

Origin and Scope of Hexavalent Chromium In North Carolina Groundwater

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EXECUTIVE SUMMARY

Potential groundwater contamination from coal ash ponds is a current public health concern in North Carolina (NC) surrounded by controversy. Recently, the focus has expanded beyond the initial concern regarding coal ash contamination degrading the quality of local water supplies. The issue now includes concern about the inherent water quality of the state's groundwater.

A 2015 report from the North Carolina Department of Environmental Quality (NC DEQ) disclosed elevated levels of trace metals in domestic wells near coal ash ponds. The presence of hexavalent chromium (Cr(VI)) in some of these wells was attributed to contamination from the coal ash ponds, but a 2016 study by Vengosh et al. found elevated Cr(VI) levels in domestic wells located far away from coal ash ponds. The geochemical analysis of the samples revealed a geogenic source – the ultramafic rock formations composing the Piedmont aquifers.

This study expands upon the 2016 work by Vengosh et al. that examined chromium (Cr) in domestic wells within the Piedmont of North Carolina. To identify the populations at risk of Cr exposure, the geogenic source(s) and the distribution of total chromium (CrT) and its toxic form, Cr(VI), need to be studied more thoroughly.

With over 3 million NC residents relying on groundwater as their primary water supply, results from this research will strengthen the foundation for understanding which residents of NC may be at risk of drinking groundwater that exceeds a safe level for Cr. The findings from the new study will help inform state and federal agencies, as well as the public and scientific communities, of the potential exposure and risk of adverse health effects for the populations of NC that rely solely on groundwater for drinking water.

The research objectives of this project are as follows:

- (1) establish a large water quality dataset through new sampling combined with assembly of archive data;
- (2) map the occurrence of CrT and Cr(VI) in groundwater resources with respect to aquifer lithology distribution; and
- (3) evaluate the speciation of chromium in groundwater across different North Carolina aquifers.

To meet the objectives of this study, samples of the groundwater from domestic wells and springs were collected from random locations in the mountain, Piedmont, and coastal region of North Carolina. Monitoring wells in the coastal region were obtained in collaboration with the NC DEQ. Chemical analyses of these samples were performed at Duke University by members of the Vengosh laboratory. Additional data from public water supplies were obtained by aggregating data from the Environmental Protection Agency's Unregulated Contaminant Monitoring Rule 3 (EPA UCMR3) program and NC DEQ's Source Water Assessment Program (SWAP).

Geospatial analysis was conducted in ArcMap Version 10.5.1. to extrapolate the aquifer lithology for each groundwater sample. Afterwards, statistical analysis was performed in RStudio Version 1.0.153 by using a Spearman's rank correlation test to assess the relationship between Cr(VI) and CrT, and a Kolmogorov-Smirnov rank test to assess the relationship between levels of Cr and the aquifer lithology (major mafic, significant minor mafic, possible mafic, and unlikely to contain mafic).

The main findings of this study are:

- (1) Cr concentration increases with the mafic contents in the aquifer rocks
 - a. major mafic and significant minor mafic > possible mafic > unlikely to contain mafic
- (2) Strong, positive correlation between Cr(VI) and CrT

These new results support previous findings and provide additional evidence that Cr(VI) is the predominant species of CrT, and that groundwater in aquifers with lithology containing mafic constituents will have elevated levels of Cr when compared to aquifers in non-mafic lithology.

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1 INTRODUCTION

1.1 PROBLEM IDENTIFICATION AND APPROACH

Potential groundwater contamination from coal ash ponds has become a major public health concern in North Carolina (NC) that has spurred research into the levels of various contaminants in drinking well water near the ponds. One of the suspected contaminants is chromium (Cr), with concern focusing on the hexavalent form (Cr(VI)) due to its potential carcinogenicity and association with coal combustion residues. In 2015, the NC Department of Environmental Quality (NC DEQ) found elevated levels of Cr in groundwater samples from domestic wells located within close proximity to the coal ash ponds. Of the 14 coal-fired power plant sites in North Carolina, one had wells with Cr levels exceeding the state's groundwater standard of 10 ug/L for total chromium (CrT) and six had wells with levels exceeding either the NC Department of Health and Human Services' (NC DHHS) health screening level of 0.07 ug/L for Cr(VI) (NC DEQ, 2015).

The NC groundwater standard is a legal mandate that incorporates economic feasibility while the health screening level is a recommendation designed to protect public health. Private drinking water wells are loosely regulated in NC and are not required to conform to the state's groundwater standards. The 0.07 ug/L health screening level for Cr(VI) is "based on an increased one-in-a-million risk of an average person developing cancer as a result of consuming well water over a lifetime of approximately 70 years" (Dockham, 2015). Based on above results, the NC DHHS issued "Do Not Drink" letters to residents residing near the six locations, where

the groundwater exceeded the health screening levels. But shortly thereafter, the NC DHHS rescinded the “Do Not Drink” letters because the water was legally safe to drink. These actions created public confusion over whether the groundwater is safe for consumption.

Adding complexity to North Carolina’s chromium conundrum, a 2016 study on Cr(VI) and CrT in groundwater from the Piedmont Aquifers of North Carolina found that Cr may be more prevalent than previously thought due to geogenic sources from water-rock interactions and that CrT in the water may be predominantly in the more toxic and mobile form, Cr(VI) (Vengosh et al., 2016). This study provides evidence that the coal ash ponds are not the source of Cr in the wells, but rather that the Cr is naturally-occurring. While the prevalence of Cr in drinking water wells across all of North Carolina is not well studied, the distribution of the ultramafic and igneous rocks that are associated with elevated levels of Cr suggests that many aquifers could be impacted (Figure 1).

To identify the populations at risk of Cr exposure, the geogenic source(s) and the distribution of Cr and its toxic form Cr(VI) need to be studied more thoroughly. This project will extend the dataset and analyze the concentrations of Cr in groundwater samples from wells across North Carolina with relation to lithology as categorized by mafic content to explore the origin of naturally-occurring Cr in different aquifers. Additionally, this project will evaluate the relative proportion of Cr(VI) to CrT.

With over 3 million NC residents relying on groundwater, results from this research will strengthen the foundation for understanding which residents of NC may be at risk of drinking groundwater that exceeds a safe level for Cr (NC DHHS, 2016). Additionally, results will further

investigate if Cr(VI) is indeed the predominant Cr form in drinking water wells in NC as previously suggested by Vengosh et al. (2016). Combined, the findings from the new study will help inform state and federal agencies, as well as the public and scientific communities, of the potential exposure and risk of adverse health effects for the populations of NC that rely solely on groundwater for drinking water.

