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Road salting and natural brine migration revealed as major sources of groundwater contamination across regions of northern Appalachia with and without unconventional oil and gas development

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ABSTRACT

High methane and salt levels in groundwater have been the most widely cited unconventional oil and gas development (UOGD) related water impairments. The attribution of these contaminants to UOGD is usually complex, especially in regions with mixed land uses. Here, we compiled a large hydrogeochemistry dataset containing 13 geochemical analytes for 17,794 groundwater samples from rural northern Appalachia, i.e., 19 counties located on the boundary between Pennsylvania (PA; UOGD is permitted) and New York (NY; UOGD is banned). With this dataset, we explored if statistical and geospatial tools can help shed light on the sources of inorganic solutes and methane in groundwater in regions with mixed land uses. The traditional Principal Component Analysis (PCA) indicates salts in NY and PA groundwater are mainly from the Appalachian Basin Brine (ABB). In contrast, the machine learning tool – Non-negative Matrix Factorization (NMF) highlights that road salts (in addition to ABB) account for 36%–48% of total chloride in NY and PA groundwaters. The PCA fails to identify road salts as one water/salt source, likely due to its geochemical similarity with ABB. Neither PCA nor NMF detects a regional impact of UOGD on groundwater quality. Our geospatial analyses further corroborate (1) road salting is the major salt source in groundwater, and its impact is enhanced in proximity to highways; (2) UOGD-related groundwater quality deterioration is only limited to a few localities in PA.

1. Introduction

The increase in natural gas supply within the United States (U.S.) since 2008 is mainly driven by advancements in horizontal drilling and high-volume hydraulic fracturing (HVHF) enabling widespread implementation of unconventional oil and gas development (UOGD) (USEIA, 2022). HVHF is widely used during UOGD to enhance the rock permeability via the injection of pressurized chemical fluids, proppants, and large volumes of water into low permeability rocks, e.g., shale, to produce economic quantities of gas (Clark et al., 2022; USEPA, 2015).

The Marcellus shale, located in the northeastern U.S. and covering five states, including Pennsylvania (PA) and New York (NY), is one of the most prolific shale gas plays in the U.S. The rapid boom in UOGD within the Marcellus shale has spurred public concern over its impact on groundwater quality. Methane migration (Wen et al., 2018; Woda et al., 2018) and spills of drilling/produced fluids (i.e., water returned to the surface with crude oil and natural gas) (Brantley et al., 2014; Patterson et al., 2017) are the most widely reported UOGD-related water contamination incidents. Drilling and produced fluids from UOGD usually contain health concerning chemical species such as high salt content (e.g., sodium and chloride) and heavy metals (e.g., barium). Such water contaminations, if occurring, could pose a severe safety and health risk, particularly in rural areas where domestic wells are the primary drinking water source for residents, e.g., high salt contents in water can increase the risk of high blood pressure and heart disease. In addition, high levels of methane trapped in confined space can lead to explosion and asphyxiation (Hammond et al., 2020). Dissolved methane in the water can also mobilize other inorganic solutes that could pose a health risk, e.g., sulfide and arsenic (Siegel et al., 2015b; Soriano et al., 2020).

Methane has been reported as one of the most common contaminants associated with UOGD by the Pennsylvania Department of Environmental Protection (PADEP). Unconventional oil and gas wells (UOG wells) might act as conduits to facilitate the migration of natural gas

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stored in the targeted geologic formation or a penetrated shallow gas reservoir to shallow groundwater when the casing and/or cementing of UOG wells are faulty (e.g., Darrah et al. 2014). However, many studies have shown that elevated levels of naturally-occurring methane in the Marcellus are not uncommon (Siegel et al., 2015a; Wen et al., 2019). Drilling and produced fluids used in UOGD contain a high level of salt (i.e., sodium and chloride) and other toxic constituents. The improper storage and disposal of these fluids can degrade water quality (Cantlay et al., 2020a) through either chemical spills (e.g., Patterson et al. 2017) or subsurface migration (e.g., Soriano et al. 2020). In regions where UOGD overlaps with other land uses, salt contents in groundwaters might also come from other non-UOGD related sources, e.g., road salting, septic effluents, and the naturally-migrated Appalachian Basin Brine (ABB) from deeper formations (e.g., Brantley et al. 2014, Cantlay et al. 2020a, Lautz et al. 2014, Warner et al. 2012), which is often hard to distinguish from UOGD sources. To note, surface runoff flushing the highway will carry the applied road salt and enter nearby shallow aquifers (also domestic water wells) (Jain, 2018; Pieper et al., 2018). Septic effluents can seep into the nearby shallow aquifers potentially contaminating groundwater while ABB has been found to be able to migrate into the shallow aquifer via geologic faults and fractures (e.g., Warner et al. 2012). The impact of ABB and road salting on groundwater quality is relatively more regional compared to septic effluents, the impact of which is usually limited to rural regions. Additionally, ABB naturally migrated into a shallow formation can mix with meteoric recharge water, acting as a source of salt in groundwater although it presents much lower concentrations of salt-related analytes compared to the pristine ABB. In addition, as suggested by the literature (Shaheen et al., 2022), rainwater contains low concentrations of chloride. As infiltrating and percolating into the aquifer, meteoric recharge water might mix with organic wastes that are relatively geochemically non-distinct and near-surface sourced.

Recent studies have attempted to address the spatiotemporal extent of UOGD impacts on groundwater quality within the Marcellus shale footprint by using hydrogeochemical (e.g., Soriano et al. 2020, Warner et al. 2012), statistical (e.g., Siegel et al. 2015a), and geospatial tools (e.g., Li et al. 2017, 2016, Wen et al. 2019b, 2018). Warner et al. (2012) utilized geochemical analytes (Br, Cl, Na, Ba, Sr, and Li) measured in shallow groundwater to explore the natural migration of deep brine unrelated to shale gas drilling. Geochemical tracers showed no significant UOGD impact on groundwater salinity. Siegel et al. (2015a) analyzed a large groundwater quality dataset collected prior to shale gas drilling (i.e., "pre-drill") in the Appalachian Basin, concluding there was little to no significant impact from UOGD on regional groundwater quality. Wen et al. (2018) used a geospatial analysis tool, i.e., Sliding Window Geospatial Tool (SWGT), first developed by Li et al. (2016, 2017), to evaluate the geospatial correlations between methane concentrations in northeastern PA groundwater and the proximity to various features of interest. This study revealed the regional control of geologic features, e.g., anticlinal folding and faults, on elevated dissolved methane in groundwater. Potentially UOGD-related methane contamination was observed in only a few localities. Based on compiled groundwater quality data in UOGD regions, Wen et al. (2019b, 2021) developed empirical and machine learning-based models to predict the incidents of methane migration near shale gas wells, also revealing a limited number of methane migration incidents present in UOGD regions both with and without legacy conventional oil and gas development (COGD). Fewer comparative studies were conducted in regions that differ with respect to UOGD but are otherwise hydrogeologically comparable (e.g., similar topography and geology), which may provide an ideal study area to quantitatively separate potential UOGD impacts from other non-UOGD impacts.

