrome	Y	7.5	7.7	596	0.19	0.1
70010	17S 1W-23.1e	U-OR	05/29/13	na	Brass	na	7.8	23.4	307	0.08[6]	0.5[6]

Appendix 1. Well and surface-water intake information, field characteristics of water quality, and concentrations of hexavalent chromium and total chromium in samples from selected source-water aquifers and surface waters used for public supply in Illinois, 2013.—Continued

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; ft, feet below land surface; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; do., ditto; na, not applicable; N, no; Y, yes; ?, uncertain; ??, unrecorded; <, less than; chrome, chrome-plating or similarly appearing metallic plating; galv, galvanized; PVC, polyvinyl chloride]

IEPA well or intake number	USGS well or intake name	Aquifer and principal lithology or glacial provenance and surface-water body	Sample date	Depth of well, total (ft)	Sample-tap material	Lime[1] treatment	pH, water, whole, field (standard units)	Temperature, water (°C)	Specific conductance (µs/cm)	Hexavalent chromium, dissolved (µg/L)	Chromium, total (µg/L)
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.06[6]	<0.1[6]
do.	do.	do.	do.	do.	Brass	N	do.	do.	do.	0.09	0.1
70290	5S 2E-35.3g	IE-L	01/17/13	na	Brass	na	7.8	4.8	300	0.05	0.4
do.	do.	do.	do.	do.	Chrome	Y?	??	??	??	1.1	1.5
do.	do.	do.	do.	do.	Brass	Y?	do.	do.	do.	1.0	1.4
70550	10S 2W-12.2a	U-L	02/07/13	na	Chrome	na	7.9	5.6	106	0.04	0.4
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.04	<0.1
do.	do.	do.	do.	do.	Chrome	N	do.	do.	do.	0.04	<0.1
70620	8S 3W-26.5h	IE-L	02/28/13	na	Brass	na	7.6	5.5	162	0.05	0.3
do.	do.	do.	do.	do.	Chrome	N	??	??	??	0.05	0.2
do.	do.	do.	do.	do.	Copper	N	do.	do.	do.	0.05	0.1
70811	13S 3E-4.8e	IE-L	10/31/13	na	Brass/rubber	na	7.3	15.9	174	0.09	0.1
do.	do.	do.	do.	do.	Chrome	N	8.1	18.0	209	0.08	<0.01
do.	do.	do.	do.	do.	Chrome	N	8.1	18.6	204	0.10	0.1
71531	1N 9E-17.5g1	PV (S)	04/17/13	215	Brass	na	7.7	14.5	1,780	<0.02	0.1

[1] Listing of facilities using lime differed slightly between the two references; for the questionable facilities, treatment was determined by change in water chemistry.

[2] For surface-water facilities, the first sample listing represents raw source water, the second listing represents treated water near the point of treatment, and the third listing represents treated water near the end point of distribution.

[3] It is suspected that this recorded measurement is in error. Efforts to confirm were unsuccessful.

[4] Insufficient volume of buffer solution was added to sample upon collection; laboratory reports pH of sample was within acceptable range upon receipt.

[5] Measurements made without use of flow-through cell attached to the water-quality meter.

[6] Sample temperature was 12.4 °C upon receipt at laboratory.

Appendix 2. Protocols for collecting representative samples of untreated source water and treated water

[Developed by the UL[1] wet chemistry laboratory and modified by the U.S. Geological Survey]

A. Hexavelent Chromium (CrVI) (Method 218.6)

Please read all the instructions before sampling to ensure accurate test results.

Before Sampling

- Check UL-supplied sampling kit for sample bottle, beaker, syringe, filter, and pH buffer solution.
- Remove blue refrigerant (ice) packs from the UL-supplied foam-insulated shipping container and place packs in freezer. They must be completely frozen before returning samples to the laboratory.
- Plan to have samples collected after 11 a.m. and prior to the normal pick-up time of your overnight carrier.
- Don protective gloves (nitrile or latex), replacing ones used for attaching/removing water-quality meter or handling spigot.
- Use previously unused gloves ONLY for handling sampling equipment (after shipping box opened) and collecting sample.

Sampling Steps for Finished Drinking Water

1. Flush the cold water line for 10-15 minutes prior to sample collection, while collecting stabilized field water-quality values.
2. Remove the snap-cap security sample bottle from the bubble-wrap sleeve and open the sample bottle. Do not touch around the edge and interior of the sample bottle and bottle cap.
3a. Sample bottle rinse: fill 1/4 full, close cap, shake, and pour out rinse water; Repeat.
3b. Collect 100 mL sample (i.e. to the 100 mL mark).
4. Pour the entire 1.0 mL pH buffer solution into the 100 mL sample.
5. Push the snap cap back to close the sample bottle and to put the security tab to the secure position. Secure the tab in place with the plastic locking strip.
6. Indicate sampling date, time and name of sampler on both the bottle labels and the enclosed Chain of Custody form. Information on the Chain of Custody and labels must match the sample locations and be complete.
7. Place sample bottle in sealed bubble-wrap sleeve and then into the shipping container.

