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Stephen Van Ryswick, Director

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**CHARACTERIZATION OF CHLORIDE SOURCES IN GROUNDWATER
IN THE PIEDMONT, BLUE RIDGE, RIDGE AND VALLEY, AND
APPALACHIAN PLATEAU PHYSIOGRAPHIC PROVINCES OF
MARYLAND**

by

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ABBREVIATIONS AND SYMBOLS APPEARING IN THIS REPORT

CBE	Charge Balance Error
Ca:Cl	Calcium:Chloride
Cl:Br	Chloride:Bromide
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
K:Cl	Potassium:Chloride
MCL	Maximum Contaminant Level
MDE	Maryland Department of the Environment
MDOT	Maryland Department of Transportation
Mg:Cl	Magnesium:Chloride
MGS	Maryland Geological Survey
NaCl	Sodium Chloride
POE	Point of Entry
QA/QC	Quality Assurance and Quality Control
SHA	State Highway Administration
SMCL	Secondary Maximum Contamination Level
TDS	Total Dissolved Solids
TN	Total Nitrogen
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
ft	feet
gal/day	gallons per day
kg/year	kilogram per year
meq L ⁻¹	milliequivalent per liter
mg/L	milligrams per liter
μ	micron
μg/L	microgram per liter
μS/cm	microsiemens per centimeter at 25 degrees Celsius
<	less than

KEY RESULTS

Groundwater and wastewater samples were collected from 28 sites across central and western Maryland to evaluate chloride sources and associated geochemical indicators. Samples were collected from septic effluent, wells at municipal landfills, agricultural wells, road salt-impacted wells, natural formation brine-affected wells, domestic wells, and a saltwater treated swimming pool. Chemical analyses included major ions, minor halides, nutrients, trace metals, and wastewater tracers (artificial sweeteners and caffeine). The purpose of this study was to: (1) characterize chloride concentrations across distinct sources, and (2) evaluate geochemical ratios and tracers that support source identification. Key results from this investigation are:

- Piper diagram analysis showed two dominant water types: Ca–Mg–HCO₃ waters, representative of natural and agricultural influences; and Na–Cl waters, characteristic of anthropogenic inputs (septic effluent, landfill leachate, road salt). Septic and formation brine samples plotted toward the Na+K field, while agricultural and landfill monitoring well water clustered in the Ca–Mg field.
- Chloride concentrations varied widely across source categories. Septic effluent samples exhibited the broadest concentration range from 37 to 4,000 mg/L (median 215 mg/L). Municipal landfill wells contained 20–110 mg/L chloride (median 65 mg/L), whereas agricultural well water ranged from 2.5 to 8.5 mg/L (median 3 mg/L), with elevated values observed near livestock facilities. Road salt-impacted wells showed the greatest variability among groundwater sources, with concentrations ranging from 26 to 750 mg/L (median 455 mg/L), and the highest value measured at a salt storage facility. Formation brine-affected wells contained 86–170 mg/L chloride, whereas the saltwater treated swimming pool sample exhibited 1,700 mg/L. Chloride concentration ranged from 11 mg/L to 910 mg/L in the two domestic well waters sampled.
- Sample pH values ranged from 5.8 to 8.7. Domestic well samples were acidic (5.9–6.5), whereas septic effluent and formation brine affected samples were neutral to alkaline (7.1–8.7). Specific conductance was strongly correlated with chloride ($R^2 = 0.986$). The highest conductance (12,000 $\mu\text{S}/\text{cm}$) and TDS (6,600 mg/L) occurred in a septic effluent sample, consistent with concentrated wastewater affected by water-softener brine.
- Septic effluent exhibited generally low dissolved oxygen (DO) concentrations (median < 5 mg/L) and elevated dissolved organic carbon (DOC) (up to 65 mg/L). Landfill monitoring well samples exhibited very low DO (<1 mg/L) and low DOC (≤ 4.2 mg/L). Domestic wells were generally oxidic with low DOC, formation brine affected well water was oxygen-depleted (<1 mg/L). In contrast road salt-impacted wells showed variable DO conditions, ranging from oxygen-depleted (<1 mg/L) to well-oxygenated (>7 mg/L), with DOC not detected. Agricultural well waters were well-oxygenated with low DOC.
- Box-plot analysis of ion-to-chloride and nutrient-to-chloride ratios reveals distinct but overlapping chloride source signatures based on the combined MGS dataset and literature-derived source ranges (Panno and others, 2005). Na:Cl ratios in road salt-impacted samples cluster near and below halite mass ratios with a narrow interquartile range (MGS median: 0.289), whereas septic effluent exhibits frequent sodium enrichment (Na:Cl > 0.60). Calcium and magnesium display greater variability, with elevated ratios most pronounced in agricultural wells (Ca:Cl > 3.0), while road salt- and brine-affected samples remain consistently low. Landfill-affected groundwater exhibits an intermediate Na:Cl median of approximately 0.38, distinguishable from septic systems by lower sodium enrichment and from road salt by increased divalent cation variability. K:Cl and especially TN:Cl ratios provide additional discrimination, as they are elevated in septic effluent and animal-waste-affected samples, but remain low in mineral salt-dominated sources.
- When interpreted together, geochemical ratios provide practical fingerprints for chloride source identification. Road salt-impacted groundwater is characterized by Na:Cl ratios near and below that of

halite and consistently low Ca:Cl, Mg:Cl, K:Cl, and TN:Cl. Septic effluent exhibits elevated Na:Cl, K:Cl, and TN:Cl and is uniquely associated with wastewater tracers. Agricultural groundwater is distinguished by elevated Ca:Cl and Mg:Cl ratios relative to sodium, often at low chloride concentrations. Landfill-affected groundwater shows intermediate Na:Cl ratios with elevated bromide (lower Cl:Br) and greater divalent-cation variability. Formation brine-affected groundwater is identified by low Cl:Br ratios and strontium enrichment. However, care must be taken in using ratios with cations for source identification, which can be affected by adsorption and desorption on subsurface materials during transport.

- Chloride:bromide ratios for septic effluent (246–3,649) and road salt-impacted wells (1,143–2,778) overlapped in the zone characteristic of rock salt (halite) inputs. Landfill wells exhibited moderate ratios (177–1,806), while formation brine samples plotted at lower ratios (142–156) due to bromide enrichment relative to chloride. Agricultural wells showed ratios of 264–708 that mainly reflect uncontaminated fresh groundwater (with respect to chloride). Domestic wells were variable, with one well plotting among the highest ratios.
- Chloride:bromide versus chloride concentration mixing curves provide the best differentiation of chloride sources in Maryland waters. Points for septic effluent and road salt affected waters trended towards the high-ratio halite end members for the chloride sources, landfill wells plotted along mixing zones toward the moderate ratio end members, and formation brine-affected wells formed a zone towards distinct low-ratio end members. The close agreement between observed field data and locally derived mixing trajectories demonstrates the value of Maryland-specific endmembers for chloride source interpretation. All of the agricultural well waters had low chloride concentration (<10 mg/L) such that no significant trend towards a high chloride source could be conclusively determined. If animal waste had produced substantially elevated chloride, a trend towards slightly higher Cl:Br might be expected based on literature data.
- Septic effluent samples clustered at high total nitrogen and high chloride with elevated Cl:Br, while agricultural wells showed high nitrogen and low chloride. Road salt impacted well water samples exhibited high chloride and Cl:Br and negligible nitrogen. Formation brine affected well waters also had low nitrogen and had low Cl:Br. This dual-tracer approach provided effective separation of sources where Cl:Br alone overlapped.
- Strontium showed the strongest correlation with chloride ($\rho = 0.71$, $p < 0.0001$) with enrichment in formation brine-affected wells. Barium showed a moderate overall correlation with chloride ($\rho = 0.54$, $p = 0.0030$) while a strong relationship was observed within the limited dataset of road salt-impacted wells ($R^2 = 0.991$), although this observation should be interpreted with caution. One well near a salt storage facility exceeded the USEPA MCL of 2.0 mg/L. Lithium showed weak correlation with chloride and limited tracer utility. These minor cations are also affected by cation exchange so care must be taken in interpretation. Other metals (Fe, Mn, As, Pb, Cu) were primarily controlled by redox, chemical precipitation, and adsorption/desorption conditions rather than salinity.
- Artificial sweeteners (acesulfame and sucralose) were detected at elevated concentrations in septic effluent and at lower concentrations in domestic and landfill well waters. Trace levels of acesulfame were detected in two road salt-impacted wells, indicating localized septic influence or mixed-source conditions. Caffeine was not detected in any samples.
- Many groundwater samples exhibited geochemical signatures consistent with contributions from more than one chloride source. The integrated use of Cl:Br ratios versus chloride mixing plots, other ion-to-chloride ratios, nitrogen, and wastewater tracers provided a regional-scale framework for constraining chloride sources, while recognizing that complete separation is not always possible in areas with overlapping land uses and complex hydrogeologic and geochemical conditions.

INTRODUCTION

Chloride (Cl^-) in groundwater and surface water poses a significant risk to water quality and can create substantial challenges for both private well owners and municipal water suppliers. Naturally occurring chloride is commonly present in the solid form as sodium chloride (NaCl) or potassium chloride (KCl), with precipitation (derived primarily from seawater) also representing a natural source. In Maryland, background chloride concentrations in groundwater are typically low ($<5\text{--}10\text{ mg/L}$) in the absence of anthropogenic inputs or formation brine influence; however, concentrations can be elevated through numerous natural and anthropogenic processes. These include water–rock interactions, upward migration of deep formation brines, coastal saltwater intrusion, evapotranspiration concentration of atmospheric deposition, road salt application, and discharges from water softeners, septic systems, saltwater swimming pools, landfills, and agricultural activities (Hingst and others, 2023; Panno and others, 2002). The U.S. Environmental Protection Agency (USEPA) has established a secondary maximum contaminant level (SMCL) of 250 milligrams per liter (mg/L) for chloride in public drinking water supplies. Although SMCLs are non-enforceable, they serve as guidelines for public water systems to manage aesthetic qualities such as taste, odor, and color. Elevated chloride concentrations can also accelerate the corrosion of plumbing, appliances, fixtures, and water distribution systems (DeSantis and others, 2009; Ng and Lin, 2016; Pieper and others, 2018; Stets and others, 2018).

Because chloride can enter water supplies from multiple sources, distinguishing between natural and anthropogenic inputs is critical for managing risks to water quality and infrastructure. One of the most widely used techniques for source identification is the chloride-to-bromide ($\text{Cl}:\text{Br}$) ratio, which is particularly effective in differentiating between halite and brine sources of salinity in groundwater (Richter and Kreidler, 1993; Panno and others, 2005). Previous studies conducted by the Maryland Geological Survey (MGS) have applied this method to evaluate chloride sources in the Piedmont Physiographic Province. VanDerwerker (2019) sampled 25 wells and analyzed for major ions, trace metals, nutrients, radionuclides, and bromide to assess chloride distribution and potential sources. Elevated chloride was attributed to road de-icing salts in 10 wells, agricultural operations in two wells, and septic effluent in one well. A subsequent MGS study (VanDerwerker, 2020, in review) reported that 74% of wells exceeded 50 mg/L chloride, with an average concentration of 140 mg/L. Among 59 wells with complete chloride and bromide data, $\text{Cl}:\text{Br}$ ratios indicated road salt was the likely source in 40 wells, septic effluent in four wells, and agricultural effluent in two wells. However, these studies did not directly sample source end members (e.g., septic effluent, road-salt stockpiles/runoff, agricultural drainage), so fingerprints were not validated against measured source compositions or external reference datasets such as Panno and others (2005).

Although comparing $\text{Cl}:\text{Br}$ ratios provide a useful and relatively simple approach to source identification, they are not always definitive, as ratios from different sources, particularly road de-icing salt and septic, may overlap. In addition, mixing of freshwater with saline water or saltwater can produce ratios that are intermediate between those for the freshwater and saline water/saltwater end members. An improvement over just comparison of ratios is the mixing curve approach that shows the location of points on $\text{Cl}:\text{Br}$ versus chloride concentration plots within zones of conservative mixing between end members (Davis and others, 1998; Panno and others, 2006; Whittemore, 1995). Limitations of overlapping ratios for end members have been addressed by incorporating additional tracers in groundwater studies, including isotopes (Appelo and Postma, 1994; Panno and others, 2005), and trace metals such as strontium (Sr), barium (Ba), potassium (K), and lithium (Li) (VanDerwerker, 2019; Wilhelm and others, 2019). Nutrients such as total nitrogen (TN) have also been used alongside $\text{Cl}:\text{Br}$ ratios to help distinguish chloride sources, as elevated nitrogen concentrations often accompany septic or wastewater influences but are typically absent in road-salt-impacted groundwater (Panno and others, 2006). In recent years, wastewater tracers such as artificial sweeteners (Buerge and others, 2010) have also been applied to identify human-derived inputs. Compounds like sucralose are highly soluble, resistant to degradation, and exhibit minimal sorption to solid phases, making them effective markers of wastewater influence (Oppenheimer and others, 2011). Their widespread production and consumption further contribute to their utility in tracing wastewater movement.

PURPOSE AND SCOPE

This study documents the sources of chloride affecting groundwater in central and western Maryland. We analyze waters for major ions, trace metals, nutrients, caffeine, and artificial sweeteners to (1) identify likely

chloride sources and (2) evaluate associations between chloride and co-occurring analytes that can serve as source-specific indicators. Where feasible, we incorporate direct measurements of potential sources based on previous publications to strengthen fingerprinting and resolve overlaps among road-salt, wastewater, agricultural, landfills, saltwater treated swimming pools, and natural salinity signatures.

LOCATION OF THE STUDY AREA

The study area extends across central and western Maryland, west of the Fall Line, and includes portions of the Piedmont, Ridge and Valley, and Appalachian Plateaus physiographic provinces (fig. 1); although the Blue Ridge Province was included in the project proposal, no suitable sampling locations were identified, and it is therefore not represented in this study. These provinces differ in geology, topography, and aquifer characteristics, which collectively influence groundwater occurrence and quality.

Counties within the study area include Baltimore, Howard, Montgomery, Frederick, Carroll, Washington, Allegany, and Garrett. Land use is diverse, with suburban and urban development concentrated in Baltimore, Howard, and Montgomery Counties, extensive agricultural activity in Frederick, Carroll, and Washington Counties, and largely forested landscapes in Allegany and Garrett Counties. This range of land uses creates multiple potential sources of chloride, including road de-icing, septic systems, and agriculture.

Water supply in the region is derived from both surface water and groundwater. While larger municipalities, particularly in Baltimore, Montgomery, and Howard Counties, are primarily served by surface water, rural communities across Frederick, Carroll, Washington, Allegany, and Garrett Counties rely heavily on domestic wells. The combination of population growth, land-use pressures, and dependence on private groundwater supplies highlights the need to better understand chloride impacts in this part of Maryland.

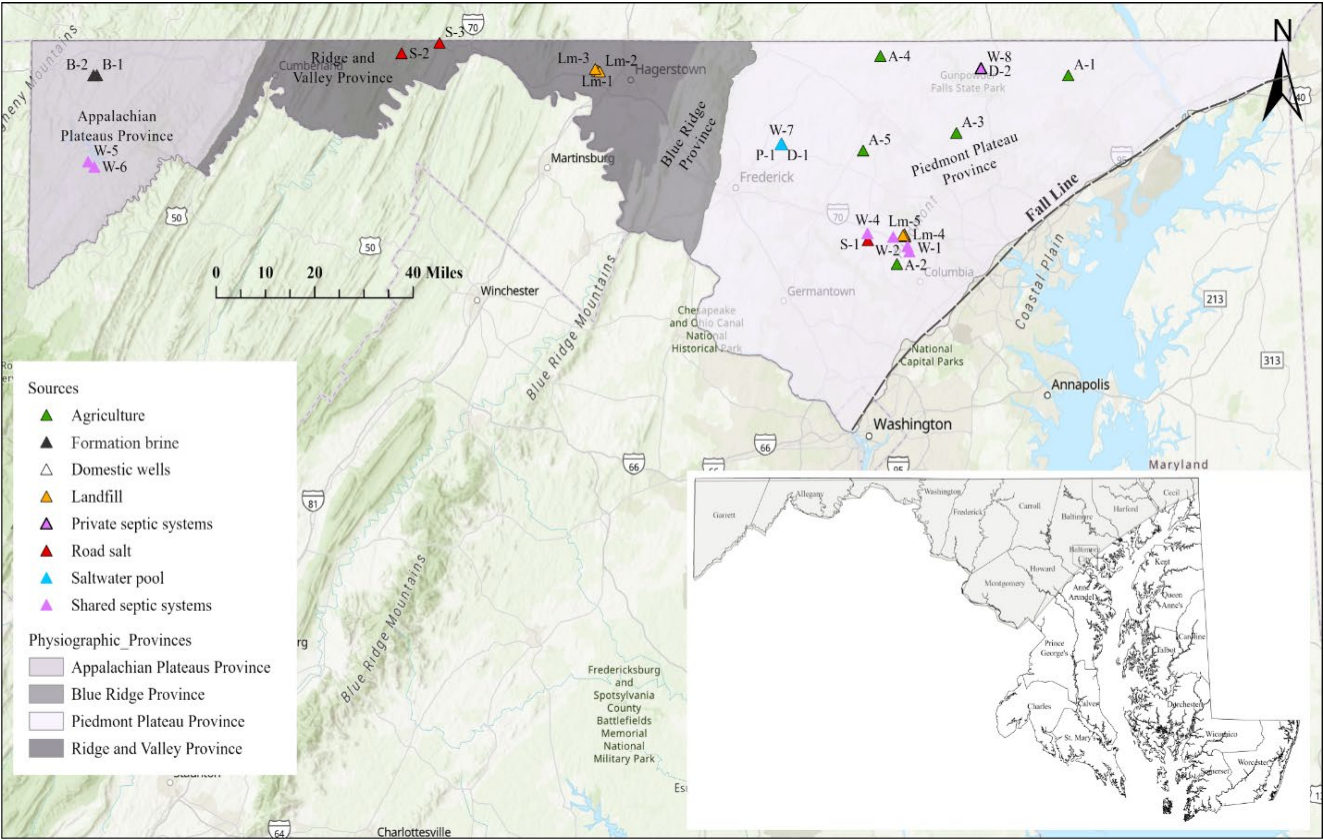


Figure 1. Location of study area in the fractured rock zone of Maryland.

GEOLOGICAL SETTING

The study area spans the Appalachian Plateau, Ridge and Valley, and Piedmont physiographic provinces (fig. 1).

The Appalachian Plateau is underlain by a gently folded Paleozoic sedimentary section of Devonian–Permian age composed of interbedded sandstone, siltstone, shale, conglomerate, limestone, and coal (Brezinski and Conkwright, 2013). Folds trend northeast – southwest (NE–SW) and include broad anticlines and synclines. Several Pennsylvanian coal seams have been mined from synclinal troughs, while the Accident Dome and Deer Park anticlines produced gas from the Devonian Needmore–Oriskany–Helderberg interval; the Accident Field has served as a natural-gas storage reservoir for decades (Schwarz, 1996). The Marcellus Shale, a Devonian, organic-rich dark shale with limestone and siltstone interbeds, is interpreted as an important gas source in the Accident structure (Brezinski, 2012) and outcrops east of the Plateau. These structural and stratigraphic relations control groundwater storage and flow within interbedded clastics and carbonates and influence geochemical evolution.

The Ridge and Valley Province consists of strongly folded and faulted Paleozoic sedimentary rocks arranged in long, linear ridges separated by parallel valleys. The eastern part forms a broad carbonate valley developed on Cambrian–Ordovician limestone and dolomite, characterized by widespread karst. Westward, a more rugged terrain reflects Silurian–Mississippian shale and sandstone, with additional valleys locally underlain by Silurian–Devonian limestones.

