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# Trace Metal Characterization and Ion Exchange Capacity of Devonian to Pennsylvanian Age Bedrock in New York and Pennsylvania in Relation to Drinking Water Quality

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#### **Abstract**

I report the results of an evaluation on the factors that control the quality of potable water produced in domestic and other wells in the shallow sedimentary rock formations of the Appalachian Basin. I collected 49 samples from the upper 120 meters of Devonian to Pennsylvanian aged bedrock between Marcellus, NY and State College, PA and analyzed their bulk geochemical composition. In particular, I quantified the mobile and total metals for which there are health concerns related to unconventional gas exploitation in the Appalachian Basin; Fe, Mn, Sr, Ba, As, and Pb. Measured bulk concentrations for several formations reached maximum concentrations of 65 ppm As, 4,900 ppm Ba, 63,000 ppm Fe, 130 ppm Ni, and 68 ppm Pb.

To assess the mobility of these metals in the subsurface I used a variation of the U.S. Geological Survey Field Leaching Test. Metals such as Al, Zn, and U potentially can be leached from aquifer rocks naturally under acidic conditions, such as where pyrite might oxidize, to above current allowable regulatory values for these metals (2 mg/L, 5 mg/L, and 0.03 mg/L respectively) from some of the clay-rich formations. Small percentages (typically <1%) of the bulk concentrations were mobilized into solution but were still sufficient to exceed current EPA drinking water maximum contaminant levels (MCL) in many of the samples. In total, 74% of our samples exceeded MCL values for Al, 18% for As, 6% for Fe, 12% for Mn, 98% for Pb (above MCL Goal of 0 ppb), and 70% for U (above MCL Goal of 0 ppb).

Groundwater analyses from both New York and Pennsylvania show that natural ion exchange occurs along flow paths from ridge tops to valleys. I measured the total cation exchange capacity (CEC) of the samples and observed that they do not span the expected values for illite-rich clays (typically 10-40 milliequivalents/100g) commonly found in the Appalachian Basin. Instead, 88% of the samples had CEC values below 10 meq/100g with only 1 sample

above 20 meq/100g. I quantified the hypothetical ground water flow path lengths necessary for the observed cation exchange to occur along fracture planes by combining CEC values with surface area measurements on three samples which ranged from 10.32-13.59  $\text{m}^2/\text{g}$ . These three estimates resulted in plausible flow path lengths of 2 km, 3 km, and 30 km.

Many state and federal regulations do not require water from domestic wells or groundwater samples collected for metal analysis to be filtered. I argue that these regulations expose residents to drinking water with turbidity caused by suspended minerals that have metals attached leading to total concentrations at or above the Environmental Protection Agency's (EPA) MCL levels. I quantified the effects of turbid water at the EPA MCL of 5 NTU and improper filtration of turbid groundwater samples at the EPA MCL of 10 NTU on total metal concentrations used to trigger regulatory compliance related to possible contamination and health effects.

Along with this broad scale study area I compared my geochemical results to the Fiorentino II (2015) study on a Devonian outcrop 4 miles North of Cortland, NY to evaluate small-scale trace metal heterogeneity within a single stratigraphic section. My regional collection of single data points at outcrops plotted within the  $10<sup>th</sup>$  and  $90<sup>th</sup>$  percentiles of the small-scale outcrop study. Together these two studies provide important information to determine the extent to which ground water might be naturally high in trace metal composition, either because of geochemical conditions or entrainment of suspended material not removed prior to sampling.

# **Trace Metal Characterization and Ion Exchange Capacity of Devonian to Pennsylvanian Age Bedrock in New York and Pennsylvania in Relation to Drinking Water Quality**

by:

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B.S., The University of Texas at Dallas, Dallas, Texas 2013

#### MASTERS THESIS

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#### **Introduction**

In the Appalachian Basin, people are concerned that hydraulic fracturing of shales to obtain gas may contaminate their water with metals introduced from produced water or metals solubilized by the introduction of stray methane into shallow ground water. Hydraulic fracturing, in short, is the practice of producing fractures in a rock formation that stimulate the flow of natural gas or oil and increases the volumes that can be recovered. These fractures are created by injecting large quantities of high pressure fluids down a wellbore and into the target formation (EPA, 2014). Typically these fluids consist of water (98-99.2%) with various chemical additives along with sand, ceramic pellets, or other incompressible particles added to hold open the newly created fractures. Current chemical additives to the fracturing fluids include friction-reducing additives to allow the fluids to be pumped at a higher rate and biocides to reduce microorganism growth. Oxygen scavengers are also added to reduce the corrosion of wellbore pipes along with miscellaneous acids to remove drilling mud from the pipe (GWPC & IOGCC, 2015).

Once the injection process is complete, the internal pressure of the rock formation causes the injected fluid to return to the surface through the wellbore. This resulting fluid, known as "flow back water" contains the original additives along with any brines, metals, radionuclides, and/or hydrocarbons it may have come into contact with in the subsurface (EPA, 2014). Flow back water is stored in tanks or pits at the surface prior to treatment which typically involves either re-injection of the water well below the water table or having it processed by a wastewater facility, if possible. The flow back water disposal process poses potential risks to groundwater resources via improper containment of flow back water at the surface, leaks in injection well casings, or the newly created fractures serving as migratory pathways for methane gas (EPA, 2014).

The process of hydraulic fracturing is especially important in Pennsylvania and New York State due to the presence of the Marcellus shale. Starting in 2003, drilling companies noticed that this formation, which spans across much of New York, Pennsylvania, and West Virginia, contained trillions of cubic feet of natural gas that could be utilized as a resource. Since the discovery of the Marcellus shale gas there are now over 16,000 operating gas wells permitted in the state of Pennsylvania alone (Pennsylvania DER, 2015). High volume hydraulic fracturing is currently banned in the state of New York although the risk of groundwater contamination is still present from other drilling operations.

Most domestic water wells in Appalachia are drilled in bedrock, and are up to 400 feet deep. These obtain their water from fractures in uncased bedrock, open holes which act as cisterns, storing water during dry months when recharge is minimal. The rocks from which people obtain their drinking water in the northern Appalachian Basin contain metals common to those found in produced water from oil and gas.

Under certain geochemical conditions, these metals can naturally be released from the bedrock into the groundwater. For example, under anoxic and/or acidic conditions, iron and manganese as well as arsenic can be leached from oxides in shales (Brumsack, 2006). Most clastic rocks contain significant amounts of clay that can accumulate at the bottom of open-hole wells as the well lining fractures.

The United States Environmental Protection Agency (EPA) has long recognized that improperly completed monitoring wells can produce water with so many clay-sized particles that the water becomes turbid and cloudy (Barcelona et. al., 2005), a property which can be measured using an instrument called a nephelometer. The EPA establishes drinking water standards and

maximum contaminant levels (MCL) for both personal and industrial water. An MCL is defined as "the level of a contaminant in drinking water below which there is no known or expected risk to health" (EPA, 2009). The MCL standards established by the EPA for turbidity in drinking water are in question as part of this study. Turbidity measures water clarity with respect to the suspended (0.004 mm to 1.0 mm) particles in the water. Turbidity increases in water due to high pumping rates or inadequate drinking water well construction. For decades, the regulatory industry has tried to evaluate the degree to which turbidity and associated mineral matter containing metals of regulatory interest reflects what may be consumed by people, rather than an artifact of sampling protocols. I hope to settle this question.

Many regulations do not call for water from domestic wells to be filtered, under the assumption that the wells have been completed properly to avoid turbidity. But it is clear that over-pumping uncased bedrock wells can produce turbidity, and the mineral matter causing it contains metals of regulatory interest; Al, Fe, Mn, Sr, Pb, etc. When samples of water are collected for metals analysis, they are acidified to pH less than 3 to insure any metals in solution will remain in solution. However, adding acid to water with mineral particles in it will dissolve the minerals, completely or in part and desorb metals loosely bound to clays as well. The question I address is to what extent turbidity in drinking water in Appalachia can be the cause of high concentrations of metals, producing a false positive with respect to characterizing dissolved metal concentrations that MCLs are based on.

I focused on metals of environmental importance (Fe, Mn, Sr, Ba, As, and Pb) related to health or aesthetic concerns. My work will provide guidance about potential natural trace metal contamination in ground water found in shallow rock aquifers to help homeowners select

locations and depths to drill water wells that minimize their exposure to natural contaminants, be they in dissolved or particulate state.

To assess the potential for the natural mobility of dissolved trace metals and other elements, I simulated acidic conditions mimicking that expected from possible oxidation of pyrite combined with records of acid rain. In cases with circumneutral pH, most trace metals are effectively immobile except under anoxic conditions. Since the solubility of trace metals under anoxic conditions generally is similar, within an order of magnitude, to those under very acidic conditions, my experiments conceptually address both situations leading to metal solubility (Hem, 1978).

Groundwater analyses in both New York State and Pennsylvania show a tendency for natural ion exchange to occur, wherein clay minerals remove natural water hardness (Ca and Mg) and release sodium (Na) (Siegel et. al., 2014). Groundwater samples collected from southcentral New York, northeastern Pennsylvania, Ohio, and West Virginia show a clear natural geochemical progression from  $Ca + Mg$ ,  $HCO<sub>3</sub> + SO<sub>4</sub>$  type waters at ridge tops along short flow paths to Na,  $HCO<sub>3</sub> + SO<sub>4</sub>$  type waters along slope faces with intermediate flow path lengths to Na + Cl type waters in discharge valleys with long flow path lengths (Molofsky et. al., 2013 and Siegel et. al, 2014). This change in groundwater hydrogeochemistry, prior to modification of the local groundwater by anthropogenic water softening is clear. The cation exchange capacities of the formations of interest are currently not well known. Therefore, I also explored whether cation exchange actually causes major hydrogeochemical changes in water types along flow paths in the shallow Appalachian Basin.

