



Detecting anomalous methane in groundwater within hydrocarbon production areas across the United States



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ABSTRACT

Numerous geochemical approaches have been proposed to ascertain if methane concentrations in groundwater, [CH₄], are anomalous, i.e., migrated from hydrocarbon production wells, rather than derived from natural sources. We propose a machine-learning model to consider alkalinity, Ca, Mg, Na, Ba, Fe, Mn, Cl, sulfate, TDS, specific conductance, pH, temperature, and turbidity holistically together. The model, an ensemble of sub-models targeting one parameter pair per sub-model, was trained with groundwater chemistry from Pennsylvania ($n=19,086$) and a set of 16 analyses from putatively contaminated groundwater. For cases where [CH₄] ≥ 10 mg/L, salinity- and redox-related parameters sometimes show that CH₄ may have moved into the aquifer recently and separately from natural brine migration, i.e., anomalous CH₄. We applied the model to validation and hold-out data for Pennsylvania ($n=4,786$) and groundwater data from three other gas-producing states: New York ($n=203$), Texas ($n=688$), and Colorado ($n=10,258$). The applications show that 1.4%, 1.3%, 0%, and 0.9% of tested samples in these four states, respectively, have high [CH₄] and are $\geq 50\%$ likely to have been impacted by gas migrated from exploited reservoirs. If our approach is indeed successful in flagging anomalous CH₄, we conclude that: i) the frequency of anomalous CH₄ (# flagged water samples / total samples tested) in the Appalachian Basin is similar in areas where gas wells target unconventional as compared to conventional reservoirs, and ii) the frequency of anomalous CH₄ in Pennsylvania is higher than in Texas + Colorado. We cannot, however, exclude the possibility that differences among regions might be affected by differences in data volumes. Machine learning models will become increasingly useful in informing decision-making for shale gas development.

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1. Introduction

If natural gas production in the United States (US) doubles from 2000 to 2050 as expected, shale gas production will account for more than three-quarters of this natural gas production (U.S. Energy Information Administration, 2018). This development is largely driven by the combined usage of high-volume hydraulic fracturing and horizontal drilling (U.S. Energy Information Administration, 2018). Other countries and regions (e.g., China, Canada, Middle East) are also ramping up their natural gas production from newly discovered technically recoverable shale reserves (U.S. Energy Information Administration, 2017). In the meantime, putative incidents of deterioration of water quality caused by shale gas development have been investigated throughout the

US (Brantley et al., 2014; Darrah et al., 2014; Guo et al., 2014; Nicot and Scanlon, 2012; Vidic et al., 2013; Wen et al., 2019b, 2019a; Woda et al., 2018; Yang et al., 2013), where it is not rare to see that hydrocarbon wells show signs of compromised well integrity (Lackey et al., 2021). Proving that contamination was caused by shale gas development activities is always difficult, and estimating the frequency of problems is even more problematic. However, for the public to make decisions about granting social license for shale gas development requires some information about the frequency of problems. In this paper we explore the use of a machine learning model developed with large groundwater datasets from one region to see if such data-driven models can be used in other regions to assess incidents of contamination.

We developed the model by application to data from Pennsylvania (PA), the state in the US with the longest history of conventional oil/gas (OG) drilling and coal mining. PA has become a leading area for shale gas production through use of horizon-

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tal drilling and high-volume hydraulic fracturing to extract gas and liquids from the Marcellus and Utica shales. The contaminant that has been identified as the most common problem in PA is methane (CH_4), the chief component of natural gas (Brantley et al., 2014). Many studies investigating groundwater quality in shale gas basins have focused on contamination by such anomalous CH_4 (Hammond, 2016; Hammond et al., 2020; Li and Carlson, 2014; Molofsky et al., 2013; Nicot et al., 2017c; Osborn et al., 2011; Sherwood et al., 2016; Siegel et al., 2015a,b, 2016; Smith et al., 2016; Wen et al., 2017, 2016). Here 'anomalous CH_4 ' is used to denote dissolved or free-phase CH_4 found in groundwater that is putatively derived from the effects of recent human activities related to shale gas development. In general, naturally occurring CH_4 may have long affected an aquifer whereas anomalous CH_4 represents a relatively new source at the impacted site.