The Piedmont Plateau Province is a belt of hard, crystalline igneous and metamorphic rocks extending from the inner Coastal Plain to the Blue Ridge boundary. Bedrock is dominated by schist, gneiss, and gabbro, locally intruded by granitic plutons and pegmatites (Bennett and Meyer, 1952; Dingman and Meyer, 1954); domal Precambrian gneiss mantled by quartzite, marble, and schist produces distinctive relief through differential erosion. Inliers include the Frederick Valley (Cambrian–Ordovician limestone and dolomite) and scattered Triassic red-bed basins (shale, siltstone, sandstone). Together these materials form a coupled regolith–fracture aquifer system in which storage resides largely in the weathered mantle while transmissivity is controlled by fractures at depth (Pavich, 1989).

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METHODS OF INVESTIGATION

CHARACTERIZING LOCATIONS

Samples were collected from sites distributed across the physiographic provinces west of the Fall Line (fractured-rock zone) to characterize chloride from multiple sources (fig. 1). Sites included shared and private septic systems, municipal landfills, a saltwater treated pool, agricultural properties, domestic wells, formation

brine-affected wells, and road-salt-impacted wells (tab. 1). Sampling occurred from September 2024 through April 2025 and comprised 28 representative samples and 11 field blanks.

Shared and private septic systems

According to the Maryland Department of the Environment (MDE), approximately 420,000 septic systems are installed across the state, providing wastewater treatment for many homeowners who often also rely on private wells for their drinking water (MDE, 2020). Because septic systems consolidate and store human waste, they can provide useful insights into substances that people are exposed to in their daily lives, whether through ingestion or environmental pathways. For this study, septic effluent samples were collected from six shared septic systems, each serving between four and eleven homes (sample IDs W-1 to W-6), as well as from two private septic systems (W-7 and W-8), for a total of eight septic effluent samples (fig. 1; tab. 1).

Municipal landfills

Housing over six million people in Maryland requires large areas of land dedicated to the collection and management of solid waste generated from daily activities. Although modern landfills are engineered with multiple components and processes designed to minimize environmental impacts, they remain a potential source of pollution and groundwater contamination. According to the USEPA's Landfill and Landfill Gas Energy Database (U.S. EPA, 2025), Maryland currently has 47 municipal landfills (both open and closed) that collectively store approximately 198 million tons of waste. For this study, seven groundwater samples were collected from monitoring wells at two sites: Alpha Ridge Landfill in Howard County and Forty West Landfill in Washington County (Lm-1 to Lm-7) (fig. 1; tab. 1).

Saltwater swimming pool

Saltwater treated swimming pools offer an alternative to traditional chlorine-based pool water treatment. As pool water passes through the salt cells of the treatment system, the salt is broken down through electrolysis which produces chlorine to treat the water. Water was collected as a grab sample from one saltwater treated pool (P-1) (fig. 1; tab. 1). For the remainder of the report, the saltwater treated pool is termed as the saltwater pool.

Agricultural sources

Agriculture remains a major land use in Maryland, with approximately two million acres devoted to farming, primarily in the north-central and eastern regions of the state. As population growth increases demand for food and agricultural products, farmers have adopted a range of practices to improve yields, including the widespread use of chemical fertilizers and pesticides. In addition, long-term agricultural practices in Maryland include liming (CaO application), which contributes calcium to soils and may influence groundwater chemistry. However, excessive application of agricultural inputs can have significant environmental consequences, as runoff from agricultural lands enters natural and engineered drainage systems and ultimately flows into Chesapeake Bay. In addition, animal waste can contain elevated chloride and impact groundwater. To evaluate potential impacts to groundwater quality from agricultural practices, five groundwater samples were collected from wells located on agricultural properties situated at a substantial distance from urban development (A-1 to A-5) (fig. 1; tab. 1).

Formation brine water-affected wells

Formation waters, especially those at great depths, can contain very high concentrations of dissolved salts, which are from ancient trapped and altered seawater or can form naturally when groundwater interacts with salt deposits or other evaporite minerals. In Maryland, these formation waters can be brine that is present within deep sedimentary aquifers of the Appalachian Plateau Province in Garrett County. Although contamination of groundwater by brines brought to the surface by oil and gas exploration and production is present in many other states, Maryland no longer has any substantial oil and gas production. However, significant quantities of gas were produced, primarily in Garrett County, during 1951–1973. Gas production has appreciably declined since then (Schwarz, 1996). Contamination by brine that came to the surface during the exploration and production of gas in the past and was not properly handled could potentially be present as legacy pollution. Previous studies identified several wells in Garrett County with evidence of formation brine influence (Gemperline and Adams, 2022; VanDerwerker and others, 2018). For this study, two groundwater samples were collected from wells previously

identified as affected by natural brine (B-1 and B-2) (fig. 1; tab. 1). For the remainder of the report the formation, brine affected wells are termed as brine wells.

Table 1. List of sample names and locations.

SITE NAME	SAMPLE ID	SOURCE OF SAMPLE
Brantwood	W-1	Effluent sample from shared septic system, Ellicott City, Howard County.
Willow Ridge	W-2	Effluent sample from shared septic system, Ellicott City, Howard County.
Lyndonbrook	W-3	Effluent sample from shared septic system, West Friendship, Howard County.
Riggs Meadow	W-4	Effluent sample from shared septic system, Glenwood, Howard County.
Blakeslee	W-5	Effluent sample from shared septic system, Garrett County, Garrett County.
Crescent Shores	W-6	Effluent sample from shared septic system, Garrett County, Garrett County.
WB-3	W-7	Effluent sample from private septic system, Woodsboro, Frederick County.
FL-2	W-8	Effluent sample from private septic system, Freeland, Baltimore County.
FW-1	Lm-1	Groundwater sample from landfill monitoring well at Forty West landfill site, Washington County.
FW-2	Lm-2	Groundwater sample from landfill monitoring well at Forty West landfill site, Washington County.
FW-3	Lm-3	Groundwater sample from landfill monitoring well at Forty West landfill site, Washington County.
ARL-1	Lm-4	Groundwater sample from landfill monitoring well at Alpha Ridge landfill site, Howard County.
ARL-2	Lm-5	Groundwater sample from landfill monitoring well at Alpha Ridge landfill site, Howard County.
ARL-3	Lm-6	Groundwater sample from landfill monitoring well at Alpha Ridge landfill site, Howard County.
CML-1	Lm-7	Groundwater sample from landfill monitoring well at Alpha Ridge landfill site, Howard County.
WB-1	D-1	Groundwater sample from private well in Woodsboro, Frederick County.
FL-1	D-2	Groundwater sample from private well in Freeland, Baltimore County.
WB-2	P-1	Sample of saltwater pool water from Woodsboro, Frederick County.
Accident-1	B-1	Groundwater sample from a well affected by brine, Accident, Garrett County.
Accident-2	B-2	Groundwater sample from a well affected by brine, Accident, Garrett County.
Glenwood library-GWL	S-1	Groundwater sample from a well near slated roads, Glenwood, Howard County.
Town Hill Satellite-SHA-1	S-2	Groundwater sample from SHA monitored well at the Town Hill Satellite salt storage facility, Allegany County.
Sideling Hill Rest area-SHA-2	S-3	Groundwater sample from SHA monitored well near salted roads at the Sideling Hill Rest Area, Washington County.
Jarrettsville-JV-1	A-1	Groundwater sample from a private well adjacent to a horse stable, Jarrettsville, Harford County.
LPF-1	A-2	Groundwater sample from a well on farm, Howard County.
Reisterstown-RT-1	A-3	Groundwater sample from a well on farm, Reisterstown, Baltimore County.
Westminster-WM-1	A-4	Groundwater sample from a well on farm, Westminster, Carroll County.
Westminster-WM-2	A-5	Groundwater sample from a well adjacent to a horse stable, Westminster, Carroll County.

Road salt-affected wells

The application of de-icing salts and brines to roadways is one of the most common and cost-effective methods of maintaining safe driving conditions during winter weather events. However, road salt is a well-documented

source of chloride contamination in groundwater. As ice and snow melt, the dissolved salt generates chloride-rich runoff that infiltrates unpaved surfaces and enters stormwater drainage systems. According to the United States Geological Survey (USGS), road salt application is a major contributor to elevated chloride levels in groundwater across the northeastern United States (USGS, 2023). Three groundwater samples (S-1 to S-3) were collected in March 2025 from wells located near major roadways and a road salt storage facility managed by the Maryland State Highway Administration (SHA) (fig. 1; tab. 1). These sites were selected to represent groundwater with known or suspected impacts from road salt storage or application.

Domestic wells

According to MDE, approximately 13% of Maryland's population relies on domestic groundwater wells for their drinking water supply (MDE, 2025). These residents typically live outside more developed cities and towns in areas where municipal water systems are unavailable. For this study, two groundwater samples were collected from locations where private septic effluent samples were also obtained to evaluate potential septic influence on groundwater quality or determine whether the groundwater remains relatively pristine. Additionally, one of these sites included a saltwater pool, providing an opportunity to assess its possible contribution to chloride concentrations in groundwater. These groundwater samples are identified as D-1 and D-2 (fig. 1; tab. 1).

Locations with multiple source samples

At two sampling locations, multiple types of samples were collected. In Woodsboro, Frederick County, samples D-1 (well water), P-1 (saltwater pool water), and W-7 (septic effluent) were obtained from the same property. Similarly, in Freeland, Baltimore County, samples D-2 (well water) and W-8 (septic effluent) were collected at a single property (fig. 1; tab. 1).

SAMPLE COLLECTION

Except for the grab samples (septic and saltwater pool samples), groundwater samples were collected in accordance with the USGS groundwater sampling protocol (USGS, 2006) wherein water is purged at a constant and low rate and field parameters are recorded every five minutes. Field parameters were measured with a YSI EXO™¹ multiparameter sonde attached to a flow-through cell. When field conditions did not allow the use of a flow-through cell, approximately three gallons of water were collected in a 5-gallon bucket and field parameters were recorded. Once the field parameters stabilized within appropriate ranges, the sampling tubing was removed from the flow-through cell, and a sample was collected. The field parameters recorded were temperature, pH, specific conductance, dissolved oxygen, and turbidity. Field parameters for the grab samples were recorded at the time of sample collection.

Unfiltered samples were collected first, either directly from a spigot or through silicone tubing. Orthophosphate and dissolved organic carbon samples were required to be field filtered for analysis. When samples were collected through silicone tubing directly from the well, a 350 cm² 0.45-micron filter was attached to the tubing and a sample was collected. Depending on the sample collection limitations for some locations, raw water was first collected in a glass beaker and a peristaltic pump equipped with silicone tubing and an inline 0.45-micron filter was used to obtain the filtered samples.

Landfill samples were collected directly from groundwater wells using either a peristaltic pump or a preinstalled pump, when present. Shared and private septic systems were sampled using a grab method by utilizing a plastic container attached to an 8-foot pole and skimming the surface of the water to avoid collecting solids. The saltwater pool sample was collected as a grab sample using a glass container filled with pool water to fill the sample bottles. All other samples were collected from spigots or taps associated with groundwater wells prior to any water quality treatment or filtration systems. All samples were collected in laboratory-supplied bottles preloaded with preservatives and were immediately stored in ice filled coolers until delivery to the laboratory for analysis. Groundwater samples were manually titrated in the field to calculate alkalinity values. In addition, a field blank was collected at the end of each sampling day.

¹ The use of brand names in this report is for identification purposes only and does not constitute endorsement by Maryland Geological Survey.

The sampled wells had casing diameters ranging from four to six inches. Total well depths ranged from 19 to 600 feet (ft) below land surface (bls) and casing depths ranged from 7 to 109 ft bls. Well construction materials included steel and PVC casings, with PVC screens or open boreholes. Available well construction information for the sampled wells is included in Appendix A and Table A-1.

STATE HIGHWAY ADMINISTRATION DATA

Since 1999, SHA has responded to well-owner complaints regarding domestic well water quality by collecting groundwater samples for laboratory analysis. The resulting data, provided by SHA, were incorporated as supplemental information in this study's analyses where applicable. However, the SHA dataset is limited in scope, as not all analytes included in this project were measured, most notably bromide concentrations, thereby restricting its use in certain geochemical comparisons. To protect homeowners' privacy, data are not presented; however, selected results are shown in figures.

ANALYTICAL PROCEDURES

Samples were collected and transferred to Eurofins Laboratories in Lancaster, Pennsylvania, with courier pickup occurring within 24 hours of sample collection. A complete list of analytes and corresponding analytical methods is provided in Appendix B (tabs. B-1 and B-2). Major cations and anions, nutrients, and trace metals were analyzed using Standard Methods (SM) and U.S. Environmental Protection Agency (USEPA) methods specified by the laboratory. Seventeen samples were analyzed for caffeine, acesulfame, and sucralose to evaluate potential wastewater influence (app. B, tab. B-3). With the exception of the saltwater pool sample, at least one sample from each potential chloride source category (for example, septic systems, landfills, agricultural settings, domestic wells, brine-affected wells, and road-salt-impacted wells) was analyzed for these tracers.

Quality assurance and quality control (QA/QC) procedures were applied to verify that all data met established quality standards. Field blanks ($n = 11$) accompanied routine sampling. Non-detect results were retained as reported by the laboratory and not substituted in statistical summaries. Electroneutrality was evaluated for each sample using cation and anion sums milliequivalent per liter (meq L^{-1}). All samples fell within the acceptance threshold of charge balance error $|\text{CBE}| \leq 10\%$. Hydrochemical relationships were evaluated using Spearman's rank correlation coefficient (ρ), a nonparametric measure of monotonic association, to assess relationships between chloride and selected trace metals (strontium, barium, and lithium). Spearman's correlation was selected because it does not assume normality and is less sensitive to outliers and non-linear relationships than Pearson correlation. Statistical significance was evaluated using p-values.

RESULTS AND DISCUSSION

GENERAL WATER CHEMISTRY

A summary of the chemical analysis data is provided in Appendix B (tab. B-3), and detailed descriptions of the sample locations are presented in Table 1. The Piper diagram (fig. 2) illustrates the hydrochemical facies of samples collected from distinct chloride sources, including septic systems, landfills, domestic wells, saltwater pool, brine, road salt, and agricultural sites. In the cation triangle, agricultural and domestic well samples, as well as landfill monitoring wells, generally plot toward the Ca–Mg field, whereas septic, brine, and saltwater pool samples exhibit elevated Na+K proportions. Road salt samples cluster near the center of the cation triangle, consistent with cation-exchange processes in which sodium from halite is partially exchanged with calcium and magnesium in the aquifer matrix. In the anion triangle, most septic, brine, and road salt samples are strongly enriched in $\text{Cl}+\text{NO}_3$, while agricultural samples show higher contributions from HCO_3+CO_3 , consistent with carbonate dissolution and nutrient cycling. Overall, two dominant water types are evident: Ca–Mg– HCO_3 waters, representative of natural background and agricultural influences, and Na–Cl waters, characteristic of anthropogenic sources such as septic effluent, landfill leachate, road salt, and brine.

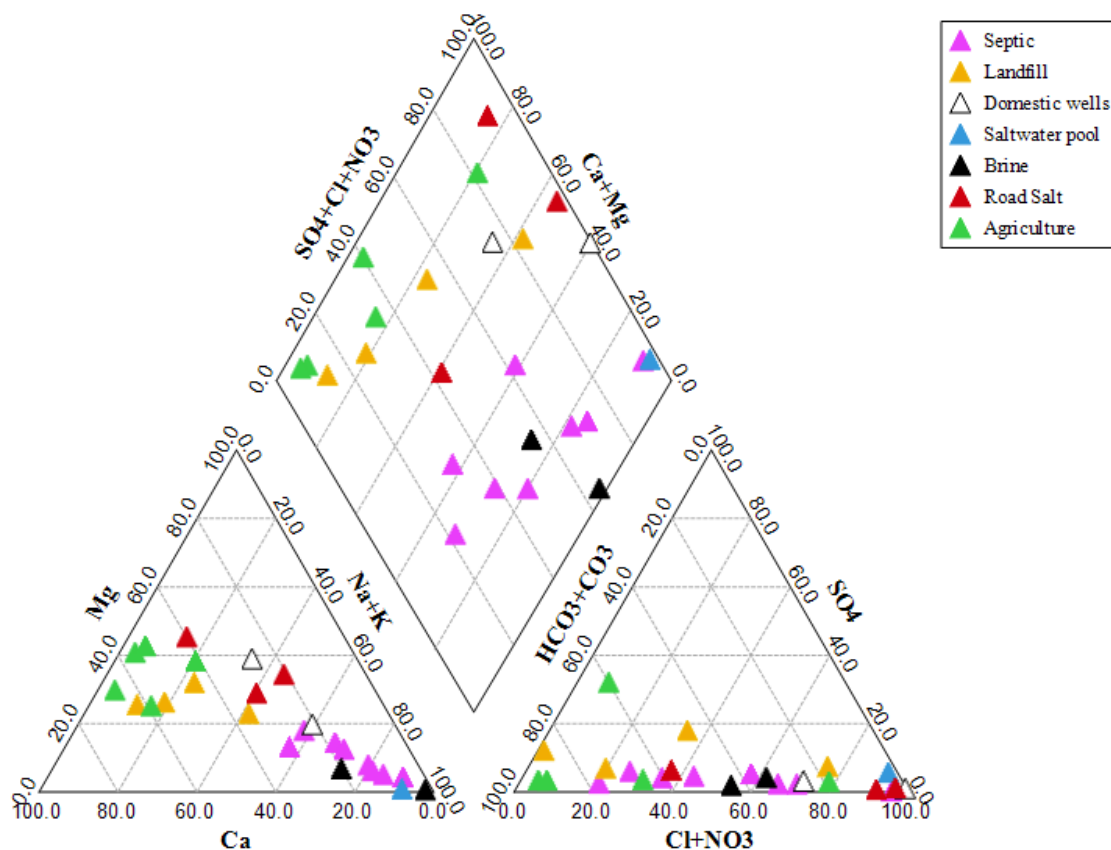


Figure 2. Piper diagram of grab and groundwater samples.

pH

Sample pH values ranged from 5.8 to 8.7 across all sites. Septic (W-series) and brine (B-series) samples were generally neutral to alkaline (7.1–8.7), whereas domestic wells (D-series) were the most acidic (5.9–6.5). Landfill (Lm-series) and agricultural (A-series) sites exhibited intermediate to variable pH (5.8–8.2), reflecting mixed geochemical and anthropogenic influences. Road salt-impacted sites (S-series) were near neutral to slightly alkaline (7.0–7.6). The acidic conditions in domestic wells may reflect natural soil or bedrock geochemistry, whereas elevated pH in septic and brine samples likely reflects alkalinity contributions from wastewater and concentrated salts.

Total Dissolved Solids and Specific Conductance

Figure 3 illustrates a strong positive correlation between specific conductance and chloride ($R^2 = 0.986$), with a slope of 0.33 and an intercept of -113, indicating chloride as the major driver of salinity in the dataset. Both specific conductance and total dissolved solids (TDS) vary substantially among sites, reflecting source-specific inputs. Septic effluent samples show the highest values, with an extreme outlier at site W-7 (12,000 $\mu\text{S}/\text{cm}$ conductance; 6,600 mg/L TDS), likely influenced by concentrated wastewater or water softener brine (app. B, tab. B-3). Elevated values are also observed at the saltwater swimming pool site (P-1) and one domestic well (D-1). In contrast, landfill and agricultural sites generally exhibit lower conductance and TDS relative to the range of values measured in this dataset, suggesting either limited chloride loading or dilution effects. Road salt, brine, and landfill samples fall within intermediate ranges, while agricultural samples cluster toward the lower end, underscoring distinct source-specific signatures across sites sampled during this project (fig. 3). These signatures are indicative rather than strictly diagnostic given the limited sample size. Additional sampling may increase variability and overlap among sources; however, the strong specific conductance–chloride relationship is expected to persist, reflecting chloride’s dominant contribution to conductivity.