Generally, clay sized minerals in Appalachian Basin shales have minimal ion-exchange capacity, associated primarily with the clay mineral illite (Drever, 1982). Hosterman and

Whitlow (1981) analyzed the clay-sized fraction of Upper Devonian Appalachian Basin black shales and found that 60% of the samples consisted of clay. Of this fraction, the clay minerals consisted of the following average percentages: illite, 59; chlorite, 17; mixed-layer illitesmectite, 23; kaolinite, 1; mixed-layer illite-chlorite, trace amounts. If the Devonian aged rocks we sampled have low CEC values, then another mechanism for the observed ion exchange needs to be considered. The question I seek to answer is, given a Ca concentration in a ground water, how long would it take for the observed ion-exchange to occur and how long would the hypothetical flow path have to be?

#### **Geologic Setting**

The Appalachian Basin,  $536,000 \text{ km}^2$  in area, extends from southern Quebec to northern Alabama (Ettensohn, 2008). The sediments record nearly one billion years of tectonic history, including late Proterozoic supercontinent formation and breakup, the formation of the Appalachian orogen in the Paleozoic and the transition from an active to passive margin during the disassembly of Pangea in the Mesozoic (Faill, 1997). The formation of the Appalachian Basin began during the Taconic orogeny, the second of four major orogenic events that shaped the region. Microcontinents and magmatic arcs from prior rifts accreted onto the existing carbonate shelf along the eastern margin of Laurentia during the Taconic orogeny (Faill, 1997). During the early Silurian (443-427 Ma), coarse-grained clastic rocks were deposited in the basin as a result of erosion from the newly created highlands uplifted during the Taconic orogeny (Faill, 1997).

Beginning in the early to middle Devonian, the Acadian orogeny ended the previous deposition of inter-fingered continental and marine sediments during the late Silurian, by introducing more siliciclastic material into the basin (Faill, 1997). This uplift was caused by the oblique collision between Laurentia and a microcontinent, or a number of terranes referred to as Avalon (Rast and Skehan, 1993). Ettensohn (1998) proposed that the extensive black shale deposits in the Appalachian Basin formed in response to foreland basin subsidence associated with the Acadian orogeny. Accumulation of high organic-carbon (>10%) black shales was associated with the deepening of the foreland basin formed under widespread anoxia beneath a permanent pycnocline (Ettensohn, 1985b, 1998).

Uplift and erosion of siliciclastic material continued throughout the Devonian to form the Upper Devonian Catskill Delta (Faill, 1997) and continued into the late Carboniferous and earliest Permian period when west Gondwana and Laurentia converged to produce the Permian Alleghanian Orogeny in the Appalachians (Faill, 1997). The tectonics of this period were defined by fold and thrust belts creating long, curved folds within the Appalachian basin (Ettensohn, 2008). Crustal extension within the late Triassic and early Jurassic created numerous closed basins within the larger Appalachian Basin (Dennison, 1989). The cyclical orogenesis and erosion in this region over millions of years resulted in a complex basin with a variety of rock types and geochemical properties. The Devonian and Carboniferous sediments in this study are of particular importance because presently they constitute the upper bedrock from which groundwater is being collected in the region.

#### **Description of Study Area**

The study area lies along a 354 km transect between Marcellus, NY and State College, PA (Figure 1) This area is located in the north central Appalachian Basin where the Marcellus formation is exposed at the surface in north central New York and is being hydraulically fractured further south in Pennsylvania. These surface exposures provide a mechanism to interpret the potential groundwater hazards associated with bedrock at depth in other locations.

This region contains multiple depositional cycles consisting of a basal black shale overlain by lighter gray shale, siltstone, and sandstone with limestone beds at the top. An example of a complete cycle is the Devonian Hamilton Group sampled in this study. This cycle contains the basal black Marcellus and Skaneateles shales, the overlying Moscow and Ludlowville shales and the Tully limestone at the top of the sequence (Roen, 1983). Sampling varying lithologies from different depositional environments allowed us to better characterize the potential hazards that these formations present to drinking water.



**Figure 1 – Google Earth image of regional study area and zoom in image of 49 sample locations between Marcellus, NY and State College, PA**

From Marcellus, NY to the south rock units generally become coarser in texture from the fine grained Marcellus shale, to the Lock Haven shales and siltstones, and finally the Catskill formation sandstones and siltstones. A more detailed description of each formation sampled for this project is as follows.

#### **Sample Collection**

The forty nine samples were collected from exposed outcrops of Devonian to Pennsylvanian age bedrock in the study area. The outcrops were chosen by a combination of literature review and Google Earth, then cross referenced with geologic maps. Although the sample locations were limited by both outcrop exposure and quality, a generally even sample distribution was achieved (Figure 1; Table 1).

A bulk sample (>150-200 grams), GPS coordinates, and a general lithologic description were obtained at each outcrop. Samples were excavated deeper than 10 cm into the outcrop to reach fresh sample. Samples are organized by the state they were collected in (NY or PA) and the number of the sample ranging from 1-29.

At each sample location, if possible, a fine grained shale sample was collected rather than a coarser grained sample. At outcrops where shale samples were heavily weathered, a sample from a coarser grained unit was collected instead. I chose this protocol to attempt to emphasize finer grained clastics which, by virtue of greater internal surface area, will solubilize faster and are most susceptible to be mobilized in particulate form. A detailed description of the number of samples collected from each formation can be found in Table 1.

Along with this regional scale geochemical study, I compared my results to a more detailed study of the total metals content of an outcrop of the upper Devonian Genesee Group 4 miles north of Cortland, NY, where Fiorentino (2015) evaluated small-scale trace metal heterogeneity within a single stratigraphic section. Together these two studies provide important information to determine the extent to which groundwater might be naturally high in trace metal composition, either because of geochemical conditions or entrainment of suspended material not removed prior to sampling or drinking. The concentrations of various trace metals were compared from this single outcrop to our regional data for the same group to provide context for our reported values. (Figure 6).

#### **Lithologic Descriptions**



**Figure 2 – Generalized Devonian age stratigraphy of New York State (modified from New York State Geological Survey Highway Map, 1990)**

Stratigraphically, sampling began with the lower Devonian Helderberg Group (423-393 Ma) with one sample from the Manlius Limestone from a 20 m thick outcrop 4 km north of Marcellus, NY. The group contains carbonate intervals of limestone and dolostone which stratigraphically underlies the Oriskany sandstone.

Nine samples were collected from the Lock Haven formation within the Susquehanna Group (419-382 Ma) in New York State. This formation consists primarily of interbeds of horizontally laminated olive-gray mudstone, siltstone, and sandstone with thin layers of conglomerate and black shale with graded bedding (Slingerland et. al, 2009). Outcrops sampled were approximately 50 m high with moderate weathering of mudstone units. This group stratigraphically underlies the Catskill Formation.

Ten samples were collected from the middle Devonian Hamilton group (419-382 Ma) from multiple formations in New York State. The basal formation is the Marcellus shale sampled from multiple sub-members, including the Union Springs shale, Chittenango shale, Cardiff shale, and Solsville shale. These members consist of fissile gray-black to black colored, thinly laminated shale with sparse marine fauna. The Moscow shale is the uppermost member of the Hamilton Group in New York State. This shale member consists of shale and sandstone interbeds with our sample being collected from a quarry 9 km west of Hamilton, NY.

Three samples were collected from the upper Devonian (382-358 Ma) Renwick shale member of the Genesee group in New York State. This formation overlies the Hamilton group and consists of black, greyish-black to olive back shale to medium grey shale with small amounts of nodular limestone, argillaceous siltstone, and on rare occasion fine sandstone. The formation at outcrops was approximately 15 m thick with few fossils and is overlain by the Ithaca member of the Genesee formation (de Witt and Colton, 1978). The uppermost portion of the Genesee group consists of non-marine fluvial clastic sediments from the Oneonta formation (Selleck, 2010).

Three samples were collected from the upper Devonian (382-358 Ma) Sonyea group in New York State consisting of a generally east-west oriented belt about 320 km long, extending from Lake Erie on the west to the Catskill Mountains in the east. These samples were collected in the vicinity of Ithaca, NY, which consists of about 215 m of alternating unfossiliferous siltstones and shales (Sutton et al., 1970). The Sonyea Group includes rocks deposited in a variety of deltaic environments from non-marine flood plains on the east, through a marine shelf, to deeper slope and basin deposits on the west (Sutton et al., 1970).

Five samples were collected from the upper Devonian West Falls Group (382-358 Ma) in New York State. It consists of a lower black shale member known as the Rhinestreet shale and an upper gray shale and mudstone section with abundant limestone nodules, the Angola Shale member (Pepper et al., 1956). Both members interfinger to the east into an eastward-thickening sequence of siltier and sandier rocks. The Rhinestreet shale is approximately 30 m thick and is split into four members including the Dunn Hill shale and Roricks Glen shale. The Angola shale member further east includes the upper Walton sample location and interfingers with the Gardeau formation to the west.