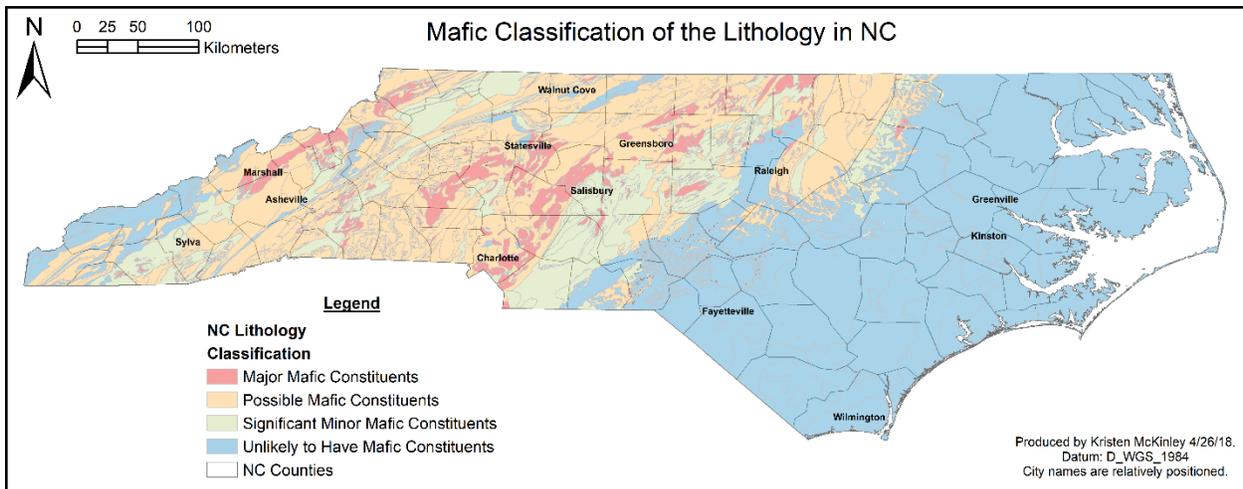


Figure 1 – Geographic distribution of the lithology in North Carolina as categorized by mafic content. The blue area represents formations that are unlikely to contain mafic constituents, while the green, yellow, and red areas represent regions that are likely to contain significant minor mafic constituents, possible mafic constituents, or major mafic constituents, respectively.

1.2 BACKGROUND

1.2.1 Chromium in the Environment

In aquatic systems such as groundwater, Cr exists primarily in the oxidation states of trivalent chromium (Cr(III)) or hexavalent chromium (Cr(VI)), with the speciation being pH- and redox-dependent (Kota & Stasicka, 2000; McNeill, Mclean, Edwards, & Parks, 2012). Cr(III) occurs as a cation that is dominated by insoluble hydroxide complexes, while Cr(VI) occurs as the oxyanion species dichromate ($\text{Cr}_2\text{O}_7^{2-}$), or monovalent chromate (HCrO_4^-) below pH 6.5 and divalent chromate (CrO_4^{2-}) above pH 6.5 (Kota & Stasicka, 2000). Many of the Cr(VI) forms are water soluble and thus mobile in groundwater.

While historically assumed to be a strictly anthropogenic contaminant from industrial activities, current literature points to ultramafic rocks as a geogenic source of Cr(VI) in groundwater, which have elevated levels of Cr (>200 mg/kg) as compared to other rock types (Kazakis et al., 2015; Oze, Bird, & Fendorf, 2007; Vengosh et al., 2016). Experimental work finds that “rates of aqueous Cr(VI) production are primarily controlled by the solubility and dissolution rates of Cr(III) host minerals, the solution pH, and the accessibility of aqueous Cr(III) to mixed valence Mn(VI/III)-oxides that coat mineral surfaces and pore spaces in sediments and soils of ultramafic and related rocks” (Oze et al., 2007). When manganese-iron oxides co-exist with Cr(III)-bearing minerals from ultramafic and serpentinite rocks, Cr(III) oxidation by Mn(V)-oxides can occur on the mineral surface, generating Mn(II) and Cr(VI) that dissolve into groundwater and migrate away from the site of origin (Kazakis et al., 2015; Oze et al., 2007; Trebien, Bortolon, Tedesco, Bissani, & Camargo, 2011).

1.2.2 Chromium Toxicity

Cr(III) is considered an essential nutrient, though the biological target is unknown and limited evidence exists for chromium deficiency (ATSDR, 2012). Conversely, Cr(VI) is classified as a known human carcinogen based on sufficient evidence from “the combined results of epidemiological studies, cancer studies in experimental animals, and evidence that chromium(VI) ions generated at critical sites in the target cells were responsible for the carcinogenic action observed” (NTP, 2016). The carcinogenicity is limited to respiratory cancer, primarily bronchogenic and nasal, from the inhalation route of exposure (ATSDR, 2012).

Oral exposure by ingestion of low to moderate levels in drinking water lacks sufficient evidence to be classified as carcinogenic (ATSDR, 2012; Nickens, Patierno, & Ceryak, 2010). Despite the lack of evidence for carcinogenicity from oral exposure of Cr(VI), evidence does exist for other adverse health outcomes such as gastrointestinal effects like abdominal pain, vomiting, ulcers, and diarrhea; hematological effects such as microcytic, hypochromic anemia; and even dermal effects such as exacerbated dermatitis in sensitized individuals (ATSDR, 2012).

The minimal risk level, which is “an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse effects (noncarcinogenic) over a specified duration of exposure”, is 0.0009 mg Cr(VI)/kg/day for a chronic (\geq 1 year) oral route of exposure (ATSDR, 2012).

1.2.3 Chromium Regulation

The national maximum contaminant level (MCL) for CrT was established in 1991 at 100 ug/L as authorized by the Safe Drinking Water Act (SDWA) (US EPA, 2017). The maximum contaminant level goal (MCLG), a level designated to protect public health from adverse effects, is also 100 ug/L for CrT. As a conservative approach to “ensure that the greatest potential risk is addressed”, the MCL and MCLG assume that CrT is entirely the most toxic form Cr(VI) (US EPA, 2017). A review is in process by the EPA since 2008 to determine if Cr(VI) should have a separate standard.

Instead of adopting the EPA’s MCL, some states have set their own standards for Cr at lower concentrations. In 1977, California adopted a MCL of 50 ug/L for CrT. In 2014 California became the first state to create a specific MCL for Cr(VI) when the California Department of Public Health (CDPH) created a state MCL of 10 ug/L Cr(VI) in response to concerns about the potential carcinogenicity of Cr(VI) when ingested (CalEPA, 2018). However, the Superior Court of Sacramento County ruled the Cr(VI) MCL as invalid because the CDPH did not adequately document the economic feasibility of small water systems complying with the Cr(VI) MCL. The court ordered the State Water Board to adopt a new Cr(VI) MCL that is between the public health goal level (PHGL) of 0.02 ug/L Cr(VI) and the MCL of 50 ug/L CrT (Super. Ct. Sacramento County, 2017). As of September 11, 2017, the Cr(VI) MCL has been deleted from the California Code of Regulations and only the original 50 ug/L CrT MCL remains (CalEPA, 2018).

North Carolina officials have responded in a similar fashion to public concern regarding Cr in drinking water by investigating a specific MCL for Cr(VI). Groundwater usage and protection as a high-quality drinking water supply in NC is regulated by the Environmental Management Commission (EMC) under Title 15A Subchapter 02L of the North Carolina Administrative Code (Young, 2016). The NC groundwater standards are specifically described as “the maximum allowable concentrations resulting from any discharge of contaminants to the land or waters of the state, which may be tolerated without creating a threat to human health or which would otherwise render the groundwater unsuitable for its intended best usage” and that “development does not require efforts to reduce or eliminate the presence of dissolved constituents which are indigenous to the ground water quality in that area” (Groundwater Quality Standards, 2013, Standards of Construction: Water Supply Wells, 2009). Additionally, the Director of the Division of Water Resources (DWR) can set the standards to match the background concentration for specific wells and areas where the groundwater naturally exceeds the groundwater standards (Young, 2016).