The identification of new (anomalous) CH_4 is difficult at least partly because naturally occurring CH_4 is common in many basins, including in PA groundwater (Baldassare et al., 2014; Siegel et al., 2015b; Wen et al., 2019b). In a limited number of areas, the causes of elevated CH_4 in groundwater have been attributed to OG production activities (conventional or unconventional) (Darrah et al., 2014; Grieve et al., 2018; Hammond, 2016; Hammond et al., 2020; Jackson et al., 2013; Osborn et al., 2011; U.S. Environmental Protection Agency, 2015; Warner et al., 2012; Wen et al., 2019b; Woda et al., 2018). Identification of anomalous versus natural CH_4 in groundwater often relies on measurement of carbon isotopes in the gas (e.g., Baldassare et al., 2014; Jackson et al., 2013), but this is somewhat expensive and seldomly definitive. Researchers have also sometimes used other hydrogeochemical patterns to identify anomalous CH_4 . For example, the migration of natural CH_4 from deeper formations into shallow groundwater in the Appalachian Basin is often accompanied by salt-containing waters, which leads to slightly elevated salt contents in the shallow aquifer and distinctive chemical signatures (Siegel et al., 2015a, 2015b; Warner et al., 2012; Wen et al., 2019b). Therefore, major and trace elements (e.g., calcium, sodium, and bromide) (Brantley et al., 2014; Cantlay et al., 2020b; Grieve et al., 2018; Lu et al., 2015; McMahon et al., 2017b; Schout et al., 2018; Warner et al., 2012; Wen et al., 2019b; Woda et al., 2018) have been proposed to distinguish varying sources of subsurface fluids. In addition, electron acceptors can be reduced (e.g., SO_4 can be reduced to sulfide) by bacteria that use CH_4 as an electron donor (McMahon et al., 2017b; Schout et al., 2018; Van Stempvoort et al., 2005; Woda et al., 2018). The concentration of sulfate in waters has sometimes been used to detect anomalous CH_4 as it is easier to collect and analyze water samples for sulfate than sulfide. Other tracers were also proposed recently to detect anomalous CH_4 in groundwater, e.g., strontium isotopes (Warner et al., 2012; Woda et al., 2018), lithium and boron isotopes (Warner et al., 2014), and noble gas isotopes (Darrah et al., 2015, 2014; Wen et al., 2017, 2016; Woda et al., 2018). These latter isotopic tools require a high level of expert knowledge and advanced (and expensive) analytical facilities to ensure proper data acquisition and interpretation. Such characteristics so far have prevented these tracers from being applied widely for monitoring of baseline water quality in the area of shale gas production.

Among these hydrogeochemical tracers, no single parameter is characteristic of a particular source for anomalous CH_4 (Cantlay et al., 2020b). In past studies determining the attribution of anomalous CH_4 , bivariate plots were often used, in which the variables are generally concentrations of hydrogeochemical parameters (e.g., chloride) and/or concentration ratios (e.g., Ca/Na). No single bivariate plot has been suggested that provides definitive answers about whether anomalous CH_4 is present. Instead, the source of elevated CH_4 is more likely to be identified through a combination of parallel bivariate plots (Cantlay et al., 2020b; Wen et al., 2019b; Woda et al., 2018).