One such region exists in northern Appalachia, where UOGD is permitted in PA but is strictly banned in NY, providing a valuable opportunity to assess the occurrence and origin of dissolved solutes (i.e., methane and salt contents) in regions with and without UOGD. Other land uses, such as highways and associated highway maintenance (e.g., road salting), are common in both states. This enables us to test analysis tools to separate UOGD-derived contaminants from non-UOGD-derived contaminants. McMahon et al. (2019) previously studied groundwater samples from 50 domestic wells from the state boundary region between NY and PA identifying non-UOGD sources of dissolved methane in groundwater, but analysis of larger datasets in such a region enables a more robust comparison of contamination frequencies across regions with and without UOGD. Here, we attempted to apply multiple statistical and geospatial analysis tools to delineate the anthropogenic and natural sources of methane and salts (e.g., Cl) in groundwater using the NY – PA state boundary as our study area (Fig. 1). Since dissolved methane in groundwater of the UOGD region was widely studied, we mainly focused on the delineation of salt sources in PA and NY groundwaters. Two end-member-mixing analysis methods – Principal Component Analysis (PCA) and Non-negative Matrix Factorization (NMF) were applied to a compiled hydrogeochemistry dataset to delineate potential salt sources in NY and PA groundwaters. Additionally, the SWGT (Li et al., 2017, 2016; Wen et al., 2018) was also used to detect individual localities where solute concentrations in groundwater increased with proximity to unconventional gas wells and non-UOGD-related features (i.e., conventional oil/gas wells, faults, stream flowline, and highway). We sought to address two questions: (1) What is the spatial distribution and extent of UOGD impact on dissolved methane and salt contents in groundwater? and (2) How does the impact of UOGD compare to that of other non-UOGD-related land uses?

2. Methods and materials

2.1. Study area

The study area, located within the Appalachian Basin Province, extends across ten NY counties (from west to east: Chautauqua, Cattaraugus, Allegany, Steuben, Chemung, Tioga, Broome, Delaware, Sullivan, Orange) and nine PA counties (from west to east: Erie, Warren, McKean, Potter, Tioga, Bradford, Susquehanna, Wayne, and Pike; Fig. 1). Except for Orange, Sullivan, and Chautauqua counties in NY, and Pike and Erie counties in PA, all counties are underlain by the Marcellus shale. The study area is primarily underlain by clastic unconsolidated sedimentary rocks and glacial material deposited in Devonian, Ordovician, and Mississippian ages (Christian et al., 2016; Williams, 2010) (Figs. S1 and S2). The major thrust faults in the study area are predominantly located in Bradford County, PA. A detailed description of geologic and hydrogeological setting of the study area is included in the supporting information.

2.2. Dataset collection

Groundwater quality measurements were obtained from four publicly accessible databases: Community Science Institute (CSI) (CSI, 2021), Shale Water Interaction Forensic Tools (SWIFT) (Christian et al., 2016; Lautz, 2020), Shale Network Database (Brantley, 2015), and Water Quality Portal (WQP) (Read et al., 2017) to increase the number of groundwater sampling sites / samples. The compiled dataset included 17,794 groundwater samples reporting 13 chemical analytes: potassium (K), iron (Fe), methane (CH_4), bromide (Br), calcium (Ca), barium (Ba), chloride (Cl), pH, specific conductance (SC), manganese (Mn), sodium (Na), strontium (Sr), and sulfate (SO_4). These analytes were chosen because they either were indicative of potential UOGD impacts or had the largest number of measurements. Any censored values (i.e., below the detection limit) were replaced with the corresponding detection limit (Tables S1 and S2). The sampling date of these water samples ranges from 1927 to 2020 with 16,460 (92.5% of all water samples) samples collected post-1980 and 15,346 (86.2%) collected post-2004.

The location and spud date of both unconventional and conventional oil and gas wells were downloaded from the PADEP (PADEP, 2021) and