The oversight and enforceability of the standards depends on the classification of the water supply. Only public water supplies, those that service at least 15 connections or those that regularly serve at least 25 residents, are consistently monitored and required to meet MCL’s (NC DHHS, 2016). The water quality of public water supplies is regulated under Title 15A Subchapter 18C of the North Carolina Administrative Code. Aside from arsenic, iron, and manganese, the legally enforceable MCL’s for inorganic chemicals are the same as the national standards required by the SWDA (NC DHHS, 2016; Water Supplies, 1990). For the 6.2 million NC residents that rely on public water supplies, approximately 44.5% of the supply originates from

groundwater sources (Maupin et al., 2014). The remaining 3.3 million NC residents rely on self-supplied groundwater as their primary source of water and are independently responsible for the water quality.

Domestic wells in NC are rarely tested for contaminants as the responsibility lies on the homeowner. From 2000 to 2010, less than 200,000 domestic wells were tested for water quality (NC DHHS, 2016). Since 2008, newly constructed private drinking water wells are required to be tested for 20 contaminants, including CrT, by the local health department within 30 days of issuing a certificate of completion as described in G.S. 87-97(h) (Young, 2016). The statute does not stipulate the consequences for wells that exceed the health screening levels or the groundwater standards. According to the DEQ, if a well exceeds the drinking water or groundwater standards for a contaminant, then the local health department and DHHS will provide the well owner with information on the contaminant, including steps to address the contamination (NC DEQ, n.d.-a). The underlying goal of NC's groundwater regulation is to maintain the natural state of the groundwater as public resource, with the protection of public health being a secondary goal.

In 2013, North Carolina set a groundwater standard of 10 ug/L for CrT and a public health screening level of 0.07 ug/L for Cr(VI). DWR is awaiting action on Cr(VI) regulations by the EPA before advancing on a Cr(VI) specific groundwater standard (Young, 2016). Sampling of NC groundwater has found Cr(VI) concentrations up to 22.9 ug/L and CrT concentrations up to 33.8 ug/L (Vengosh et al., 2016). While under the EPA threshold of 100 ug/L, these values exceed the stricter standards of California and North Carolina.

1.3 STATEMENT OF OBJECTIVES & HYPOTHESES

The research objectives of this project are (1) establish a large water quality dataset through new sampling combined with assembly of archive data; (2) mapping the occurrence of Cr and Cr(VI) in groundwater resources with respect to aquifer lithology distribution; and (3) evaluate the speciation of chromium in groundwater across different North Carolina aquifers. The overall question this project will address is whether the distribution of subsurface geology can predict the presence and magnitude of chromium in North Carolina groundwater?

2 METHODS

2.1 APPROACH

To meet the objectives of this study, samples of the groundwater from domestic wells and springs were collected from random locations in the mountain, Piedmont, and coastal region of North Carolina. Generally, residential wells were identified through a self-selection process of homeowner requests to our laboratory. Some of the areas for residential wells were specifically targeted by our lab, such as the community of Walnut Cove in the Piedmont (in collaboration with UNC) or the community of Marshall in the mountains. Monitoring wells in the coastal region were obtained in collaboration with the North Carolina Department of Environmental Quality (NC DEQ). Additional data from public water supplies were obtained by aggregating data from the EPA's UCMR3 program and NC DEQ's Source Water Assessment Program (SWAP) (NC DEQ, n.d.-b; US EPA, 2018).

2.2 SAMPLE COLLECTION & DATA PREPARATION

For samples collected by our lab, well water was flushed for 30 minutes prior to sampling to clear the well of standing water. Additionally, the samples were not collected until the physical parameters of the water stabilized, indicating water representative of the raw groundwater was discharging from the wellhead. If a spigot was not accessible at the wellhead, the nearest spigot on the house was used for collection. Before collection, the physical parameters of the groundwater were recorded for pH, oxidation-reduction potential (ORP), temperature, dissolved oxygen, and specific conductivity (SPC). These measurements were

taken using a multimeter calibrated the morning of sample collection. Additionally, spatial measurements such as geographic coordinates and well depth were recorded.

For chemical parameters, six bottles of groundwater were collected using clean hand techniques directly from the source for each sample for the different laboratory analyses performed at Duke University. To supplement the data for private wells, additional data from previous studies by the Vengosh research group were included in the final analysis. These samples were collected under the same conditions as described above. Samples received from the DEQ and UNC collaboration projects were collected with similar protocols. The monitoring wells sampled by DEQ were flushed of water equal to three times the well volume prior to sampling. Analysis methods in the lab are described in the publication of the prior study (Vengosh et al., 2016).

2.3 ADDITIONAL DATA SOURCES

2.3.1 EPA UCMR3

An additional data source for Cr(VI) and CrT concentrations in drinking water was the EPA's Unregulated Contaminant Monitoring Rule (UCMR) program. "The monitoring provides EPA and other interested parties with nationally representative data on the occurrence of contaminants in drinking water, the number of people potentially being exposed, and an estimate of the levels of that exposure. These data can support future regulatory determinations and other actions to protect public health" (US EPA, 2018). Cr(VI) and CrT were two of the 30 contaminants measured as part of the UCMR3 program that was conducted from

2013 to 2015. Results from UCMR3 were published in January of 2017 and are available for public download from the EPA's website (US EPA, 2018). Generally, each public water supply (PWS) had two separate sample collection events during this time, though some PWS's only had one sampling event. CrT was measured under EPA Method 200.8 and Cr(VI) was measured under EPA Method 218.7 (US EPA, 2018)

To prepare this data for inclusion in my analysis, I developed a tool for ArcMap that extracts only the records for a specified state and contaminant. I used this tool to extract the records for NC for Cr(VI) and CrT. These records were exported to an Excel document. Then, I filtered the records to only include samples where the source of water was groundwater (FacilityWaterType = GW) and where the sample was taken at the entry point to the distribution system (SamplePointType = EP). Samples for surface water, groundwater under the direct influence of surface water, or a mix of sources, as well as samples from the distribution system at maximum residence, were excluded from the analysis.

While the dataset did include zip codes for the locations of the PWS's being tested, it did not include location information, such as geographic coordinates, for the individual sampling points. Therefore, to confidently assign a subsurface geology category for each sampling location, I had to link the EPA dataset with a dataset provided by North Carolina's Source Water Assessment Program (SWAP).

2.3.2 NC Source Water Assessment Program (SWAP)

To comply with Section 1453 of the SWDA Amendments of 1996, North Carolina established a Source Water Assessment Program (SWAP) in 1999 (NC DENR, 1999). One product of these efforts was a complete inventory of the state's PWS's using geographic information systems (GIS). The GIS files for all active permanent drinking water sources in NC as of 2015 are available for public download (NC DEQ, n.d.-b). Since both the SWAP shapefile and the EPA table contained an attribute field for the PWSID, I was able to join these two datasets to create a sub-dataset of PWS entry points with chemical and geographic data for inclusion in my analysis (n=332).

2.4 GEOSPATIAL ANALYSIS

After obtaining the chemical and physical parameters for the above data sources, I mapped each point in ArcGIS using ArcMap Version 10.5.1 (Figure 2). Using a shapefile provided by the Vengosh lab where the USGS geology information had been classified into major mafic, possible mafic, significant minor mafic, and unlikely to contain mafic formations for the previous study, I was able to intersect the geographic coordinates of the individual data points to extract the subsurface geology category. This table was exported to an Excel document to utilize in RStudio Version 1.0.153 for statistical analyses (n=907). Samples without geographic coordinates linkable to subsurface geology were excluded from analysis (n=873). At this point, samples that were not representative of raw groundwater, such as filtered samples, were also excluded (n=865).