We wanted to test machine learning approaches to identifying anomalous CH_4 in multiple shale gas plays. Logistic Regression (LR), introduced in the late 1980s (McCullagh and Nelder, 1989), is a type of machine learning algorithm used to make dichotomous prediction (e.g., whether the dissolved CH_4 concentration is higher or lower than a threshold value). LR has been used in environmental science to predict the presence of certain redox-sensitive contaminants in groundwater, e.g., arsenic (Ayotte et al., 2016), nitrate (Nolan et al., 2002), and the redox state (Tesoriero et al., 2015). LR was also used to predict the probability of CH_4 occurrence in aquifers in Alberta (Canada) (Humez et al., 2019). In these studies, a LR model was built based on a few selected categorical or continuous variables. No interactions between variables were explicitly considered. For example, Humez et al. (2019) used sulfate and total dissolved solids as input variables to predict the presence of CH_4 , but no concentration ratios of these variables were ever explicitly considered. Recognizing that the concentrations of chemical constituents in groundwater are prone to differences in the baseline effects of local geology, topography, and hydrology, we suspected that the exclusion of concentration ratio variables in these previously used models largely hampered investigators' ability to generalize the models and findings to other areas. In addition, in the above-mentioned studies, all variables were fed into a single LR model to generate the final dichotomous prediction, and this made it difficult to completely understand how each variable contributed to the prediction.

In this study, we developed an ensemble LR model trained with data (Shale Network, 2015) from the northern Appalachian Basin in PA. Each sub-model focusses on a pair of hydrogeochemical parameters. More complex classifiers like Random Forest or XGBoost (Chen and Guestrin, 2016) were not used because their outputs are harder to explicitly interpret and visualize. We considered predictor features themselves and their interactions. We then explored use of the refined ensemble model on additional hold-out hydrogeochemistry data from PA and other data from New York, Texas, and Colorado (Fig. 1). To the best of our knowledge, this study is the first to apply an ensemble LR model to predict whether CH_4 in groundwater is anomalous or natural. With the improved availability of hydrogeochemistry data, such a prediction model could be potentially beneficial for other areas in the US and even for other countries/regions with existing or planned OG production. Although we do not have definitive evidence for which groundwater sample(s) in each basin are affected by anomalous methane, we validated the model against a dataset of 13 sites with high [CH_4] presumed to be caused by gas development activity and 1 site with high [CH_4] thought to be unaffected by anthropogenic activities. We also explored the model by testing it against the following hypotheses we derived from the literature: i) the frequency of detection of anomalous methane (# impacted water samples / total water samples tested) in the Appalachian Basin is greater where gas wells target unconventional as compared to conventional reservoirs (Brantley et al., 2014; Ingraffea et al., 2014), and ii) the frequency of detection of anomalous methane in groundwater in the Marcellus/Utica shale play is higher than in western shale plays such as those in Texas and Colorado (e.g., Brantley et al., 2014; Hammond et al., 2020; McMahon et al., 2017a; Sherwood et al., 2016; Woda et al., 2018).

2. Methods and materials

2.1. Groundwater quality data used in model development and application

We collated groundwater chemistry analyses from basins that contain some of the largest shale plays in the U.S. and that also are associated with large groundwater datasets: the Appalachian