**Figure 3 – Generalized Devonian to Mississippian age stratigraphy of Pennsylvania State (modified from Milici and Swezey, 2006)**

Fourteen samples were collected from the 850 m thick upper Devonian (382-358 Ma) Catskill formation in Pennsylvania consisting of siltstone or sandstone with few shale samples. The lithologies at the outcrops were arranged in upward fining cycles with thin interbeds of conglomerate and were commonly red and green-gray in color. The red in many of the samples is caused by increased hematite content and the green-gray color of the siltstones is due to the presence of chlorite.

Two samples were collected from the late Devonian to early Mississippian (372-346 Ma) Huntley Mountain formation in Pennsylvania consisting of upward fining cycles of greenishgray to olive-gray sandstone with siltstone and shale interbeds and sparse plant fossils. The Huntley Mountain formation is a 150-215 meter thick boundary between the underlying Catskill formation and the overlying Burgoon sandstone (Skehan et al., 1979).

Two samples were collected from the Mississippian age (358-346 Ma) Burgoon sandstone, the upper portion of the Pocono formation, in Pennsylvania. This formation is approximately 110 meters thick at its maximum and consists of medium to coarse grained light gray sandstone with thin dark shale and siltstone interbeds with plant fossils commonly present (Skehan et al., 1979).

One sample was collected from the Mississippian age (330-323 Ma) Mauch Chunk formation in Pennsylvania consisting of non-marine grayish-red shale and siltstone with some light gray sandstone. The maximum thickness of this formation is uncertain but is estimated to be approximately 2,450-2,750 m, our sample location had 40 m of exposed rock (Skehan et al., 1979).

One final sample was collected from the lower to middle Pennsylvanian age (323-315 Ma) Pottsville formation in Pennsylvania consisting of gray conglomerate, fine to coarse grained sandstone, and is known to contain limestone, siltstone and shale, as well as anthracite and bituminous coal although no coal was observed at our sample location (Levine and Slingerland,

1987). The Pottsville formation ranges in thickness from 6-75 meters and was approximately 10 meters tall at this sampling location.



**Table 1 – Summary of 49 samples collected from various geologic formations/groups in the study area. Adapted from U.S. Geological Survey Geology by State Database**

#### **Methods**

#### **XRF Analysis**

All samples were analyzed for total metals and trace element composition at the Peter Hooper GeoAnalytical Lab at Washington State University by using X-ray fluorescence instrumentation. Approximately 80-100 grams of each sample was ground using tungsten carbide ring mills with 8-10 drops of Vertrel as an evaporative lubricant for 2 minutes each. Between 3.5000 to 3.5050 g of the resulting clay-sized powder was weighed out and mixed in a 1:2 ratio with the fusion additive di-Lithium Tetraborate (Conrey, 2014). The samples were fused at 1000°C for 40 minutes then allowed to cool. Each sample bead was re-ground to clay powder for 30 seconds in the ring mills to ensure homogeneity of the sample from the initial

fusion process. The sample powder was then fused again at 1000°C for another 40 minutes to create the final bead for analysis (Conrey, 2014).

Loss on Ignition (LOI) was measured for each sample by measuring between 0.5-2 grams of the same clay sized sample into a glass crucible (without a fusion additive), recording the weight, and firing the sample at 900°C for 16 hours and recording the final weight after cooling.

Samples were analyzed using a ThermoARL Advant'XP+ sequential X-ray fluorescence spectrometer. This instrument has an auto-sample feature which allowed all 49 samples to be analyzed in the same batch with three randomly selected duplicates to ensure precision. Eleven major elements were analyzed for in oxide form:  $SO_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $Al_2O_3$ ,  $FeO$ ,  $MnO$ ,  $MgO$ , CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>. In addition, twenty trace elements were analyzed for: Ni, Cr, Sc, V, Ba, Rb, Sr, Zr, Y, Nb, Ga, Cu, Zn, Pb, La, Ce, Th, Nd, U, and As.

X-ray fluorescence, simply put, works by bombarding homogeneous sample pellets made with a focused X-ray beam. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation energy is characteristic of a transition between specific electron orbitals in a particular element. The resulting fluorescent Xrays can be used to detect the abundances of elements that are present in the sample (Conrey, 2014).

#### **Leaching Experiments**

The XRF data provides bulk concentrations of trace metals and elements in the sandstone, shale, and siltstone samples. When attempting to quantify the potential hazards these rocks can impose on drinking water, the leachable amount of metals needs to be assessed. To test this, I used a variation of the USGS Field Leach Test for Assessing Water Reactivity and Leaching Potential (Hageman, 2007). This method consists of a simple 15 minute experiment with nearly identical results to EPA Method 1312 which uses an 18 hour agitation process and more specialized equipment (Hageman, 2007).



**Figure 4 - Adapted from Hageman, 2007 to illustrate results of leaching experiments using the EPA Method 1312 and the USGS Field Leach Test methods**

The leaching procedure utilized a 5 gram sample of the remaining clay sized powder from the XRF lab work. This sample was mixed in a 1:20 ratio with a pH 4.0 diluted sulfuric acid solution in 125 mL high density polyethylene plastic bottles with head space and agitated for 5 minutes, then allowed to settle for 10 minutes. The sulfuric acid solution was made by mixing 5  $\mu$ L of H<sub>2</sub>SO<sub>4</sub> with 1 L of de-ionized water to produce a pH of approximately 4.0.

After the agitation process was completed and the particles settled, the unfiltered sample was analyzed for pH and specific conductance. The leachate was filtered through a 60 mL Luer Lock syringe fitted with a 0.45 µm nitrocellulose capsule filter (Hageman, 2007). The resulting filtered sample was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ICP optical omission spectroscopy (ICP-OES) at The State University of New York College of Environmental Science and Forestry (SUNY ESF) for trace metals and elements.

ICP-MS works by introducing the sample as a solution which is converted by a nebuliser into an aerosol and dispersed into an argon gas plasma at temperatures ranging from 6,000- 10,000 Kelvin (Jarvis, 1997). The plasma torch consists of three concentric glass tubes between which an inert gas, commonly argon, is passed. The sample aerosol upon entering the high temperature region of the ICP is volatilized, dissociated, and ionized (Jarvis, 1997). The sample exits the mouth of the torch as a mixture of atoms, ions, unvolatilized particles, and molecular fragments. The resulting ions are extracted into the mass spectrometer via a decrease in pressure from the axial zone of the torch (Jarvis, 1997). The ions are then transmitted through a lowvacuum region (about 0.005 atmospheres) and focused into a narrow beam via two conical nickel apertures, the sampling cone and the skimmer. These apertures allow the ions to pass through into the mass analyzer but deflect away a majority of uncharged molecules and atoms (Jarvis, 1997). The most common form of mass analyzer is a quadrupole mass filter which allows ions of only one mass/charge ratio through the detector for each combination of potentials applied to the pair of rods. Ion detection is typically accomplished using electron multiplier detectors. These detectors are able to count individual ions and due to the low background signals, a high sensitivity for most elements is achieved (Jarvis, 1997). A relative measurement is then reported which compares the number of ions in the sample to that of a standard solution.

Multiple elements can be analyzed simultaneously which makes ICP-MS a very effective technique. However, ICP-MS is limited by the fact that the quadrupole mass filter cannot resolve the small differences in mass which separate elemental peaks from polyatomic ions that may interfere at the same nominal mass number (Jarvis, 1997). Due to this, other analytical techniques can be used in conjunction with ICP-MS to do metal analysis, such as ICP optical emission spectroscopy (ICP-OES).

ICP-OES begins the same way as ICP-MS, by introducing an aerosol sample into argon plasma which ionizes the sample at temperatures greater than 7000°C (Walsh, 1997). When energy is transferred to a ground-state atom, electrons may be promoted to vacant higher-energy levels. As the atom moves to a lower-energy state as it exits the plasma, this electron may drop back to the lower-energy level and energy will be radiated in the form of a photon (Walsh, 1997). For each specific transition, light of a specific wavelength is generated and is referred to as an emission spectral line. Every element has its own set of emission lines, and samples that are mixtures of multiple elements will emit a range of spectral lines contributed by the elements present (Walsh, 1997). By measuring the intensities of selected spectral lines, the spectrometer provides a quantitative measure of the concentration of each analyte and reports those values to the computer. The fact that mass-to-charge ratios are ignored and instead the optical emissions are quantified into concentrations of elements based on the intensity of the emitted light allows for a different range of elements to be analyzed for than on ICP-MS alone.

These results were compared to the solid rock bulk concentration data to determine how effectively metals can be mobilized under acidic conditions. The pH 4.0 value was selected to attempt to simulate the most acidic recorded pH of acid rain in the region (pH 4.1-4.4) along with natural pyrite oxidation in the subsurface. More acidic solutions could have been used to achieve maximum leaching of the metals in question but that would be unreasonable for simulating common natural conditions in these formations. Clay sized powder was used rather than larger sized particles to maximize the surface area exposed to the leaching solution. This increased surface area was important for the experiment because of the limited agitation time with the acidic leaching solution before the sample was filtered.

#### **Ion Exchange**

Ion exchange is defined as the total sum of the exchangeable ions of similar size and charge between a solution and an insoluble solid at a specific pH (Chapman, 1965). Since most trace metals are cations and the surfaces of many clay minerals and organic materials have net negative charges, cation exchange can occur along the exchanger sites located on the surfaces of clays and organic matter (Horowitz, 1985). This process is commonly utilized in water softening systems by exchanging "hard water" cations  $(Ca^{2+}$  and  $Mg^{2+})$  for "soft water" cations (Na<sup>+</sup>) via artificial ion exchange resin columns. The process of natural ion exchange is governed by the presence of clay minerals, organic matter, and metal oxy-hydroxides which can sorb charged ions on to their surfaces (Horowitz, 1985).