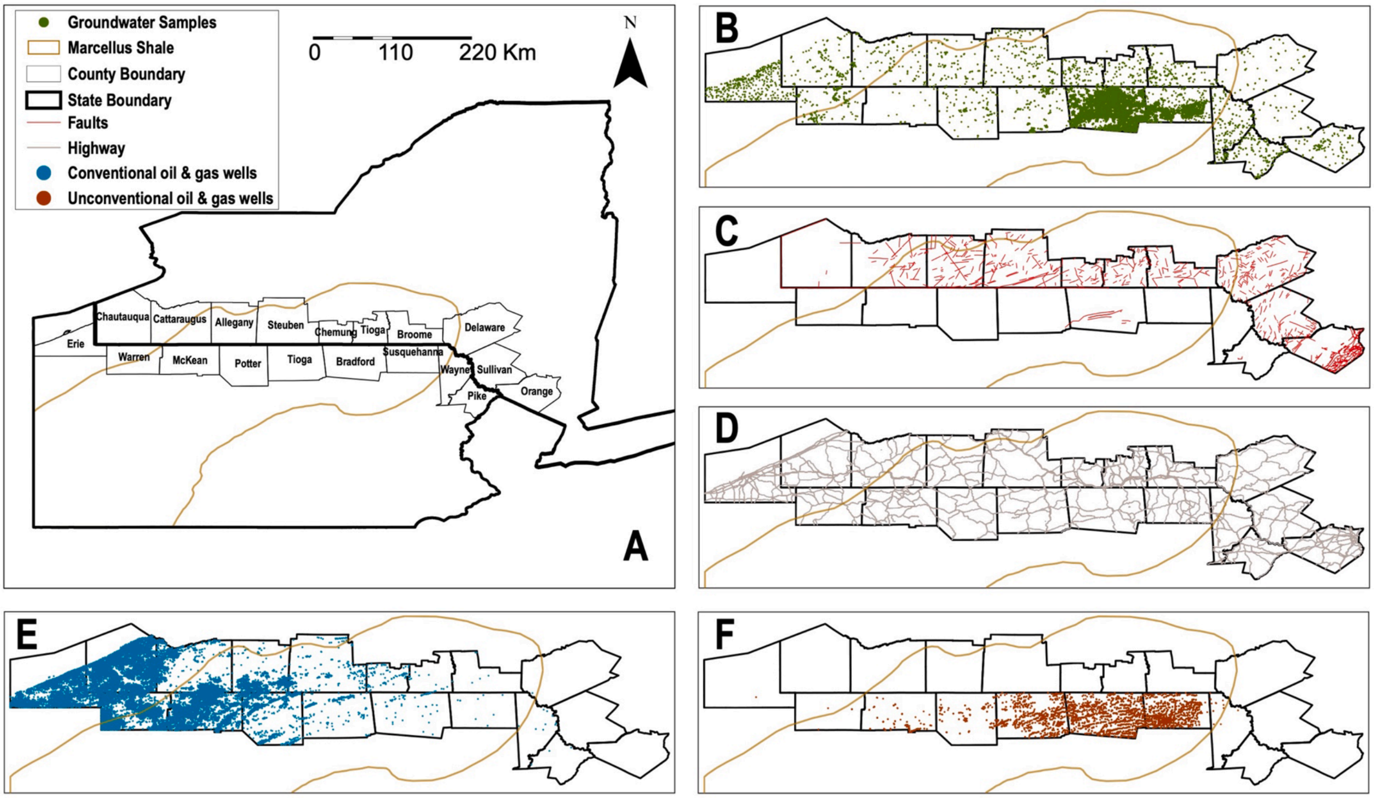

Fig. 1. Maps of (A) our study area covering nineteen counties along the New York – Pennsylvania State boundary underlain by Marcellus shale extent, and locations of (B) groundwater samples, (C) faults, (D) highways, (E) conventional oil and gas wells, and (F) unconventional oil and gas wells.

the New York Department of Environmental Conservation (NYDEC, 2021). The 'Near' function in the ArcGIS Pro (Version 2.8.3) was used to calculate the distance between geochemical analytes and the nearest features of interest (i.e., highways and faults). Due to the high density of UOGD within the past decade, many oil and gas wells that did not exist at the moment of water sampling were subsequently drilled around nearby water samples. These oil and gas wells should not be considered as hydrocarbon wells that might have contaminated the corresponding water sample. To address this, the distance between groundwater samples and oil and gas wells (unconventional and conventional) was calculated using R codes to exclude oil and gas wells drilled after the groundwater sample collection. Distance calculations using both ArcGIS Pro and R refer to the planar distance between water chemistry measurements and the nearest features of interest. The PA and NY bedrock geology was derived from the USGS (USGS, 2021) and New York State Museum (NYSM, 2022).

2.3. Endmember mixing analysis

When applied to water quality data, Principal Component Analysis (PCA) can extract the principal components (PCs) of the dataset, where each component represents a linear combination of water quality parameters. These components can be interpreted as distinct solute/water sources based on domain knowledge. The minimum number of PCs was determined by comparing the total variance explained by the selected PCs to a threshold of 90%. The greater the explained variance, the more information from the original dataset is retained in the selected PCs (Grunsky et al., 2014). Pearson correlations between water quality variables were evaluated to identify linearly correlated variables. Only intercorrelated analytes were considered in PCA to derive solute/water sources (Saporta and Niang Keita, 2009).

Non-negative Matrix Factorizations (NMF) is an unsupervised machine learning algorithm that delineates the endmembers (solute/water sources) mixing proportions in each groundwater sample by solving the equation, $V = W \times H$, where V is the groundwater sample matrix, W is the endmember mixing proportions, and H represents the endmember chemical composition. Unlike traditional inverse models, NMF delineates the endmembers (water types) mixing proportions without prior knowledge or assumptions about the endmember compositions (Shaheen et al., 2022; Shaughnessy et al., 2021). The performance of NMF in identifying salinity sources using a previously published synthetic dataset was tested (Lautz et al., 2014; Shaheen et al., 2022). Here, NMF was applied to quantitatively assess mixing proportions of salt/water sources (e.g., brine and road salting discharge) in NY and PA. Before performing NMF, the molar ratios of Na, K, Ba, Ca, and SO_4, to Cl were calculated and normalized to the corresponding highest ratio. The only hyperparameter of NMF was the number of endmembers, which was assumed to be the minimum number of PCs of PCA results using the same set of analytes as NMF. For the PA and NY datasets, the NMF was run using 10,000 iterations, initiated with a different random state each time to avoid initialization bias. Only model outputs with mixing proportions of all endmembers summing up within 1.00 ± 0.05 were kept. Retained models were ranked by error sum of squares, and only the top 5% of the best-fitting models were used to calculate the average chemical composition of endmembers and their contribution to each water sample.

2.4. Geospatial and statistical analysis

In this study, Sliding Window Geospatial Tool (SWGT), first developed by Li et al. (2016, 2017), was performed in Python 3.9.9 to highlight hotspots with elevated Cl, Na, SC, Ba, and CH_4 in proximity to features of interest (i.e., faults, highways, and unconventional and conventional oil and gas wells). SWGT results can indicate the contribution of natural processes and various human activities to salt and methane contents in groundwater. These five analytes were selected as they were most representative of UOGD-related contamination with respect to methane migration and salt contamination incidents. Note: water samples from the CSI database were excluded in the SWGT analysis due to the lack of precise locations. A detailed description of the SWGT can be found in the literature (Wen et al., 2018). The SWGT outputs a "heatmap" with the intensity of Kendall rank correlations between analyte concentration and distance to the feature of interest color-coded. On the heatmap, gray color denotes areas without sufficient data density for the SWGT calculation, while white areas represent regions where no statistically significant correlations are present. Red (or blue) color denotes areas where analyte concentration negatively (or positively) correlates with the proximity to features of interest.

Although these three methods, i.e., PCA, NMF, and SWGT, can all shed light on the contribution of sources of dissolved solute in groundwater, the type of application they are most suitable for varies. Both PCA and NMF are commonly used to delineate the 'principal' components of dissolved solute in groundwater, while PCA might fail to identify secondary components and NMF can be geared towards deriving information for the sources of a specific analyte (e.g., chloride). Unlike NMF and PCA, SWGT is a geospatial tool that incorporates geospatial context in the analysis which provides important implications for not only the solute sources but also the potential pathways of solute migrating from its source to the mixing water.

Wilcoxon-Mann-Whitney (WMW) test was used in this study to compare the distribution of concentration of chemical analytes between two sample groups, which can be treated as a test of median values of two sample groups. WMW test is a non-parametric test that requires no normal distribution of the tested population (i.e., sample group). Because species concentrations in groundwater samples tend to be highly skewed, the WMW test is thus well-suited for statistical comparison across sample groups.