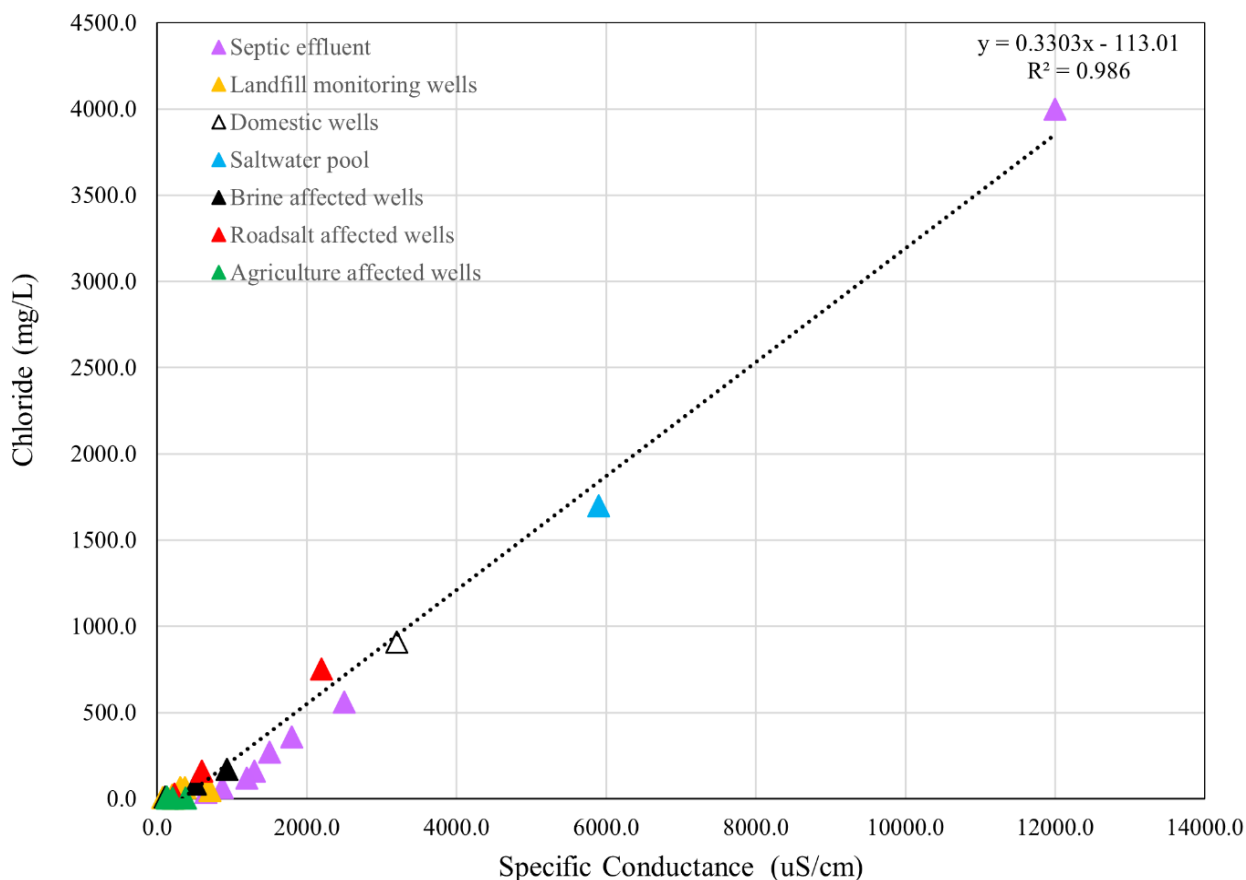


Figure 3. Relationship between specific conductance and chloride.

Dissolved Oxygen and Organic Carbon

Dissolved oxygen (DO) and dissolved organic carbon (DOC) varied widely among sites, reflecting differences in redox conditions and organic matter inputs (app. B, tab. B-3). For discussion, DO conditions are defined as low (<1 mg/L), moderate (1–5 mg/L), and high (>5 mg/L). Septic effluent samples exhibited DO concentrations ranging from 1.7 to 7.5 mg/L (median <5 mg/L) and elevated DOC, with sites W-3 and W-4 reaching 52–65 mg/L, indicative of substantial organic loading. Landfill sites showed extremely low DO (<1 mg/L) and low DOC (≤ 4.2 mg/L), consistent with strongly reducing conditions and limited biodegradable organic content. Domestic wells were characterized by high DO (7–9 mg/L) and low DOC, typical of oxic groundwater. Natural brine impacted samples displayed very low DO (<1 mg/L), suggesting oxygen depletion likely associated with high ionic strength or reducing environments. In contrast, road salt-impacted wells showed variable DO conditions, ranging from oxygen-depleted (<1 mg/L) to well-oxygenated (>7 mg/L), with DOC not detected. Agricultural wells were generally well oxygenated (1–15 mg/L DO) with low DOC (<1 mg/L) (app. B, tab. B-3). Overall, septic effluent sites contained the highest concentrations of organic carbon, while landfill and brine sites represented the most oxygen-depleted conditions.

CHLORIDE SOURCES

SEPTIC EFFLUENT

Chloride in wastewater may come from a variety of discharges from residential, commercial, and industrial sources (Granato and others, 2015). Apart from commercial activities, domestic sources also add significant chloride in septic effluent with water softener discharge being a dominant contributor. Ion exchange water softeners, which are commonly used to reduce water hardness, release significant amounts of chloride into wastewater during the regeneration cycle, where NaCl brine is flushed through the resin (Thomas, 2000; Wilhelm and others, 1994). Other contributors include human waste, food waste, detergents, and cleaning products, all of which contain varying levels of chloride (U.S. EPA, 2002). In areas with extensive use of water softeners, chloride concentrations in septic effluent can exceed 100 mg/L, sometimes reaching several hundred mg/L (Wilhelm and others, 1994). Unlike nutrients such as nitrogen or phosphorus, chloride is highly mobile and conservative in groundwater, meaning it does not readily degrade or attenuate, making it a valuable tracer for assessing wastewater impacts on groundwater quality (Robertson and others, 1991).

Septic effluent samples in this study included six shared septic systems, discharging between 2,250 to 7,500 gallons per day (gal/day), and two private systems discharging approximately 1,000 to 1,500 gal/day (tab. 1; app. A, tab. A-2). Chloride concentrations in the shared systems ranged from 64 to 560 mg/L, while the private systems exhibited a much broader range: one sample (W-7) recorded the highest chloride concentration of 4,000 mg/L, whereas another (W-8) was among the lowest at 37 mg/L (app. A, tab. A-2). The median chloride concentration across all systems was 215 mg/L (tab. 3). Elevated sodium, chloride, and other ion concentrations, such as those observed in W-7 are often linked to the regeneration cycle of water softeners. These point-of-entry (POE) systems function by exchanging hardness-causing calcium and magnesium for sodium and are widely used in regions where groundwater is the primary drinking water source. All shared systems sampled in this study rely on groundwater except W-2, which is connected to a public water supply. Consistent with this difference, W-2 exhibited the lowest sodium, chloride, and overall ion concentrations among the shared systems (app. A, tab. A-2). A study from a small, mostly forested watershed in Baltimore County reported that 14-20% of chloride contributions were derived from water softeners and human waste (Moore and others, 2017). These results highlight the substantial contribution of water softeners to chloride loading in domestic wastewater. Nationwide, an estimated 10 million residential water softeners are currently in use, with adoption rates increasing by up to 20% annually (Cartwright and Cartwright, 2022; Jankowski and others, 2023).

MUNICIPAL LANDFILLS

A total of seven groundwater samples were collected from monitoring wells at municipal landfills in Washington and Howard Counties. Landfill leachate is typically enriched in a wide range of dissolved constituents, including major cations and anions, as well as tritium (^3H) (Ramaroson and others, 2018; Sankoh and others, 2021). Trace elements such as boron (B) and lithium (Li), which normally occur in groundwater at low concentrations (1–100 $\mu\text{g/L}$; Wedepohl, 1970), may be substantially elevated in leachate-impacted groundwater, often reaching 1–5 mg/L for boron and 100–500 $\mu\text{g/L}$ for lithium (Bassett and others, 1995; Hogan and Blum, 2003). Consistent with these patterns, boron concentrations in landfill monitoring wells from this study ranged from 0.017 to 2.2 mg/L, with the highest value (2.2 mg/L) aligning with leachate-impacted groundwater reported in previous studies. In contrast, lithium concentrations were relatively low, ranging from 0.012 to 0.023 mg/L (12 $\mu\text{g/L}$ to 24 $\mu\text{g/L}$), remaining close to natural background levels (Hem, 1985) (app. B, tab. B-3).

Wells located downgradient of the landfill in the direction of groundwater flow (Lm 1, 2, 4, 5, and 6) exhibit elevated concentrations of TDS, major cations and anions, trace metals, and chloride (up to 110 mg/L) compared to upgradient wells (Lm 3 and 7), which more closely reflected ambient groundwater chemistry and therefore were not included as landfill-impacted wells (app. B, tab. B-3). The median chloride concentration across downgradient wells was 65 mg/L (tab. 2). This pattern indicates a leachate influence on downgradient groundwater, with chloride serving as a conservative tracer of contaminant migration.

Table 2. Descriptive statistics for sodium (Na), chloride (Cl), and total nitrogen (TN), and ranges of chloride-to-bromide ratios (Cl:Br) for samples collected in this study, grouped by chloride source. Statistics are presented in the following order: mean, median, and range.

Sample type and source	n	Na ⁺ (mg/L)	Cl ⁻ (mg/L)	Br ⁻ (mg/L)	Cl:Br	TN (mg/L)
Septic Effluent (6 shared, 2 private)	8	462.5 145 47 - 2600	696.37 215 37 - 4000	0.2675 0.112 0.032 - 1.1	246.7 – 3,649	50.86 49.47 39 - 63
Road Salt – affected wells	3	41.6 48 10 - 67	312 455 26 - 750	0.14 0.14 0.012 – 0.14	1,142.8 – 2,777.7	1.77 0.92 0 – 4.4
Landfill leachate – monitoring wells*	5	19.82 24 8.1 - 26	61.4 65 20 - 110	0.1652 0.078 0.036 – 0.38	177 – 1,806	0.639 0.11 0.059 – 1.1
Brine – affected wells	2	141.5 141.5 83 - 200	128 128 86 - 170	0.875 0.875 0.55 – 1.2	141.66 – 156.36	0.069 0.069 0.057 – 0.081
Agriculture – affected wells	5	2.79 3 0.96 – 4.2	4.86 3.7 2.5 – 8.5	0.0054 0.013 0.012 – 0.014	264.3 – 708.3	4.3 2.8 1.6 – 9.9
Saltwater swimming pool	1	1,100	1,700	0.05**	34000	12.5

* Data summarized for downgradient wells only.

** Br value set to RL for Cl:Br calculations

AGRICULTURAL

According to the U.S. Geological Survey 2024 Mineral Commodity Summaries, total U.S. salt consumption in 2023 was approximately 41 million metric tons, of which about 3% (1.23 million metric tons) was used in agriculture. The primary agricultural use of salt is as a feed additive for livestock. Large animal confinement facilities require substantial feed inputs and generate manure that is often enriched in sodium and chloride. When stored or applied to fields, this manure can contribute to elevated chloride in surface water and groundwater (Kelly and others, 2008; Panno and others, 2006). In addition, the widespread use of potash (potassium chloride, KCl) as fertilizer represents an additional source of chloride; for example, Overbo and others (2021) identified fertilizer as a major contributor and the second-largest source of chloride in Minnesota. Fertilizer-derived chloride may increase concentrations in the environment, particularly under conditions that promote leaching or runoff.

Five groundwater wells were sampled in areas suspected to be influenced by agricultural activities and livestock facilities but located away from direct road salt application. Wells situated near livestock operations (A-1 and A-5) contained slightly higher chloride concentrations (6.4–8.5 mg/L) compared to wells primarily used for irrigation (2.5–3.7 mg/L) (app. B, tab. B-3). Nitrate (NO₃⁻) showed a similar trend, with higher concentrations in livestock-associated wells (5.2–9.9 mg/L) relative to irrigation wells (1.6–2.8 mg/L) (app. B, tab. B-3). Across all agricultural wells sampled for this project, the median chloride concentration was 3.0 mg/L and the median nitrate concentration was 2.8 mg/L (tab. 2). These patterns suggest a possible influence of livestock presence on groundwater quality, likely related to manure management practices or localized nutrient loading. In contrast, wells on farmland without livestock exhibited lower nutrient and ion concentrations, which may reflect effective land management, limited fertilizer use, or off-season sampling conditions that reduce nutrient leaching. However, given the limited number of samples and overlapping concentration ranges, the observed differences are not statistically significant. The low chloride concentrations observed indicate that the agricultural sources did not produce substantial salinity of concern for the sites sampled.

ROAD-DEICING SALT

Road salt, primarily NaCl, is widely used as a de-icing agent due to its low cost and effectiveness. However, repeated seasonal applications lead to environmental and infrastructural concerns. Chloride is highly soluble and

mobile, accumulating in soils, aquifers, and surface waters long after winter, often exceeding the USEPA chronic exposure criterion of 230 mg/L for aquatic life (Corsi and others, 2010; Moore and others, 2020; Szklarek and others, 2022; U.S. EPA, 1988). Elevated chloride also accelerates corrosion of infrastructure, including bridges, roads, and drinking water systems, resulting in billions of dollars in repair costs annually (Kaushal and others, 2005; NACWA & AMWA, 2009).

The Maryland Department of Transportation (MDOT) maintains an annual stockpile of approximately 386,000 tons of rock salt, stored at 87 locations across the state. During the 2024–2025 winter season, approximately 201,165 tons of salt were used for road treatment. SHA has significantly reduced salt application on a per event basis over the past five years through increased use of salt brine pretreatment and improved spreading technology. In addition to rock salt, SHA stores over 1.6 million gallons of salt brine to enhance road safety and minimize environmental impact. These operational strategies reflect ongoing efforts by the MDOT to reduce salt dependency while maintaining effective winter road maintenance (Johnson and others, 2015).

Three groundwater samples (S-1 to S-3) were collected from areas with potential road salt exposure. Sample S-1, from a county park, contained 160 mg/L chloride, reflecting historical road salt influence, as communicated by county officials familiar with long-term water-quality issues at the site. Sample S-2, located near a salt storage facility, had the highest concentration (750 mg/L chloride), indicating direct contamination. In contrast, sample S-3, from a rest area near Interstate 70, showed relatively low chloride (26 mg/L), conductivity, and TDS, suggesting minimal road salt impact.

SALTWATER SWIMMING POOL

Saltwater swimming pools rely on NaCl dissolved in the pool water, typically maintained at concentrations around 2,700–3,500 ppm (0.27–0.35%), about one-tenth the salinity of seawater (~35,000 ppm NaCl). These systems generate chlorine electrochemically by passing an electric current through the saline solution, producing chlorine in situ for disinfection purposes (NCCEH, 2014). In this study, only one saltwater pool (P-1) was sampled. The sample showed elevated sodium and chloride concentrations of 1,100 mg/L and 1,700 mg/L, respectively. Boron was detected at 8 mg/L, likely originating from borate additives used in pool maintenance. Borates are commonly added to saltwater pools as algacides, pH buffers, and stabilizers that improve water clarity and swimmer comfort (Taylor Technologies, 2020). The presence of nitrate and ammonium (NH_4^+) may reflect either swimmer waste or contamination present in the fill water source (WHO, 2006). The property at which the pool is located relies on domestic well water for household water needs. The pool is situated upgradient of the well. The corresponding well water sample (D-1) contained elevated nitrate, which may be the source of the nitrate detected in the pool sample. However, because the pool also contains elevated sodium and chloride, it may represent a potential contributing source to groundwater salinity. Historical data indicate that the domestic well has consistently exhibited elevated levels of chloride, nitrate, and *E. coli* (well-test data shared by a county representative).

BRINE

Previous studies have suggested that many wells in the Accident Dome area of Garrett County have chloride derived from brackish or deep formation brine sources (Bolton and others, 2014; Gemperline and Adams, 2022). Two samples (B-1 and B-2), which were analyzed during Phase I of this study and previously linked to deep brine sources due to elevated chloride levels and relatively low Cl:Br ratio, were resampled to evaluate temporal changes in chloride and other analyte concentrations. Chloride concentrations of 170 mg/L and 86 mg/L were reported from samples B-1 and B-2, respectively, compared to 144 mg/L and 139 mg/L, respectively, reported in the earlier study (Gemperline and Adams, 2022). The USGS also sampled well B-1 in 2014 and reported a chloride concentration of 197 mg/L. These differences in chloride concentrations likely reflect seasonal variability, dilution from groundwater recharge, and changes in aquifer flow conditions at the time of sampling, all of which can alter the proportion of deeper brine-influenced water mixing into the well over time.

The source of the saline water could possibly be natural flow of brackish water or saltwater from strata below the level of the fresh groundwater, such as in valleys where upward groundwater flow can occur. However, the source could also be legacy contamination from natural gas exploration and production that occurred in the past

as indicated earlier. The first deep well found to discover hydrocarbons in Maryland was drilled in 1944. Major natural gas deposits were then discovered during 1949–1966 and major gas production occurred during 1951–1973 primarily in Garrett County (Schwarz, 1996). Although the Marcellus Shale is present in western Maryland, the state banned hydraulic fracturing in 2017 for environmental protection (Maryland General Assembly, 2017).

ELEMENTAL RELATIONSHIP

Graphical analysis methods were used to characterize potential sources of contamination in water samples by examining differences in trace element composition, as demonstrated by Panno and others (2005). In this study, samples were collected from known sources, such as septic systems, landfills, and road salt-impacted wells, to aid in source identification. These techniques allowed for visual comparison and helped group the samples based on similarities or patterns that may reflect distinct contaminant origins. The approaches discussed below were particularly useful in highlighting distinctions among the samples and linking them to their likely source materials.

CHLORIDE VS CATIONS

Na vs. Cl: The bivariate plot in Figure 4 illustrates a strong positive correlation ($R^2 = 0.97$) between sodium and chloride concentrations across all sample types from this study, with a slope of approximately 0.63. This relationship spans the full concentration range from the lowest values observed in agricultural and upgradient landfill wells to the highest values in saltwater pool and septic effluent samples. The pattern reflects a concentration-dependent trend, with the strongest NaCl signatures occurring in relatively undiluted sources such as septic effluent and the saltwater pool. In contrast, agricultural, some landfill wells and one domestic well show lower NaCl concentrations, indicating dilution within the groundwater system.

