Origin of Hexavalent Chromium in Drinking Water Wells from the Piedmont Aquifers of North Carolina

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S *Supporting Information*

ABSTRACT: Hexavalent chromium $[Cr(VI)]$ is a known pulmonary carcinogen. Recent detection of $Cr(VI)$ in drinking water wells in North Carolina has raised public concern about contamination of drinking water wells by nearby coal ash ponds. Here we report, for the first time, the prevalence of Cr and $Cr(VI)$ in drinking water wells from the Piedmont region of central North Carolina, combined with a geochemical analysis to determine the source of the elevated $Cr(VI)$ levels. We show that $Cr(VI)$ is the predominant species of dissolved Cr in groundwater and elevated levels of Cr and $Cr(VI)$ are found in wells located both near and far (>30 km) from coal ash ponds. The geochemical characteristics, including the overall chemistry, boron to chromium ratios, and strontium isotope ($^{87}Sr/^{86}Sr$) variations in groundwater with elevated $Cr(IV)$ levels, are different from those of coal ash leachates. Alternatively, the groundwater chemistry and Sr isotope variations are consistent with water−rock interactions as the major source for $Cr(VI)$ in groundwater. Our results indicate that $Cr(VI)$ is most likely naturally occurring and ubiquitous in groundwater from the Piedmont region in the eastern United States, which could pose health risks to residents in the region who consume well water as a major drinking water source.
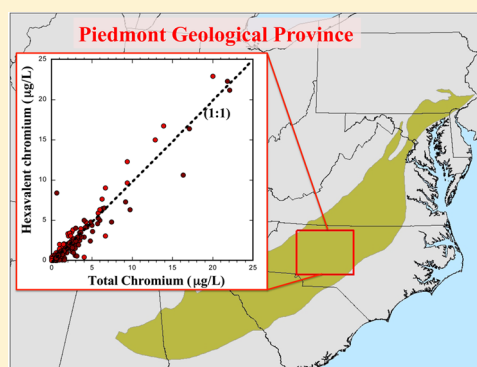
INTRODUCTION

Since the early findings of hexavalent chromium $[Cr(VI)]$ in drinking water in the Hinkley community of San Bernardino County, California, presumably from $Cr(VI)$ additives at water-cooling towers from gas compressor facilities, there has been a persistent controversy about the sources of $Cr(VI)$ in groundwater and its human health impacts.[1] Most Cr in aquatic systems occurs as either the trivalent chromium $[Cr(III)]$ cation Cr^{3+} or $Cr(VI)$ oxyanions, such as the monovalent $HCrO_4^-$ and divalent CrO_4^{2-} species.[2−4] All $Cr(VI)$ compounds are strong oxidizing agents and are recognized by the World Health Organization (WHO) as "carcinogenic to humans (Group 1)",[15] and $Cr(VI)$ is recognized as a pulmonary carcinogen.[5−14] However, the U.S. Environmental Protection Agency (EPA) does not regulate individual Cr species, and the drinking water standard includes only total Cr $[Cr_T,$ maximum contaminant level (MCL) of 100 $\mu g/L];[4]$ the most updated 2003 WHO guidelines for drinking water include only total Cr with an upper limit of 50 $\mu g/L.[15]$ The absence of $Cr(VI)$ from the drinking water regulations was explained by analytical limitation and the assumption that the speciation of Cr favors the predominance of the less toxic $Cr(III)$ under typical environmental conditions.[4,15] To date, only the state of California has issued a specific MCL of 10 $\mu g/$

L and a public health goal (PHG) of 0.02 $\mu g/L$ for $Cr(VI)$ in drinking water.[16]