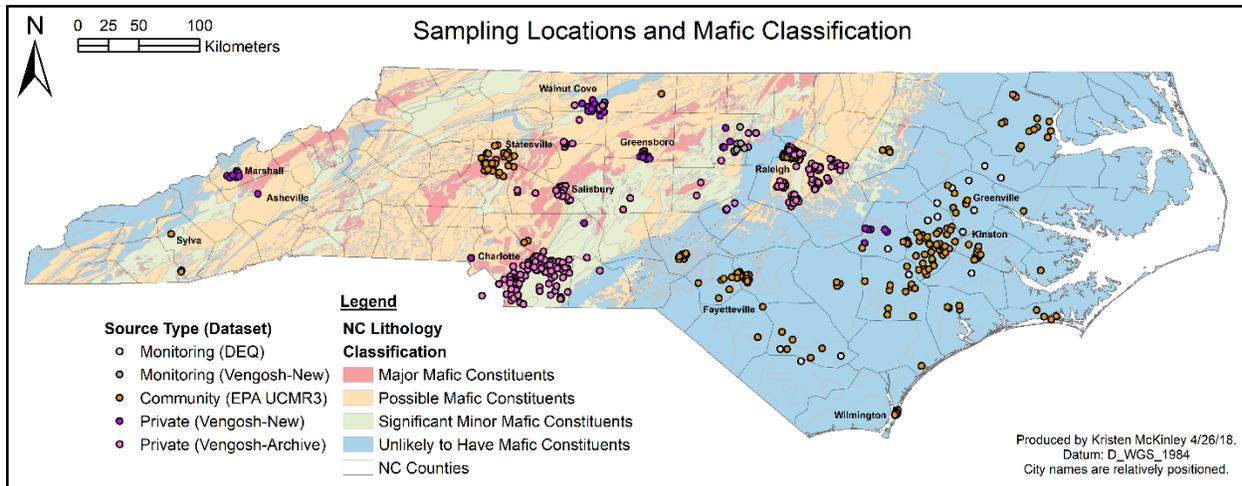


Figure 2 – Locations of all samples available in the new water quality dataset (n=907). Samples are classified according to the type of water source and the dataset from which the observation was obtained.

2.5 STATISTICAL ANALYSES

Because the data was not normally distributed, I had to employ non-parametric tests. To meet my objectives, I performed a Spearman’s rank correlation test for Cr(VI) versus CrT, and a Kolmogorov-Smirnov rank test to assess the relationship between levels of Cr and the subsurface geological formation categories.

For the correlation tests, I wanted only samples that had quantifiable levels of both Cr(VI) and CrT so that I could determine a representative ratio of Cr speciation in groundwater. To this end, I eliminated any samples that did not have quantifiable levels of either compound. Then I parsed the dataset down to samples where both Cr(VI) and CrT were above the respective minimum reporting levels (MRL) (Table 1). A correlation test was performed on the overall dataset (n=179), as well as on the separate Vengosh and EPA datasets (n=112, n=67 respectively). Correlation tests were also performed on subsets of the data as classified by

subsurface geology. The sample sizes were sufficient to test for correlation for the categories of major, possible, and unlikely, but not for minor (n=37, n=47, n=22, n=6, respectively).

For the Kolmogorov-Smirnov tests, I split the data into a Cr(VI) dataset (n=573) and a CrT dataset (n=840). For each analyte, the samples were grouped by their respective subsurface geology category. Then Kolmogorov-Smirnov two-sample tests were performed for each possible pair of subsurface geology. To account for samples below the detection limit in the Kolmogorov-Smirnov statistical analysis, these samples were randomly assigned a value falling on a random uniform distribution between 0 and one-half the respective MRL.

Table 1 – Minimum reporting levels based on analytical capability and the corresponding sample sizes.

Analyte	Dataset	MRL (ug/L)	No Data (n)	Data (n)	< MRL (n)	>= MRL (n)
Cr6	Vengosh lab	0.012	292	242	74	168
	EPA	0.03	0	331	157	174
CrT	Vengosh lab	0.003	25	509	71	438
	EPA	0.2	0	331	182	149

3 RESULTS

3.1 OVERALL DESCRIPTION

Data was obtained from three sources: (1) measurements of samples collected and analyzed at Vengosh lab (n= 458); (2) data from monitoring wells throughout NC (n= 76); and (3) EPA archive data (n=331). Results are presented in Table 2. 40.3% of data points (n=231) were below the respective minimum reporting levels (Table 1) for Cr(VI) (30.6% < 0.012 ug/L samples measured at Vengosh lab; 47.4% < 0.03 ug/L EPA) and 30.1% for CrT (13.9% < 0.003 ug/L Vengosh lab; 55% < 0.2 ug/L EPA). While the EPA samples include only community wells, the Vengosh samples include private wells and monitoring wells. For private wells, 17.8% were below the MRL for Cr(VI) and 12.2% were below the MRL for CrT. For monitoring wells, 60.3% were below the MRL for Cr(VI) and 27.6% were below the MRL for CrT.

1.5% of total samples (n=13) exceeded NC's 02L groundwater standard of 10 ug/L (0.698% >10 ug/L Cr(VI); 1.4% >10 ug/L CrT). The highest concentration for Cr(VI) detected in North Carolina groundwater is 22.9 ug/L in Salisbury, NC. The highest concentration for CrT detected in North Carolina groundwater is 33.8 ug/L in Monroe, NC. All samples exceeding the 10 ug/L standard were located in aquifers associated with major mafic rocks, significant minor mafic rocks, or possible mafic rocks. When considering NC DHHS's health screening level of 0.07 ug/L, 38.2% of samples were above the level for Cr(VI) (n=219) and at least 72.7% were above the level for CrT.

When categorized by geology, the median value of Cr(VI) and CrT tended to increase with the magnitude of mafic constituents in the aquifer rocks (Table 2). For Cr(VI), major mafic formations had a median of 0.84 ug/L while formations unlikely to contain mafic constituents had a median of 0.012 ug/L (Figure 3). Similarly for CrT, major mafic formations had a median of 0.64 ug/L, while formations unlikely to contain mafic constituents had a lower median value of 0.09 ug/L (Figure 4).

Table 2 – Sample sizes and median concentrations for hexavalent chromium (Cr(VI)) and total chromium (CrT) as categorized by geological formations then source type. The median concentration for Cr(VI) is ~70x higher in major mafic formations (~0.8 ug/L) as compared to formations unlikely to contain mafic rocks (~0.01 ug/L). The median concentration for CrT is ~3x higher in major mafic formations (~0.6 ug/L) as compared to formations unlikely to contain mafic rocks (~0.09 ug/L).