Clay minerals have large surface areas and CEC increases with decreasing grain size. (Horowitz, 1985). The clay minerals in Devonian age shales in the Appalachian Basin consist mostly of illite, chlorite, and kaolinite with illite ranging from 40-90% of the clay composition (Hosterman and Whitlow, 1983). The ion exchange capacity of illite is generally low (10-40 meq/100 g) compared to mixed layered clays (80-150 meq/100g) (Drever, 1982).

I used the analytical procedure adapted from Chapman (1965) to measure CEC in the crushed samples. The sediment was leached with 250 ml of 1N ammonium chloride at a rate of 30 drops per minute, washed with 200 ml of 95% isopropyl alcohol at a rate of 30 drops per minute, and leached with 250 ml of 10% acidified sodium chloride at a rate of 30 drops per minute (Chapman, 1965). The resulting leachate was transferred into a Kjeldahl flask and washed with sodium chloride to completely transfer the leachate (Chapman, 1965). In a separate Erlenmeyer flask, 50 ml of 4% boric acid was combined with 3 drops (0.15 ml) of pH indicator solution. The flask was connected to the distillation apparatus and 150 ml of distillate was

collected for titration. Finally, I titrated the distillate with 0.1 N HCl until the indicator solution in the Erlenmeyer flask turns from blue to pink. The CEC in meq/100 g is calculated from the following calculation:

**CEC (meq/100 g) = (T-B) x N x 100/S**

Where: **T** is the amount titrated for sample

**B** is the amount titrated for sample blank

**N** is the normality of standardized acid

**S** is sample weight in grams

In addition to the total CEC of each sample, surface area measurements of selected samples were obtained to more accurately quantify the potential cation exchange that can occur along a flow path. Particle Technology Labs completed 3-point Brunauer–Emmett–Teller (BET) surface area measurements on three samples (1 organic rich shale and 2 siltstones). This analysis measures the adsorption of nitrogen gas on to a surface at a given pressure and is able to calculate the surface area  $(m^2/g)$  based on this amount of gas.

Once the surface area was known it was used in conjunction with the CEC values to estimate the amount of milliequivalents (meq) of cations in a gram (g) of sample that can be exchanged by dividing the meq/g by the surface area of our samples. This calculation gives us the ability as a first approximation to hypothesize whether the natural ion exchange as observed by Siegel et al. (2014) is reasonable or not in terms of the necessary flow path length for cation exchange to occur. This calculation was completed via a conceptual model of water flowing through a 1 m long and 0.001 m wide fracture in the subsurface bounded on both sides by sediment with our CEC values and surface area measurements. For the model, I calculated the volume of water in a 1 m<sup>2</sup> x 1 mm x 1 m<sup>2</sup> square parallelepiped piece of the fracture system to be 1 liter. The hypothetical length of a subsurface flow path wherein Ca is exchanged for Na was

calculated by dividing the observed meq/L of Ca from groundwater analyses by the amount of milliequivalents of cations that the sample can exchange on both sides of the fracture plane. The resulting flow path length through the fracture is how far groundwater would hypothetically need to travel in order for the cation exchange to occur. The time that this flow path would take is dependent on the groundwater velocity, which we calculated to be 10m/year for this first approximation conceptual model.

#### **Turbidity**

I designed experiments to test how much metal of environmental concern would be in water that met the regulatory drinking water MCL of 5 NTU along with the regulatory sampling MCL of 10 NTU. The experiment involved mixing 100 mg of clay sized sediment into 1 L of deionized water. This solution was agitated to ensure that the clay particles were in suspension and the initial turbidity measurement was recorded using a nephelometer. Due to the intrinsic nature of darker materials to typically absorb more light than light colored materials, turbidity values are influenced by the color of sediment suspended in solution. Higher turbidity values are often associated with lighter colored suspended solids when comparing equal masses of light and dark colored suspended solids in turbid water. To combat this logistical problem of turbidity depending on sample color, the same experiment was done 8 times with varying samples with different colors; black, gray, white, red, and brown. The 100 mg/L solution had initial turbidity values ranging between 27 NTU and 78 NTU depending on the color of the suspended solids. A series of dilutions (5x, 10x, and 25x) were collected from the solution and their resulting turbidity values were recorded. This collection of data points for each sample was plotted on a graph of turbidity vs dilution with a power law relationship. The number of dilutions necessary to calculate a turbidity of 5 NTU and 10 NTU for each sample was achieved from this method.

Once the number of necessary dilutions for the sample was known, the resulting mass of sediment required to bring 1 L of water to 5 NTU or 10 NTU for that sample could be calculated from the initial mass of 100 mg. For example, if one sample required a 7.5 dilution from the initial 100 mg/L concentration, then 100mg/7.5 would result in a mass of 13.3 mg to be added to 1 L of water in order to achieve a turbidity of 5 NTU. These masses for the 8 samples were calculated, and a resulting mass for several trace elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ni, Cr, Ba, Sr, Cu, Zn, Pb, U, and As) was plotted. The resulting range of concentrations for each element was plotted in a box plot with the corresponding MCL for each element (where applicable) to illustrate the potential range of health hazards associated with consuming drinking water at a turbidity value of 5 NTU (Figure 8). Any exceedances of drinking water MCL values are considered health concerns that need to be addressed.

#### **Total Organic Carbon**

Ten samples were selected to be analyzed for total organic carbon (TOC). All samples selected were shale from the Hamilton group, West Falls group, or Genesee Formation except for one siltstone sample from the Catskill Formation. These samples were presumed at have the greatest potential for TOC in our dataset which can be used to correlate with the concentrations of other trace elements such as Mo, V, Cu, Zn, or U that are typically enriched in organic carbon rich sediments (Goldschmidt, 1954).

The methods for analyzing TOC in our samples are as follows: A ceramic crucible was heated to 1000 $^{\circ}$  C for at least one hour and cooled to room temperature. Next,  $0.025 \pm 0.004$ grams of crushed sample  $( \leq 0.8 \text{ mm in size}, \text{No. 20 sieving mesh})$  was added into the crucible inside of a glass beaker. The beaker was placed on a 115° C hot plate and the sample was washed twice with 5N hydrochloric acid and allowed to dry. The sample was then analyzed on a LECO C230 carbon/sulfur analyzer for TOC values.

#### **Rock Evaluation**

Bulk rock evaluation was completed on all ten samples to identify their organic matter type and hydrocarbon potential. For this analysis, the same mesh size for the TOC analysis was used and  $0.065 \pm 0.010$  g of sample was weighed out and placed in a graphite crucible. The sample was then heated from 300° C to 650° C at a rate of 25° C/minute in a controlled inert atmosphere of nitrogen and helium. A flame ionization detector measures the quantity of free hydrocarbons in the sample along with the amount of hydrocarbons and oxygen containing compounds  $(CO<sub>2</sub>)$  that are produced during the thermal cracking of the insoluble organic matter in the sample. These data were then reported and used to confirm the terrestrial origin of each sample and its level of hydrocarbon maturity in relation to the buried and more mature formations in Pennsylvania currently being hydraulically fractured for oil and natural gas.

#### **Results**

Results of key trace elements provide a framework in which to visualize variations in concentrations between the formations over time (Figure 5). Measured bulk concentrations for several formations reached maximum concentrations of 65 ppm As, 4,900 ppm Ba, 63,000 ppm Fe, 130 ppm Ni, and 68 ppm Pb. Figure 5 illustrates the range of concentrations of 20 key elements in the 49 samples. The data are stratigraphically arranged by the age of the formation sampled and also color coded. For example, to study the range of observed Sr concentrations in the Catskill Formation the reader would locate the Sr graph and focus on the orange bar corresponding to the Catskill Formation.

The comparison of the regional bulk geochemical data with the Fiorentino (2015) study of a single outcrop of the Genesee Group provided a context in which to interpret the confidence in our dataset. The mean concentration of my three regional samples collected from the Genesee Group plotted within the  $10<sup>th</sup>$  and  $90<sup>th</sup>$  percentile values of the small scale study for all 8 elements analyzed while 5 of the 8 elements plotted within the  $25<sup>th</sup>$  and  $75<sup>th</sup>$  percentile values (Figure 6). The Fiorentino (2015) study sampled a single outcrop at a high resolution ( $\sim$  every 30 cm) to characterize single outcrop heterogeneity. These results suggest that the data from my regional study with fewer samples in each unit are sufficient to broadly characterize, as a first approximation, the trace element composition of the rock units.

Some bulk rock concentrations are above the maximum contaminant level (MCL) values for groundwater (Figure 5). The EPA recommends MCL-based and human health risk-based soil screening levels (SSL) for elements of concern in soil that interacts with groundwater. These SSL values are risk-based concentrations derived from standardized equations combining exposure information assumptions with EPA toxicity data (EPA, 2014). As of 2014, applicable MCL-based SSL values of 0.29 ppm As, 82 ppm Ba, and 14 ppm Pb illustrate that the sampled formations exceed certain MCL based soil risk levels by over an order of magnitude (EPA, 2014). This should be considered when selecting formations to extract drinking water from.