Sampling Steps for Raw Water

1. Flush the cold water line for 10-15 minutes prior to sample collection, while collecting stabilized field values.
2. Do not touch around the edge and interior of the sample bottle, bottle cap, beaker, and syringe tip, and filter connections.
3. Use the beaker to collect at least 20 mL (1/4 full) sample and swirl the beaker to rinse all inner surfaces of the beaker. Repeat.
4a. Fill beaker to about 100 ml. Pre-rinse filterless syringe by filling ½ full with water from beaker, shake, push water through syringe, Repeat.
4b. Draw up 10 mL of the sample from the beaker into a syringe by placing the tip of the syringe into the sample and pulling up the plunger slowly to the 10 mL mark.
5. Connect the 45-µ syringe filter to the syringe tip.
6. Push the plunger using gentle pressure to filter 10 mL of the sample through the filter as waste; place syringe and filter on clean piece of aluminum foil.
7a. Remove the snap-cap security sample bottle from the bubble-wrap shipping sleeve and open the sample bottle. Do not touch around the edge and interior of the sample bottle and bottle cap.

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[1] The UL Company was formerly known as Underwriters Laboratory.

7b. Remove filter, placing on clean aluminum foil; Draw up 20 ml of the sample from the beaker into the syringe; replace the filter and discharge 10 ml (1/2 syringe volume) of water into the sample bottle; close cap, shake, discharge water; Repeat with remaining 10 ml of water in syringe. Make sure that no water from the syringe drops on the exterior of the filter and into the sample bottle.

7c. Dump any remaining sample from the beaker as waste.

8. Use the rinsed beaker to recollect at least 100 mL sample.

9. Disconnect the filter from the syringe tip and put the filter on a clean surface (e.g. a clean paper towel).

10. Draw up 20 mL of the sample from the beaker into the syringe by placing the tip of the syringe into the sample and pulling up the plunger slowly to the 20 mL mark.

11. Connect the rinsed filter back to the syringe tip. Make sure that no water from the syringe drops on the exterior of the filter and into the sample bottle.

12. Push the plunger using gentle pressure to filter the sample through the filter into the 120 mL sample bottle.

Quantity

☐

13. Repeat Steps 9-12 for 4 more times for a total volume of 100 mL. Make sure that the sample upper level is on the 100 mL mark.

14. Pour the entire 1.0 mL pH buffer solution into the 100 mL sample.

15. Push the snap cap back to close the sample bottle and to put the security tab to the secure position. Secure the tab in place with the plastic locking strip.

16. Indicate sampling date, time and name of sampler on both the bottle labels and the enclosed Chain of Custody form**.** Information on the Chain of Custody and labels must match the sample locations and be complete.

17. Place sample bottle in sealed bubble-wrap sleeve and then into refrigerated foam shipping container.

18. If filter clogs with sediment during steps 12-13, repeat steps 4b, 5, and 6 with extra filter(s) available from drinking-water sampling kits.

Shipping Instructions

- Place 2-3 frozen blue refrigerant packs and the Chain of Custody form into the shipping container along with the chromium (VI) and total chromium samples, and return the container and contents to the laboratory immediately after sample collection.
- Samples must be shipped to the laboratory by an overnight carrier or hand delivered..
- The laboratory must be notified on the day of sample collection of their scheduled arrival at the laboratory on the following day.

THERE WILL BE NO SATURDAY DELIVERIES

Additional Supplies:

- Aluminum foil for placement of sampling equipment during sample collection (store aluminum foil in clean, sealed plastic bag).

2-inch packing tape for sealing tops/bottoms of UL shipping boxes or other larger shipping boxes containing multiple samples.

Refrigerant Packs

- Freeze refrigerant packs prior to use in the foam-insulated shipping containers. Store with other packs in larger cooler when transporting to the field for final use and shipment to help retain their frozen state.

Field Notes/Chain-of-Custody

- Chain of Custody form also will be used to list final stabilized field water-quality values and for field notes of conditions that might affect sample results, including air temperature, weather, composition and cleanliness of sample tap, conditions of sample location and facility, lot number and expiration date of inorganic blank water.