3. Results

3.1. Overview of groundwater quality data and county categorization

The compiled dataset in this study includes 17,794 groundwater samples with 13 geochemical analyses grouped into cations, anions, and others (Tables S1 and S2). A total of 16,175 and 1619 water samples are collected from PA and NY, respectively. Analyte concentrations in most groundwater samples ($>$ 80% of all samples) fall below the respective USEPA drinking water standard with the exception of Fe and Mn (Fig. S3), which is consistent with previous literature (e.g., Siegel et al. 2015b, Wen et al. 2018). A detailed overview of the groundwater quality data is available in the supporting information.

To assess the regional impact of UOGD and COGD on groundwater quality, NY and PA counties with $>$ 999, 1–999, or 0 conventional wells (or $>$ 299, 1–299, or 0 unconventional wells) were labeled as counties with heavy, moderate, or non COGD (UOGD) counties (Table S3). The selection of above threshold numbers of oil and gas wells was not fully arbitrary, given that many more conventional oil and gas wells (COG wells) were drilled than unconventional oil and gas wells (UOG wells). In addition, an unconventional well may potentially yield a larger-scale environmental impact than a COG well due to horizontal drilling and HVHF practices. Therefore, a smaller threshold number of UOG wells, i.e., 299, was selected to define a heavy-UOGD county compared to heavy-COGD counties.

Wilcoxon-Mann-Whitney (WMW) tests showed no monotonic trend in CH_4, Na, Cl, SC, Ba, Sr, Mn, or K concentrations in groundwaters from heavy- to moderate- and non-UOGD counties (Table S4), suggesting that UOGD might not be a source of these solutes (particularly dissolved CH_4 and salts) in groundwater on a regional scale. CH_4 levels remained unchanged from heavy to moderate COGD counties and decreased from moderate to non-COGD counties, suggesting that COGD might be one of the sources of dissolved CH_4 in PA-NY groundwater, although such an impact might not be significant on a regional scale (Table S4). Na concentrations increased from heavy to moderate COGD counties (Table S4). However, Na concentrations remained the same between moderate and non-COGD counties (Table S4). Unlike Na, SC and Cl concentrations decreased from heavy to moderate COGD counties and stayed constant from moderate to non-COGD counties (Table S4). Such inconsistent trends in salt-related parameters suggest that the impact of COGD on groundwater salinity is not significant on a regional scale, which is also consistent with the non-monotonic trend in Sr concentration from heavy- to moderate- and non-COGD counties. Although SO_4, Mn, and Fe levels decreased from heavy to moderate COGD counties, only Mn and Fe further decreased from heavy to non-COGD, pointing to COGD as a presumable source of elevated regional levels of dissolved Mn and Fe (Table S4). Ba concentrations decreased from heavy- to moderate- and non-COGD counties, suggesting a regional impact of COGD on Ba concentration in groundwater. Such regional impact, however, might be explained by a few local COGD-related water contamination events in heavy- and moderate-COGD counties as previously suggested by Shaheen et al. (2022).

3.2. Endmember mixing analysis

A cross-correlation was calculated for all 13 analytes of NY and PA samples to identify intercorrelated analytes. Fig. 2 shows Na, Cl, Br, K, Sr, SC, and CH_4 are intercorrelated for the NY samples, while Na, Cl, Ba, Sr, and SC are intercorrelated for PA samples.

PCA was applied to the NY and PA datasets separately, considering only the above-intercorrelated analytes. A minimum number of one and two PCs were needed to account for at least 90% variance of the original data for the NY (92.8%) and PA (91.8%) datasets (Fig. S4). For NY samples, PC1 showed positive loadings on all solutes, especially Na, Cl, SC, and Br (Fig. S5). Therefore, PC1 was interpreted as the Appalachian Basin Brine (ABB). PC1 is unlikely to be road salting or septic effluent due to the positive loading in Br since these two sources are not enriched in Br as much as ABB. For PA samples, PC1 was assumed to be ABB as well as it exhibited a similar pattern to NY-PC1. PA-PC2 yielded negative loadings on Cl, Na, and SC while positive loadings on Ba and Sr (Fig. S5), indicative of water/solute originated from a mix of rainwater (or shallow freshwater recharge; negative loadings on Cl, Na, and SC) and brine (positive loadings on Ba and Sr). Our PCA results showed that ABB plays a dominant role in characterizing PA and NY groundwater chemistry with regards to the largely salinity-related suite of analytes considered in our analysis, especially for NY samples. PCA, however, failed to detect other secondary water/solute sources for NY samples, while ABB-derived water/solute was not separated from that originated from non-ABB sources for PA samples. Therefore, an alternative method was needed to quantitatively assess the contribution of analyte-specific sources in groundwater.

To further investigate endmember analyte sources in groundwater, including assessing potential UOGD impacts on groundwater quality, we further applied a machine learning-based approach, NMF, to delineate salt sources in PA/NY water. Salt-related analytes (e.g., Cl) in groundwater can serve as effective geochemical tracers to illustrate the sources of water and other dissolved solutes (e.g., Cantlay et al. 2020a, 2020b, Warner et al. 2012, Wen et al. 2019).

Ba, K, Ca, SO_4, Na, and Cl were selected for inclusion in the NMF analysis, where Cl was used as a proxy for salt inputs, given its generally conservative behavior in the environment. This combination of analytes retained the most groundwater samples while allowing as many analytes as possible to be included in the NMF analysis. Only water samples reporting measurements for all the selected analytes were included in the NMF analysis. As a result, 610 out of 1619 NY samples and 2653 out of 16,175 PA samples were retained. Ba/Cl, K/Cl, Ca/Cl, SO_4/Cl, and Na/Cl molar ratios were calculated and normalized to the highest respective value before feeding into NMF. PCA analysis of these molar ratios indicated three endmembers were needed to explain at least 90% variance of the original data. Three NMF-derived endmembers were