It is commonly assumed that the occurrence of $Cr(VI)$ in drinking water wells is directly associated with human activities, and any detection of $Cr(VI)$ infers anthropogenic contamination.[4,15] However, recent reports have established that naturally occurring $Cr(VI)$ is prevalent in groundwater from specific aquifer systems composed of ultramafic rocks, known to be enriched with Cr relative to other rock types.[17] Elevated $Cr(VI)$ levels were reported in groundwater associated with ultramafic aquifers in California,[18−21] Arizona,[22] Mexico,[23] Argentina,[24] Brazil,[25] Italy,[26] and Greece.[27] Experimental work demonstrated that the presence of manganese oxide minerals within ultramafic- and serpentinite-derived soils and/or sediments can trigger the oxidation of Cr, leading to the presence of naturally occurring $Cr(VI)$ in aquifers.[28]

Recent detection of $Cr(VI)$ in drinking water wells near coal ash ponds in North Carolina[29] has been attributed to leaking from nearby coal ash ponds because an elevated Cr levels have been reported in coals and coal ash residuals (CCRs).[30−33] This
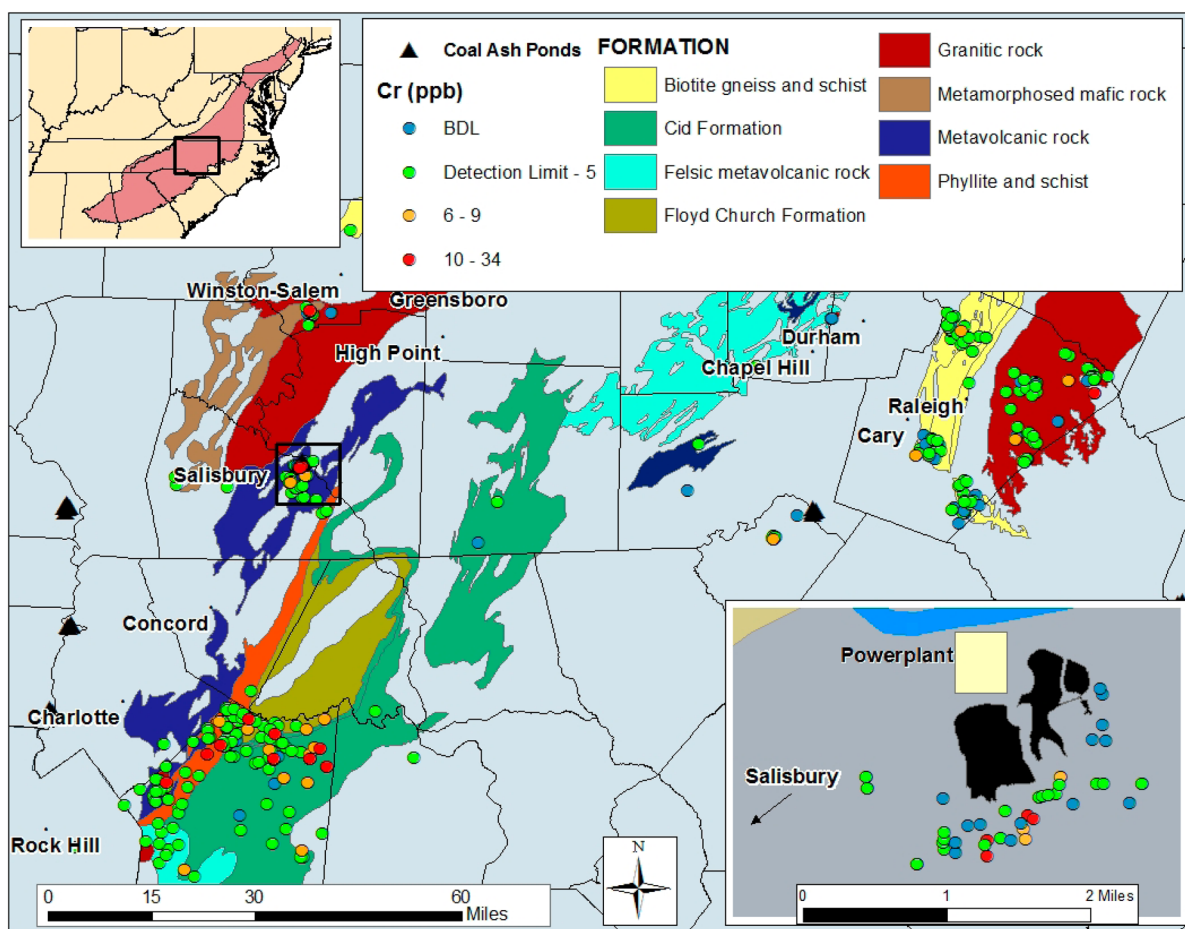
Figure 1. Distribution of total Cr concentrations (ranked by color, in micrograms per liter) in drinking water wells, coal ash ponds, and selective geological formations in the Piedmont region of North Carolina. The small inset map at the top left shows the distribution of the Piedmont geology in the southeastern United States. The bottom inset map shows the distribution of Cr near coal ash ponds close to Salisbury, NC. The felsic metavolcanic rock and granitic rock categories are primarily felsic formations. The Cid, Floyd Church, metamorphosed mafic rock, and metavolcanic formations are of mixed character with varying levels of mafic components. The biotite gneiss and schist and phyllite and schist categories are characterized as general metamorphic bodies. The Cr concentrations in groundwater from the different formations are reported in Table S2. Geological data and location of coal ash ponds were retrieved from U.S. Geological Survey database[44] and Southern Alliance for Clean Energy.[45]