However, the total concentrations of metals from the source rocks do not directly dissolve into the local groundwater (McLean and Bledsoe, 1992). To more accurately quantify the amounts of contaminants that can potentially enter the local groundwater, it was necessary to compare the bulk rock concentrations with the results of the acid leaching experiments.

![](_page_32_Figure_0.jpeg)

**Figure 5** - Trace element concentrations in mg/kg by formation. Red line denotes median concentration

The results of the acid leaching experiments are shown in Figure 7. The percent of each element mobilized was compared to the bulk concentration of that element. For example, Arsenic values across all 49 samples had a median concentration of 5,950 ppb but the highest concentration able to be mobilized was 9.17 ppb. The SMCL (blue line) for As is 2 ppb and the MCL (red line) is 10 ppb which illustrates that even this small percentage of the median concentration was sufficient to exceed the SMCL and nearly the MCL values currently in place by the EPA.

![](_page_33_Figure_1.jpeg)

**Figure 6 - Box plot displaying the 10th, 25th, median, 75th, and 90th percentile values for the regional and small scale single outcrop study (Fiorentino II, A J., 2015). Smaller shaded boxes represent 21 randomly generated sample intervals at the single outcrop. The mean of the 3 regional data points is correlated to the corresponding stratigraphic unit represented by the grey boxes.**

Mobilized percentages of each element ranged from 0.001% of the bulk concentration of Fe up to 34.8% of the bulk concentration of Mn. However, less than 1% of the total concentration was mobilized for all elements analyzed except for Mn (34.8%) and Zn (1.6%). However, even small percentages of the bulk concentrations mobilized into solution were

sufficient to exceed current EPA drinking water MCL, SMCL (Secondary MCL), or SDWR (Secondary Drinking Water Requirement) values in many of the samples. In total, 74% of our samples exceeded the MCL for Al, 18% for As, 6% for Fe, 12% for Mn, 98% for Pb (above MCL Goal of 0 ppb), and 70% for U (above MCL Goal of 0 ppb (Table 2).

The resulting values for CEC on our samples did not span the expected 10-40 meq/100g range expected for the illite rich samples of the Appalachian Basin. Instead, 88% of our samples had CEC values under 10 meq/100g with one siltstone sample from the Devonian Catskill formation having a CEC of 23.90 meq/100g and one shale sample from the Late Devonian-Early

![](_page_34_Figure_2.jpeg)

**Figure 7 – Median bulk trace element concentration (ppb) with corresponding maximum concentration mobilized into solution during leaching experiments on all 49 samples. Horizontal bars denote EPA drinking water MCL, SMCL, or SDWR values, where applicable.** 

![](_page_35_Picture_323.jpeg)

**Table 2 – Summary of leaching experiment results with each element's EPA MCL or other regulatory value with corresponding percentage of the 49 samples which exceeded the EPA limit and the maximum amount mobilized from our dataset**

Mississippian Huntley Mountain Formation having a CEC of 19.04 meq/100g as the two highest

measured values.

Three samples were measured for total surface area. The first sample was the organic-rich

Union Springs shale in the Hamilton Group. The second sample was a siltstone from the Catskill

Formation and the third sample was another siltstone from the Huntley Mountain Formation.

![](_page_35_Picture_324.jpeg)

**Table 3 – Surface area and cation exchange capacity of the three samples with results of estimated flow path lengths and travel times for 10 meq of Ca to exchange for Na, multiplied by 10 to correct for 1 order of magnitude offset between clay sized samples and the natural environment.**

Using this information I estimated the hypothetical lengths of subsurface flow paths

where Ca might exchange for Na. To estimate a fast cation exchange scenario, I chose sample

PA-3 with a CEC of 23.90 meq/100g and a surface area of 10.32  $m^2/g$ . Using these values and assuming ground water moves through a 1 m<sup>2</sup> x 1 mm x 1 m<sup>2</sup> square parallelepiped piece of the fracture system with an assumed velocity of 10 meters/year; I calculated the necessary flow path length for cation exchange to completely occur as 216 meters, along which water would take 21.6 years to pass. Another estimate for the flow path calculation was done for sample NY-1 with a surface area of 13.59  $\frac{m^2}{g}$  and a CEC of 2.10 meq/100g which resulted in a flow path length of 3,236 meters which would take 324 years for water to pass. Of course, flow velocities may not be this fast, so the time for exchange to occur could be far shorter.

I understand these flow path estimates were calculated using data from our clay sized ground sediment to maximize surface area—unrealistic compared to the natural environment. In addition, groundwater does not typically flow within the same formation for the duration of its entire flow path due to fracture patterns and vertical geological heterogeneities. This implies that groundwater could briefly travel through formations with varying values for both cation exchange capacity and surface area. Therefore, my calculations may be an order of magnitude faster than what would occur when groundwater passes through competent heterogeneous rock/sediment lining fractures not composed entirely of clay-sized material. The results of my calculations with one order of magnitude corrections for this are listed in Table 3. In any case, the results show that cation exchange hypothetically can lead to the changes in hydrogeochemistry found in the groundwater, even with illite being the major exchanger.

The turbidity experiments showed that the mass of clay sized sample necessary to bring 1 L of deionized water to a turbidity value of 5 NTU depended on the color of the sample, ranging from 4.17 mg to 14.29 mg with an average mass of 9.78 mg. Initial turbidity values in the 100

mg/L solutions ranged between 27 NTU and 78 NTU, prior to dilutions, with color being a

controlling factor in the recorded values (Table 4).

![](_page_37_Picture_151.jpeg)

**Table 4 – Results of laboratory turbidity experiments showing initial turbidity values based on sample color for 100 mg/L solutions prior to dilutions to reach 5 and 10 NTU regulatory values**

Applying this mass to the bulk concentration for each element provided the mass of each trace element in the solid phase in turbid water. Results shown in Figure 8 show concentrations in the solid phase above current EPA MCL, SDWR, or MCLG values for drinking water for the elements Al, Fe and Pb at a turbidity of 5 NTU. Concentrations for Al ranged between 560- 1,269 ppb (parts per billion), orders of magnitude above the current SDWR of 50 ppb. Concentrations for Fe ranged between 26.5-379.0 ppb, some above the current SMCL of 300 ppb. Finally, concentrations for Pb ranged between 0.025-0.213 ppb which is below the EPA action limit of 15 ppb but still above the MCLG of 0 ppb. Low concentrations of Pb observed in the data have been attributed to the step dilutions completed during the experiment which muted the Pb concentration. All other elements analyzed were below current MCL values, should one exist for that element.

I had total organic Carbon (TOC) analyzed on 10 samples across varying lithologies to characterize its weight percent in relation to trace elements. Values for TOC on the 10 samples ranged between 0.10-8.45 weight percent (wt%) of the samples. The Union Springs Shale and Chittenango Shale members of the Marcellus Formation had TOC of 8.45 wt% and 1.75 wt%, respectively, with the other eight samples ranging between 0.10-0.87 wt% organic carbon. In comparison, values for LOI on all 49 samples ranged between 0.9-42.5 wt% of the sample depending on the chemical composition. Rock evaluation (RE6) analysis for these two Marcellus

Shale samples illustrated their TOC values and remaining hydrocarbon potential to be classified under the category of immature source rock based on the low ratio of total petroleum hydrocarbons to TOC.

![](_page_38_Figure_1.jpeg)

**Figure 8 – Box plot showing the range of trace element concentrations for eight samples at a turbidity of 5 NTU. Outer bars denote 10th and 90th percentile, colored rectangle encompasses the 25th and 75th percentile with median concentration in between. Red lines denote drinking water MCL, MCLG or secondary MCL values where applicable.** 

#### **Discussion**

Initial trends extracted from the dataset show large variability in the trace element concentrations between the formations. The Marcellus Formation, Catskill Formation, and West Falls Group each have wide ranges of metal concentrations which can span over an order of magnitude on a regional scale. Despite this variability, overall trends can be inferred from the dataset by plotting median concentrations in each formation to reduce outlier data points from otherwise skewing the average concentrations.

Beginning with the middle Devonian Hamilton Group and continuing into the late Devonian Huntley Mountain Formation spikes in Al, As, Ce, Cr, Fe, K, Mn, Na, Pb, Si, Zn, and Zr occur in the stratigraphic profile. One explanation for this increase in concentrations may be increased chemical weathering rates with higher mountain ranges during the Acadian orogeny which would sequester more heavy metals in the anoxic conditions of the restricted Appalachian Sea (Algeo and Maynard, 2008). A eustatic transgression occurred during this time (Johnson et al., 1985). This increase in sea level and a strong restriction of the Appalachian Sea from the open ocean created deep anoxic waters in portions of the Appalachian basin which allowed for the preservation of metals and organic matter (Algeo and Maynard, 2008). The ocean water column anoxia occurred seasonally (Murphy et al., 2000 a,b,c) which may explain some geochemical heterogeneities observed in the outcrop sections sampled in this study due to anoxic events being strongly correlated with trace metal preservation.

Acid leaching experiments illustrated that concentrations above current EPA MCL values can be mobilized into drinking water, even when the samples are only exposed to the acidic conditions for 15 minutes before being filtered. Dissolved constituents; As, Mn, Fe, Pb, and U have both health and aesthetic related impacts on drinking water quality. It is our recommendation that homeowners who use water wells in the study area consult their well construction records (screen interval, total depth, etc.) for what formation they are extracting drinking water from in order to understand their potential health hazard exposure. In addition, laboratory analysis of home drinking water quality should be completed, if possible, to characterize any trace element hazards.