Appendix 2. Protocols for collecting representative samples of untreated source water and treated water—Continued

[Developed by the UL[1] wet chemistry laboratory and modified by the U.S. Geological Survey]

B. Total Chromium (Method 200.8)

Please read all the instructions before sampling to ensure accurate test results.

Before Sampling

- Check UL-supplied sampling kit for sample bottle**.**
- Remove blue refrigerant (ice) packs from the UL-supplied foam-insulated shipping container and place packs in freezer. They must be completely frozen before returning samples to the laboratory.
- Plan to have samples collected after 11 a.m. and prior to the normal pick-up time of your overnight carrier.
- Don protective gloves (nitrile or latex), replacing ones used for attaching/removing water-quality meter or handling spigot.
- Use previously unused gloves ONLY for handling sampling equipment (after shipping box opened) and collecting sample.

Sampling Steps for Raw and Finished Drinking Water

1. Flush the cold water line for 10-15 minutes prior to sample collection, while collecting stabilized field water-quality values.
2. Unscrew the cap from the sample bottle. Do not touch around the edge and interior of the sample bottle and bottle cap.
3a. Sample bottle rinse: fill 1/4 full, replace cap, shake, and pour out rinse water; Repeat.
3b. Collect 100 mL sample (to the neck of the bottle).
4. Screw the cap back to close the sample bottle.
5. Indicate sampling date, time and name of sampler on both the bottle label and the enclosed Chain of Custody form. Information on the Chain of Custody and labels must match the sample locations and be complete.

Shipping Instructions

- Place 2-3 frozen blue refrigerant packs and the Chain of Custody form into the shipping container along with the total chromium and chromium (VI) samples, and return the container and contents to the laboratory immediately after sample collection.
- Sample bottles must be shipped to the laboratory by an overnight carrier or hand delivered.
- The laboratory must be notified on the day of sample collection of their scheduled arrival at the laboratory on the following day.

THERE WILL BE NO SATURDAY DELIVERIES

Additional Supplies:

- Aluminum foil for placement of sampling equipment during sample collection (store foil in clean, sealed plastic bag).

2-inch packing tape for sealing tops/bottoms of UL shipping boxes or other larger shipping boxes containing multiple samples.

Refrigerant Packs

- Freeze refrigerant packs prior to use in the foam-insulated shipping containers. Store with other packs in larger cooler when transporting to the field for final use and shipment to help retain their frozen state.