study aims to determine whether coal ash ponds are causing the Cr(VI) contamination in local aquifers or if Cr(VI) is naturally occurring and ubiquitously distributed in groundwater across the Piedmont region. The study is based on systematic measurements of Cr_T and Cr(VI) in groundwater from different aquifers and varying distances from coal ash ponds in the Piedmont region of North Carolina, combined with geochemical and strontium isotope tracers known to be indicative of coal ash contamination and water–rock interactions.[34−36] Previous studies have observed elevated Sr (>150 μg/L) and B (>100 μg/L) levels and distinct Sr isotope ratios ($^{87}Sr/^{86}Sr$ = 0.7095−0.7120) in effluent discharged from coal ash ponds and in contaminated surface and groundwater.[34−36] The Sr and B tracers are particularly useful for delineating the release of coal ash pond water because they are sensitive to very small contributions of contaminated water to the environment.[35,36] We hypothesize that Cr(VI) contamination from coal ash ponds will be associated with modification of the chemical and isotope compositions of the groundwater toward a coal ash geochemical signature.[34−36]

MATERIALS AND METHODS

Water samples in the study were collected from domestic groundwater wells in central North Carolina and were analyzed for major and trace elements (n = 376). A subset of these groundwater samples were analyzed for Cr(VI) (n = 77) and stable isotopes of strontium ($^{87}Sr/^{86}Sr$; n = 45). Water samples were collected before any treatment systems following standard methods.[37] Anions were measured by ion chromatography (IC) on a Dionex IC DX-2100 instrument; major cations were measured by direct current plasma optical emission spectrometry (DCP-OES) and trace elements by a VG PlasmaQuad-3 inductively coupled plasma mass spectrometer (ICP-MS). The DCP and ICP-MS instruments were calibrated to the National Institute of Standards and Technology 1643e standard. The detection limit of ICP-MS for each element was determined by dividing 3 times the standard deviation of repeated blank measurements by the slope of the external standard. Cr(VI) was measured as chromate according to a modified version of U.S. EPA Method 218.6.[38] This method is based on anion exchange chromatography on a Thermo Scientific Dionex IonPac AS7 column (4 mm × 250 mm) with a method detection limit (MDL) for chromate of 0.004 μg/L and a reporting limit of 0.012 μg/L (see the text of the Supporting

Information). Strontium isotopes were analyzed by thermal ionization mass spectrometry (TIMS) on a ThermoFisher Triton instrument at Duke University. The external reproducibility of $^{87}Sr/^{86}Sr$ ratios was comparable to standard NIST987 (0.710265 ± 0.000006).