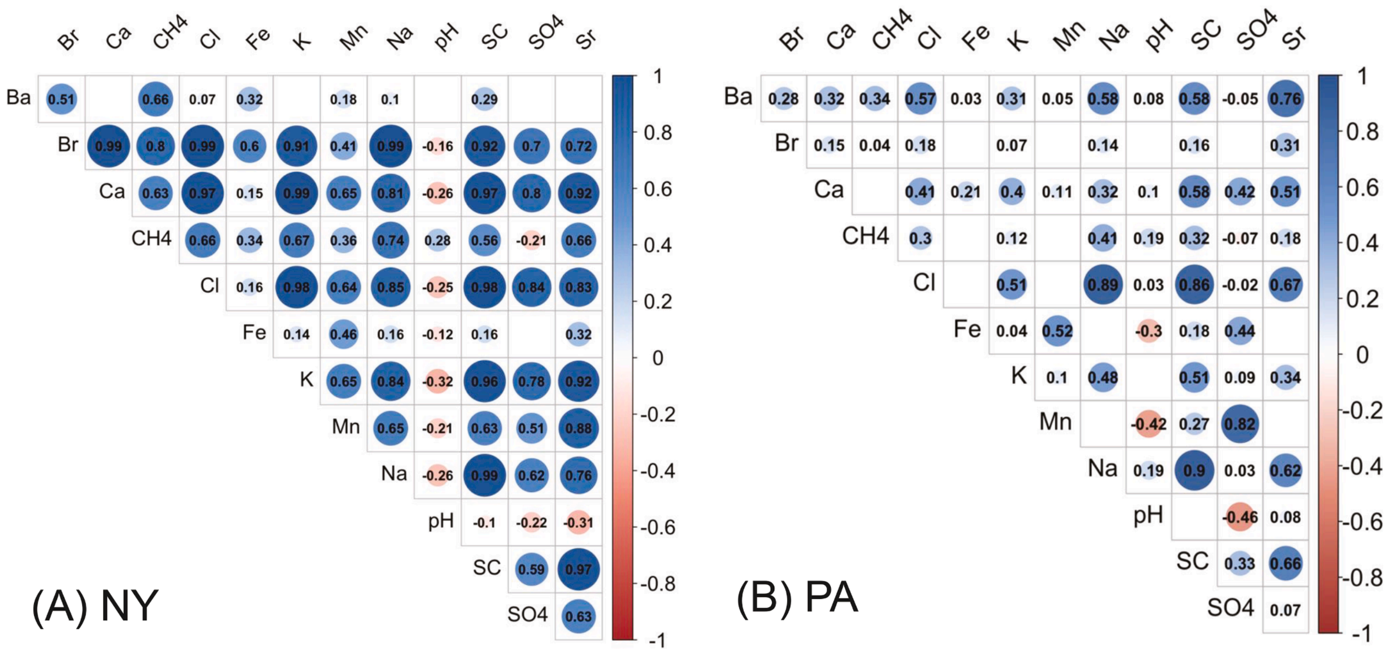

Fig. 2. Cross correlation matrix for (A) NY and (B) PA groundwater samples based on Pearson correlation. Cells with blue and red circles denote positive or negative correlations that are statistically significant ($p < 0.05$). Using the correlation coefficient threshold of 0.5, it is determined that Na, Cl, Br, K, Sr, Ca, SC, CH4 are intercorrelated for NY samples while Na, Cl, Ba, Sr, and SC are intercorrelated for PA samples.

interpreted as Cl sources (i.e., ABB or brine, road salts, and shallow freshwater recharge) based on their molar ratio characteristics: (1) a higher Ba/Cl ratio suggests a larger ABB/brine impact, (2) elevated Ca/Cl and SO_4/Cl ratios can be interpreted as more contribution from the shallow freshwater recharge endmember since shallow freshwater recharge is typically less saline and more oxidizing, and (3) an elevated Na/Cl ratio compared to the other analyte ratio indicates a larger input from road salt (Table S5). Road salts, shallow freshwater recharge, and ABB were the dominant (i.e., ≥50%) Cl source in 147 (24%), 39 (6%), and 79 (13%) NY groundwater samples (Fig. 3). Cl content in 236 (9%), 765 (29%), and 601 (23%) PA water samples was dominated by brine-, shallow freshwater recharge-, and road salt-derived Cl (Fig. 3).

It is important to note that ABB might represent salt-containing briny water either naturally migrated from deeper formations to the shallow aquifer or leaked briny wastewater produced during UOGD/COGD. To try to separate these two sources, we further applied the SWGT to assess the geospatial relationship between salt contents (i.e., Na, Cl, SC) in groundwater and the proximity to conventional and unconventional oil / gas wells, highways, and faults. The SWGT was also applied to Ba and CH_4 because (1) Ba serves as an effective proxy for the environmental impact of oil and gas production in PA (Niu et al., 2018; Warner et al., 2012) and (2) dissolved CH_4 in PA groundwater has been widely studied (e.g., Wen et al. 2018), which can be cross-checked with our CH_4 results to further determine the accuracy of the SWGT results for other analytes

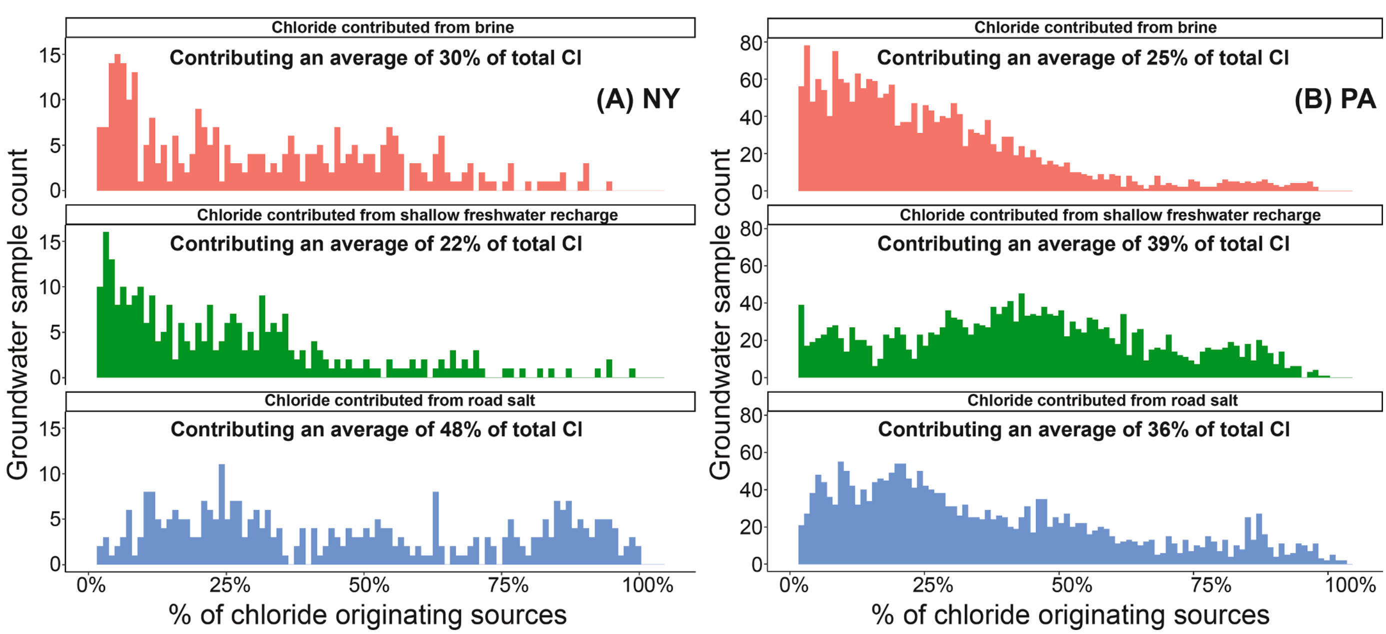

Fig. 3. Histogram showing the count of (A) NY and (B) PA groundwater samples for the given percentage of chloride originated from each of the three endmembers (brine, shallow freshwater recharge, and road salt).