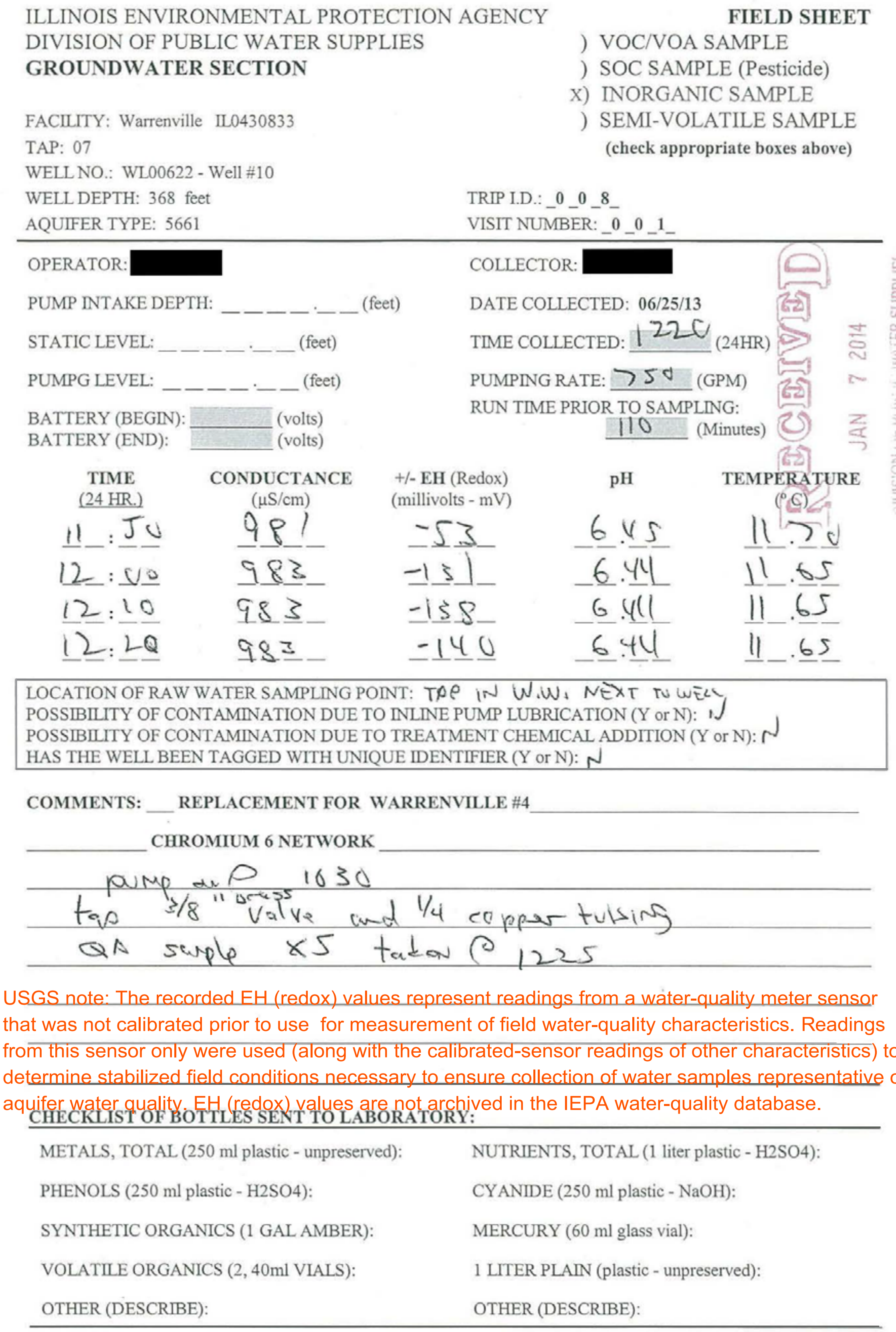
Field Notes/Chain-of-Custody

- Chain of Custody form also will be used to list final stabilized field water-quality values and for field notes of conditions that might affect sample results, including air temperature, weather, composition and cleanliness of sample tap, conditions of sample location and facility, lot number and expiration date of inorganic blank water.

---

[1] The UL Company was formerly known as Underwriters Laboratory.

Appendix 3. Example Illinois Environmental Protection Agency field sampling record



ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
DIVISION OF PUBLIC WATER SUPPLIES
GROUNDWATER SECTION

FIELD SHEET
( ) VOC/VOA SAMPLE
( ) SOC SAMPLE (Pesticide)
(x) INORGANIC SAMPLE
( ) SEMI-VOLATILE SAMPLE
(check appropriate boxes above)

FACILITY: Warrenville IL0430833
TAP: 07
WELL NO.: WL00622 - Well #10
WELL DEPTH: 368 feet
AQUIFER TYPE: 5661

TRIP I.D.: _0_0_8_
VISIT NUMBER: _0_0_1_

OPERATOR: [redacted]
COLLECTOR: [redacted]

PUMP INTAKE DEPTH: _____.__ (feet)
STATIC LEVEL: _____.__ (feet)
PUMPG LEVEL: _____.__ (feet)
BATTERY (BEGIN): ____ (volts)
BATTERY (END): ____ (volts)

DATE COLLECTED: 06/25/13
TIME COLLECTED: 1220 (24HR)
PUMPING RATE: 750 (GPM)
RUN TIME PRIOR TO SAMPLING: 110 (Minutes)

RECEIVED
JAN 7 2014
DIVISION OF PUBLIC WATER SUPPLIES
ENVIRONMENTAL PROTECTION AGENCY
STATE OF ILLINOIS

TIME (24 HR.)	**CONDUCTANCE** (µS/cm)	**+/- EH** (Redox) (millivolts - mV)	**pH**	**TEMPERATURE** (°C)
11:50	981	-53	6.45	11.70
12:00	983	-131	6.44	11.65
12:10	983	-138	6.44	11.65
12:20	983	-140	6.44	11.65

LOCATION OF RAW WATER SAMPLING POINT: TAP IN W.W. NEXT TO WELL
POSSIBILITY OF CONTAMINATION DUE TO INLINE PUMP LUBRICATION (Y or N): N
POSSIBILITY OF CONTAMINATION DUE TO TREATMENT CHEMICAL ADDITION (Y or N): N
HAS THE WELL BEEN TAGGED WITH UNIQUE IDENTIFIER (Y or N): N

COMMENTS: ___ **REPLACEMENT FOR WARRENVILLE #4** ___
___ **CHROMIUM 6 NETWORK** ___
pump on @ 1630
tap 3/8" brass Valve and 1/4 copper tubing
QA sample x5 taken @ 1225

USGS note: The recorded EH (redox) values represent readings from a water-quality meter sensor that was not calibrated prior to use for measurement of field water-quality characteristics. Readings from this sensor only were used (along with the calibrated-sensor readings of other characteristics) to determine stabilized field conditions necessary to ensure collection of water samples representative of aquifer water quality. EH (redox) values are not archived in the IEPA water-quality database.