Geospatial analysis of data was conducted using ArcMap version 10.3.1. The background on the hydrogeology and geological map is provided in the text of the Supporting Information. Statistical analyses were performed using R (version 3.2.0). All correlations were Spearman nonparametric correlations, and the reported r is the Spearman rank coefficient, rho. The nonparametric Wilcoxon rank sum test was used to determine if concentration mean ranks differ between different populations.

■ RESULTS AND DISCUSSION

Geochemical Characteristics of Piedmont Groundwater. Total Cr (Cr_T) concentrations ranged from below the reporting limit (0.0016 μg/L) to 33.8 μg/L (Figure 1). In the subset of samples ($n = 77$) analyzed for Cr(VI), Cr(VI) concentrations varied from below the reporting limit (0.012 μg/L) to 22.9 μg/L and were highly correlated to Cr_T [slope of ~1; $r^2 = 0.93$; $p < 0.001$ (Figure 2)]. Our data are consistent
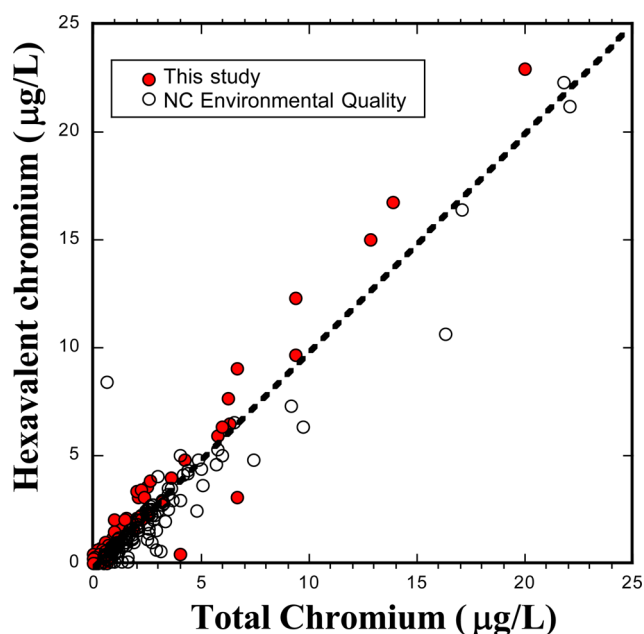

Figure 2. Hexavalent chromium concentration vs total Cr concentration in groundwater analyzed in this study (red circles) and reported by the North Carolina Department of Environmental Quality[25] (○). Note the high correlation of Cr(VI) to Cr_T in both data sets with an r^2 of 0.93 ($p < 0.001$; $n = 77$) reported in this study and an r^2 of 0.90 ($p < 0.001$; $n = 129$) in NC-DEQ data. The ~1:1 ratio in most of the samples indicates that Cr(VI) is the predominant species of dissolved Cr in the Piedmont groundwater.

with data reported by the North Carolina Department of Environmental Quality[25] for residents near coal ash impoundments ($n = 129$) that show the same range of Cr(VI) concentrations and a high correlation between Cr(VI) and Cr_T [slope of ~0.9; $r^2 = 0.90$; $p < 0.001$ (Figure 2)]. The average Cr(VI)/Cr_T ratio of ~1 indicates that Cr(VI) is the predominant species of dissolved Cr in groundwater and accounts for nearly all of the dissolved Cr. While the NC-DEQ

data are restricted to wells located near coal ash ponds, our data collection included wells located far (up to 75 km) from coal ash impoundments (Figure 1).