Comparison with overlaid reference data from Panno and others (2005) and SHA chloride–sodium datasets further highlight source-specific patterns and reactions affecting sodium and chloride differently. Samples influenced by septic effluent and road salt align closely with the high Na–Cl trend observed in both reference datasets, while agricultural and pristine samples deviate from this trend, showing lower sodium relative to chloride (fig. 4). Many points for SHA data cluster where those for Panno’s values are located, reinforcing their shared NaCl signature. The distribution of data points close to the linear regression at higher chloride concentrations indicates dissolution of halite as the dominant process. The divergence of many points from the regression line is probably related to the cation adsorption and desorption of sodium on mineral surfaces, especially clays. When a chloride source with sodium migrates into a location containing clay and that is equilibrated with a lower sodium concentration in soil moisture or groundwater, cation exchange can occur whereby sodium is adsorbed, and calcium and magnesium are released from clay. This lowers the Na:Cl ratio because chloride is chemically conservative. If a location that had been affected for some time by a higher source of NaCl undergoes dilution by fresher recharge, sodium can be desorbed from the clay and replaced by calcium and magnesium such that the Na:Cl ratio increases. These effects are similar to what happens to the water passing through the exchange media in a conventional water softener. The cation exchange effect of adsorption of sodium during the influx of saline water from road salt dissolution is likely to have caused the band of lower sodium concentration in the group of SHA data on Figure 4.

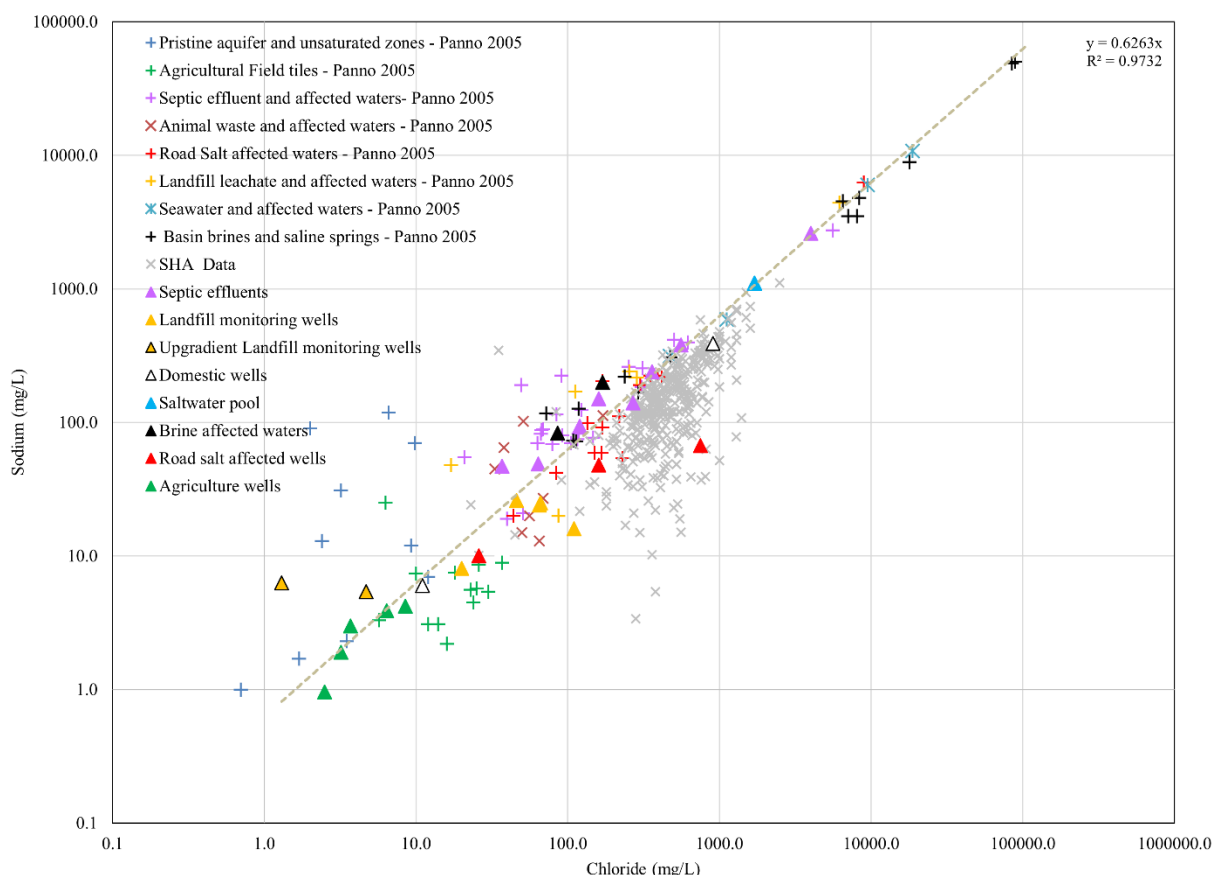


Figure 4. Scatter plot showing the relationship between chloride and sodium concentrations for grab and groundwater samples from all contaminant sources, with State Highway Administration (SHA) data and reference data from Panno and others (2005) included for comparison. The linear regression (dashed line) was calculated using only MGS data collected in this study ($R^2 = 0.9732$).

While the Na versus Cl scatter plot illustrates overall sodium–chloride relationships and confirms halite-controlled trends, such bivariate plots are influenced by dilution, concentration, and cation exchange effects, allowing samples from different chloride sources to follow similar trends despite distinct geochemical origins. To minimize these effects and emphasize source-specific signatures, cation-to-chloride ratios were utilized. Normalizing major cations to chloride, which behaves conservatively in groundwater, highlights processes such as halite dissolution, mineral weathering and surface reactions, and wastewater inputs (Hem, 1985; Whittemore, 1995). These ratios are presented as box plots (fig. 5) to summarize source-level variability and reduce the influence of outliers.

Na:Cl: To evaluate chloride source signatures, box plots of Na:Cl ratios were developed for both the MGS dataset which includes data from this study as well as previously published MGS investigations (Gemperline and Adams, 2022; VanDerwerker, 2019; VanDerwerker and others, 2018) and published values from Panno and others (2005), minimizing the influence of individual data points while emphasizing source-level patterns. Sodium-to-chloride ratios are presented as mass ratios (mg/L Na ÷ mg/L Cl). For reference, pure halite dissolution yields a Na:Cl mass ratio of approximately 0.65 (which is equivalent to the 1:1 molar ratio), whereas seawater has a slightly lower mass ratio of approximately 0.56. These reference values are shown to aid interpretation (fig. 5A). Because chloride behaves conservatively in groundwater, the Na:Cl ratio provides a robust indicator of chloride origin and post-input geochemical modification, including cation exchange with aquifer material and wastewater inputs.

Road salt-affected samples in both datasets plot predominantly below the halite mass-ratio reference line, reflecting chloride enrichment relative to sodium following halite dissolution and subsequent geochemical modification such as cation exchange, or mixing with ambient groundwater. The relatively narrow interquartile

range for road salt samples (MGS median = 0.289; Panno median = 0.534) indicates post-input geochemical alteration (fig. 5A).

Septic effluent and septic-affected groundwater display broader Na:Cl distributions, reflecting sodium enrichment associated with household water softener discharge and wastewater-related ion exchange processes. Brine-affected wells generally exhibit elevated Na:Cl ratios relative to road salt, and notably high median ratio (0.882). Devonian age formation waters in Maryland are expected to have Na:Cl ratios in the range 0.3–0.5 that are similar to Devonian brines in Pennsylvania (Warner and others, 2012). The higher Na:Cl ratios for the brine-affected wells suggest that the elevated chloride could derive from legacy contamination from natural gas exploration and production activities, whereby the chloride pollution is being diluted, and sodium is being desorbed from clays as described earlier. Agricultural and field-tile-drained waters tend to plot at lower Na:Cl ratios, reflecting greater relative contributions of divalent cations derived from mineral dissolution. Animal waste-affected waters exhibit variable and often elevated Na:Cl ratios (Panno median = 0.526), reflecting biological processes, feed-derived inputs, and possible cation exchange rather than halite dissolution (fig. 5A).

Landfill samples exhibit intermediate and variable Na:Cl mass ratios, reflecting heterogeneous leachate composition, mixing with ambient groundwater, and cation exchange rather than simple halite dissolution. Although some overlap with septic-affected waters occurs in Na:Cl space, landfill samples are distinguished by generally lower nitrogen concentrations, as shown in the TN-based analyses (fig. 8).

Outliers observed across several source categories represent localized geochemical conditions or mixed-source influences rather than analytical artifacts, underscoring the importance of evaluating Na:Cl distributions rather than individual values.

Ca:Cl and Mg:Cl: To further refine source differentiation beyond sodium, Ca:Cl and Mg:Cl mass ratios were evaluated using box plots for the MGS and referenced datasets (figs. 5B and 5C). Because chloride behaves conservatively, variability in these divalent cation ratios reflects subsurface processes, such as carbonate dissolution, silicate weathering, and cation exchange, that modify the original chloride signal.

Road salt-affected samples and geologic brines in the MGS dataset exhibit consistently low Ca:Cl and Mg:Cl ratios with narrow interquartile ranges, reflecting halite-dominated chloride inputs in which divalent cations are either low in the source or depleted through prolonged water-rock interaction and cation exchange processes. In the Panno dataset, these ratios are also generally low but show a broader range. In contrast, agricultural and field-tile-drained waters display elevated and highly variable Ca:Cl and Mg:Cl ratios, consistent with carbonate-rich soils, mineral weathering, and enhanced mobilization of calcium and magnesium during recharge and drainage.

The particularly high ratios observed in the MGS agricultural dataset may be partially amplified by lower absolute chloride concentrations; however, the persistent pattern of broad variability and elevated medians indicates that water-rock interaction dominates over simple dilution effects (Appelo and Postma, 2005; Hem, 1985). Field-tile drainage samples from the Panno dataset exhibit similar enrichment patterns, reinforcing the reliability of divalent cation-to-chloride ratios as possible indicators of agricultural influence (fig. 5B).

Septic effluent in the MGS dataset generally exhibits lower Ca:Cl and Mg:Cl ratios than road salt-impacted samples, reflecting mixed influences from wastewater inputs, background groundwater chemistry, dilution, and cation exchange. Animal waste-affected waters display moderate Ca:Cl and Mg:Cl ratios with some variability, reflecting manure-derived inputs, biological processing, and groundwater mixing. Landfill-affected groundwater exhibits elevated Ca:Cl and Mg:Cl ratios in the MGS dataset, whereas these ratios are more variable in the Panno dataset, consistent with heterogeneous waste composition and geochemical evolution. A notably elevated Mg:Cl outlier in the Panno dataset (approaching 6.0) highlights the potential for magnesium enrichment under certain landfill conditions (fig. 5C).

Overall, Ca:Cl and Mg:Cl ratios can distinguish carbonate- and soil-influenced agricultural sources from halite-dominated chloride sources and complement Na:Cl ratios by emphasizing mineral weathering and ion exchange processes.

K:Cl: Potassium-to-chloride (K:Cl) mass ratios provide additional separation among anthropogenic chloride sources, particularly those influenced by organic matter, wastewater, and waste-derived inputs (fig. 5D). Road salt-affected samples exhibit uniformly low K:Cl ratios in both datasets, consistent with halite-derived chloride and minimal potassium contribution. Brine-affected samples similarly display low and tightly clustered K:Cl ratios, possibly from potassium-depleted formation waters or by potassium adsorption and fixation on clays. In contrast, septic effluent and septic-affected groundwater display elevated K:Cl ratios relative to road salt, with greater variability, particularly in the Panno dataset, reflecting potassium inputs from wastewater, detergents, and household water use. Animal waste-affected waters also show elevated K:Cl ratios, consistent with potassium-rich feed additives and biological cycling, aiding differentiation of organic waste sources from mineral road salt (fig. 5D).

Agricultural samples exhibit higher K:Cl ratios than those in the Panno field-tile dataset and are also elevated relative to road salt, brine, and septic effluent samples, reflecting limited potassium mobility relative to calcium and magnesium in soil systems.

Landfill leachate and landfill-affected groundwaters exhibit broad and variable K:Cl distributions that overlap with septic and animal waste sources (fig. 5D). This variability reflects heterogeneous waste composition, organic matter degradation, ash and debris contributions, and variable geochemical attenuation processes.

Elevated potassium concentrations may reflect inputs from septic effluent, urea-based wastewater, or agricultural fertilizers, and therefore K:Cl ratios should be interpreted as a general nutrient-related indicator rather than a unique tracer of septic systems.

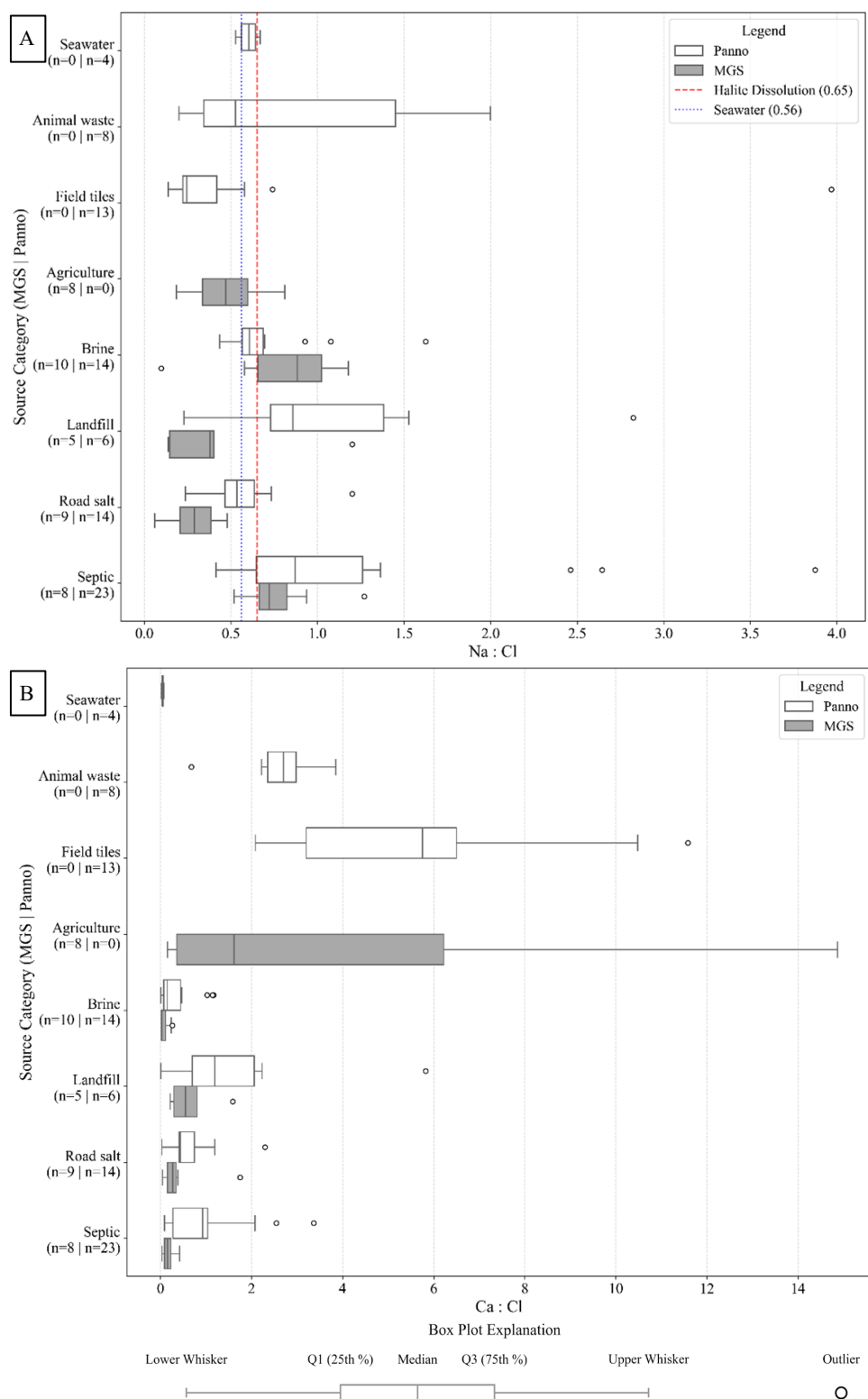


Figure 5. Box plots of mass-ratio distributions for major chloride sources based on the Maryland Geological Survey (MGS) compiled data and published data from Panno and others (2005), showing (A) sodium-to-chloride (Na:Cl), (B) calcium-to-chloride (Ca:Cl), (C), magnesium-to-chloride (Mg:Cl), and (D) potassium-to-chloride (K:Cl) ratios.

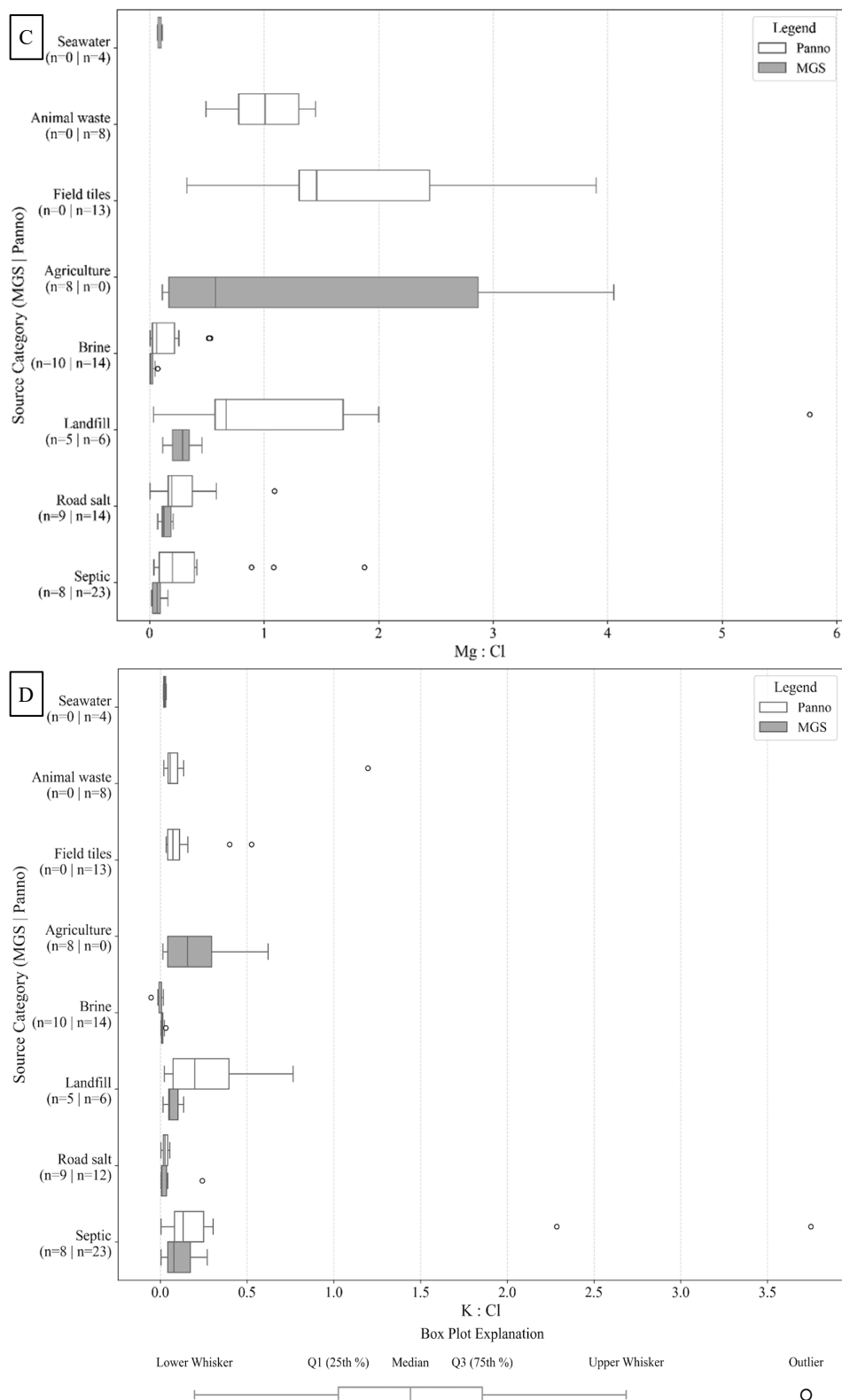


Figure 5 (cont.). Box plots of mass-ratio distributions for major chloride sources based on the Maryland Geological Survey (MGS) compiled data and published data from Panno and others (2005), showing (A) sodium-to-chloride (Na:Cl), (B) calcium-to-chloride (Ca:Cl), (C), magnesium-to-chloride (Mg:Cl), and (D) potassium-to-chloride (K:Cl) ratios.