CHECKLIST OF BOTTLES SENT TO LABORATORY:

METALS, TOTAL (250 ml plastic - unpreserved):
PHENOLS (250 ml plastic - H2SO4):
SYNTHETIC ORGANICS (1 GAL AMBER):
VOLATILE ORGANICS (2, 40ml VIALS):
OTHER (DESCRIBE):

NUTRIENTS, TOTAL (1 liter plastic - H2SO4):
CYANIDE (250 ml plastic - NaOH):
MERCURY (60 ml glass vial):
1 LITER PLAIN (plastic - unpreserved):
OTHER (DESCRIBE):

Appendix 4. Example analytical result report and quality-assurance documentation provided by UL laboratory

LABORATORY REPORT

This report contains 10 pages.
(including the cover page)

If you have any questions concerning this report, please do not hesitate to call us at (800) 332-4345 or (574) 233-4777.

This report may not be reproduced, except in full, without written approval from UL.

NELAC NARRATIVE PAGE

Client: Illinois Environmental Protection Agency Report #: 300502NP

Underwriters Laboratories is a NELAP accredited laboratory. All reported results meet the requirements of the NELAC standards, unless otherwise noted.

UL contact person: [redacted]

NELAP requires complete reporting of deviations from method requirements, regardless of the suspected impact on the data. Quality control failures not reported within the report summary are noted here.

Method 218.6

In the Method 218.6 analysis, the Hexavalent Chromium recovery in the MSD (114%) was outside the acceptance limits of 90-110%.

There were no additional quality control failures.

Note: This report may not be reproduced, except in full, without written approval from UL. UL is accredited by the National Environmental Laboratory Accreditation Program (NELAP).

[redacted]	Senior Project Manager	Digitally signed by j[redacted] Date: 2013.08.21 13:40:57 -04'00'
Authorized Signature	Title	Date

Laboratory Report

Client:	Illinois Environmental Protection Agency	Report:	300502
Attn:	[redacted]	Priority:	Standard Written
	1021 North Grand Avenue East	Status:	Final
	Springfield, IL 62702	PWS ID:	IL1795780

Copies to: [redacted]

Sample Information

UL ID #	Client ID	Method	Collected Date / Time	Collected By:	Received Date / Time
2865219	WL50051 #3	218.6	07/25/13 11:40	Client	07/26/13 09:45
2865220	WL50051 #3	200.8	07/25/13 11:40	Client	07/26/13 09:45

Report Summary

Note: See attached page for additional comments.

Project: North Tazewell PWD

Detailed quantitative results are presented on the following pages. The results presented relate only to the samples provided for analysis.

We appreciate the opportunity to provide you with this analysis. If you have any questions concerning this report, please do not hesitate to call [redacted]

Note: This report may not be reproduced, except in full, without written approval from UL. UL is accredited by the National Environmental Laboratory Accreditation Program (NELAP).

[redacted] Senior Project Manager Digitally signed by j[redacted]
Date: 2013.08.21 13:41:05 -04'00'

Authorized Signature	Title	Date

Client Name: Illinois Environmental Protection Agency
Report #: 300502

Client Name: Illinois Environmental Protection Agency Report #: 300502

Sampling Point: WL50051 #3 PWS ID: IL1795780

General Chemistry

Analyte ID #	Analyte	Method	Reg Limit	MRL†	Result	Units	Preparation Date	Analyzed Date	UL ID #
18540-29-9	Chromium, Hexavalent	218.6	---	0.02	**0.28**	ug/L	---	07/26/13 17:03	2865219

Metals

Analyte ID #	Analyte	Method	Reg Limit	MRL†	Result	Units	Preparation Date	Analyzed Date	UL ID #
7440-47-3	Chromium, LL	200.8	---	0.1	**0.5**	ug/L	---	08/05/13 12:47	2865220

† UL has demonstrated it can achieve these report limits in reagent water, but can not document them in all sample matrices.

Reg Limit Type:	MCL	SMCL	AL
Symbol:	*	^	!

Lab Definitions

Continuing Calibration Check Standard (CCC) / Continuing Calibration Verification (CCV) / Initial Calibration Verification Standard (ICV) / Initial Performance Check (IPC) - is a standard containing one or more of the target analytes that is prepared from the same standards used to calibrate the instrument. This standard is used to verify the calibration curve at the beginning of each analytical sequence, and may also be analyzed throughout and at the end of the sequence. The concentration of continuing standards may be varied, when prescribed by the reference method, so that the range of the calibration curve is verified on a regular basis.