Geology	Hexavalent Chromium		Total Chromium	
Source Type	n	Median (ug/L)	n	Median (ug/L)
Major Mafic Constituents	66	0.839	124	0.642
Community Well	25		25	
Monitoring Well	1		1	
Private Well	40		98	
Possible Mafic Constituents	193	0.137	321	0.365
Community Well	112		112	
Monitoring Well	0		0	
Private Well	72		200	
Spring	9		9	
Significant Minor Mafic Constituents	43	0.015	120	0.871
Community Well	8		8	
Monitoring Well	11		9	
Private Well	23		102	
Spring	1		1	
Unlikely to Have Mafic Constituents	271	0.012	275	0.090
Community Well	186		186	
Monitoring Well	61		48	
Private Well	24		41	
Grand Total	573	0.028	840	0.221

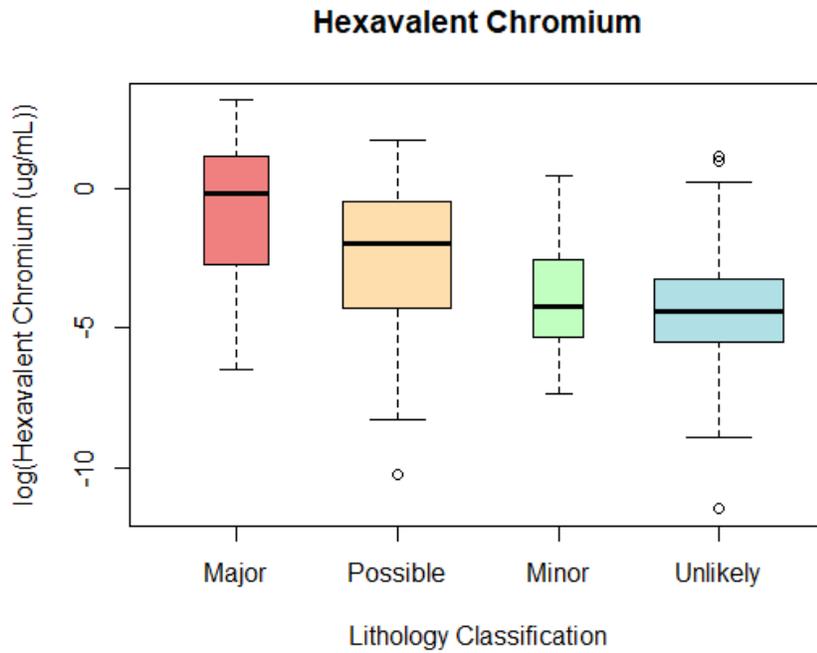


Figure 3 – Percentiles of log-transformed concentrations of Cr(VI) as categorized by subsurface geological formations.

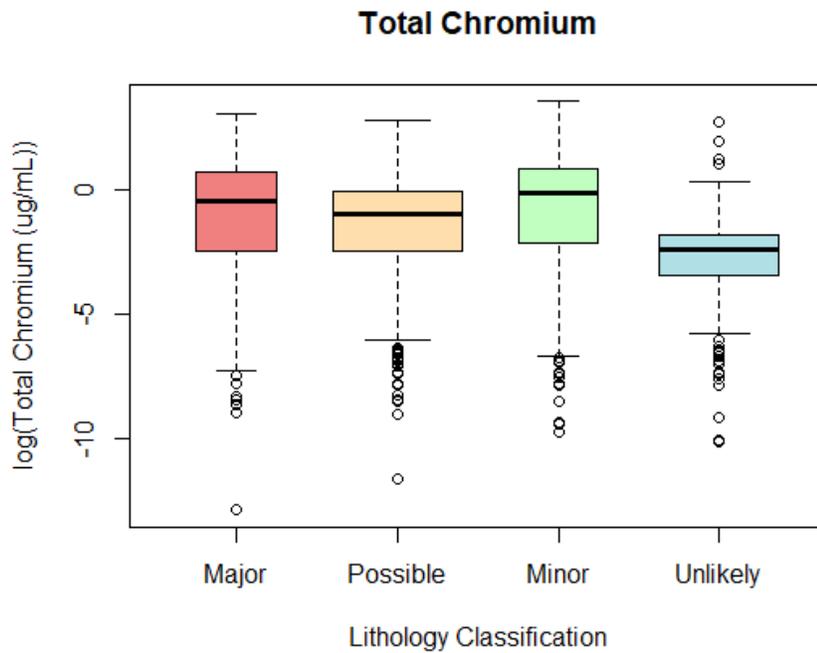


Figure 4 - Percentiles of log-transformed concentrations of CrT as categorized by subsurface geological formations.

3.2 CORRELATION OF CR(VI) TO CRT

Overall, Cr(VI) has a very strong, positive correlation with CrT (slope of ~ 1.1 , $r^2=0.876$, $p < 0.0001$; Figure 5). The Vengosh laboratory data (slope of ~ 1.1 , $r^2=0.862$, $p < 0.0001$; Figure 6) are consistent with the data reported by the EPA (slope of ~ 0.8 , $r^2=0.920$, $p < 0.0001$; Figure 7) and with that reported in the previous study (Vengosh et al., 2016).

With regards to lithology, the sample sizes were sufficient to test for correlation for the categories of major, possible, and unlikely, but not for minor. Cr(VI) has a very strong, positive correlation with CrT for both major mafic (slope of ~ 1.2 , $r^2=0.913$, $p < 0.0001$; Figure 8) and possible mafic (slope of ~ 0.98 , $r^2=0.880$, $p < 0.0001$; Figure 9) formations. Cr(VI) has a moderate, positive correlation with CrT for formations that are unlikely to contain mafic constituents (slope of ~ 0.41 , $r^2=0.493$, $p = 0.021$; Figure 11). These results support the hypothesis that hexavalent chromium is the predominant species of total chromium in North Carolina groundwater.

Ratio of Cr6/CrT for Overall Dataset

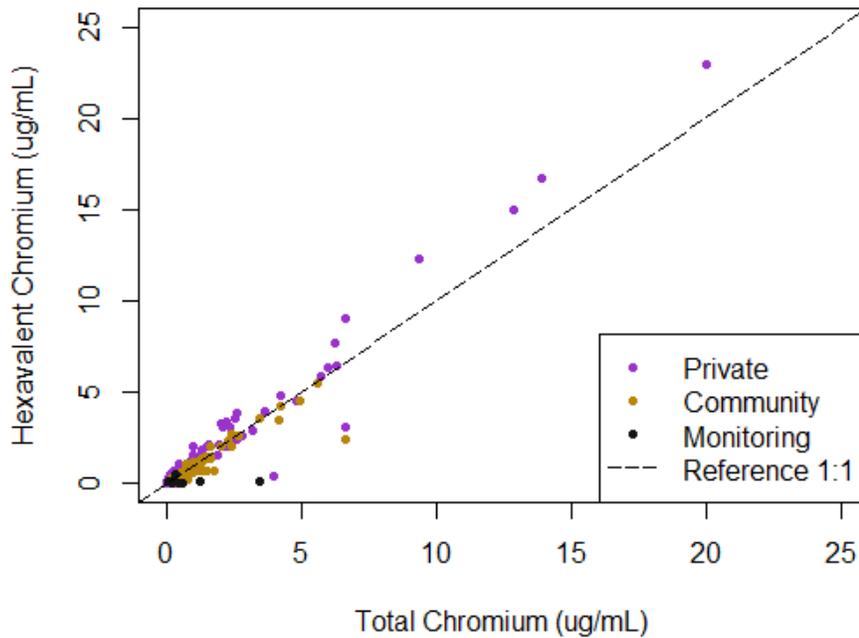


Figure 5 – Overall correlation of Cr(VI) to CrT for samples exceeding the respective MRL’s for both analytes. The dashed line represents a 1:1 ratio.

Ratio of Cr6/CrT for Vengosh Dataset

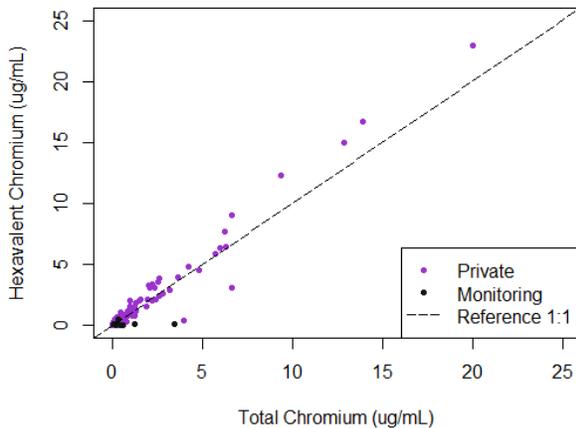


Figure 6 – Correlation for samples from the Vengosh dataset (n=112), shown as private wells (n=103) in purple and as monitoring wells (n=9) in gray.