(i.e., Na, Cl, SC, Ba).

3.3. Sliding window geospatial technique (SWGT)

In a limited number of localities in UOGD-present counties, Cl, SC, and Na levels in groundwater increased closer to the UOG wells (red zones in Figs. 4, S6 and S7), suggesting a localized impact of UOGD on groundwater quality with respect to salt content in these areas. In the heatmap of Ba and CH_4 levels, a few red hotspots were also identified (Figs. S8 and S9). Hotspots for the above five analytes were not present across the entirety of northeastern PA, indicating the UOGD impact on groundwater quality is likely not significant on a regional scale. Particularly, CH_4 results generally agreed with the previous studies (e.g., Wen et al., 2018) which used a slightly smaller groundwater quality dataset from Bradford County, PA, suggesting that SWGT was indeed effective in detecting localities with presumable UOGD-related water impairments.

In COGD counties, SWGT detected hotspots where Cl, Na, and SC concentrations increase closer to conventional oil and gas wells, suggesting COGD impact in these subregions but not on a regional scale (Figs. S10–S12). SWGT heatmaps also showed a few subregions with increasing CH_4 and Ba concentrations near COG wells (Figs. S13 and S14).

The geospatial relationship between analyte concentrations and the proximity to geologic faults was also assessed by the SWGT (Figs. S15–S19). Many fault-related hotspots overlapped with COGD/UOGD related hotspots, suggesting detected COGD/UOGD hotspots might be alternatively explained by the methane-containing ABB naturally migrated from the deep formation along the geologic faults. This was also suggested by many previous studies (e.g., Li et al. 2017, 2016, Warner et al. 2012, Wen et al. 2018). Compared to heatmaps for COGD, UOGD, and faults, many more hotspots were present in the heatmaps for highway and salt analytes (Figs. 5, S20 and S21), indicating a more widespread and potentially regional impact of highway (i.e., road salt containing discharge) on PA/NY groundwater quality.

4. Discussion

4.1. Sources of dissolved methane in PA and NY groundwater samples

Our analysis of the distribution and sources of dissolved CH_4 in PA-NY groundwater provides insight into (1) UOGD and COGD impacts on regional dissolved CH_4, and (2) the effectiveness of the SWGT method in NY with less dense groundwater samples.

The WMW test showed no simple monotonic trend in the dissolved CH_4 in PA-NY water from non- to moderate- and heavy-UOGD/COGD counties, suggesting insignificant regional impacts of COGD or UOGD on dissolved CH_4. SWGT results further corroborated this conclusion, revealing a limited number of isolated hotspots where CH_4 levels increased nearby oil and gas wells in the study area, mostly in Bradford and Susquehanna counties in PA (Figs. S9 and S14). The hotspots in Bradford were previously identified by Wen et al. (2018) and Li et al. (2016). We searched the PADEP violation database (PADEP, 2022) for unconventional oil and gas wells with citations categorized as (1)

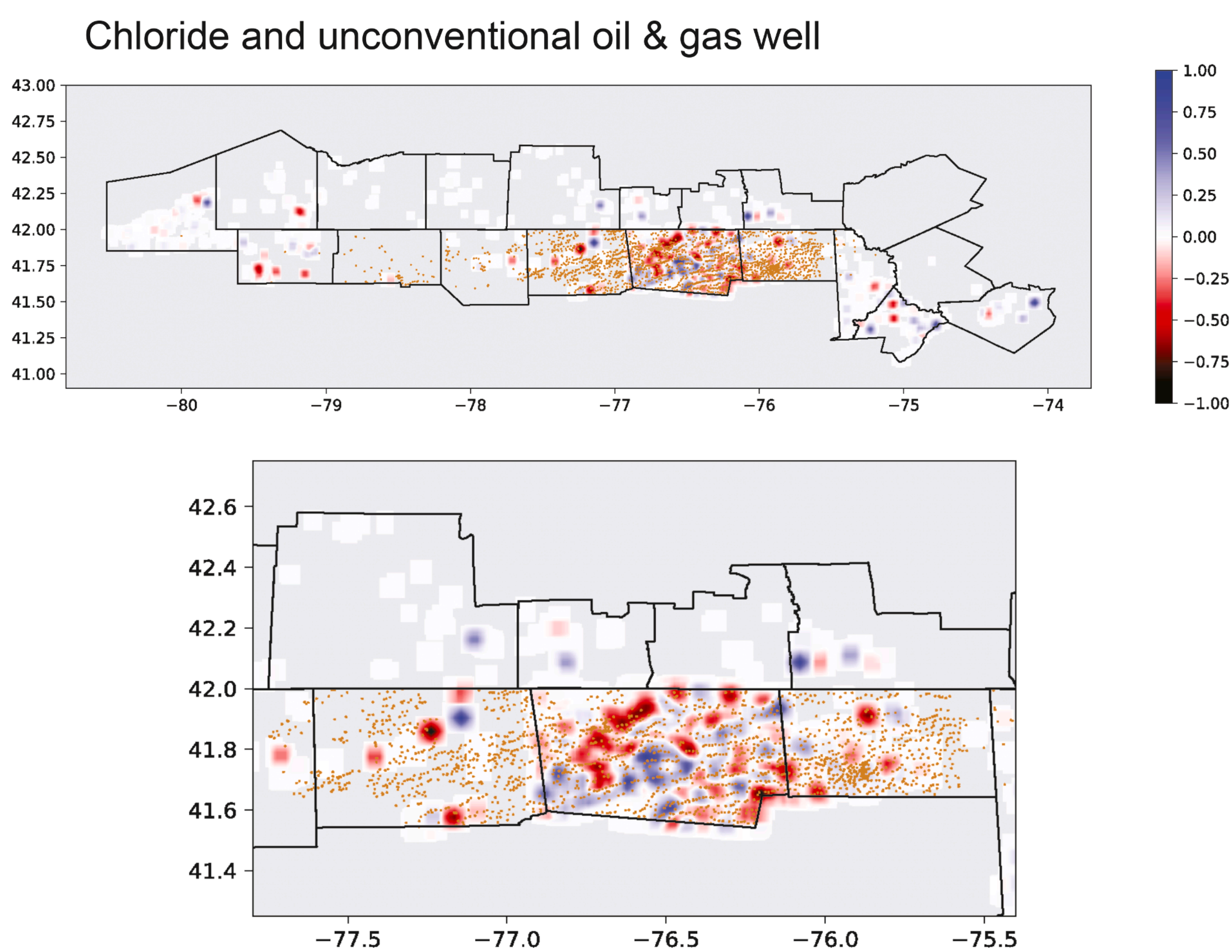

Fig. 4. Heatmap of correlations between chloride concentrations and the distance to the nearest unconventional oil and gas (UOG) well. Brown circles represents locations of UOG wells. Red (blue) color indicates regions where chloride increases (decreases) nearby UOG wells. Color intensity corresponds to the relative frequency of significant positive (red) or negative (blue) correlations.