Internal Standards (IS) - are pure compounds with properties similar to the analytes of interest, which are added to field samples or extracts, calibration standards, and quality control standards at a known concentration. They are used to measure the relative responses of the analytes of interest and surrogates in the sample, calibration standard or quality control standard.

Laboratory Duplicate (LD) - is a field sample aliquot taken from the same sample container in the laboratory and analyzed separately using identical procedures. Analysis of laboratory duplicates provides a measure of the precision of the laboratory procedures.

Laboratory Fortified Blank (LFB) / Laboratory Control Sample (LCS) - is an aliquot of reagent water to which known concentrations of the analytes of interest are added. The LFB is analyzed exactly the same as the field samples. LFBs are used to determine whether the method is in control.

Laboratory Method Blank (LMB) / Laboratory Reagent Blank (LRB) - is a sample of reagent water included in the sample batch analyzed in the same way as the associated field samples. The LMB is used to determine if method analytes or other background contamination have been introduced during the preparation or analytical procedure. The LMB is analyzed exactly the same as the field samples.

Laboratory Trip Blank (LTB) / Field Reagent Blank (FRB) - is a sample of laboratory reagent water placed in a sample container in the laboratory and treated as a field sample, including storage, preservation, and all analytical procedures. The FRB/LTB container follows the collection bottles to and from the collection site, but the FRB/LTB is not opened at any time during the trip. The FRB/LTB is primarily a travel blank used to verify that the samples were not contaminated during shipment.

Matrix Spike Duplicate Sample (MSD) / Laboratory Fortified Sample Matrix Duplicate (LFSMD) - is a sample aliquot taken from the same field sample source as the Matrix Spike Sample to which known quantities of the analytes of interest are added in the laboratory. The MSD is analyzed exactly the same as the field samples. Analysis of the MSD provides a measure of the precision of the laboratory procedures in a specific matrix.

Matrix Spike Sample (MS) / Laboratory Fortified Sample Matrix (LFSM) - is a sample aliquot taken from field sample source to which known quantities of the analytes of interest are added in the laboratory. The MS is analyzed exactly the same as the field samples. The purpose is to demonstrate recovery of the analytes from a sample matrix to determine if the specific matrix contributes bias to the analytical results.

Quality Control Standard (QCS) / Second Source Calibration Verification (SSCV) - is a solution containing known concentrations of the analytes of interest prepared from a source different from the source of the calibration standards. The solution is obtained from a second manufacturer or lot if the lot can be demonstrated by the manufacturer as prepared independently from other lots. The QCS sample is analyzed using the same procedures as field samples. The QCS is used as a check on the calibration standards used in the method on a routine basis.

Reporting Limit Check (RLC) / Initial Calibration Check Standard (ICCS) - is a procedural standard that is analyzed each day to evaluate instrument performance at or below the minimum reporting limit (MRL).

Surrogate Standard (SS) / Surrogate Analyte (SUR) - is a pure compound with properties similar to the analytes of interest, which is highly unlikely to be found in any field sample, that is added to the field samples, calibration standards, blanks and quality control standards before sample preparation. The SS is used to evaluate the efficiency of the sample preparation process.

110 S. Hill Street
South Bend, IN 46617
T: 1.800.332.4345
F: 1.574.233.8207

235175
Order # 231902
Batch # 365562

www.ul.com/water

Shaded area for UL use only

CHAIN OF CUSTODY RECORD

Page 1 of 1

REPORT TO:

BILL TO:

SAMPLER (Check ONE)
☒ Ryan Bennet
☐ Ed Wagner
☐ Alan Fuhrmann
☐ Joe Konczyk
☐ Greg White

SYSTEM ID: IL 1795780

STATE (sample origin):

PROJECT NAME:

PO#:

Compliance: Yes ☐ No ☐

POPULATION SERVED:

SOURCE WATER:

LAB Number	COLLECTION DATE	COLLECTION TIME	AM	PM	SAMPLE LOCATION (SITE)	FACILITY	TEST NAME	CHLORINATED YES	CHLORINATED NO	# OF CONTAINERS	MATRIX CODE	TURNAROUND TIME
1 2865219	7-25	11:40	X		WL 50051 #3	North Tazewell PWD	Chromium 6					
2 ↓ 220	7-25	11:40	X		WL 50051 #3	North Tazewell PWD	Total Chromium, LL					

Field Parameter			Code
Pump Rate:	1009	(gal/min)	9997
Conductance:	770		9910
Field EH:	200		9998
Field pH:	739		1926
Field Temp:	12.41	° C	9911
Run Time:	60	min	6002
Static Level:		ft.	6000
Pumping Level:		ft.	6001

USGS note: The recorded EH (redox) values represent readings from a water-quality meter sensor that was not calibrated prior to use for measurement of field water-quality characteristics. Readings from this sensor only were used (along with the calibrated-sensor readings of other characteristics) to determine stabilized field conditions necessary to ensure collection of water samples representative of aquifer water quality. EH (redox) values are not archived in the IEPA water-quality database.