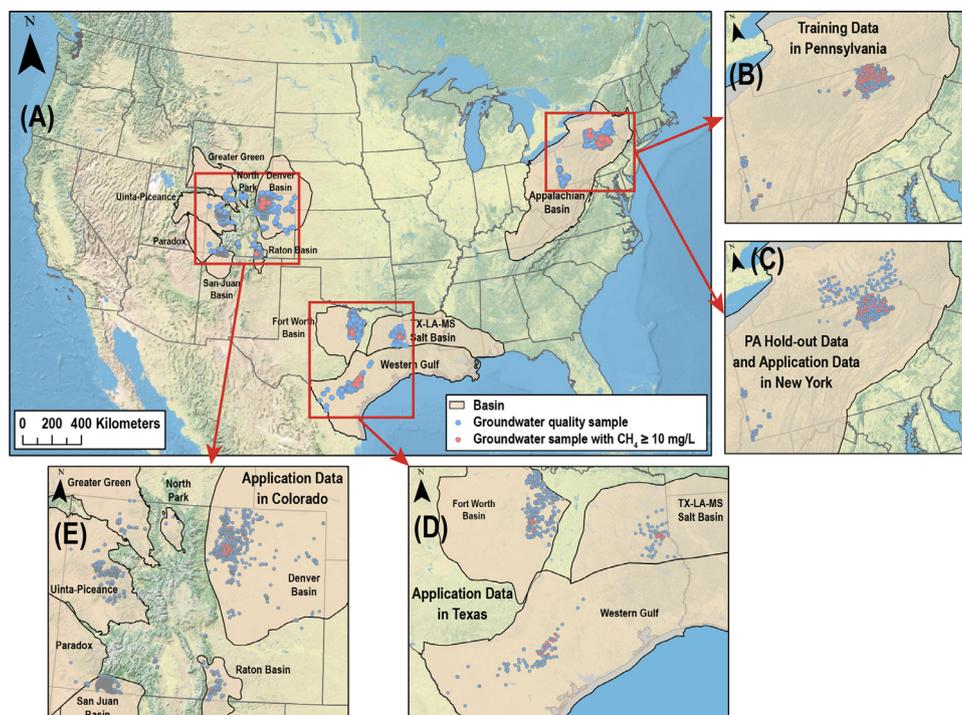


Fig. 1. Location of groundwater quality data used in the model development and application in this study. This map layer of basins producing shale gas is adapted from the map of U.S. Energy Information Administration (<https://www.eia.gov/maps/maps.htm>).

Table 1
Overview of the datasets for model development, validation, and application

Dataset	N_1^a	N_2^b	N_2/N_1	N_3^c	N_3/N_2	N_4^d	N_4/N_1
Model Development							
Shale Network - training	19086	11875	62.22%	258	2.17%	390	2.04%
Known problematic sites - training	16	16	100%	16	100%	16	100%
Model Validation							
Known problematic sites	13	13	100%	13	100%	13	100%
Model Application							
Shale Network - hold-out	4772	2969	62.22%	64	2.16%	98	2.05%
New York	203	78	38.42%	5	6.41%	7	3.45%
Colorado	10258	457	4.46%	58	12.69%	756	7.37%
Texas	688	338	49.13%	34	10.06%	40	5.81%

^a N_1 refers to the number of groundwater samples with reported values for at least one predictor feature

^b N_2 refers to the number of groundwater samples with reported values for all predictor features

^c N_3 refers to the number of groundwater samples with methane concentration at least 10 mg/L and also meet the definition of N_2

^d N_4 refers to the number of groundwater samples with methane concentration at least 10 mg/L regardless of whether they had all the analytes

Basin within Pennsylvania ($n=23,858$; [Shale Network, 2015](#)); the Fort Worth, TX-LA-MS Salt, and Western Gulf basins within Texas ($n=688$; [Darvari et al., 2017](#); [Nicot et al., 2017a, 2017b, 2017c](#)); and the Denver-Julesburg, Raton, San Juan, Paradox, Uinta-Piceance, Greater Green, and North Park basins within Colorado ($n=10,258$; <https://cogcc.state.co.us/>). We decided not to include some shale plays such as the Fayetteville shale in Arkansas in our study because 1) that play has shown little evidence for gas migration ([McMahon et al., 2017a](#); [Warner et al., 2013](#)); 2) we were unaware of a large dataset of groundwater chemistry for analysis; and 3) this region is not one of the major shale gas production areas. The samples we analyzed were compiled from a variety of data sources ([Fig. 1](#); [Table 1](#)). A relatively small dataset of groundwater quality in the counties of New York ($n=203$; [Christian et al., 2016](#)) that neighbor Pennsylvania was also tested for comparison because it represents a region of long-standing exploitation of conventional but not unconventional hydrocarbon reservoirs. More detailed descriptions of these datasets and sources are included in the sup-

porting information. All datasets discussed in this study will be released at: <https://doi.org/10.26208/qs4c-ks39>.