CHLORIDE VS ANIONS

Cl vs Cl:Br: Halides such as chloride, bromide, and iodide behave conservatively in groundwater, making them effective tracers for identifying solute sources (Davis and others, 1998; Katz and others, 2010). A chloride versus chloride-to-bromide (Cl:Br) plot provides insight into potential contamination sources by evaluating differences in halide ratios in relation to chloride concentration (Alcalá and Custodio, 2008; Cartwright and others, 2023; Panno and others, 2006; Whittemore, 2005) (tab. 3). To establish an initial reference framework, a Cl versus Cl:Br plot was constructed using the published mixing curves of Panno and others (2006), with both the Panno dataset and available SHA bromide data overlaid for comparison (fig. 6). This reference plot illustrates the expected separation among major chloride sources based on published endmembers. Table 3 summarizes Cl:Br ratios from this study alongside published values for representative chloride sources.

Table 3. Ranges of chloride-to-bromide (Cl:Br) ratios, chloride concentrations, and bromide concentrations (mg/L) for selected sources, compiled from literature and from this study. NA, no data available.

Chloride sources and references	Chloride(mg/L)	Bromide (mg/L)	Cl:Br
Pristine groundwater			
Davis and others, 1998	NA	NA	< 200
Septic effluent			
Thomas, 2000; Jagucki and Darner, 2001	69	NA	460
Katz and others, 2010	20 – 136	0.02 – 0.25	544 – 1,150
Davis and others, 1998	NA	NA	300 – 600
Panno and others, 2006	91	0.118	769
Dumouchelle, 2006	NA	NA	1,167
This study	37 – 4,000	0.032 – 1.1	246.7 – 3,649
Road salt			
Davis and others, 1998	NA	NA	1,000 – 10,000
Granato, 1995: Highway runoff	80,000	NA	3,300
Granato, 1995: Road salt analysis	10,000	1.5	6,667
Granato, 1996: First flush winter storm	17,000	NA	58,621
Panno and others, 2006; analysis of deicing salt	NA	NA	13,497
Gemperline and Adams, 2022	78 – 466	<0.1	780 – 4,660
VanDerwerker, 2019	61.8 – 571	<0.1 – 0.2	1,579 – 15,261
This study	26 – 750	0.012 – 0.27	1,143 – 2,778
Brine and brine-affected water			
Warner and others, 2012, Devonian brine in PA	35,400 – 207,000	349 – 1,350	79.8 – 183
Panno and others, 2006, basin brine	64,600	NA	406
Davis and others, 1998	NA	NA	200 – 400
Gemperline and Adams, 2022	139 – 144	0.83 – 0.95	146.32 – 173.49
This study	86 – 170	0.55 – 1.2	142 – 156
Landfill			
Panno and others, 2006, median of 10 leachate samples from Illinois	1,284	7.81	193
Mullaney and others, 1999, landfill leachate affected groundwater	247	1.4	173
This study, landfill leachate affected groundwater	1.3 – 110	0.011 – 0.38	100 – 1,806
Agriculture			
Panno and others, 2006, fertilizer	40	NA	510
VanDerwerker, 2019	81.8 – 175	0.1 – 0.2	818 – 875
This study	2.5 – 8.5	0.012 – 0.014	264 – 708
Saltwater pool			
This study	1,700	0.05*	34000

* Br value set to RL for Cl:Br calculations.

Samples from this study generally fell within the broad source areas defined by Panno and others, (2006), including high Cl:Br ratios for halite-derived inputs (road salt and septic systems) and lower or intermediate ratios for landfill, agricultural, and brine-affected waters. Septic effluent exhibited a wide Cl:Br range (246–3,600), consistent with NaCl-based wastewater inputs with minimal bromide. Road-salt-impacted samples and SHA data plotted in the high-ratio halite zone, consistent with reference values (1,000 to >58,000) reported by Granato (1995), Davis and others (1998), and VanDerwerker (2019). Agricultural and landfill samples plotted in moderate-ratio zones, while brine samples plotted at low ratios, aligning with previously documented brine signatures. This comparison confirms that Maryland groundwater samples fit broadly within established source fields when viewed through the Panno mixing framework.

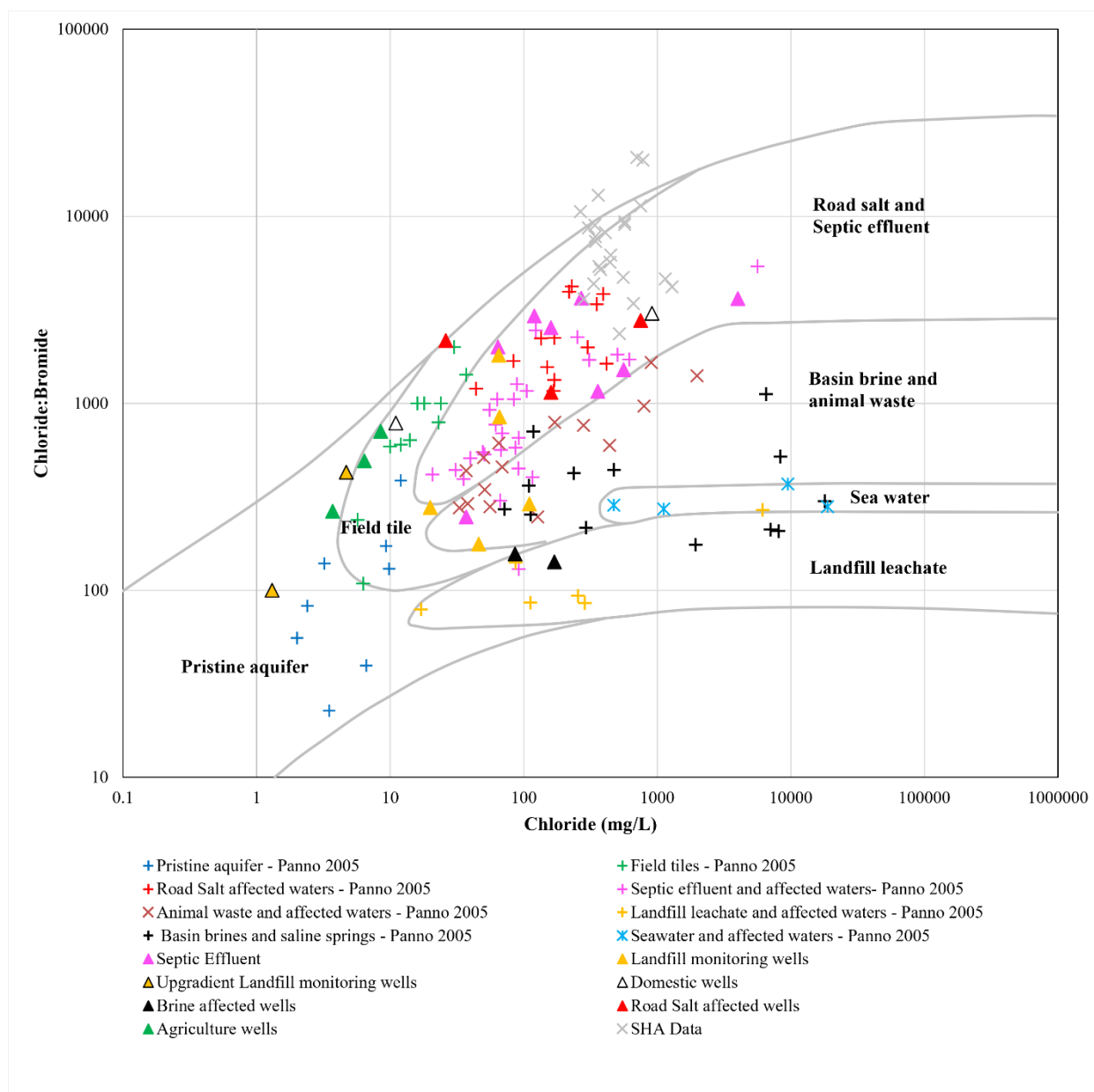


Figure 6. Chloride concentration versus chloride-to-bromide (Cl:Br) ratio for samples from this study, shown with a mixing curve modified after Panno and others, (2006). Reference data from Panno and others (2005) and State Highway Administration (SHA) samples (where bromide data were available) are included for comparison.

To more accurately evaluate chloride sources under Maryland-specific hydrogeochemical conditions, a second mixing plot was constructed using endmembers derived entirely from Maryland data (fig. 7). In this plot, chloride and bromide relationships among septic effluent, SHA road-salt-impacted wells, agricultural wells, landfill monitoring wells, domestic wells, saltwater pool water, and brine-affected wells demonstrate clearer source separation than in the generalized Panno framework. Maryland road-salt-impacted wells, including SHA well data, and previous MGS studies from Piedmont and Appalachian regions (Gemperline and Adams, 2022; VanDerwerker, 2019; VanDerwerker and others, 2018), cluster tightly at high Cl:Br ratios along the halite mixing trajectory, reflecting low bromide relative to high chloride content. The upper mixing curve in Figure 7 represents the upper boundary of a mixing zone between freshwater and rock salt (halite) used for road deicing, water softeners, and saltwater pools; the next lower curve indicates the lower bound of the mixing zone. The point for the saltwater pool in Figure 7 was determined using the reporting limit for bromide (app. B. tab. B-2). Septic effluents and affected wells occupy a broad intermediate-to-high ratio band, overlapping the halite field but forming a distinct group shaped by variable sodium and chloride inputs from wastewater and water-softener discharge.

Maryland landfill wells plot at lower to moderate Cl:Br ratios, with upgradient wells showing low Cl and Br and downgradient wells showing elevated bromide and reduced ratios due to leachate influence. Brine-affected wells from the Accident Dome fall within a narrow low-ratio range (142–156), consistent with deeper formation-water chemistry and previously reported methane-rich conditions at these sites (Gemperline and Adams, 2022). The Cl:Br ratios for the brine wells lie within the range of Devonian formation saltwaters in Pennsylvania listed in Warner and others (2012). Gas production in western Maryland is derived from Devonian age formations. Agricultural wells remain at low chloride concentrations but plot within moderate Cl:Br ratios, reflecting manure or fertilizer contributions to shallow groundwater. Notably, most agricultural samples from this study fall within or near the pristine groundwater mixing zone, indicating limited chloride enrichment despite localized nutrient inputs (fig. 7). Together, these patterns demonstrate that when Maryland-specific endmembers are used, the resulting mixing trajectories align closely with observed field data and improve differentiation among local chloride sources.

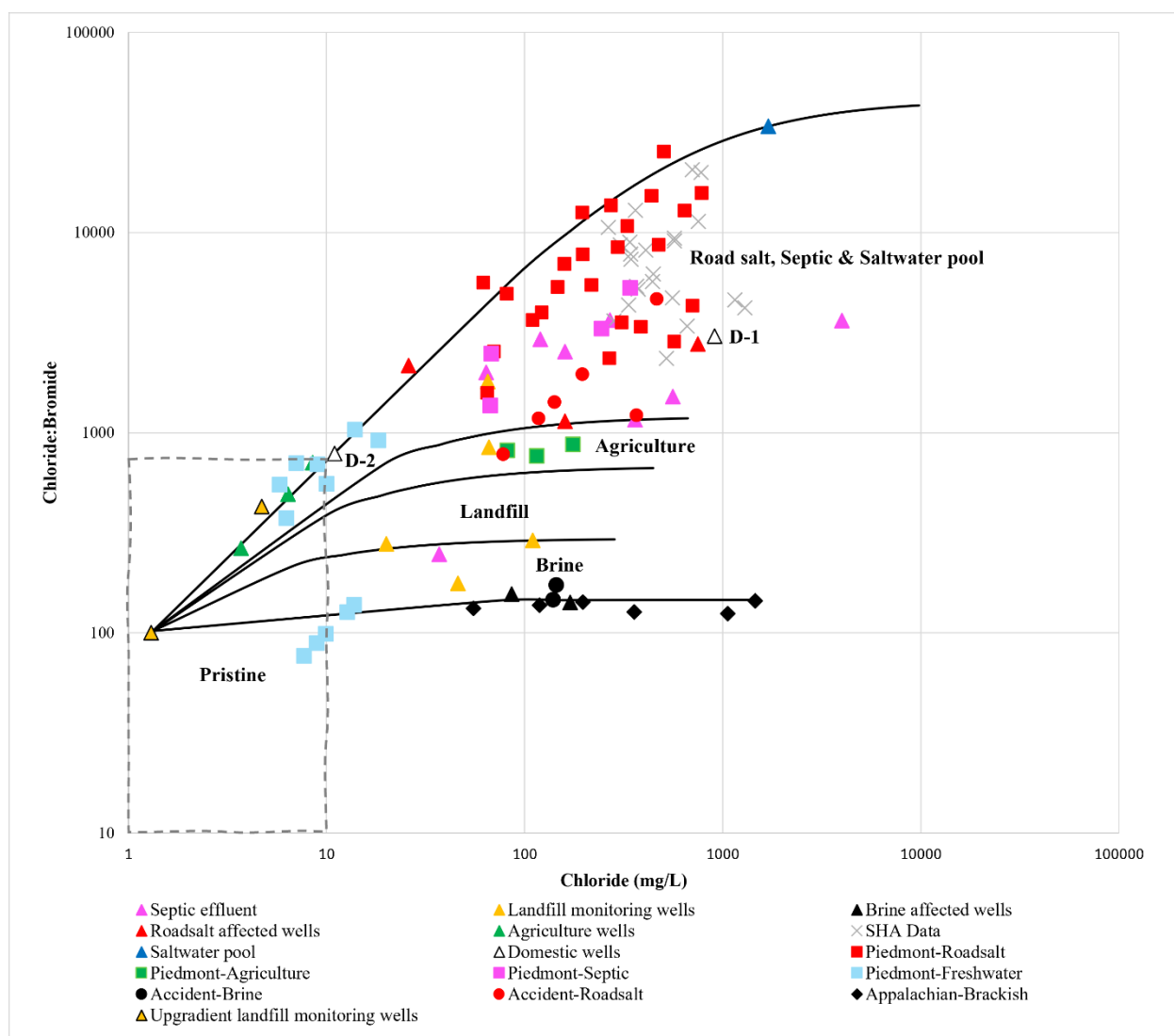


Figure 7. Maryland-based chloride:bromide (Cl:Br) mixing curves and sample distributions for major chloride sources. Samples collected for this study are plotted alongside reference data from Gemperline and Adams (2022; Accident), VanDerwerker (2019; Piedmont), and VanDerwerker and others (2018; Appalachian) to verify and strengthen the Maryland-based mixing model.

Two domestic wells (D-1 and D-2) further illustrate the value of the Maryland-based mixing curves. D-1, long known for elevated chloride, plotted at one of the highest Cl:Br ratios in this dataset (though lower than many Piedmont values) and had a Na/K ratio of 100, strongly indicating septic influence, or potentially contributions from an onsite saltwater swimming pool. Although D-2 plotted at a much lower Cl:Br ratio (785), it is within the mixing zone of very freshwater and rock salt affected waters; although the low chloride concentration indicates minimal signs of anthropogenic impact the slightly higher chloride than most of the pristine waters could also reflect a very small impact of road or water softener salt. These site-specific observations reinforce the importance of using both Cl:Br ratios and supporting geochemical indicators when interpreting chloride sources in Maryland groundwater.

Overall, the comparison between the Panno reference plot and the Maryland-based mixing curve demonstrates that while published frameworks provide useful context, Maryland-specific endmembers offer clearer and more accurate source discrimination for Maryland groundwater samples. Septic effluent and road salt consistently plot in the high Cl:Br zone characteristic of halite-derived inputs, whereas landfill, brine, and agricultural wells occupy

distinct lower or intermediate ranges shaped by local hydrogeochemical processes. This highlights the need to combine Cl:Br ratios with additional indicators (e.g., nutrients, or site conditions) to reliably distinguish overlapping sources such as septic effluent and road salt.

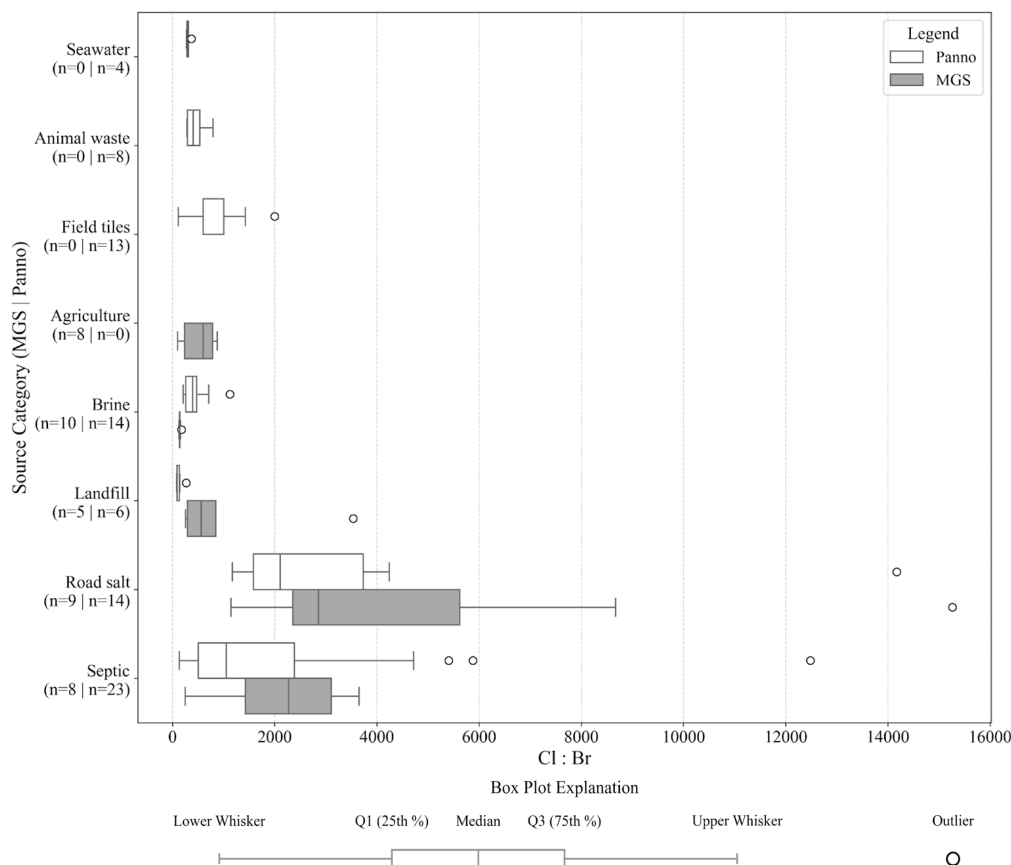


Figure 8. Box plots of chloride-to-bromide (Cl:Br) mass-ratio distributions for major chloride sources based on Maryland Geological Survey (MGS) compiled data and published data from Panno and others (2005).