Strontium concentrations in the groundwater ranged from the detection limit (0.25 μg/L) to 3426 μg/L, with low Sr/Ca ratios [<0.006 (Figure 3A)]. Groundwater from a Cr(VI)-rich
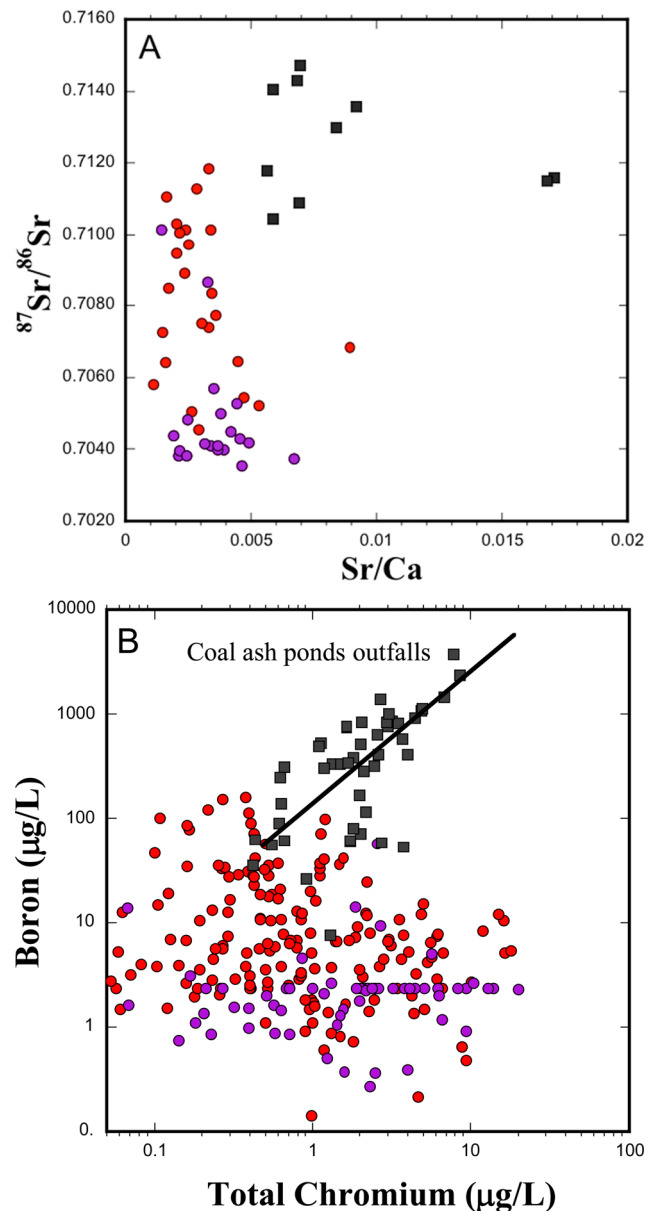

Figure 3. Variations of (A) $^{87}Sr/^{86}Sr$ vs Sr/Ca and (B) B vs total Cr (log scale) in groundwater from the Piedmont region (red and purple circles) as compared to that of effluent discharge from coal ash ponds' outfalls in North Carolina (black squares; data from ref 31). The data show systematically lower $^{87}Sr/^{86}Sr$, Sr/Ca, and B/Cr ratios in groundwater than in coal ash effluents. Groundwater from aquifers composed of metavolcanic rocks (purple circles) is characterized by distinctively lower $^{87}Sr/^{86}Sr$, Sr/Ca, and B contents relative to those of groundwater from other aquifers and coal ash effluents. The combined data indicate that the chemistry of the Piedmont groundwater is different from the composition of coal ash waters, particularly for groundwater from metavolcanic aquifers that are located near coal ash ponds ($n = 16$), thus ruling out the possibility of the contamination of drinking water wells by coal ash ponds.