Ratio of Cr6/CrT for EPA Dataset

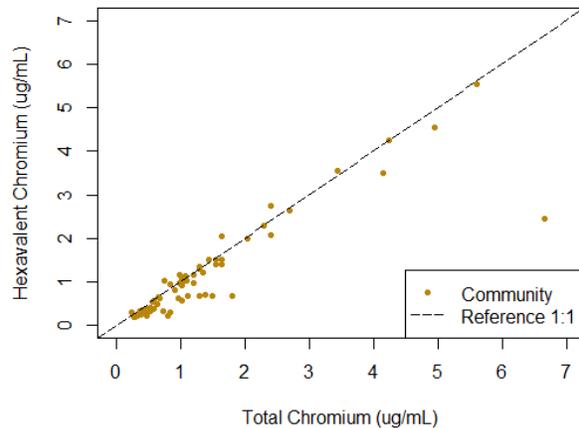


Figure 7 – Correlation for samples from the EPA dataset (n=67) that are all community wells.

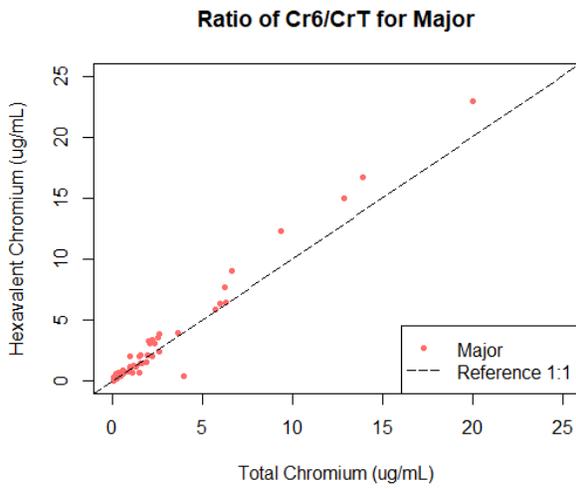


Figure 8 – Correlation for samples with major mafic lithology (n=37).

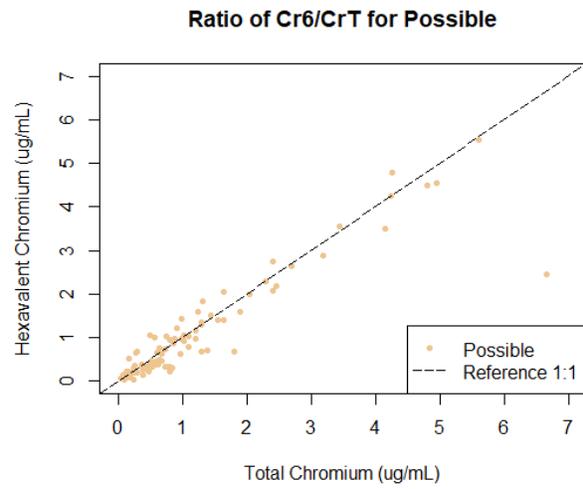


Figure 9 – Correlation for samples with possible mafic lithology (n=47).

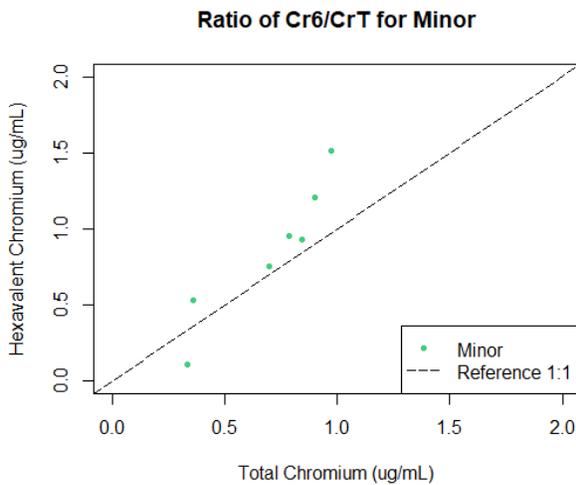


Figure 10 – Correlation for samples with significant minor mafic lithology (n=6).

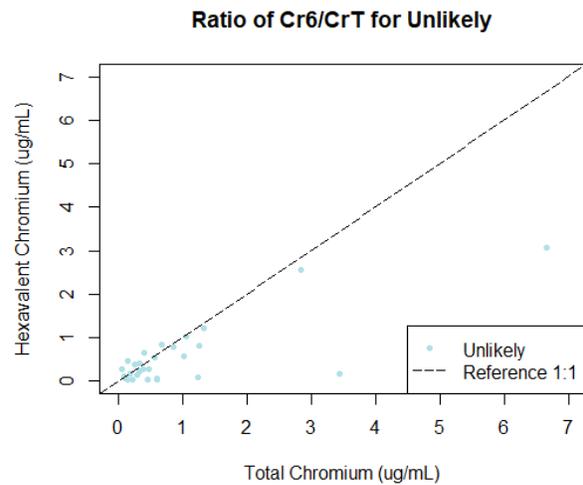


Figure 11 – Correlation for samples with lithology that is unlikely to contain mafic constituents (n=22).

3.3 SUBSURFACE GEOLOGY

In support of the observed trends in the boxplots and the geospatial analysis, groundwater sources in mafic formations have elevated levels of Cr(VI) and CrT as compared to groundwater sources in non-mafic formations (Table 3; Figure 12). The difference in the results for Cr(VI) and CrT regarding the minor mafic category is likely due to the difference in sample sizes. The minor mafic dataset had a lower sample size for Cr(VI) (n=43) than for CrT (n=120).

Major mafic formations and significant minor mafic formations have similar levels of CrT to each other (p-value = 0.6635). Possible mafic formations have lower levels of Cr when compared to major mafic formations and significant minor mafic formations (p-values < 0.001) and higher levels of Cr when compared to formations unlikely to contain mafic material (p-values < 0.001). Formations unlikely to contain mafic material have lower levels of Cr compared to mafic formations (p-values < 0.001), except for in the comparison to significant minor mafic formations for Cr(VI) as described previously (p-value = 0.3366). The results support the hypothesis that Cr concentrations will be elevated in groundwater from aquifers composed of mafic formations compared to groundwater from non-mafic formations.

Table 3 – Sample size and significance for pairs of geological formations used in the two-sample Kolmogorov-Smirnov tests to evaluate the effect of aquifer lithology categorized by mafic content on chromium concentrations in groundwater.