To further evaluate source differentiation beyond theoretical mixing relationships, the distribution of Cl:Br mass ratios across source categories is shown in Figure 8. The box plots are based on the combined MGS dataset and reference data from Panno and others (2005), providing a broader context for comparison with established chloride source signatures. Road salt samples exhibit the highest Cl:Br ratios and the greatest variability, consistent with halite-derived inputs characterized by elevated chloride relative to bromide. In contrast, septic effluent displays comparatively lower Cl:Br ratios with moderate spread, reflecting bromide enrichment associated with wastewater sources. Landfill and brine-impacted samples generally plot at lower Cl:Br ratios than road salt, indicating non-halite influences and potential mixing with formation waters. Although some overlaps occur among sources, particularly between septic and lower-range road salt samples, the overall distribution patterns support the use of Cl:Br as a robust diagnostic indicator for distinguishing halite-dominated inputs from wastewater, agricultural, and natural brine sources within the study area. However, because the mixing curves in Figure 7 illustrate that Cl:Br ratios change with increasing chloride concentration for the same source (especially dissolved rock salt), care must be taken when comparing ratios without considering chloride content.

I vs Cl: In addition to bromide, iodide (I^-) was also examined as a potential supplementary tracer for differentiating chloride sources. Previous work (e.g., Panno and others, 2006) has demonstrated that iodide can provide useful source discrimination when measured at very low concentrations. In the present dataset, however, iodide was

detected in only two samples, reflecting the relatively high analytical detection thresholds used for this study. The method detection limit for iodide was 0.15 mg/L, and the reporting limit was 1 mg/L, which exceeds the concentration range in which iodide is typically informative for environmental fingerprinting. Because iodide concentrations in groundwater and wastewater are generally well below 0.05 mg/L, and often near or below 0.01 mg/L, the analytical sensitivity required to evaluate iodide signatures was not achieved. As a result, iodide is not discussed further in this section, but it may warrant reconsideration in future studies using lower-level detection methods.

Total Nitrogen vs Cl: Nitrate (NO_3^-) is a potential indicator of groundwater contamination from sewage (Whitemore, 2005). Panno and others (2006) suggested that total nitrogen (TN), calculated as the sum of nitrate-N, nitrite-N, and total Kjeldahl nitrogen (TKN), provides a more comprehensive and reliable indicator of wastewater influence. Because ammonium ($\text{NH}_4\text{-N}$) is already included in TKN, it was not added separately when TKN results were available; in cases where only $\text{NH}_4\text{-N}$ was reported and TKN was not analyzed, $\text{NH}_4\text{-N}$ was used in place of TKN for TN calculation.

Building directly on the chloride fingerprinting framework established by the Cl:Br versus Cl plot, TN concentrations were plotted against Cl:Br ratios to evaluate the co-occurrence of nutrient and halide signals (fig. 9). The TN versus Cl:Br plot reveals distinct clustering of groundwater samples associated with different contamination sources. Septic effluent and animal waste-impacted waters cluster at elevated TN concentrations (>10 mg/L) and moderate Cl:Br ratios, reflecting combined inputs of organic nitrogen and chloride from wastewater and manure. Agricultural samples exhibit elevated TN but relatively low chloride and Cl:Br ratios, consistent with fertilizer-derived nitrogen that is comparatively chloride-poor.

Landfill samples display variable chloride and generally low to moderate TN, reflecting heterogeneous waste composition, landfill age, and attenuation processes. In contrast, road salt and brine-affected samples are characterized by very high chloride and negligible TN, consistent with inorganic chloride sources lacking associated nitrogen. The saltwater pool sample plots at high chloride with moderate TN, suggesting mixing with organic inputs such as human-derived waste or decomposing debris; alternatively, the nitrogen signal may reflect contaminated source water, as the domestic well on the same property is also impacted by septic discharge.

To reduce dilution effects and emphasize source-specific nitrogen enrichment relative to conservative chloride behavior, TN:Cl mass ratios were evaluated using box plots for the MGS and Panno and others (2005) datasets (fig. 10). Septic effluent and septic-affected groundwater exhibit the highest TN:Cl ratios and the broadest distributions, reflecting elevated nitrogen loading from wastewater combined with variable attenuation processes such as nitrification, denitrification, and dilution during subsurface transport. Agricultural and field-tile-drained waters also display elevated and variable TN:Cl ratios, consistent with nitrogen-rich fertilizer inputs and rapid transport pathways in shallow subsurface systems.

In contrast, road salt-affected samples plot at consistently low TN:Cl ratios, reflecting chloride inputs largely decoupled from nitrogen sources. Brine-affected wells similarly exhibit very low TN:Cl ratios with minimal variability, consistent with geologic chloride sources that contain negligible nitrogen. Landfill leachate and landfill-affected groundwater show intermediate and variable TN:Cl ratios, reflecting heterogeneous waste composition and differing degrees of nitrogen mobilization and attenuation. Animal waste-affected waters exhibit moderate TN:Cl ratios and partially overlap with septic and agricultural sources, consistent with manure-derived nitrogen inputs and biological processing.

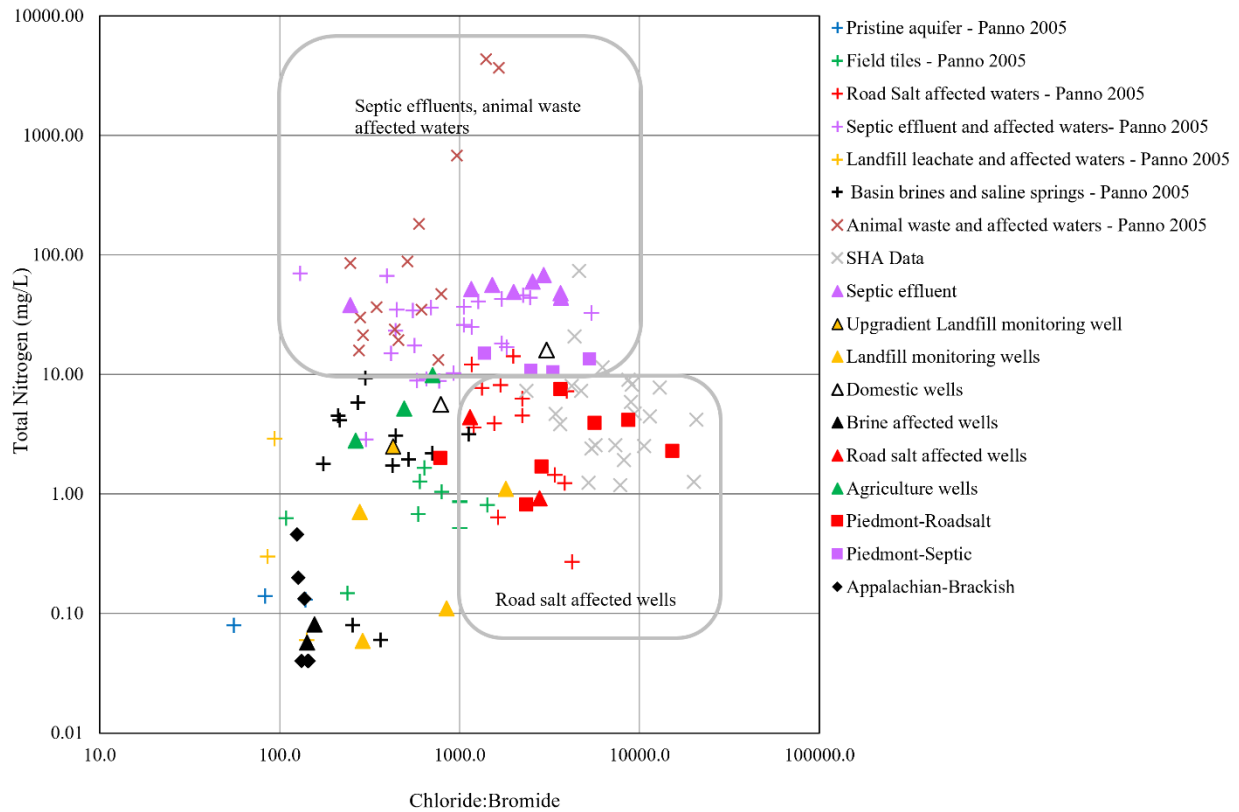


Figure 9. Total nitrogen (TN) versus chloride-to-bromide (Cl:Br) ratios for samples from this study, VanDerwerker and others (2018; Appalachian-Brackish), VanDerwerker (2019; Piedmont), and reference data from Panno and others (2005); State Highway Administration (SHA) samples shown for comparison.

Overall, the combined use of TN versus Cl:Br relationships and TN:Cl ratios provides a robust diagnostic framework for distinguishing groundwater contamination sources. While chloride and Cl:Br ratios alone may show overlap between septic effluent and road salt, including total nitrogen significantly improves source separation by explicitly accounting for nutrient inputs. Results from this study align closely with previously published datasets (Panno and others, 2005), and inclusion of SHA samples indicates that most plot within the road salt field, with a subset overlapping septic and animal waste signatures, suggesting localized wastewater influence. Together, these analyses demonstrate that nitrogen and chloride function as complementary co-tracers, improving the identification of groundwater contamination pathways compared to reliance on halide-based indicators alone. Median ion-to-chloride and halide ratio patterns derived from this study and published datasets are summarized in Table 4 to synthesize characteristic chloride source signatures.

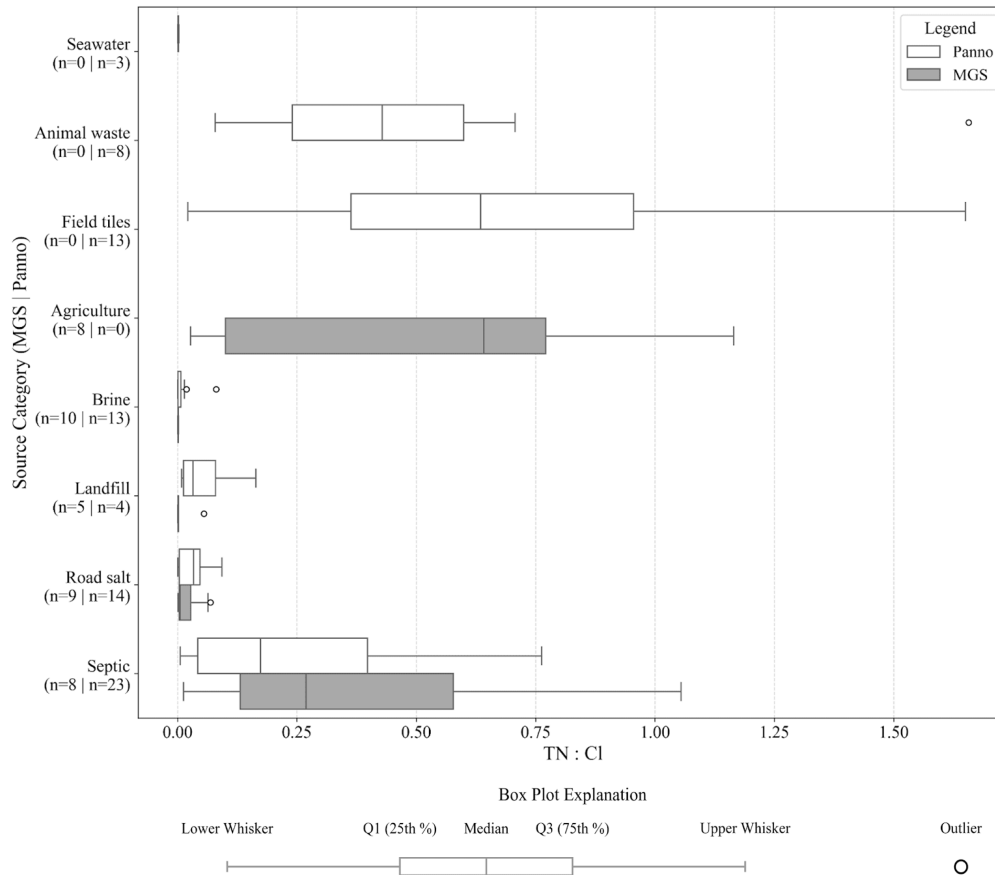


Figure 10. Box plots of total nitrogen–to–chloride (TN:Cl) mass-ratio distributions for major chloride sources based on Maryland Geological Survey (MGS) compiled data and published data from Panno and others (2005).

Table 4. Median ion-to-chloride and halide ratios derived from the combined Maryland Geological Survey (MGS) and published datasets used to characterize major chloride sources[†].

Sources	Na:Cl	Ca:Cl	Mg:Cl	K:Cl	Cl:Br	TN:Cl	Diagnostic Forensic Signature
Road Salt	0.42	0.38	0.17	0.02	2855	0.008	High-purity halite; minimal organic or divalent mass.
Septic Effluent	0.82	0.42	0.12	0.11	1514	0.17	Sodium & potassium enrichment; strong organic nitrogen signal.
Agriculture	0.47	1.62	0.58	0.15	600	0.64	High divalents from carbonate weathering; low relative sodium.
Landfill	0.76	0.85	0.45	0.135	250	0.01	Elevated Mg relative to chloride
Geologic Brine	0.68	0.08	0.03	0.005	213	0.0007	Distinctly low Cl:Br with elevated Na:Cl
Field tiles	0.24	5.75	1.45	0.07	1000	0.63	Extremely high divalent ratios
Animal waste	0.52	2.7	1	0.056	398	0.42	High organic nitrogen (TN:Cl) and elevated divalent cations relative to mineral salts.
Saltwater pool	0.64	0.04	0.002	0.007	34000	0.007	Extremely high Cl:Br ratio; nearly pure NaCl with negligible secondary ions.
Seawater	0.6	0.04	0.08	0.02	282	0.001	Low Cl:Br ratio and low Ca:Cl relative to terrestrial or anthropogenic sources.

[†] Median values were calculated using data from this study (MGS) together with published values from Panno and others (2005) to better represent characteristic chloride source behavior. Ratios are expressed as mass ratios and are intended as screening-level indicators; overlap among sources may occur where mixed inputs or site-specific hydrogeologic conditions are present.

Although animal waste and agricultural field tile sources show overlapping median ion-to-chloride ratios (tab. 4), additional clarification is warranted regarding how these influences are interpreted in this study. Distinguishing animal waste from fertilizer-related agricultural field tile sources based solely on major-ion chemistry is inherently challenging, as both sources can exhibit elevated nitrate and divalent cation concentrations. Definitive separation typically requires additional tracers, such as nitrate isotopes or organic markers, which were not evaluated in this study. However, systematic differences are evident within the dataset. Samples associated with animal waste exhibit moderate nutrient-to-chloride ratios (TN:Cl) accompanied by enrichment in calcium and magnesium, consistent with organic nitrogen inputs. In contrast, field tile samples are characterized by higher TN:Cl ratios, elevated Ca:Cl and Mg:Cl ratios, and low Na:Cl, reflecting fertilizer inputs and water–rock interaction associated with carbonate dissolution rather than dominant organic waste sources. These patterns are influenced by the prevalence of carbonate-rich soils and underlying bedrock in the Illinois study area, where the field tile samples were collected, and may not be broadly applicable to all settings. These relative differences support interpretation of animal waste and field tile drainage as distinct but potentially overlapping agricultural chloride influences, while acknowledging that complete source separation is not possible with the available data. Although Table 4 indicates an elevated Na:Cl ratio for groundwaters affected by geologic brine, the expected Na:Cl for saltwater in Devonian aged formations underlying western Maryland is lower than 0.5 (in the range 0.3 – 0.5) based on the same aged formations in Pennsylvania. As indicated earlier, the elevated Na:Cl ratio could represent the dilution of legacy brine contamination from gas production with subsequent sodium desorption from geologic materials containing the groundwater.

RELATIONSHIP OF TRACE METALS TO CHLORIDE CONCENTRATIONS

Trace metals were evaluated in relation to chloride concentrations across multiple sources to assess whether they provide additional insight into groundwater contamination pathways. Previous studies have reported such relationships. Granato and others (1995) observed positive correlations between chloride, strontium, and barium, with elevated concentrations of these trace metals in downgradient wells impacted by contamination, while VanDerwerker (2019) documented moderate correlations in Piedmont samples. In contrast, this study found only weak overall correlations between chloride and trace metals ($R^2 < 0.05$). However, when evaluated by source type, distinct patterns emerged, suggesting that certain trace metals may be more strongly associated with specific inputs such as brine, septic effluent, or landfill leachate. Chloride serves here as a reference indicator of anthropogenic influence, allowing comparison of how trace metals behave under different contamination scenarios.

Strontium

Strontium (Sr) exhibited the strongest and most statistically robust association with chloride in the dataset ($\rho = 0.71$, $n = 27$, $p < 0.0001$) (fig. 11A). Naturally, Sr occurs at low concentrations in groundwater, derived primarily from the weathering of carbonate and silicate minerals (Skougstad and Horr, 1963). Elevated Sr concentrations are often associated with mixing of deep brine sources (Gosselin and others, 2004; Skougstad and Horr, 1963) and in certain cases, can serve as a useful tracer of road salt and oil-field brines (Vengosh and others, 2013). The strong Sr–chloride coupling observed in this work indicates a common salinity source and/or concentration mechanism, such as evaporite dissolution or mixing with saline end members.

In aquifer systems, Sr commonly substitutes for Ca in carbonate lattices and is released both through mineral weathering and via cation-exchange reactions, where sodium from road salt or brine displaces Ca and Sr from mineral surfaces. This geochemical behavior enhances Sr mobility in saline environments.

The value of Sr as a tracer lies in its ability to corroborate source interpretations based on halide ratios. While Cl:Br and Na:Cl ratios are widely used to differentiate chloride sources (e.g., halite dissolution, septic effluent, or road salt), overlaps between sources can complicate interpretation. Elevated Sr concentrations, when occurring alongside halite-like Cl:Br and Na:Cl signatures, provide an independent line of evidence that strengthens attribution of chloride inputs to brine or road salt, as opposed to wastewater or agricultural contributions. However, interpretation must consider the timing of chloride sources because of the cation exchange of Sr. As described

earlier, the movement of chloride sources with high sodium into a location can cause increases in doubly charged cations (and thus Sr), and the dilution of existing contamination by fresh recharge can result in desorption of sodium and adsorption of doubly charged cations.

Lithium

Lithium (Li) typically occurs at low concentrations in natural groundwater but can be enriched in systems influenced by geothermal fluids, oil-field brines, or landfill leachates (Hogan and Blum, 2003). Its mobility is governed by pH, mineral interactions, and localized anthropogenic inputs (Wadepohl, 1970). In this study, Li concentrations were generally very low and exhibited only a weak, non-significant association with chloride ($\rho = 0.18$, $n = 13$, $p = 0.5511$) (fig. 11B). The limited sample size and the presence of mixed sources likely obscure clearer patterns; within brine-dominated subsets, Li commonly co-varies with chloride, but this trend disappears when all sources are pooled. Overall, Li does not appear to function as a consistent tracer of chloride contamination in the study area.

Barium

Barium (Ba) occurs naturally in groundwater at generally low concentrations, primarily due to the low solubility of barite (BaSO_4) and other barium-bearing minerals. Its mobility is strongly influenced by both redox and sulfate conditions (Skougstad and Horr, 1963; Shand and Edmunds, 2008) as well as by carbonate concentrations and cation exchange. Elevated barium concentrations have also been associated with oil-field brines and deep formation waters (White and others, 1963).