Cation exchange capacity and surface area measurements for our three samples illustrated a plausible hypothesis that natural cation exchange in the subsurface can account for the

geochemical evolution of groundwater along a flow path observed by Siegel et. al., 2014 (Figures 9 and 10). Our findings suggest that 2-3 km long flow paths would be sufficient for the observed ion exchange to occur, although this requires further investigation. New York State contains many groundwater discharge points due to a broad network of surface water bodies. These discharge points make it unlikely that a 30 km continuous flow path exists in the subsurface.

![](_page_40_Figure_1.jpeg)

**Figure 9 - Piper trilinear plot of predrilling samples in Northeastern Pennsylvania in four categories of sodium concentration. Circles in the diamond field are scaled to the concentrations of TDS in the sample (Siegel et. al., 2014)**

The experiments investigating turbidity in relation to drinking water have both health and regulatory implications. The Pennsylvania Department of Environmental Protection (PADEP) does not regulate the construction of private wells (Pennsylvania DEP, 2015). This lack of regulation on drinking water wells in the state of Pennsylvania exposes homeowners to unnecessary health risks via open-hole drinking water wells. Groundwater pumping rates of greater than 100 ml/min can induce the movement of particulates into water wells from the surrounding rock when the proper filtration is not in place (EPA, 2013).

![](_page_41_Figure_0.jpeg)

**Figure 10 - Conceptual figure illustrating the geochemical evolution of groundwater in local, intermediate, and regional flow cells observed in Northeastern Pennsylvania, Ohio, and West Virginia from over 21,000 groundwater samples (Siegel et. al., 2014)**

The New Hampshire Department of Environmental Services states that the recommended pump rate of satisfactory domestic water wells is approximately 5 gallons per minute (NHDES, 2010). This pumping rate is far above what can potentially induce turbidity in open-hole wells. New York State implements regulations set forth by the New York Department of Environmental Conservation which require a well completion report be filed upon completion of a water well (New York DEC, 2015). This water well completion report ensures that all registered personal wells are constructed properly to reduce the potential hazards to the consumer.

These turbidity results also have implications for national groundwater regulatory processes. The EPA allows turbidity values of up to 5 NTU in drinking water and up to 10 NTU in sample collection for groundwater analysis so long as the parameters during low-flow pumping (turbidity, dissolved oxygen, temperature, conductivity, etc.) are stable.

The EPA defines parameter readings to be stable and acceptable for sample collection "when turbidity values remain within 10%, or within 1 NTU if the turbidity reading is less than 10 NTU" (EPA, 2013). The presence of particles in the solid phase during groundwater analysis can result in false positive results for metal concentrations being reported if the samples are not filtered prior to analysis. Per EPA regulation, "… ground water samples will not be filtered for routine analysis or to correct for improperly designed or constructed monitoring wells, inappropriate sampling methods, or poor sampling technique" (EPA, 2013).

Figure 11 illustrates concentrations of trace elements similar to Figure 8 but at 10 NTU, the EPA turbidity limit for groundwater sample collection, instead of 5 NTU. Exceedances for MCL values still occurred for the elements Al, Fe, and Pb but at approximately twice the concentration from those at 5 NTU. Concentrations for these elements reached 742 ppb Fe (379 ppb at 5 NTU), 2,448 ppm Al (1,269 ppb at 5 NTU), and 0.497 ppb Pb (0.213 ppb at 5 NTU). No other MCL exceedances occurred in other elements but it is worth noting that nearly doubling the concentrations of what is allowed in drinking water by sampling groundwater up to 10 NTU can create false positive values in regulatory sampling. The lack of sample filtration on routine groundwater analyses is a regulatory standard that I think should be amended.

The regulations the EPA adapted under the Clean Water Act instruct that groundwater samples be field-filtered 15 minutes after collection only when analyzing for dissolved metals. However, those regulations allow a state to propose alternative monitoring methods. As of 2009, many states' statutes and regulations for the filtering of groundwater samples differed from those of the EPA. Seventeen states did not allow any filtration of groundwater samples, two states always allowed filtration, and thirty-one states sometimes allowed filtration of samples depending on the scope of the project (Figure 11). This disparity between the state and federal

regulations on sample filtration along with regulatory inconsistency at the state level is another problem which I recommend needs to be addressed in future studies.

![](_page_43_Figure_1.jpeg)

**Figure 11 – Box plot showing the range of trace element concentrations for eight samples at a turbidity of 10 NTU. Outer bars denote 10th and 90th percentile, colored rectangle encompasses the 25th and 75th percentile with median concentration in between. Red lines denote drinking water MCL, MCLG or secondary MCL values, where applicable.**

![](_page_43_Figure_3.jpeg)

**Figure 12 – Depiction of state regulations (as of 2009) on filtration of groundwater samples prior to analysis. Regulations vary between no filtration (red), mandatory filtration (blue), and inconsistent filtration (purple/gray)**

#### **Conclusions**

The chemical composition of forty nine samples collected from Devonian to Pennsylvanian age shale, siltstone, and sandstone outcrops between Marcellus, NY and State College, PA was analyzed. These formations are commonly used for domestic drinking water wells but to our knowledge no empirical studies regarding their potential natural hazards have been completed to date. Trace elements related to groundwater quality were tested for their ability to be mobilized into solution in the subsurface under acidic conditions. Small percentages (<2% except for Mn, 34%) of the total amounts of each trace element leached into solution were still sufficient to exceed multiple EPA drinking water maximum contaminant levels.

Natural cation exchange occurs in groundwater as it travels along subsurface flow paths and interacts with the rock and sediment which can alter groundwater quality. Our calculations for the minimum length of a subsurface flow path sufficient to exchange 10 meq/L of Ca for 10 meq/L Na resulted in plausible scenarios of 2 km, 3 km, and 30 km, depending on several factors. This hypothesis is the first attempt to understand the natural geochemical evolution of groundwater along flow paths in the subsurface but future work is required to more accurately constrain these estimates.

Our investigations of turbidity in drinking water due to inadequate well construction, high pumping rates, or improper filtration illustrated that human health hazards exist at the currently accepted EPA value for turbidity of 5 NTU. Drinking water quality exceedances for the elements Al, Fe, and Pb in our experiments illustrate the importance of proper quality control in domestic water wells. The current lack of regulation in the state of Pennsylvania for drinking water well construction exposes residents to a higher risk of ingesting natural contaminants in the solid phase due to inadequate well construction. In addition, we report that the current EPA

standard of allowing up to 10 NTU in regulatory groundwater sampling produces false-positive high values for trace metals when the samples are not filtered prior to analysis.

#### **Future Work and Recommendations**

It is recommended that all regulatory groundwater samples be filtered for standard groundwater quality analyses due to erroneous trace metal concentrations in turbid samples. Personal drinking water well construction in Pennsylvania needs to be more closely regulated in order to reduce the risk of ingesting natural trace elements due to poor water filtration and turbid water. The information in this dataset is recommended as a resource to be considered for homeowners during the construction and selection of a geologic formation to extract drinking water from in the study area.

Recommended future work includes more detailed sampling of groundwater at discharge points along a flow path to more accurately quantify the geochemical evolution of groundwater due to natural ion exchange as it travels through the subsurface. These results should be modeled with various fracture patterns, groundwater flow rates, and cation exchange capacity values to achieve a better understanding of the factors that control the natural evolution of groundwater chemistry. This model could be constrained with the well logs, stratigraphy, and mineralogy of the subsurface at various sample points to make the resulting information more relevant at specific locations where water quality is in question.

**Appendices**

## Appendix 1 - Total Concentrations

![](_page_47_Picture_1675.jpeg)

## Appendix 1 - Total Concentrations

![](_page_48_Picture_1998.jpeg)

## Appendix 2 - Leaching Results

![](_page_49_Picture_1738.jpeg)

**SWDR <sup>=</sup> EPA Secondary Drinking Water Regulation N/A <sup>=</sup> No leaching data available**

**SMCL= EPA Secondary Max Contamination Limit**

**MCL= EPA Max Contamination Limit**

## Appendix 2 - Leaching Results

![](_page_50_Picture_1736.jpeg)