Relinquished by:	Date	Time
[redacted]	7-25-13	14:30 AM PM

LAB COMMENTS: Brass sample tap

Received by:	Date	Time
[redacted]	7-26-13	0945 AM PM

CONDITIONS UPON RECEIPT (check one):
X Iced: Wet / [✓ Blue]
______ Ambient
2.6 o C Upon Receipt
______ N/A

Matrix Codes	
Drinking Water	DW
Reagent Water	RW
Ground Water	GW
Surface Water	SW

TURN-AROUND TIME (TAT) - SURCHARGES

SW = Standard Written: (15 working days)	0%
RV* = Rush Verbal: (5 working days)	50%
RW* = Rush Written: (5 working days)	75%
IV* = Immediate Verbal: (3 working days)	100%
IW* =Immediate Written: (3 working days)	125%
SP* = Weekend, Holiday	CALL
STAT* = Less than 48 hours	CALL

* Please call, expedited service not available for all testing

Samples received unannounced with less than 48 hours holding time remaining may be subject to additional charges.

06-LO-F0435 Issue 2.0

UL Drinking Water Laboratory
Extended Result Record Sheet

Run Number: 182057	Instrument: IC DP	Method(s): 218.6
PC File Name: 072613A	Analyst: [redacted]	Submitted By: [redacted]
Order Number: 235175	Receipt Batch: 300502	Today's Date: 08/09/2013

Client: Illinois Environmental Protection Agency / [redacted]

Generated By: [redacted]

Sample ID: 2865948 Type: Laboratory Reagent Blank
Extracted: N/A Analyzed: 07/26/2013 15:45 Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
18540-29-9	Chromium, Hexavalent	0.02	0.0000	< 0.02	ug/L

Sample ID: 2865949 Type: Instrument Performance Check
Extracted: N/A Analyzed: 07/26/2013 15:58 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	0.9816	98	90-110	Pass

Sample ID: 2865950 Type: Quality Control Sample
Extracted: N/A Analyzed: 07/26/2013 16:11 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	1.0245	102	90-110	Pass

Sample ID: 2865951 Type: Laboratory Fortified Blank
Extracted: N/A Analyzed: 07/26/2013 16:24 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	1.0617	106	90-110	Pass

Sample ID: 2865219 Type: Field Sample Site: WL50051 #3
Extracted: N/A Analyzed: 07/26/2013 17:03 Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
18540-29-9	Chromium, Hexavalent	0.02	0.2807	0.28	ug/L

Sample ID: 2865953 Type: Matrix Spike of 2865219 Site: WL50051 #3
Extracted: N/A Analyzed: 07/26/2013 17:16 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	Parent Amt	%Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	1.3463	0.2807	107	90-110	Pass

Sample ID: 2865954 Type: Matrix Spike Duplicate of 2865219 Site: WL50051 #3
Extracted: N/A Analyzed: 07/26/2013 17:31 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	Parent Amt	%Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	1.4217	0.2807	114	90-110	Fail

Sample ID: 2865955 Type: Reporting Level Check
Extracted: N/A Analyzed: 07/26/2013 17:57 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	0.02	0.0259	129	50-150	Pass

Sample ID: 2865956 Type: Instrument Performance Check
Extracted: N/A Analyzed: 07/26/2013 18:10 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
18540-29-9	Chromium, Hexavalent	1.0	1.0023	100	90-110	Pass

NOTE: The dilution factor is included
in the percent recovery calculation.

UL Drinking Water Laboratory
Extended Result Record Sheet

Run Number: 182057
PC File Name: 072613A
Order Number: 235175

Instrument: IC DP
Analyst: [redacted]
Receipt Batch: 300502

Method(s): 218.6
Submitted By: [redacted]
Today's Date: 08/09/2013

Client: Illinois Environmental Protection Agency / [redacted]

Generated By: [redacted]

Sample ID: 2865957
Extracted: N/A

Type: Laboratory Reagent Blank
Analyzed: 07/26/2013 18:23

Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
18540-29-9	Chromium, Hexavalent	0.02	0.0000	< 0.02	ug/L

UL Drinking Water Laboratory
Extended Result Record Sheet

Run Number: 182316	Instrument: ICP-MS CN	Method(s): 200.8
PC File Name:	Analyst: [redacted]	Submitted By: [redacted]
Order Number: 235175	Receipt Batch: 300502	Today's Date: 08/09/2013