metavolcanic aquifer in Rowan County located near a coal ash pond ($n = 16$) (Figure 1) and aquifers containing mafic rocks from other counties in the Piedmont region ($n = 7$) had low $^{87}Sr/^{86}Sr$ ratios [0.7041 ± 0.0005 (Figure 3A)]. Groundwater from the other aquifers showed large variations in $^{87}Sr/^{86}Sr$ (a range of 0.7052−0.7119), with higher $^{87}Sr/^{86}Sr$ ratios in the felsic and phyllite and schist aquifers [0.7074−0.7119 (Figure S3)]. Boron concentrations from the Piedmont region were low (a range of 0.09−159.2 μg/L, median of 3.7 μg/L) with low B/Cr_T ratios [median of 8.6 (Figure 3B)]. In particular, groundwater from wells from the metavolcanic aquifer near coal ash ponds with high Cr(VI) concentrations in Rowan County (see the inset map in Figure 1) had systematically low B concentrations [median of 2.3 ± 17.3 μg/L (Figure S4)] and low B/Cr_T ratios (<200).

Tracing the Source of Hexavalent Chromium. Previous studies have shown that coal ash effluents and coal ash-contaminated groundwater have high concentrations of B and Sr with distinctive radiogenic Sr isotope ratios, which are different in some cases from those in natural waters.[34−36,39−41] Waters impacted by CCR effluents typically have high B and Sr concentrations (above background levels of 100 and 150 μg/L, respectively), high Sr/Ca ratios (>0.006), and high $^{87}Sr/^{86}Sr$ ratios (>0.70975).[34−36] In shallow groundwater monitoring wells around coal ash ponds in North Carolina, the B levels reached 5000 μg/L.[36] The low B concentrations and B/Cr_T, Sr/Ca (<0.006), and $^{87}Sr/^{86}Sr$ ratios of the Cr(VI)-rich groundwater in this study, including wells located near (<5 km) a coal ash pond, are inconsistent with the geochemistry expected for CCR-impacted water (Figure 3A). The low $^{87}Sr/^{86}Sr$ ratios observed in the groundwater in Rowan County are consistent with a nonradiogenic Sr isotope composition that is typical for the mafic rocks that are prevalent in this aquifer, indicating that Sr is derived from water−rock interactions and not from coal ash pond contamination. Higher $^{87}Sr/^{86}Sr$ ratios were observed in felsic aquifers and other nonmafic aquifers (Figure S3); however, these aquifers were not associated with high Cr(VI) and in many cases were located far from coal ash ponds.

Data from coal ash pond effluents in North Carolina[34] show that B is strongly correlated to Cr_T [$r^2 = 0.68$; $p < 0.001$ (Figure 3B)], with high B/Cr_T ratios of ∼297. In contrast, all groundwater from the Piedmont region had much lower B concentrations and B/Cr_T ratios. In particular, groundwater wells in Rowan County near the coal ash pond with a high Cr(VI) concentration had B levels and B/Cr_T ratios 2−3 orders of magnitude lower than those of coal ash pond effluents from North Carolina (Figure 3B).

In addition to the groundwater in Rowan County, samples were collected from wells in formations containing mafic rocks located in counties that did not have any coal ash ponds. Elevated Cr(VI) concentrations were detected in wells from mafic-rich aquifers in Forsyth County that are located more than 30 km from a coal ash pond. These samples had elevated Cr(VI) concentrations of up to 10 μg/L with Sr/Ca (<0.006), B/Cr_T (<20), and $^{87}Sr/^{86}Sr$ ratios similar to those of the mafic-containing aquifer near the coal ash ponds in Rowan County.