In the overall dataset, barium showed a moderate, significant positive correlation with chloride ($\rho = 0.54$, $n = 28$, $p = 0.0030$). In contrast, road salt-impacted sites exhibited an apparent linear relationship between barium and chloride; however, this trend is based on a limited number of samples from different locations and is not considered statistically robust. The highest barium concentration (2.9 mg/L) was detected at site S-2, located near a road-salt stockpile, exceeding the USEPA MCL of 2.0 mg/L. Hydrochemical characterization indicates that this sample belongs to the Ca–Mg– HCO_3 water type, suggesting that elevated barium may reflect site-specific geochemical conditions rather than direct chloride dominance. The concurrent enrichment of Ca, Mg, and Sr may be consistent with cation-exchange processes, in which sodium from road salt displaces divalent cations from mineral surfaces; however, the role of barium in this process is uncertain and likely depends on the availability of a local source. Overall, these observations suggest that increased salinity may influence barium mobility through ion exchange and desorption in some settings, but its use as a tracer of halite or brine inputs should be considered limited and supportive rather than diagnostic.

Among the trace metals evaluated, strontium and barium show source-specific associations with chloride, whereas lithium remains largely decoupled. Strontium concentrations are highest in brine-impacted wells (for example, B-1), consistent with enrichment from evaporite dissolution and saline mixing, as documented in previous studies (Davis and others, 1998; Panno and others, 2006). Barium exhibits its strongest apparent association with road-salt influence, with the highest concentration detected at a site adjacent to a salt stockpile. This observation is consistent with sodium from road salt promoting cation-exchange processes that mobilize divalent cations (e.g., Ca and Mg) from aquifer solids (Kelly and others, 2012; Panno and others, 2006). The increased solubility of strontium and barium minerals in water of higher ionic strength associated with greater dissolved solids concentration in elevated chloride solutions could also be a contributor to correlations of strontium and barium with chloride. In contrast, lithium concentrations remain uniformly low across sites and show no significant association with chloride, suggesting limited utility as a tracer in this dataset, despite reported enrichment in landfill leachates and some brine-impacted systems (Christensen and others, 2001).

Iron (Fe), manganese (Mn), arsenic (As), lead (Pb), and copper (Cu) display weak or non-significant associations with chloride. Their distributions appear to be controlled primarily by redox conditions and local geochemical processes such as adsorption/desorption rather than by salinity. For example, Fe and Mn are most elevated under reducing conditions, such as those associated with septic or landfill settings; arsenic mobility is influenced by redox- and pH-dependent sorption processes; and Pb and Cu likely reflect distribution system

contributions or particulate-associated transport. Although increased salinity may act as a secondary concentrating factor, the mobility of these elements is governed largely by redox-driven dissolution and site-specific conditions.

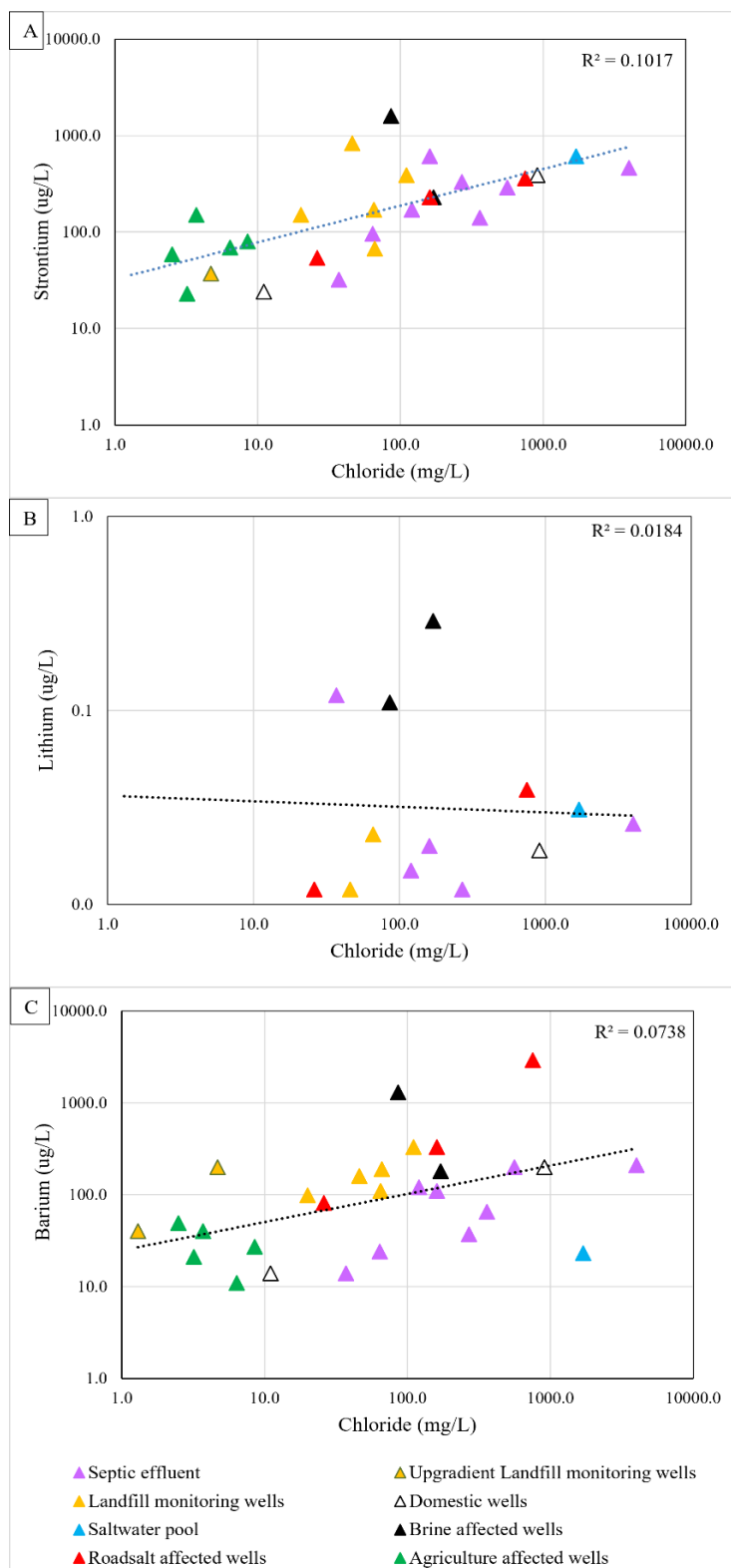


Figure 11. Relationships between chloride concentrations and (A) strontium, (B) lithium, and (C) barium for samples from all contaminant sources from this study.

ARTIFICIAL SWEETENERS AND CAFFEINE

Artificial sweeteners and caffeine have emerged as potential tracers for identifying septic system influence on groundwater. These compounds are commonly found in domestic wastewater due to their widespread use in food, beverages, personal care, and pharmaceuticals (Naik and others, 2021; Subedi and Kannan, 2014). Artificial sweeteners such as sucralose and acesulfame-K are particularly valuable indicators because they are highly water-soluble, resistant to degradation, and not prone to sorption (Buerge and others, 2009). While caffeine is more biodegradable, it can still be detected in groundwater near septic systems under conditions of limited dilution or short travel times. The USEPA has not established any MCL for caffeine and artificial sweeteners in drinking water nor federal health-based standards or advisory levels.

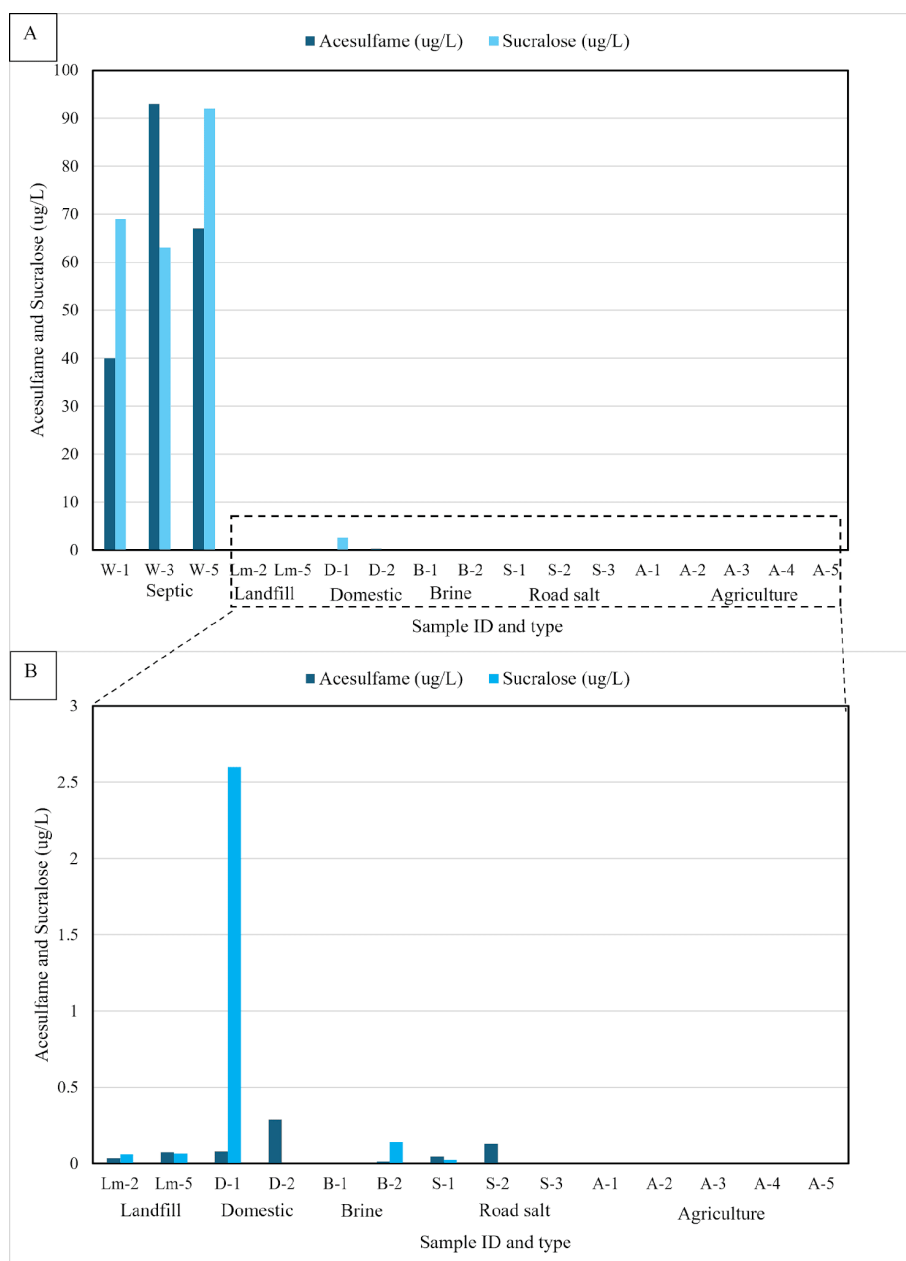


Figure 12. Bar diagrams showing concentrations of artificial sweeteners (acesulfame and sucralose in microgram/Liter (µg/L)): (A) All samples and (B) Expanded view of non-septic samples with low tracer concentrations.

A total of 17 samples were analyzed for artificial sweeteners and caffeine (fig. 12; app. B, tab. B-3). Caffeine was not detected in any samples, likely due to its rapid degradation in the environment (Buerge and others, 2009). In contrast, acesulfame and sucralose were present at elevated levels in septic effluent samples (W-1, W-3, and W-5) (fig. 12A). Agricultural wells showed no detection of these compounds, suggesting minimal or no septic contamination. Sample D-1 contained both sweeteners along with elevated nutrients and chloride, indicating a septic influence on groundwater quality. Low concentrations observed in samples D-2 and B-2 suggest a more limited impact (fig. 12B) (app. B, tab. B-3).

Artificial sweeteners were also detected at landfill sites, although concentrations were substantially lower than those observed in septic samples. This pattern is expected, as septic samples were collected directly from septic tanks or drainpipes where concentrations are highest, whereas groundwater samples reflect dilution, dispersion, and attenuation during subsurface transport. In landfill, brine, and road salt-affected samples, sucralose concentrations were generally low and often near the reporting limit ($0.1 \mu\text{g/L}$), while acesulfame was detected at low but measurable concentrations above its reporting limit ($0.02 \mu\text{g/L}$). Despite their lower concentrations, the detection of acesulfame and sucralose in groundwater provides strong evidence of wastewater influence and supports their use as diagnostic tracers. Artificial sweeteners are particularly useful for differentiating elevated chloride associated with septic effluent from chloride-only sources such as road salt, especially where Cl:Br ratios overlap and source attribution is ambiguous. Low concentrations of acesulfame were also detected in two road salt-impacted wells, likely reflecting mixed-source conditions, such as nearby septic influence or localized cross-contamination in roadway environments. Overall, the consistent association of acesulfame with septic-affected samples demonstrates its value as a supporting wastewater tracer, particularly in settings where halide ratios alone are insufficient for definitive source identification.

SUMMARY AND CONCLUSIONS

This study evaluated chloride sources and co-occurring geochemical indicators across multiple physiographic provinces in central and western Maryland. Data used for analysis and characterization of chloride sources were collected by directly sampling septic systems, landfill monitoring wells, agricultural wells, road salt-impacted sites, brine-affected wells, and a saltwater pool.

Results indicate that chloride in groundwater reflects contributions from both natural and anthropogenic sources, with anthropogenic inputs widely distributed across the study area. Road salt and septic effluent represent the dominant chloride contributors and frequently exceed the USEPA secondary maximum contaminant level of 250 mg/L . Box-plot distributions of chloride concentrations and ion-to-chloride ratios show that road salt-impacted samples are characterized by elevated chloride and Na:Cl ratios consistent with halite dissolution, whereas septic effluent exhibits greater variability and sodium enrichment associated with water-softener discharge. Brine-affected wells in Garrett County display moderate chloride concentrations and consistently low Cl:Br ratios, reflecting either discharge of natural salinity from subsurface formations or, more likely (due to elevated Na:Cl ratios), the dilution of legacy brine contamination from former natural gas production. Agricultural wells generally contain low chloride concentrations and exhibit elevated nutrient-to-chloride ratios, particularly near livestock operations.

Geochemical ratios strengthened source discrimination beyond chloride concentration alone. Analysis of Na:Cl, Ca:Cl, Mg:Cl, and K:Cl ratios revealed distinct but overlapping source signatures. Septic effluent is characterized by elevated Na:Cl and K:Cl ratios, whereas agricultural groundwater in this study exhibits higher Ca:Cl and Mg:Cl ratios consistent with soil interaction and carbonate dissolution in agricultural settings. Landfill-affected groundwater displays intermediate Na:Cl ratios with increased divalent cation variability, reflecting mixed waste inputs and geochemical exchange processes. Background groundwater shows low chloride concentrations with variable ion ratios, indicative of natural hydrogeochemical heterogeneity. Potassium enrichment, while useful as a nutrient-related indicator, may reflect inputs from septic effluent, urea-based wastewater, or agricultural fertilizers and should therefore be interpreted cautiously. The possibility of

cation:chloride ratios altered by cation exchange should be carefully considered because it can either increase or decrease the ratios from those in the original chloride sources.

Additional geochemical tracers further refined source attribution. Artificial sweeteners and total nitrogen, particularly when normalized to chloride, effectively distinguished septic effluent from chloride-dominated sources such as road salt and brine, even where Cl:Br and Na:Cl ratios overlapped. Strontium concentrations provided some evidence of halite and brine mixing. In contrast, lithium, iron, manganese, arsenic, lead, and copper did not display consistent relationships with chloride and were not reliable indicators in this dataset. Microbiological indicators were not evaluated; therefore, wastewater influence was inferred solely from chemical tracers.

A Maryland-based chloride–bromide ratio versus chloride concentration mixing curve approach developed for this study provided the best separation of locally relevant chloride sources relative to previously published frameworks. Comparison with the referenced dataset (Panno and others, 2005) demonstrates that the Maryland-derived endmembers more accurately reflect regional hydrogeochemical conditions and align closely with measured field data. This locally calibrated mixing model offers clearer differentiation among septic, road salt, landfill, agricultural, and brine influences and represents a significant advancement for interpreting chloride sources in Maryland groundwater.

Overall, the combined evidence indicates that integrating chloride concentrations with ion-to-chloride ratios, halide ratios, nutrient indicators, and wastewater tracers provides a robust framework for evaluating chloride sources in sedimentary and fractured-rock aquifers. However, the results should be interpreted as regional-scale insights rather than definitive, site-specific source determinations, given the limited sampling density, incomplete background characterization, and uncertainty in regional groundwater flow pathways. These findings contribute to the growing body of knowledge on chloride tracers in groundwater and highlight the need for expanded sampling, improved hydrogeologic characterization, and additional tracers to increase confidence in future source attribution efforts. Such approaches will be particularly important in areas where chloride signatures overlap or where complex hydrogeologic conditions influence contaminant transport.

STUDY LIMITATIONS, DISCLAIMER, AND FUTURE RESEARCH

This study provides a regional-scale evaluation of chloride sources and associated geochemical indicators in central and western Maryland; however, several limitations should be noted. Sampling density varied among source categories, and the number of samples available for some chloride sources was limited, which constrains evaluation of within-source variability. In addition, sampling did not include pristine background wells within each physiographic province or major geologic unit, limiting the ability to fully characterize baseline geochemical conditions. Regional groundwater flow pathways and residence times were not fully constrained at all sites, introducing uncertainty in the interpretation of mixing and transport processes. Microbiological indicators were not evaluated as part of this study, and therefore bacterial confirmation of wastewater influence was not assessed.

The dataset is not sufficient to support definitive, site-specific source attribution. Rather, the results presented here are intended to demonstrate the utility and limitations of multiple geochemical tracers for chloride source identification. While the findings contribute to the growing body of knowledge on chloride fingerprinting, they should not be interpreted as conclusive without additional site-specific data, supporting hydrogeologic information, and chloride source history.

Future investigations would benefit from increased sampling density across all chloride source categories, including septic systems, road salt–impacted groundwater, landfill leachate, agricultural sources, naturally occurring brines (including those brought to the surface by natural gas production), and animal waste to better characterize source-specific variability. Expanded sampling should also include pristine background groundwater from each physiographic province and major aquifer to better understand ambient groundwater geochemistry. Improved characterization of regional and local groundwater flow pathways, including hydraulic gradients and

residence times, would enhance interpretation of mixing relationships and chloride transport. Incorporation of microbiological indicators and additional wastewater tracers would further strengthen differentiation between septic effluent and other anthropogenic chloride sources. Expanded spatial and temporal sampling, combined with locally calibrated endmembers, would improve confidence in site-specific chloride source determinations.

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APPENDIXES

Appendix A. Well Construction Information

Table A-1. Summary of available well-construction details (e.g., depth, screen, aquifer where known) grouped by source type: A– agriculture, B– brine, Lm– landfill monitoring wells, S– road salt, D– domestic.

Sample id	Well depth (ft bls)	Casing type	Casing depth (ft bls)	Casing diameter (in)	Screen type	Screen or open interval (ft bls)
A-2	500	Steel	54	6	Open hole	54-500
A-3	600	Steel	40	6	Open hole	40-600
A-4	180	PVC	20	6	Open hole	20-180
A-5	270	PVC	60	6	Open hole	60-270
B-1	247	Steel	42	6	Open hole	41-247
B-2	220	Steel	63	6	PVC	20-220
D-1	402	PVC	21	6	Open hole	20-402
D-2	140	Steel	21	6	Open hole	21-140
Lm-2	20.5	PVC	10.5	4	PVC	10.5-20.5
Lm-3	55	PVC	45	4	PVC	45-55
Lm-4	300	PVC	55	4	PVC	55-65
Lm-5	31.5	PVC	20.5	4	PVC	20.5-30.5
Lm-6	19	Steel	9	4	PVC	9-19
Lm-7	300	PVC	90	4	PVC	90-105
S-1	200	Steel	40	6	Open hole	38-200
S-2	290	PVC	51	6	Open hole	239-290
S-3	500	Steel	300	6	Open hole	299-500

Table A-2. Summary of septic systems sampled in this study. Information is provided by the county officials.