Geology Pair	Hexavalent Chromium		Total Chromium	
	Sample Sizes (n)	p-value	Sample Sizes (n)	p-value
Major-Possible	66 : 193	<0.0001*	124 : 321	0.0002*
Major-Minor	66:43	<0.0001*	124 : 120	0.6635
Major-Unlikely	66 : 271	<0.0001*	124 : 275	<0.0001*
Possible-Minor	193:43	0.0002*	321 : 120	<0.0001*
Possible-Unlikely	193 : 271	<0.0001*	321 : 275	<0.0001*
Minor-Unlikely	43 : 271	0.3366	120 : 275	<0.0001*

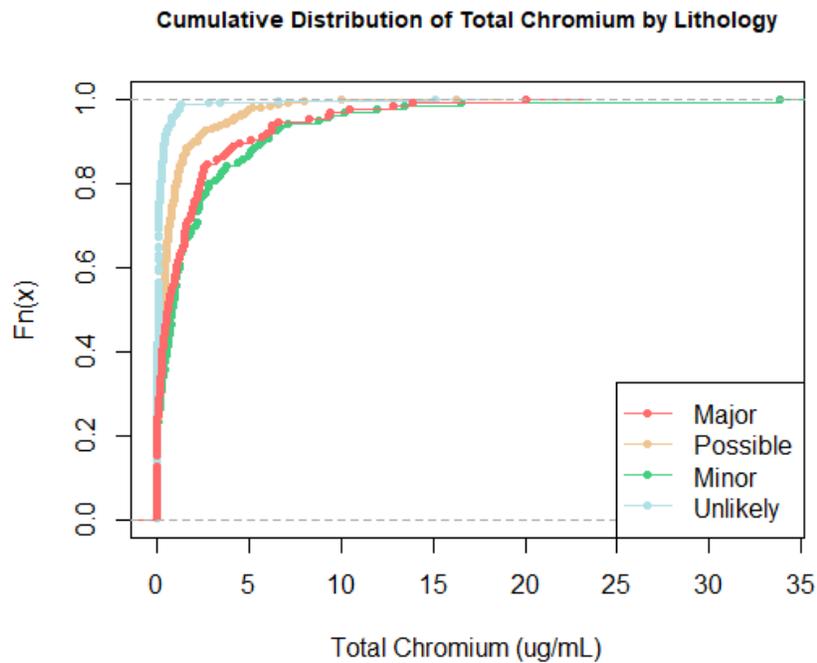


Figure 12 – Cumulative distribution functions for total chromium in NC groundwater as classified by mafic content of the aquifer lithology. Major mafic and significant minor mafic formations have similar distributions, while possible mafic rock and unlikely to have mafic rock each appear to have different distributions.

Hexavalent Chromium in NC Groundwater

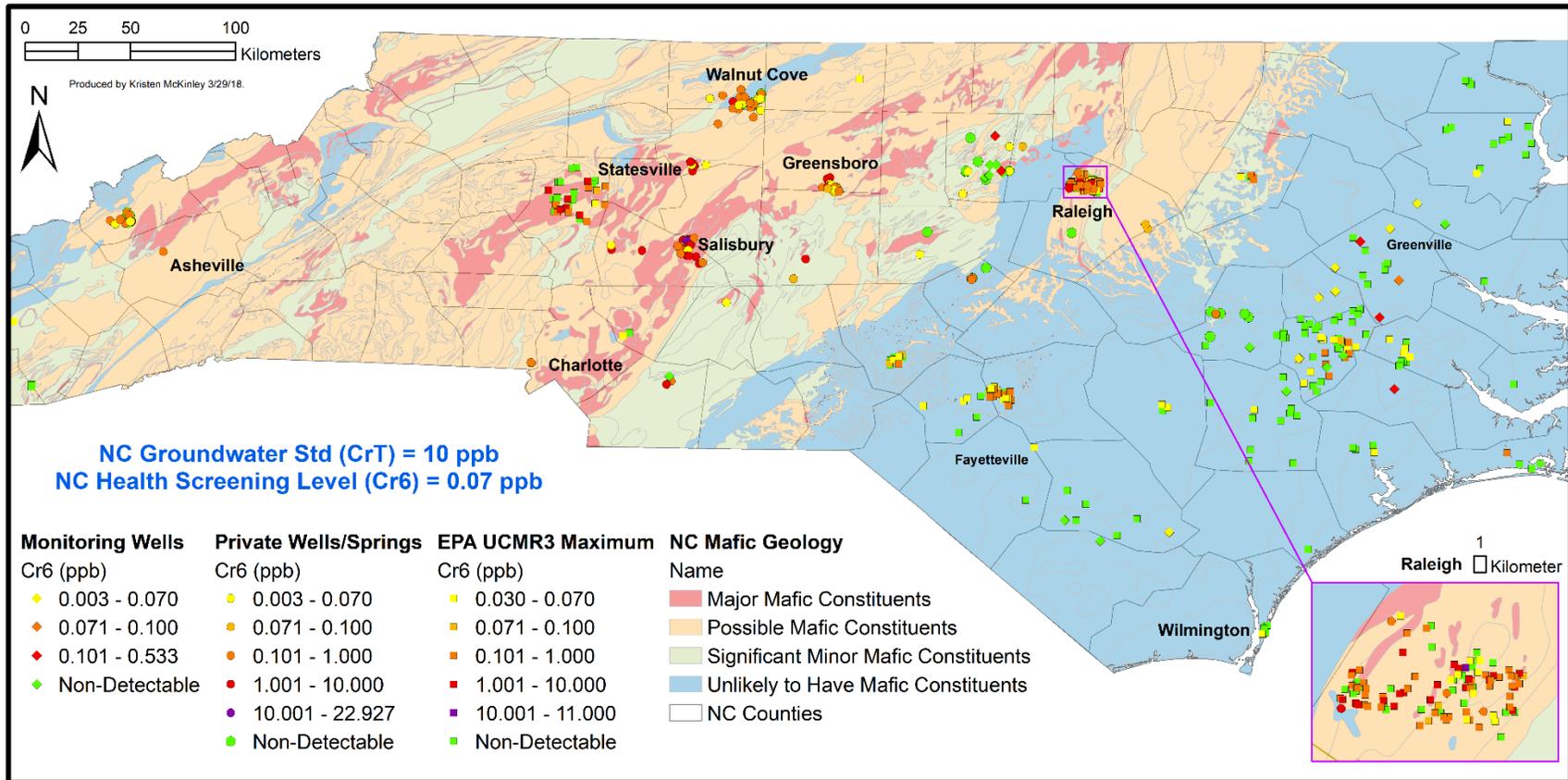


Figure 13 – Occurrence, magnitude, and distribution of hexavalent chromium in North Carolina groundwater as compared to mafic content of the aquifer lithology. Samples are color-ramped with reference to relevant standards: below the minimum reporting level (green), between the MRL and the NC Health Screening Level (yellow), between the HSL and the O2L groundwater standard (orange-red), and above the O2L groundwater standard (purple).