It is important to note that coal ash effluents that discharge from coal ash ponds in NC have high concentrations of sulfate, arsenic, selenium, molybdenum, and thallium relative to those of natural waters,[34] which are not present in the groundwater near coal ash ponds tested in this study. Furthermore, the range of Cr_T concentrations found in coal ash effluents [0.4−8.6 μg/L

(Figure S5)] is lower than those measured in nearby groundwater. Overall, the geochemical and isotopic data clearly indicate that the drinking water wells tested in this study are not impacted by CCR effluents, and therefore, the coal ash ponds are not a likely source of the elevated Cr_T and Cr(VI) concentrations found in the Piedmont groundwater. These results are further supported by the presence of Cr(VI)-rich groundwater that has similar geochemistry in wells located more than 30 km from a coal ash pond (Figure 1 and Figure S2). Total Cr concentrations were not strongly correlated with distance ($r = 0.09$) but showed a significant ($p < 0.05$) increase with distance from coal ash ponds, and concentrations of up to 34 μg/L were found in wells more than 50 km from the nearest coal ash pond. These results indicate that high Cr concentrations can be found in wells located far from coal ash ponds, which is inconsistent with the expected trend if coal ash ponds were the source of Cr contamination in nearby groundwater. The geospatial analysis therefore supports the conclusions drawn from the geochemical data.

Distribution of Chromium in the Piedmont Aquifers. While our geochemical analysis rules out contamination from nearby coal ash ponds, we present evidence of a geogenic source of Cr and Cr(VI) to drinking water aquifers. First, we show that Cr [and Cr(VI)] can be found throughout the different aquifers of the Piedmont region (Figure 1). Second, the association of $^{87}Sr/^{86}Sr$ ratios with aquifer lithology (Figure S3) indicates that the local aquifer rocks are the source of dissolved Sr and apparently Ca in groundwater, given the high correlation between Sr and Ca (Figure S6). Third, the association of Ca and Cr in groundwater from some aquifers (Figure S7) suggests that Cr, like Ca, is derived from water−rock interactions rather than an external (i.e., anthropogenic) source. The distribution of Cr_T varies among the different types of lithology (Figure S8), with the highest to lowest median Cr_T values observed in groundwater from the Floyd Church Formation, Cid Formation, mafic metavolcanic, phyllite and schist, biotite gneiss schist, felsic mica gneiss, felsic metamorphic, and granitic rocks, respectively (Table S2). The data show that groundwater from intermediate or mixed mafic metavolcanic formations has Cr_T concentrations ($p < 0.05$) significantly higher than those of groundwater from felsic formations (Table S3). These results are consistent with previous studies that have shown high Cr(VI) concentrations in groundwater from ultramafic rocks,[18−27] yet the data presented in this study infer Cr(VI) prevalence in groundwater from aquifers composed of metamorphic mafic rocks and even felsic rocks, which are highly common in the Piedmont region of the eastern United States.[42]

Environmental Health Implications. Assuming that Cr(VI) is the predominant Cr species in drinking water wells, we show that only 14 of 376 wells (∼4%) had Cr_T above the California MCL limit of 10 μg/L. At the same time, only 8 of 77 (∼10%) wells had Cr(VI) levels below the detection level (0.004 μg/L), meaning that 90% of the study wells had detectable Cr(VI), and furthermore, all of the detectable Cr(VI) was above the California PHG of 0.02 μg/L. While our sample collection was conducted in the Piedmont region of North Carolina, the distribution of the Piedmont rocks extends to other states in the eastern United States (see the top inset map in Figure 1), and a large population is potentially consuming drinking water with detectable and, in some cases, high Cr(VI) levels. Given the global distribution of aquifers composed of mafic and igneous rocks,[43] we hypothesize that

the occurrence of Cr(VI) in shallow drinking water wells is much more widespread than previously thought, with possibly millions in the eastern United States and other parts of the world directly exposed to detectable Cr(VI) from drinking water[4] impedes a large scale evaluation of the distribution of Cr(VI) in groundwater systems. Monitoring and screening for Cr(VI) levels in public and private wells are therefore essential for protecting human health in the Piedmont region and beyond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00342.

> Eight figures, three tables, information about the analytical procedure of hexavalent chromium, and background on the hydrogeology of the Piedmont area (PDF)

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Notes
The authors declare no competing financial interest.

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