**SWDR <sup>=</sup> EPA Secondary Drinking Water Regulation N/A <sup>=</sup> No leaching data available**

**SMCL= EPA Secondary Max Contamination Limit MCL= EPA Max Contamination Limit**

Appendix 2 - Leaching Results

			<b>Total</b>	Leached	% Mobilized	<b>Total</b>	Leached	% Mobilized	<b>Total</b>	Leached	% Mobilized	<b>Total</b>	Leached	% Mobilized	<b>Total</b>	Leached	% Mobilized
				No MCL			No MCL			No MCL			No MCL			MCLG 0 ppb	
				No SMCL			SDWR 50 ppb			SDWR 20,000 ppb			SDWR 100 ppb			Action Lvl. 15 ppb	
Sample ID	Formation	<b>Total CEC</b> (meq/100 g)	$\mu$ g/L	$\mu$ g/L		$\mu$ g/L	$\mu$ g/L		$\mu$ g/L	$\mu$ g/L		$\mu$ g/L	µg/L		$\mu$ g/L	$\mu$ g/L	
			Mg	Mg	$Mg\%$	Mn	Mn	Mn %	Na	Na	Na %	Ni	Ni	Ni%	Pb	Pb	Pb $%$
PA-14	Pottsville Fm (overlies Mauch Chunk)	8.62	$1.21E + 06$	3.29E+02	2.72E-02	$3.56E + 03$	$1.09E + 01$	3.05E-01	$1.19E + 04$	1.55E+03	$1.30E + 01$	$4.76E + 03$	8.36E+00	1.76E-01	$1.10E + 04$	6.98E-01	6.35E-03
PA-20	Mauch Chunk Formation	6.84	5.20E+05	$5.24E + 03$	$1.01E + 00$	$2.56E + 03$	$8.90E + 02$	$3.48E + 01$	$3.68E + 05$	$4.41E + 04$	$1.20E + 01$	8.33E+03	$3.65E + 01$	4.38E-01	$1.49E + 04$	2.97E-01	1.99E-03
PA-21	<b>Burgoon Sandstone</b>	6.67	$1.66E + 06$	$4.20E + 01$	2.52E-03	$5.08E + 03$	$2.43E+00$	4.77E-02	8.29E+04	$6.45E + 02$	7.79E-01	$5.90E + 03$	$1.62E+00$	2.75E-02	$1.48E + 04$	7.39E+00	4.99E-02
PA-6	<b>Burgoon Sandstone</b>	7.65	2.10E+06	$1.46E + 03$	6.98E-02	$1.69E + 05$	$3.26E + 02$	1.93E-01	$3.79E + 04$	8.06E+02	$2.12E+00$	$1.21E + 04$	$5.62E + 00$	4.64E-02	3.50E+03	3.45E-01	9.86E-03
PA-19	Huntley Mountain Formation	19.04	$1.46E + 07$	$1.17E + 03$	7.98E-03	9.56E+04	7.07E+00	7.40E-03	1.58E+06	$1.76E + 03$	1.11E-01	5.00E+04	1.52E-01	3.04E-04	$1.81E + 04$	3.67E-01	2.03E-03
PA-26	Huntley Mountain Formation	9.02	$3.46E + 06$	$1.05E + 03$	3.03E-02	$1.02E + 04$	$1.26E + 01$	1.23E-01	$1.67E + 0.5$	7.11E+02	4.25E-01	$2.42E + 04$	$1.07E + 00$	4.43E-03	$5.10E + 03$	2.09E-01	4.10E-03
$PA-1$	Catskill Formation	9.51	1.15E+07	2.51E+02	2.17E-03	$2.63E + 04$	$2.35E+00$	8.93E-03	$2.59E + 06$	$2.11E+03$	8.16E-02	$4.38E + 04$	1.70E-01	3.88E-04	$1.57E + 04$	8.77E-01	5.59E-03
$PA-2$	<b>Catskill Formation</b>	4.21	$3.49E + 06$	9.31E+02	2.67E-02	4.22E+05	$1.56E + 01$	3.69E-03	8.86E+05	$1.16E + 03$	1.31E-01	$1.38E + 04$	9.90E-02	7.17E-04	$1.23E + 04$	6.15E-01	5.00E-03
$PA-3$	Catskill Formation	23.90	$1.00E + 07$	1.23E+02	1.23E-03	$2.64E + 04$	2.30E+00	8.69E-03	$2.11E+06$	$1.69E + 03$	8.03E-02	$4.02E + 04$	1.41E-01	3.51E-04	$1.13E + 04$	4.75E-01	4.20E-03
PA-7	<b>Catskill Formation</b>	3.61	$9.42E + 06$	9.77E+02	1.04E-02	$2.78E + 04$	$1.13E + 01$	4.08E-02	$3.42E + 06$	$3.16E + 03$	9.22E-02	$3.42E + 04$	8.64E-01	2.53E-03	$1.28E + 04$	4.84E-01	3.78E-03
<b>PA-9</b>	<b>Catskill Formation</b>	9.55	4.88E+06	6.55E+02	1.34E-02	$1.84E + 04$	2.49E+01	1.35E-01	3.85E+06	$2.77E + 03$	7.21E-02	$2.03E + 04$	$3.09E + 00$	1.52E-02	8.50E+03	1.22E-01	1.44E-03
PA-11	<b>Catskill Formation</b>	9.48	$1.29E + 07$	5.80E+01	4.48E-04	$2.68E + 04$	8.22E-01	3.07E-03	$2.03E + 06$	1.35E+03	6.65E-02	$4.69E + 04$	2.31E-01	4.93E-04	$5.70E + 03$	$2.12E + 00$	3.73E-02
PA-12	<b>Catskill Formation</b>	8.58	$1.16E + 07$	$1.09E + 03$	9.43E-03	$9.63E + 04$	$1.56E + 01$	1.62E-02	$2.02E + 06$	$1.56E + 03$	7.71E-02	4.19E+04	1.37E-01	3.27E-04	$6.70E + 03$	6.66E-01	9.94E-03
PA-13	Catskill Formation	8.10	7.57E+06	2.55E+03	3.37E-02	$2.04E + 04$	$2.65E + 01$	1.30E-01	$3.23E + 06$	$2.04E + 03$	6.32E-02	$3.11E + 04$	8.31E-01	2.67E-03	$5.10E + 03$	1.02E-01	2.00E-03
PA-16	Catskill Formation	8.68	$3.92E + 06$	$1.69E + 03$	4.31E-02	5.22E+04	$1.04E + 02$	1.99E-01	$2.34E + 06$	$2.27E + 03$	9.71E-02	1.29E+04	4.16E-01	3.22E-03	$5.90E + 03$	1.33E-01	2.25E-03
PA-17	<b>Catskill Formation</b>	4.29	$4.71E + 06$	$1.34E + 03$	2.85E-02	$1.74E + 05$	$2.02E + 01$	1.16E-02	$4.11E + 06$	3.58E+03	8.71E-02	$1.87E + 04$	1.75E-01	9.36E-04	$1.33E + 04$	4.90E+00	3.68E-02
PA-18	<b>Catskill Formation</b>	9.16	$1.13E + 07$	7.31E+02	6.48E-03	5.23E+04	$1.29E + 01$	2.46E-02	$2.52E + 06$	$3.35E + 03$	1.33E-01	4.32E+04	2.34E-01	5.42E-04	$2.18E + 04$	1.18E-01	5.41E-04
PA-24	Catskill Formation	11.20	$1.49E + 07$	4.65E+02	3.11E-03	$2.66E + 04$	2.23E+00	8.39E-03	1.86E+06	$1.64E + 03$	8.77E-02	$5.12E + 04$	9.90E-02	1.93E-04	$1.11E + 04$	8.40E-02	7.57E-04
PA-29	<b>Catskill Formation</b>	8.73	$1.33E+07$	$2.51E + 02$	1.89E-03	$2.68E + 04$	$1.08E + 00$	4.05E-03	$2.70E + 06$	$1.87E + 03$	6.93E-02	4.33E+04	2.27E-01	5.24E-04	$1.96E + 04$	$5.09E + 00$	2.60E-02
PA-30	<b>Catskill Formation</b>	8.67	5.46E+06	9.40E+02	1.72E-02	$2.83E + 04$	$3.32E + 01$	1.17E-01	$3.49E + 06$	$2.85E + 03$	8.15E-02	2.10E+04	8.34E-01	3.97E-03	$6.70E + 03$	1.46E+00	2.17E-02
$NY-10$	West Falls Group (Dunn Hill Shale)	8.86	8.92E+06	8.44E+02	9.46E-03	$4.67E + 04$	3.95E+01	8.44E-02	$3.15E + 06$	$2.56E + 03$	8.13E-02	3.87E+04	2.09E-01	5.40E-04	$5.60E + 03$	1.17E-01	2.09E-03
$NY-16$	West Falls Group (Upper Walton)	8.57	$8.17E + 06$	2.54E+03	3.10E-02	2.73E+04	2.79E+01	$1.02E - 01$	$2.65E + 06$	$1.51E + 03$	5.69E-02	$3.66E + 04$	2.29E-01	6.26E-04	$5.32E + 04$	1.72E-01	3.23E-04
NY-18	West Falls Group (Upper Walton)	8.97	$1.08E + 07$	2.57E+03	2.39E-02	4.73E+04	$3.76E + 01$	7.96E-02	$3.07E + 06$	$1.97E + 03$	6.40E-02	4.19E+04	1.30E-01	3.10E-04	$9.40E + 03$	1.10E-01	1.17E-03
$NY-24$	West Falls Group (Upper Walton)	8.18	$7.26E + 06$	7.57E+02	1.04E-02	3.78E+04	8.53E+00	2.26E-02	$3.71E + 06$	$2.37E + 03$	6.39E-02	$3.29E + 04$	2.78E-01	8.45E-04	7.20E+03	2.65E-01	3.68E-03
NY-17	West Falls Group (Gardeau Fm)	11.00	$1.05E + 07$	$6.60E + 02$	6.31E-03	9.27E+04	$1.01E + 01$	1.09E-02	$1.79E + 06$	$1.53E + 03$	8.55E-02	4.85E+04	1.20E-01	2.47E-04	$6.71E + 04$	1.25E+00	1.86E-03