Total Chromium in NC Groundwater

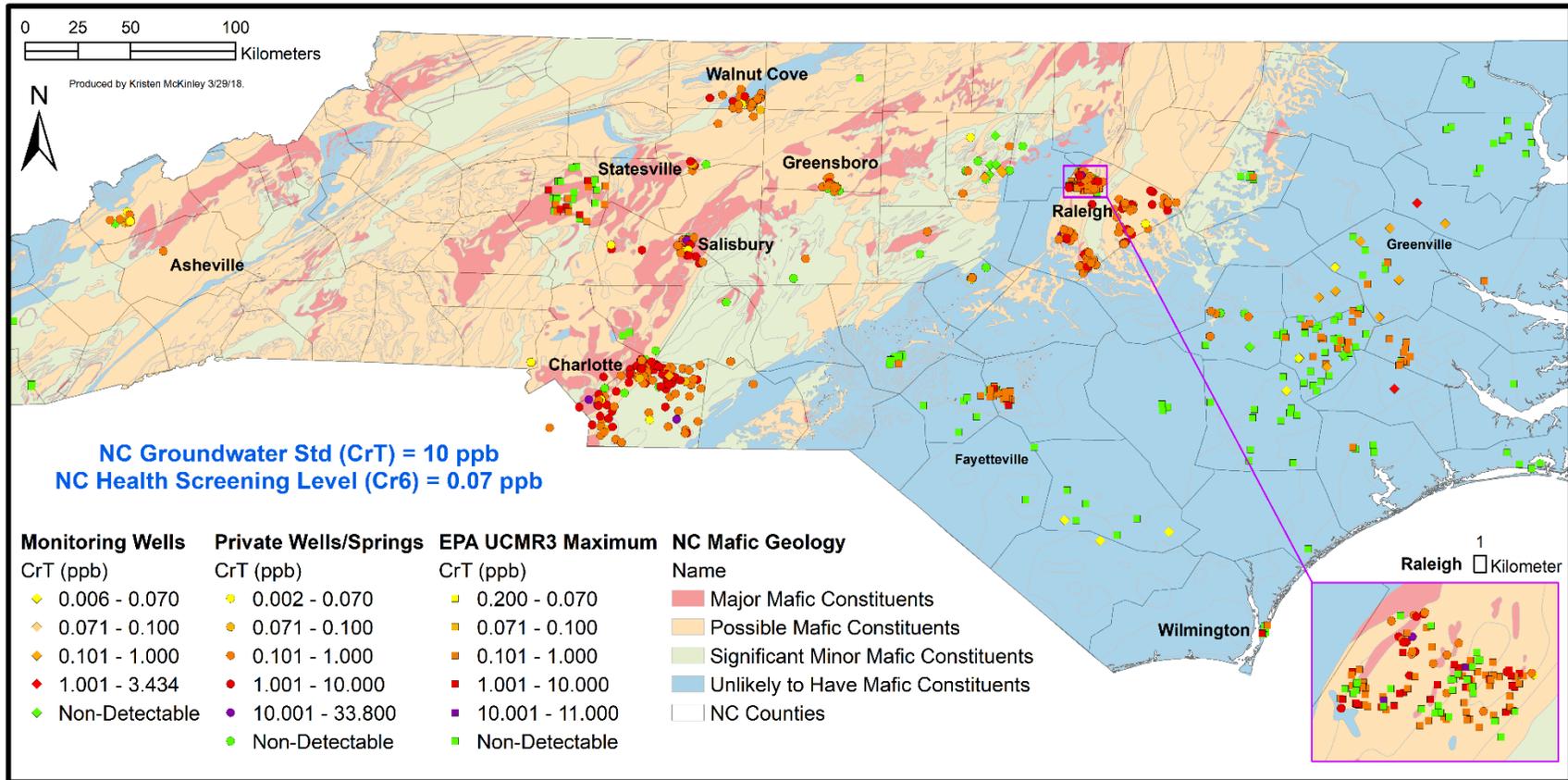


Figure 14 – Occurrence, magnitude, and distribution of total chromium in North Carolina groundwater as compared to mafic content of the aquifer lithology. Samples are color-ramped with reference to relevant standards: below the minimum reporting level (green), between the MRL and the NC Health Screening Level (yellow), between the HSL and the O2L groundwater standard (orange-red), and above the O2L groundwater standard (purple).

4 DISCUSSION

This study, building on the previous work by Vengosh et al. (2016), aimed to examine chromium distribution in North Carolina groundwater beyond the original testing constrained to the Piedmont Aquifers. Extension of the dataset included new sampling efforts and processing archive data from EPA's UCMR3; the updated dataset contains geochemical information ranging from the western mountains to the eastern coastal plains (Figure 2). A side effect of this effort was the expansion of the original dataset from domestic (private) wells, to including community wells, monitoring wells, and springs.

When examining concentrations of Cr in relation to the categorization of lithology by mafic components, both Cr(VI) and CrT are elevated in groundwater from aquifers in mafic rock formations as compared to non-mafic rock formations. While Cr(VI) and CrT had the same overall trend, the Kolmogorov-Smirnov rank test produced different results for comparisons with the minor mafic formations. The difference is likely due to the relatively small sample size for Cr(VI) in minor mafic formations as compared to the other groups. Considering the strong correlation indicating that Cr(VI) is the predominant species of CrT, the results for CrT can be interpreted for Cr(VI) as well.

For CrT, major mafic formations and significant minor mafic formations were found to have similar concentrations to each other but differing when compared to possible mafic formations or unlikely to contain mafic formations. Overall, Cr concentrations appear to increase with the mafic contents in the aquifer rocks: major mafic and significant minor mafic >

possible mafic > unlikely to contain mafic. Additionally, this study found a strong, positive correlation between Cr(VI) and CrT, in both the laboratory dataset and the EPA UCMR3 dataset.

These new results support previous findings and provide additional evidence that Cr(VI) is the predominant species of CrT, and that groundwater in aquifers with subsurface geology containing mafic formations will have elevated levels of Cr when compared to aquifers in non-mafic subsurface geology (Kazakis et al., 2015; Manning, Mills, Morrison, & Ball, 2015; Oze et al., 2007; Tziritis, Kelepertzis, Korres, Perivolaris, & Repani, 2012; Vengosh et al., 2016) More broadly, these results support previous findings from around the globe that Cr(VI) is not always an anthropogenic contaminant but also that it can originate from non-point geogenic sources with a global distribution. Since the EPA's UCMR3 dataset contains Cr(VI) and CrT concentrations for all of the United States, the statistical tests used in this study could be applied at a national level if sufficient geological characterizations can be obtained from the United States Geological Survey (USGS).

Regarding public health, Cr(VI) should have standards separate from CrT due to the difference in analytical capabilities. Under the current EPA regulations and methods, concentrations of Cr(VI) that exceed the previously mentioned public health goals but are below the 0.2 ug/L MRL for CrT would not be detectable. If groundwater was regulated and therefore analyzed specifically for Cr(VI) under EPA's Method 218.7, the MRL would be below public health goals levels, allowing for the identification of any groundwater sample potentially unsafe for human consumption. The highest MRL reported by laboratories to the EPA was 0.036 ug/L, which is less than NC DHHS's HSL of 0.07 ug/L (US EPA, 2011).

Assuming the public health goal levels to be soundly determined, the next step after this project is to identify the potential populations that may be at risk of consuming groundwater exceeding a safe level for Cr(VI) and CrT. Ideally, a tool will be developed that can help citizens predict their likelihood of their water supply exceeding a safe level. This tool will need to consider other parameters that effect the concentration and speciation of chromium, such as pH and oxidation-reduction potential (ORP), as well as well depth. When combined with geology, this could be a valuable tool to target vulnerable populations, especially citizens drinking from domestic wells as these are not regulated and therefore of unknown water quality. This research is possible as an immediate follow-up to this study as those relevant parameters are contained within this dataset.

Another branch of future research for this project is evaluating if Cr concentration differs by the type of well since this dataset can be grouped by community wells or domestic wells, which have distinctive characteristics. Domestic wells tend to be shallower with a lower flow rate than the deeper community wells. Also domestic wells are unregulated and rarely tested for water quality: from 2000-2010, less than 200,000 domestic wells were tested for contaminants (NC DHHS, 2016). As of 2010, over 3.3 million North Carolinian residents relied on self-supplied groundwater as their primary source of water with a per capita use of approximately 70 gallons per day. For the remaining 6.2 million residents, approximately 44.5% of the public water supplies also comes from groundwater sources (Maupin et al., 2014). Understanding the possible effect of well type on Cr concentration is important considering that one-third of North Carolinian residents rely on untested groundwater. With approximately 63.7% of North Carolina's personal water supply coming from groundwater, the results of this

study and future findings are necessary to understanding the role of drinking water for public health outcomes in North Carolina.

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