Client: Illinois Environmental Protection Agency / [redacted]

Generated By: [redacted]

Sample ID: 2852664 Type: Initial Cali. Verification
Extracted: N/A Analyzed: 08/05/2013 12:26 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	0.9939	99	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	1.0059	101	60-125	Pass
7440-47-3	Chromium, LL	1.0	1.0070	101	90-110	Pass

Sample ID: 2852665 Type: Initial Calibration Blank
Extracted: N/A Analyzed: 08/05/2013 12:28 Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
7440-20-2	IS-Scandium Channel 1	N/A	0.9877	99	% Recovery
7440-65-5	IS-Yttrium Channel 1	N/A	1.0000	100	% Recovery
7440-47-3	Chromium, LL	0.1	-0.0042	< 0.1	ug/L

Sample ID: 2822996 Type: Quality Control Sample
Extracted: N/A Analyzed: 08/05/2013 12:31 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	0.9939	99	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	0.9980	100	60-125	Pass
7440-47-3	Chromium, LL	5.0	5.0600	101	90-110	Pass

Sample ID: 2852666 Type: Laboratory Reagent Blank
Extracted: N/A Analyzed: 08/05/2013 12:34 Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
7440-20-2	IS-Scandium Channel 1	N/A	1.0031	100	% Recovery
7440-65-5	IS-Yttrium Channel 1	N/A	1.0040	100	% Recovery
7440-47-3	Chromium, LL	0.1	-0.0049	< 0.1	ug/L

Sample ID: 2852667 Type: Reporting Level Check
Extracted: N/A Analyzed: 08/05/2013 12:36 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	0.9939	99	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	1.0059	101	60-125	Pass
7440-47-3	Chromium, LL	0.1	0.0908	91	82-122	Pass

Sample ID: 2852668 Type: Laboratory Fortified Blank
Extracted: N/A Analyzed: 08/05/2013 12:39 Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	0.9847	98	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	0.9980	100	60-125	Pass
7440-47-3	Chromium, LL	5.0	5.0310	101	85-115	Pass

Sample ID: 2865220 Type: Field Sample Site: WL50051 #3
Extracted: N/A Analyzed: 08/05/2013 12:47 Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
7440-20-2	IS-Scandium Channel 1	N/A	1.0337	103	% Recovery
7440-65-5	IS-Yttrium Channel 1	N/A	1.0099	101	% Recovery
7440-47-3	Chromium, LL	0.1	0.4723	0.5	ug/L

NOTE: The dilution factor is included
in the percent recovery calculation.

UL Drinking Water Laboratory
Extended Result Record Sheet

Run Number: 182316
PC File Name:
Order Number: 235175

Instrument: ICP-MS CN
Analyst: [redacted]
Receipt Batch: 300502

Method(s): 200.8
Submitted By: [redacted]
Today's Date: 08/09/2013

Client: Illinois Environmental Protection Agency / [redacted]

Generated By: [redacted]

Sample ID: 2869749
Extracted: N/A

Type: Matrix Spike of 2865220
Analyzed: 08/05/2013 12:50

Site: WL50051 #3
Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	Parent Amt	%Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	1.0613	N/A	106	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	1.0277	N/A	103	60-125	Pass
7440-47-3	Chromium, LL	1.0	1.3740	0.4723	90	70-130	Pass

Sample ID: 2823004
Extracted: N/A

Type: Continuing Cali. Verification
Analyzed: 08/05/2013 12:58

Dil Factor: 1.000

CAS Number	Parameter	Target	Amount	% Rec	Limits	P/F
7440-20-2	IS-Scandium Channel 1	1.0	1.0736	107	60-125	Pass
7440-65-5	IS-Yttrium Channel 1	1.0	1.0653	107	60-125	Pass
7440-47-3	Chromium, LL	1.0	1.0880	109	85-115	Pass

Sample ID: 2823005
Extracted: N/A

Type: Continuing Calibration Blank
Analyzed: 08/05/2013 13:00

Dil Factor: 1.000

CAS Number	Parameter	MRL	Amount	Report	Units
7440-20-2	IS-Scandium Channel 1	N/A	1.0552	106	% Recovery
7440-65-5	IS-Yttrium Channel 1	N/A	1.0554	106	% Recovery
7440-47-3	Chromium, LL	0.1	0.0577	< 0.1	ug/L

NOTE: The dilution factor is included
in the percent recovery calculation.

Mills and Cobb—**Hexavalent and Total Chromium in Source-Water Aquifers and Surface Waters Used for Public Supply, Illinois**—Scientific Investigations Report 2015–5020

ISSN 2328-0328 (online)
http://dx.doi.org/10.3133/sir20155020