$NY-9$	West Falls Group (Roricks Glen Shale)	8.49	$9.21E + 06$	4.18E+02	4.53E-03	2.08E+04	1.55E+00	7.44E-03	$3.28E + 06$	2.20E+03	6.71E-02	$4.01E + 04$	1.56E-01	3.89E-04	$1.27E + 04$	6.40E-02	5.04E-04
NY-12	Enfield & Kattel Form - Sonyea Group	9.38	8.48E+06	1.95E+03	2.30E-02	4.52E+04	$1.36E + 01$	3.01E-02	$3.41E + 06$	2.70E+03	7.91E-02	3.35E+04	1.26E-01	3.76E-04	$1.31E + 04$	7.50E-02	5.73E-04
$NY-20$	Enfield & Kattel Form - Sonyea Group	8.72	$9.61E + 06$	2.39E+02	2.49E-03	$3.02E + 04$	3.73E+00	1.23E-02	$2.90E + 06$	$4.10E + 03$	1.41E-01	$4.22E + 04$	3.63E-01	8.60E-04	$2.91E + 04$	6.05E-01	2.08E-03
$NY-23$	Enfield & Kattel Form - Sonyea Group	3.79	7.70E+06	N/A	N/A	$3.62E + 04$	N/A	N/A	$3.43E + 06$	N/A	N/A	3.15E+04	1.68E-01	5.33E-04	$1.12E + 04$	7.40E-02	6.61E-04
$NY-7$	Genesee Form. (Renwick Shale)	3.51	$1.02E + 07$	$2.64E + 03$	2.58E-02	$2.65E + 04$	1.25E+01	4.71E-02	$2.36E + 06$	2.34E+03	9.92E-02	3.78E+04	1.57E-01	4.15E-04	$9.20E + 03$	6.92E-01	7.52E-03
$NY-8$	Genesee Form. (Renwick Shale)	8.64	1.25E+07	1.88E+03	1.50E-02	$4.08E + 04$	$6.85E + 00$	1.68E-02	$2.24E + 06$	$2.98E + 03$	1.33E-01	$4.67E + 04$	1.40E-01	3.00E-04	$1.69E + 04$	$1.33E + 00$	7.84E-03
$NY-19$	Genesee Form.	9.75	$1.24E + 07$	2.19E+03	1.76E-02	4.71E+04	$5.47E + 00$	1.16E-02	$2.08E + 06$	$3.44E + 03$	1.66E-01	4.89E+04	1.33E-01	2.72E-04	$1.76E + 04$	5.29E-01	3.01E-03
$NY-2$	Marcellus Form. (Chittengo)	9.30	$1.11E+07$	$9.54E + 03$	8.59E-02	2.30E+04	$3.27E + 01$	$1.42E - 01$	$5.39E + 05$	$1.85E + 03$	3.44E-01	$2.14E + 04$	9.00E-03	4.21E-05	$3.22E + 04$	2.00E-03	6.21E-06
$NY-5$	Marcellus Form. (Chittengo)	6.19	$5.14E + 06$	$1.97E + 03$	3.84E-02	$6.11E + 03$	2.95E-01	4.84E-03	7.33E+04	$1.90E + 03$	$2.60E + 00$	$4.32E + 03$	1.72E-01	3.98E-03	$1.28E + 03$	3.00E-01	2.34E-02
$NY-4$	Marcellus Form. (Solsville Shale)	9.35	$1.16E+07$	$1.91E + 03$	1.64E-02	2.28E+04	7.05E+00	3.10E-02	$1.98E + 06$	$1.92E + 03$	9.67E-02	5.14E+04	1.25E-01	2.43E-04	$1.22E + 04$	2.29E+00	1.88E-02
$NY-3$	Marcellus Form.(Cardiff)	11.25	$1.27E + 07$	3.55E+03	2.80E-02	2.96E+04	$1.07E + 01$	3.60E-02	$9.66E + 05$	$1.59E + 03$	1.64E-01	$3.34E + 04$	1.53E-01	4.58E-04	$3.32E + 04$	7.92E-01	2.39E-03
$NY-1$	Marcellus Form. (Unions Springs Shale)	2.10	$6.48E + 06$	$3.12E + 03$	4.81E-02	$1.07E + 04$	$3.01E + 00$	2.82E-02	$3.00E + 05$	$2.28E + 03$	7.61E-01	$1.21E + 05$	4.40E-02	3.64E-05	$1.90E + 03$	1.00E-02	5.26E-04
<b>PA-4</b>	Susquehanna Group (Lock Haven Form.)	6.60	$2.60E + 07$	7.46E+03	2.87E-02	5.65E+05	$5.12E + 01$	9.05E-03	$2.81E + 06$	2.59E+03	9.22E-02	$1.47E + 04$	1.55E-01	1.05E-03	$4.20E + 03$	$1.87E + 00$	4.44E-02
PA-5	Susquehanna Group (Lock Haven Form.)	8.71	7.85E+06	$1.20E + 02$	1.52E-03	1.96E+04	$1.03E + 00$	5.26E-03	$3.53E + 06$	$2.76E + 03$	7.81E-02	$3.29E + 04$	2.28E-01	6.93E-04	8.20E+03	2.29E+00	2.80E-02
$PA-10$	Susquehanna Group (Lock Haven Form.)	6.80	7.53E+06	1.54E+02	2.05E-03	$1.92E + 04$	1.78E+00	9.25E-03	$3.56E + 06$	$2.55E + 03$	7.18E-02	$2.76E + 04$	5.17E-01	1.87E-03	$9.50E + 03$	8.10E-02	8.53E-04
PA-23	Susquehanna Group (Lock Haven Form.)	7.50	$6.75E + 06$	4.46E+02	6.61E-03	$1.94E + 04$	$2.44E + 00$	1.26E-02	$3.79E + 06$	$3.02E + 03$	7.97E-02	$3.18E + 04$	1.20E-01	3.77E-04	$4.10E + 03$	4.40E-02	1.07E-03
PA-27	Susquehanna Group (Lock Haven Form.)	8.24	$6.61E + 06$	4.38E+02	6.63E-03	2.37E+04	5.95E+00	2.51E-02	$3.23E + 06$	2.70E+03	8.38E-02	$3.57E + 04$	2.75E-01	7.70E-04	7.20E+03	3.24E-01	4.50E-03
PA-28	Susquehanna Group (Lock Haven Form.)	9.44	$1.08E + 07$	7.31E+02	6.77E-03	2.65E+04	$2.09E + 00$	7.91E-03	$2.68E + 06$	$2.01E + 03$	7.50E-02	$4.16E + 04$	1.37E-01	3.29E-04	$1.22E + 04$	1.29E-01	1.06E-03
<b>PA-8</b>	Susquehanna Group (Trimmer's Rock Form)	4.48	$6.00E + 06$	1.48E+03	2.47E-02 5.62E-02	$8.22E + 03$	2.17E+00	2.64E-02	1.53E+06	1.55E+03	1.01E-01	3.47E+04	1.87E-01	5.39E-04	$6.80E + 03$	4.62E-01	6.79E-03
PA-25	Susquehanna Group (Trimmer's Rock Form)	7.71	$9.07E + 06$	$5.10E + 03$		$5.61E + 04$	$9.29E + 01$	1.66E-01	$3.06E + 06$	$2.96E + 03$	9.67E-02	$3.47E + 04$	1.91E-01	5.50E-04	$9.80E + 03$	9.00E-02	9.18E-04
$NY-6$	Hamilton Group (Moscow Formation)	4.00	$1.30E + 07$	$1.94E + 03$	1.49E-02	4.91E+04	$1.07E + 01$	2.19E-02	2.15E+06	$1.67E + 03$	7.75E-02	$6.22E + 04$	1.42E-01	2.28E-04	$1.24E + 04$	3.22E-01	2.60E-03
$NY-13$ $NY-15$	Hamilton Group (Upper Skaneateles Form.)	17.20 8.70	8.51E+06 $1.12E + 07$	$1.34E + 04$ $2.14E + 03$	1.57E-01	8.27E+03 3.29E+04	$1.86E + 02$ 8.22E+00	2.25E+00 2.50E-02	5.16E+05 $1.16E + 06$	$3.26E + 03$ 1.53E+03	6.32E-01 1.32E-01	2.56E+04 $4.84E + 04$	$4.06E + 01$ 1.29E-01	1.59E-01 2.67E-04	1.35E+04 $7.20E + 03$	2.04E-01 1.38E-01	1.51E-03 1.92E-03
$NY-21$	Hamilton Group (Upper Skaneateles Form.)	7.86	$8.52E + 06$	$2.71E + 03$	1.91E-02 3.19E-02	$4.72E + 04$	$1.31E + 01$	2.77E-02	$1.80E + 06$	$2.13E+03$	1.18E-01	$3.51E + 04$	1.40E-01	3.99E-04	$5.10E + 03$	1.21E-01	2.37E-03
$NY-14$	Hamilton Group (Upper Skaneateles Form.) Chrysler Limestone - Helderbeg Group	12.97	5.75E+07	1.65E+04	2.86E-02	$2.63E + 04$	$3.22E + 00$	1.22E-02	$1.19E + 06$	$2.10E + 03$	1.76E-01	$3.24E + 04$	3.78E-01	1.17E-03	7.30E+03	4.87E-01	6.67E-03

SWDR = EPA Secondary Drinking Water Regulation<br>SMCL= EPA Secondary Max Contamination Limit<br>MCL= EPA Max Contamination Limit **N/A <sup>=</sup> No leaching data available**

## Appendix 2 - Leaching Results

![](_page_52_Picture_1741.jpeg)

**N/A <sup>=</sup> No leaching data available**

**SWDR <sup>=</sup> EPA Secondary Drinking Water Regulation SMCL= EPA Secondary Max Contamination Limit**

**MCL= EPA Max Contamination Limit**

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