Sample Name	Sample ID	Type	No. of houses	Maximum flow (gal/day)	Cl (mg/L)
Brantwood	W-1	Shared	7	4,200	270
Willow Ridge	W-2	Shared	5	7,500	64
Lyndonbrook	W-3	Shared	11	6,600	560
Riggs Meadow	W-4	Shared	4	2,400	360
Blakeslee	W-5	Shared	5	3,000	160
Crescent Shores	W-6	Shared	5	2,250	120
WB-3	W-7	Private	1	1,500	4,000
FL -2	W-8	Private	1	1,000	37

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data

Table B-1. List of analytes measured by the laboratory.

Major Ions and Indicators			
Calcium	Chloride	Fluoride	Dissolved oxygen
Magnesium	Alkalinity	Bromide	Total dissolved solids
Sodium	Bicarbonate	Iodide	Dissolved organic carbon
Potassium	Hardness	Color	
Sulfate	Specific conductance	pH	
Trace Elements			
Arsenic	Cadmium	Lead	Mercury
Barium	Copper	Lithium	Strontium
Boron	Iron	Manganese	Zinc
Nutrients		Wastewater Tracers	
Nitrate plus nitrite	Total Kjeldahl Nitrogen (TKN)	Sucralose	
Nitrite	Phosphorus	Acesulfame	
Ammonia	Orthophosphate	Caffeine	

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data--Continued

Table B-2. Analytes measured by the laboratory, with methods, method detection limits (MDL), reporting limits (RL), and preservatives (where applicable).

Analysis Method	MDL	RL	Units	Bottle Type	Preservative
SW 846 9056 - Iodide	0.15	1.0	mg/L	Plastic - 125 ml	None
SM5310C-2014 - Organic Carbon, Dissolved	0.50	1.0	mg/L	Amber Glass Vial - 40 ml (2)	Phosphoric Acid
EPA 300.1B - Bromide	0.0095	0.05	mg/L	Plastic - 50 ml	None
SW 846 9056A_ORGFM_28D - Chloride, Fluoride Sulfate	30 0.09 0.50	75 0.2 1.5	mg/L	Plastic - 50 ml	None
EPA 350.1 - Nitrogen, Ammonia EPA 353.2_Pres - Nitrogen, Nitrate-Nitrite	0.050	0.10	mg/L	Plastic - 250 ml	Sulfuric Acid
EPA 351.2 - Nitrogen, Total Kjeldahl EPA 365.1 - Phosphorus, Total	0.75 0.05	1.5 0.1	mg/L	Plastic - 250 ml	Sulfuric Acid
SM 2320B-2011 - Alkalinity, Total and Bicarbonate; SM 4500_H+ - pH and Temperature SM 2510B -2011- Conductivity, Specific Conductance	2.6 0.01 1.7	8.0 0.01 5.0	mg/L S.U. umhos/cm	Plastic - 250 ml	None
EPA 365.3_Ortho - Orthophosphate as Phosphorus	0.006	0.02	mg/L	Plastic - 250 ml	None
SW846 6020B - 13 Metals Arsenic Barium Cadmium Calcium Copper Iron Lead Magnesium Manganese Potassium Sodium Strontium Zinc 6010D - Boron, Lithium 7470A - Mercury	0.68 0.75 0.15 50 0.36 20 0.12 16 0.95 65 90 0.39 4.0 0.012 0.079	2.0 2.0 0.50 120 1.0 50 0.50 50 2.0 200 200 1.0 10 0.05 0.20	ug/L	Plastic - 250 ml	Nitric Acid
SM 2340C-2011 - Hardness, Total (mg/l as CaCO3)	15	50	mg/L	Plastic - 250 ml	Nitric Acid
EPA 160.1_SingleDry - Solids, Total Dissolved	5.0	10	mg/L	Plastic - 1 liter	None
SOP_PPCP_NEG (LC/MS)- Acesulfame and Sucralose	0.002 0.014	0.02 0.10	ug/L	Amber Glass Vial - 40 ml	Ascorbic Acid
SOP_PPCP_POS - Caffeine	0.0052	0.010	ug/L	Amber Glass Vial - 40 ml	Ascorbic Acid

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data--Continued

Table B-3. Summary of laboratory results by site and source category. Units: mg/L (µg/L for trace metals). ND = non-detect (<RL). See Table B-2 for analytes/methods and reporting limits.

Sample ID	Temp.	Sp. Cond.	DO	Lab pH	TDS	Alkalinity	Ca	Mg	Na
	°C	(us/cm)	(mg/L)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Septic effluent									
W-1	21.9	1,500	3.7	7.2	500	300	53	24	140
W-2	23.2	870	4.4	7.3	280	280	27	7.1	49
W-3	21.3	2,500	4.4	7.2	820	370	41	12	380
W-4	23.5	1,800	3.8	7.1	640	300	33	9.8	240
W-5	17.3	1,300	7.5	7.5	470	330	22	8.2	150
W-6	17.3	1,200	6.5	7.4	400	350	21	9.5	94
W-7	17.2	12,000	4.7	7.3	6,600	300	140	65	2,600
W-8	20.8	650	1.7	7.2	250	240	12	5.9	47
Landfill monitoring wells									
Lm-1	14.5	370	0.34	6.7	210	49.0	14	19	25
Lm-2	16.8	620	0.13	7.3	310	100.0	60	22	16
Lm-3	13.5	230	0.03	7.3	140	110	30	7.4	6.3
Lm-4	15.1	710	0.06	6.6	410	290	73	21	26
Lm-5	13.3	310	1.23	6.3	160	25	19	7.4	24
Lm-6	17.7	200	0.12	6.6	110	47	16	6.9	8.1
Lm-7	13.8	78	8.92	6.3	61	16.0	5	2	5.4
Domestic Wells									
D-1	15.7	3,200	7	5.9	1,700	6.2	120	68	390
D-2	13.5	110	9.07	5.9	63	9	4.3	3.8	6
Saltwater Pool									
P-1	16.35	5,900	8.58	7	3,300	72	80	4.3	1,100
Brine									
B-1	8.21	930	0.12	8.7	430	160	3.3	0.47	200
B-2	10.2	510	0.08	7.9	260	120	20	4	83
Road Salt									
S-1	12.7	600	7.3	7	270	7.9	20	20	48
S-2	5.4	2,200	0.86	7.3	820	110	160	110	67
S-3	7.2	230	7.8	7.6	110	69	8.9	5.1	10
Agriculture sites									
A-1	13.3	130	7.55	5.8	72	5.8	8.9	5	4.2
A-2	14.4	380	6.6	8.2	220	180	55	15	3
A-3	14.6	210	15.21	7.8	110	98	22	11	1.9
A-4	12.5	140	1.06	7	75	43	15	6.7	0.96
A-5	11.4	130	7.98	6.8	64	34	14	3.6	3.9

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data--Continued

Table B-3 (cont.). Summary of laboratory results by site and source category. Units: mg/L (µg/L for trace metals). ND = non-detect (<RL). See Table B-2 for analytes/methods and reporting limits. *Reporting limit.

Sample ID	K	SO ₄	Cl	Br	I	F	As	Ba	B	Cd	Cu
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(ug/L)	(ug/L)	(mg/L)	(ug/L)	(ug/L)
Septic effluent											
W-1	15	33	270	0.074	ND	ND	ND	37	0.075	ND	16
W-2	17	19	64	0.032	ND	0.58	ND	24	0.19	ND	11
W-3	18	23	560	0.37	ND	ND	ND	200	0.34	ND	39
W-4	17	16	360	0.31	ND	ND	ND	65	0.033	ND	17
W-5	16	22	160	0.063	ND	0.32	0.73	110	0.35	ND	12
W-6	17	18	120	0.041	ND	0.38	2.7	120	0.05	ND	11
W-7	16	6.8	4,000	1.10	ND	0.25	0.69	210	0.33	ND	42
W-8	10	5.9	37	0.15	ND	ND	ND	14	0.018	ND	390
Landfill monitoring wells											
Lm-1	3.5	23	66	0.078	ND	ND	1.4	190	0.026	ND	5.5
Lm-2	1.7	23	110	0.38	ND	ND	ND	330	0.025	ND	ND
Lm-3	0.86	12	1.3	0.013	ND	0.17	ND	68	ND	ND	ND
Lm-4	4.7	21	46	0.26	0.39	ND	ND	160	2.2	ND	ND
Lm-5	3.1	8.5	65	0.036	ND	ND	ND	110	0.017	ND	0.55
Lm-6	2.7	14	20	0.072	0.38	ND	ND	99	0.06	ND	ND
Lm-7	1.8	1.8	4.7	0.011	ND	ND	ND	40	ND	ND	ND
Domestic Wells											
D-1	3.9	9.8	910	0.30	ND	ND	ND	200	0.061	ND	16
D-2	0.76	0.79	11	0.014	ND	ND	ND	14	ND	ND	25
Saltwater Pool											
P-1	12	140	1,700	0.05*	ND	0.13	2.2	23	8	ND	190
Brine											
B-1	1.3	15	170	1.20	ND	0.81	11	180	0.3	ND	0.5
B-2	2	3.7	86	0.55	ND	0.19	2.6	1,300	0.13	ND	ND
Road Salt											
S-1	3.1	2.5	160	0.14	ND	ND	0.7	330	ND	0.18	11
S-2	3.2	6.3	750	0.27	ND	ND	3.2	2,900	ND	ND	60
S-3	6.3	5.9	26	0.012	ND	0.13	16	81	0.029	0.34	29
Agriculture sites											
A-1	1.6	0.69	8.5	0.012	ND	ND	ND	27	ND	ND	2.1
A-2	2.3	5.1	3.7	0.014	ND	ND	ND	40	ND	ND	3.3
A-3	1.6	2.8	3.2	ND	ND	ND	ND	21	ND	ND	2.7
A-4	0.57	18	2.5	ND	ND	ND	ND	49	ND	ND	47
A-5	0.8	1.4	6.4	0.013	ND	ND	1.3	11	ND	ND	52

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data--Continued

Table B-3 (cont.). Summary of laboratory results by site and source category. Units: mg/L (µg/L for trace metals). ND = non-detect (<RL). See Table B-2 for analytes/methods and reporting limits.

Sample ID	Fe	Pb	Mn	Sr	Zn	Li	Hg	NO ₃ (as N)	NH ₄
	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)	(mg/L)
Septic effluent									
W-1	1,800	0.78	25	330	77	0.012	ND	ND	44
W-2	290	0.21	31	96	52	ND	ND	ND	49
W-3	210	0.47	68	290	100	ND	ND	ND	56
W-4	290	0.4	92	140	39	ND	ND	ND	52
W-5	390	0.33	130	610	51	0.02	ND	ND	60
W-6	760	0.6	83	170	64	0.015	ND	ND	68
W-7	110	0.94	670	460	120	0.026	ND	0.94	4.3
W-8	750	1.5	50	32	68	0.12	ND	ND	38
Landfill monitoring wells									
Lm-1	7,300	2.7	390	67	14	0.023	ND	ND	0.11
Lm-2	22	ND	800	390	ND	ND	ND	0.059	ND
Lm-3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lm-4	14,000	ND	14,000	830	10	0.012	ND	ND	ND
Lm-5	ND	ND	81	170	ND	ND	ND	1.1	ND
Lm-6	22	ND	220	150	4.9	ND	ND	0.71	ND
Lm-7	ND	ND	2.7	37	ND	ND	ND	2.5	ND
Domestic Wells									
D-1	31	1.3	650	390	98	0.019	ND	16	ND
D-2	ND	0.16	17	24	24	ND	ND	5.6	ND
Saltwater Pool									
P-1	ND	ND	ND	610	86	0.031	ND	7.2	1.5
Brine									
B-1	ND	0.44	5.6	230	7	0.29	ND	ND	0.057
B-2	59	ND	35	1,600	ND	0.11	ND	ND	0.081
Road Salt									
S-1	ND	4.2	140	230	98	ND	0.52	4.4	ND
S-2	89	1.2	8.6	360	49	0.039	ND	0.92	ND
S-3	47,000	18	960	54	110	0.012	ND	ND	ND
Agriculture sites									
A-1	ND	0.44	6.5	80	7	ND	ND	9.9	ND
A-2	63	ND	2.4	150	ND	ND	ND	2.8	ND
A-3	20	0.19	ND	23	6.4	ND	ND	2	0.054
A-4	92	1.8	300	59	20	ND	ND	1.6	ND
A-5	27	2.8	2.8	69	14	ND	ND	5.2	ND

Appendix B. Analytes Tested for the Study, Analytical Methods, and Water Quality Data--Continued

Table B-3 (cont.). Summary of laboratory results by site and source category. Units: mg/L (µg/L for trace metals). ND = non-detect (<RL), NT = not tested See Table B-2 for analytes/methods and reporting limits.

Sample ID	TKN	PO ₄ (as PO ₄)	Total P	DOC	Total Hardness	Caffeine	Acesulfame	Sucralose	Cl:Br
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(ug/L)	(ug/L)	(ug/L)	
Septic effluent									
W-1	44	11	5.2	31	54	ND	40	69	3,650
W-2	47	5.3	5.3	35	120	NT	NT	NT	2,000
W-3	55	5.8	5.9	52	170	ND	93	63	1,510
W-4	51	6.3	6.2	65	150	NT	NT	NT	1,161
W-5	60	7.1	7.6	19	97	ND	67	92	2,540
W-6	63	6.6	6.8	17	100	NT	NT	NT	2,930
W-7	47	4.4	6.7	50	730	NT	NT	NT	3,640
W-8	39	3.7	4.2	27	62	NT	NT	NT	247
Landfill monitoring wells									
Lm-1	ND	0.030	ND	1.3	120	NT	NT	NT	846
Lm-2	ND	0.033	ND	1.3	250	ND	0.034	0.062	289
Lm-3	ND	0.050	ND	0.78	110	NT	NT	NT	100
Lm-4	ND	0.011	ND	4.2	310	NT	NT	NT	177
Lm-5	ND	0.027	ND	ND	67	ND	0.076	0.067	1,805
Lm-6	ND	0.025	ND	1.2	69	NT	NT	NT	278
Lm-7	ND	0.026	ND	ND	21	NT	NT	NT	427
Domestic Wells									
D-1	ND	ND	ND	0.59	960	ND	0.081	2.6	3,033
D-2	ND	0.009	ND		31	ND	0.29	ND	786
Saltwater Pool									
P-1	5.3	0.400	0.39	3	310	NT	NT	NT	34000
Brine									
B-1	ND	0.071	ND	1.3	9.1	ND	ND	ND	142
B-2	ND	0.012	ND	0.89	67	ND	0.014	0.14	154
Road Salt									
S-1	ND	0.011	ND	ND	150	ND	0.048	0.025	1,143
S-2	ND	0.042	ND	ND	920	ND	0.13	ND	2,778
S-3	ND	0.012	ND	ND	67	ND	ND	ND	2,167
Agriculture sites									
A-1	ND	ND	ND	0.69	36	ND	ND	ND	708
A-2	ND	0.006	0.069	ND	43	ND	ND	ND	264
A-3	ND	0.032	ND	ND	120	ND	ND	ND	-
A-4	ND	ND	ND	ND	69	ND	ND	ND	-
A-5	ND	0.011	ND	ND	51	ND	ND	ND	492

Appendix C. Mixing Curve Methodology

Mixing curves were developed to evaluate geochemical relationships between chloride and Cl:Br ratios and to support interpretation of chloride sources in groundwater. Curves were constructed for key binary mixing scenarios using representative end members from the Maryland Geological Survey (MGS) dataset. Mixing relationships are shown in Figure 7 (Cl versus Cl:Br).

Mixing curves were generated using a two-component mass-balance approach. For any dissolved constituent, the concentration of a mixture (C_{mix}) was calculated as:

$$C_{mix} = f \cdot C_1 + (1 - f) \cdot C_2$$

where C_1 and C_2 are the concentrations of the two end members, and f is the fractional contribution of end member 1 (ranging from 0 to 1). For each mixing pair, f was varied incrementally to generate a continuous mixing curve.

Chloride-to-bromide ratios (Cl:Br) and other ratios were calculated from mixed concentrations rather than averaged directly. For example:

$$Cl:Br_{mix} = \frac{C_{Cl,mix}}{C_{Br,mix}}$$

where $C_{Cl,mix}$ and $C_{Br,mix}$ are the mixed concentrations calculated using the mass-balance equation above. This approach preserves the nonlinear behavior of ratio mixing.

End-member compositions were based on representative values from the MGS dataset. Where multiple samples were available, representative values were selected to reflect typical conditions while minimizing the influence of outliers.

The following end members were used: septic effluent, landfill-impacted groundwater, agricultural sources, formation brine, pristine groundwater, along with a halite dominated end member represented by the saltwater swimming pool sample. The pristine groundwater end member was represented by an upgradient landfill monitoring well, selected to reflect background conditions. Mixing curves were constructed for the following binary source combinations: septic effluent–pristine, brine–pristine, agricultural source–pristine, landfill source–pristine, and saltwater swimming pool–pristine. The saltwater pool–pristine mixing curve represents mixing between freshwater and a halite-dominated end member and defines the upper boundary of the freshwater–halite mixing zone. A second curve defines the lower boundary of this mixing envelope. These scenarios represent simplified binary mixing systems intended to illustrate expected trends and support interpretation of observed data.

Mixing curves represent idealized, conservative binary mixing and are subject to several sources of uncertainty. End-member variability is a primary limitation, as natural and anthropogenic sources exhibit a range of compositions, and selected values may not capture the full variability. Analytical uncertainty in chloride, bromide, and nutrient measurements also propagates into calculated ratios. In addition, while chloride and bromide are generally conservative, other constituents such as nitrogen species may be affected by biological or geochemical processes. Furthermore, groundwater samples may reflect contributions from more than two sources, which are not captured by binary mixing models. Accordingly, mixing curves are used as a conceptual and interpretive tool and are not intended to provide definitive source attribution.

Within these limitations, mixing curves provide a framework for comparing observed data to expected trends from known source combinations. Agreement between measured values and mixing curves supports interpretation of potential source contributions, whereas deviations may indicate additional processes such as ion exchange, biological transformation, or mixing of multiple sources.

Appendix C. Mixing Curve Methodology--Continued

Table C-1. End-member values used to construct mixing curves. Values were selected from representative samples in the Maryland Geological Survey (MGS) dataset. The road salt end member was derived from State Highway Administration (SHA) salt analysis data. Values represent characteristic compositions and are not intended to reflect the full range of variability within each source.

End member	Cl (mg/L)	Br (mg/L)	Source of values
Septic effluent	360	0.31	MGS dataset (this study)
Landfill-impacted groundwater	110	0.38	MGS dataset (this study)
Formation brine	1460	10	MGS dataset (Appalachian Plateau study)
Agricultural source	175	0.27	MGS dataset (Piedmont study)
Saltwater swimming pool	1700	0.05*	MGS dataset (this study)
Pristine groundwater	1.33	0.013	MGS dataset (this study, Upgradient well (background conditions))

**Rl* for *Br*.

Wes Moore
Governor



Josh Kurtz
Secretary

Aruna Miller
Lieutenant Governor

David Goshorn
Deputy Secretary

A message to Maryland's citizens

The Maryland Department of Natural Resources (DNR) seeks to balance the preservation and enhancement of the living and physical resources of the state with prudent extraction and utilization policies that benefit the citizens of Maryland. This publication provides information that will increase your understanding of how DNR strives to reach that goal through the earth science assessments conducted by the Maryland Geological Survey.

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