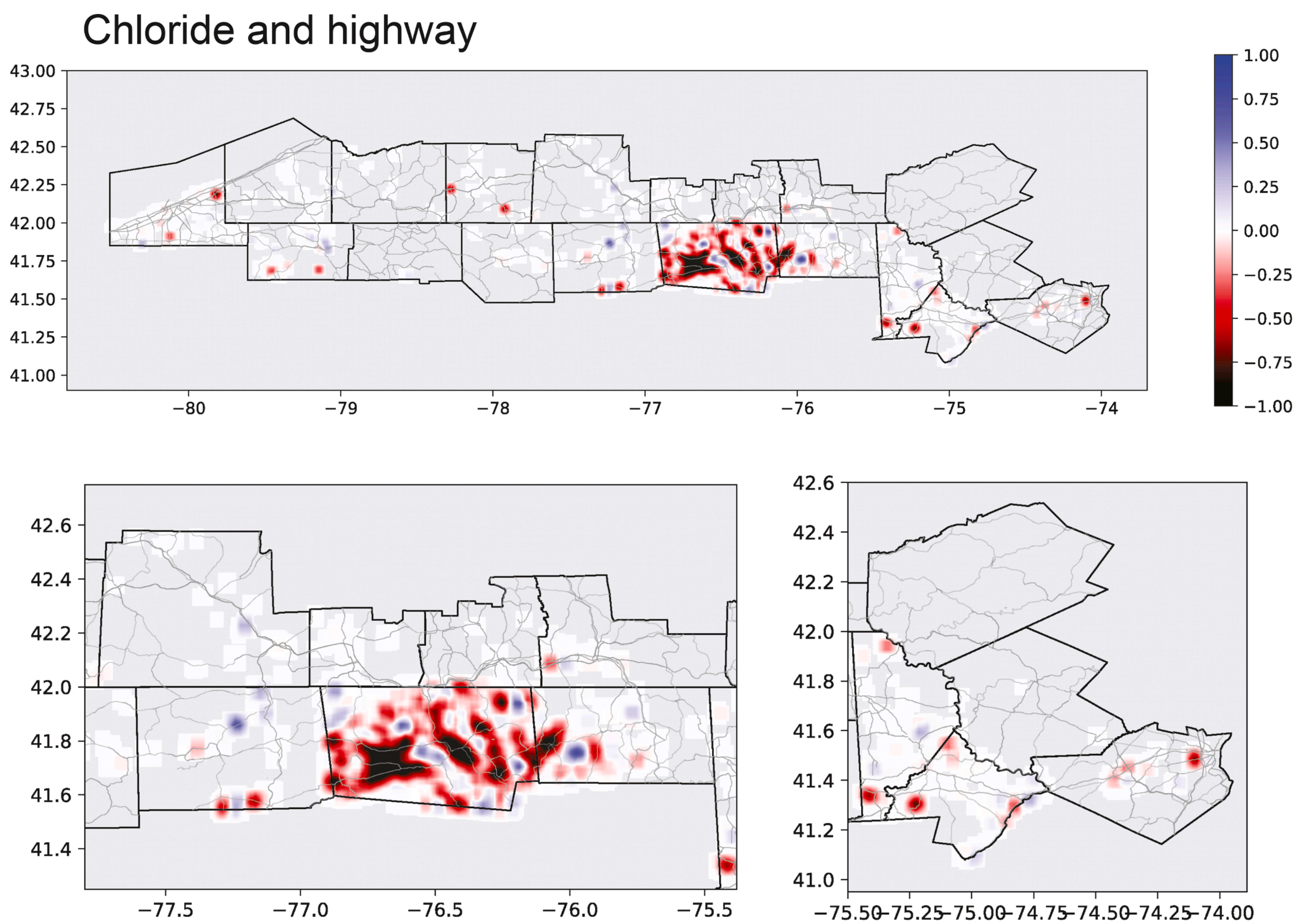

Fig. 5. Heatmap of correlations between chloride concentrations and the distance to the nearest highway for the region of interest. gray lines represent highways. Red intensities represent increasing chloride concentrations with proximity to highways while blue intensities represent decreasing chloride concentrations with proximity to highways.

cementing & casing/well construction, (2) pollution, and (3) pit & impoundment-related violations. These categories of violation were grouped and summarized by Brantley et al. (2014), and were deemed to be most likely associated with UOGD-related groundwater impairments. In Susquehanna County in PA, around the CH_4-UOGD hotspots, we found 17 violation records associated with 8 unique unconventional gas wells: 11 cementing & casing/well construction violations (associated with $n = 2$ unique unconventional gas wells), 1 pit & impoundment issue ($n = 1$), and 5 pollution incidents ($n = 5$) (Tables S6 and S7). These eight problematic unconventional wells account for 0.41% (8/1952) of all unconventional wells in Susquehanna County. Such a small fraction of unconventional oil and gas wells being presumably problematic was consistent with the previous finding in the Bradford County where 7 out of the 1385 shale gas wells were deemed problematic, which combined suggested no regional UOGD impact on dissolved CH_4 in northeastern PA.

In the heatmap of CH_4-highway, a few hotspots were identified, seemingly suggesting that highways (i.e., road salt-containing discharge) might serve as one of the major sources of dissolved methane in PA-NY groundwater (Fig. S23). Road salt-containing discharge, however, is unlikely to be enriched in CH_4. Since highways are usually constructed in valleys, typically along streams and rivers, in NY and PA (USDOT, 2013), CH_4-highway hotspots might instead be explained by the proximity to valley bottoms in these red zones. As such, these hotspots are likely instead related to the widely observed trend of increased CH_4 concentrations in topographic lows in northern PA/southern NY (e.g., Kreuzer et al., 2018; Molofsky et al., 2016).

In addition, the heatmaps for CH_4-UOGD/COGD suggested that SWGT were indeed effective in identifying localities of UOGD/COGD-related water impairments in areas where a dense groundwater quality dataset is available (e.g., Bradford and Susquehanna counties in PA). For counties (e.g., counties in western NY and PA) where no dense groundwater quality dataset is accessible, SWGT fails to yield meaningful results.

4.2. Contribution of oil and gas production practices to salt contents in NY and PA groundwater

SWGT analysis detected small, localized hotspots where salt species increased nearby UOGD/COGD. To further test if these hotspots were indeed caused by the nearby UOGD, we performed thorough scrutiny of well inspection data from the PADEP. In Susquehanna County in PA, around the hotspots in salt analytes-UOGD heatmaps, we found 158 violation records associated with 39 unique unconventional gas wells: 114 cementing & casing/well construction violations (associated with $n = 16$ unique unconventional gas wells), 17 pit & impoundment issues ($n = 12$), and 27 pollution incidents ($n = 14$) (Tables S6 and S7) with 3 wells reporting more than one type of violation. In Bradford County, PA, 98 unique unconventional wells reported 279 violation records: 98 cementing & casing/well construction violations ($n = 38$), 81 pit & impoundment issues ($n = 37$), and 100 pollution incidents ($n = 38$) with 15 wells reporting more than one type of violation. In Tioga County, PA, many fewer violations were reported with 13 unique unconventional wells cited in 48 violation records: 28 cementing & casing/well construction violations ($n = 2$), 4 pit & impoundment issues ($n = 3$), and 16 pollution incidents ($n = 10$) with 2 wells reporting more than one type of violation. Compared to CH_4 results, a lot more problematic unconventional wells as deemed by the PADEP were found in hotspots associated with salt-related analytes (Cl, Na, and SC). This suggests that water impairments caused by UOGD, if occurring, are more likely to be documented by the salt contents in groundwater than dissolved CH_4 in groundwater, although such UOGD impact on the salt content in groundwater still does not appear significant on a regional scale based on SWGT heatmaps.

Only a limited number of conventional oil and gas wells have been ever drilled in northeastern PA, i.e., Tioga ($n = 283$), Bradford ($n = 66$), and Susquehanna ($n = 9$), as compared to the orders of magnitude more unconventional oil and gas wells being drilled in these counties. A few COGD-related hotspots were still detected suggesting that the small number of legacy conventional oil and gas wells could still serve as a potential source of salt on a local scale. However, these COGD/UOGD-related hotspots for Cl, Na, and SC largely overlap with the hotspots associated with geologic faults. Therefore, we cannot rule out natural ABB migration along faults to shallow aquifer as an alternative explanation for the observed hotspots in COGD/UOGD heatmaps.

Although COGD/UOGD was not detected as an individual salt source by the NMF, the impact of UOGD/COGD might be incorporated into the ABB-derived Cl. According to NMF, ABB-derived Cl accounts for 25%−30% of total Cl in NY and PA groundwater. At the regional scale, ABB-derived salt might be derived from naturally migrated brine along geologic faults and/or salt-containing briny wastewater released by nearby COGD/UOGD. Correspondingly, WMW results revealed groundwater samples with $\geq$50% Cl originated from ABB were statistically significantly closer to conventional and unconventional wells and geologic faults than water samples with $<$ 50% ABB-derived Cl. However, SWGT analysis indicates UOGD and COGD impacts should be confined to only a limited number of localities. Resultantly, Cl content from the ABB endmember likely represents Cl sourced predominantly from naturally occurring brines, with inputs from UOGD/COGD in isolated localities.

4.3. Widespread road salt contamination in NY and PY groundwater

We used Cl concentration as a salt proxy to assess the contribution of various salt sources to NY-PA groundwater. As shown by the NMF results, for NY samples, an average of 30% of total Cl originated from the ABB, while 22% and 48% of total Cl were from shallow freshwater recharge and road salt, respectively. For PA samples, shallow freshwater recharge (39%) and road salts (36%) combined accounted for the majority of total Cl, while ABB contributed only 25% of total Cl. NMF results thus suggest road salt as the major anthropogenic source of Cl in NY and PA groundwater, between which NY samples contained more road salt-derived Cl than PA samples. A longer length of highways, and thus presumably highway density, is present in NY counties compared to PA counties (Table S3), and thus more road salt has been likely applied on NY roads. In addition, NY counties, located further north and closer to the Great Lakes, receive greater snowfall in the wintertime, which would also require more intensive road salt application. Surface runoff flushing the highway will carry the applied road salt and enter nearby shallow aquifers (i.e., also domestic water wells) (Jain, 2018; Pieper et al., 2018). In addition, WMW tests further indicated that PA and NY groundwater samples located within 1 km from highways generally had a higher Cl/Na/SC concentration than samples $>$ 1 km from highways, supporting a widespread impact of road salt on PA/NY groundwater. Such widespread impact was also evidenced by many more hotspots being detected in the SWGT heatmaps for Na, Cl, and SC vs. the proximity to highways as compared to COGD/UOGD/faults heatmaps. However, the hotspots observed for CH_4 and Ba relative to the nearest highway suggest some increases in Na and Cl nearby highways may instead reflect ABB upwelling nearby highways. Indeed, highways are usually built along valleys where more ABB tends to be present compared to ridge tops (e.g., Campbell et al., 2022, Siegel et al., 2015b).

5. Conclusions

In this study, we compiled a large hydrogeochemistry dataset containing groundwater quality data collected from 19 counties on the boundary between Pennsylvania (PA; UOGD is permitted) and New York (NY; UOGD is banned) to examine the impact of unconventional oil and gas development (UOGD) and other anthropogenic activities on groundwater quality with a particular emphasis on salts (i.e., Cl, Na, and specific conductance) and methane.

The Wilcoxon-Mann-Whitney test revealed no monotonic trend in methane and salt contents from heavy-, moderate- to non-UOGD/COGD counties, indicating no significant regional impact of UOGD/COGD on PA and NY groundwater quality. Using non-negative Matrix Factorization (NMF), the contributions of three major salt sources (Appalachian Basin Brine or ABB, shallow recharge water, and road salt) to PA and NY groundwater were separated and investigated. Road salt, applied onto highways during wintertime, accounted for 36%−48% of dissolved salt in PA/NY groundwater, indicating road salt as the dominant anthropogenic source of salt on a regional scale. Such a significant regional impact from road salts rather than UOGD was further corroborated by the geospatial analysis, which detected only a limited number of isolated localities showing UOGD impacts on groundwater quality with respect to salt and methane contents but identified widespread areas where groundwater salinity increased with the proximity to highways. NY groundwater contained more road salt-derived salt than PA samples, also consistent with a longer length of highways and a stronger lake effect (more snow in the wintertime) in NY counties than in PA counties.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All datasets in this study are accessible for downloading from the CUAHSI Hydroshare data repository via this link: http://www.hydroshare.org/resource/0539c57b68ec4b1bbac6f8c89fca8da6.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119128.

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