We trained the model to a set of 19,102 groundwater sample analyses that included a small set of groundwater quality data compiled from sites that are presumed to have been impacted by anomalous CH_4 . We then used an additional subset of analyses from such putatively contaminated samples to validate the model performance. Samples are referred to here as putatively contaminated when they were reported to be contaminated in published journal articles or government reports based on field and laboratory investigations ([Llewellyn et al., 2015](#); [U.S. Environmental Protection Agency, 2015](#); [Wen et al., 2019b](#); [Woda et al., 2018](#)). These data were divided into a set for training ($n=16$) [from Granville Road and Paradise Road (Bradford Co.), and Gregs Run (Lycoming Co.)] and a set for validation ($n=13$) [from Paradise Road (Bradford Co.) and Sugar Run (Lycoming Co.)]. An additional sample of a well-known brine spring that is naturally CH_4 -rich from northern PA was also used as part of the validation dataset. Sites were

Table 2

List of geochemical features used in machine learning models to predict methane concentration in groundwater.

Water quality parameter	Single geochemical feature (Y/N)	Reciprocal feature (Y/N)	Ratio feature (Y/N)
Bicarbonate Alkalinity	Alk	Y	Y
Calcium	Ca	Y	Y
Chloride	Cl	Y	Y
Magnesium	Mg	Y	Y
Sodium	Na	Y	Y
Sulfate	SO ₄	Y	Y
Total Dissolved Solids	TDS	Y	Y
Barium	Ba	Y	Y
Iron	Fe	Y	Y
Manganese	Mn	Y	Y
pH	pH	N	N
Hydrogen Ion ^a	H	Y	N
Specific Conductance	SC	Y	N
Temperature	T	N	N
Turbidity	Turbidity	Y	N

^a H⁺ concentration is calculated from pH

largely determined to be putatively contaminated based on temporal changes in methane concentration, carbon isotope data in collected water samples, and geological investigations.

2.2. Predictor features used in the model

We strove to develop a machine learning-based ensemble model that could use geochemical analyses to quantify the likelihood that a groundwater sample with high dissolved CH₄ had been impacted by anomalous rather than natural CH₄. A total of 118 geochemical parameters were considered as potential “predictor features” in the model. In other words, these features were tested for their ability to predict if CH₄ in a given sample was anomalous or natural. These predictor features are divided into three main sub-categories as discussed in the next paragraphs. Detailed descriptions of these predictor features can also be found in the supporting information.

Data for many of the concentrations were beneath detection (i.e., censored). For example, many of the CH₄ concentrations (31.1%) were censored (i.e., below reporting limits). To maximize the number of measurements for each feature, we chose the fifteen geochemical parameters for which the percent of non-censored measurements was $\geq 31.1\%$. These 15 features are referred to as ‘Single Geochemical Features’ or ‘SGF’ in Table 2. These 15 water quality parameters were reported in the training data from PA (Shale Network, 2015) with over 10,000 measurements each (Bicarbonate Alkalinity – Alk, Calcium – Ca, Chloride – Cl, Magnesium – Mg, Sodium – Na, Sulfate or SO₄²⁻ – SO₄, Total Dissolved Solids – TDS, Barium – Ba, Iron – Fe, Manganese – Mn, pH, Hydrogen Ion – H, Specific Conductance – SC, Temperature – Temp, and Turbidity). Specific conductance of a water solution is a measure of its ability to conduct electricity. Turbidity is a measure of the degree to which the water solution has lost transparency due to the presence of suspended particulates. pH was considered in addition to hydrogen ion concentration because pH, the more commonly reported term, is a calculated parameter [$\text{pH} = -\log(\text{hydrogen ion concentration})$] that is not directly comparable to the other concentrations.

The second and third sub-categories of predictor features are the reciprocals of the concentrations of all the SGF except for pH and water temperature ($n=13$; ‘Reciprocal Feature’), and the ratios of any two SGF (‘Ratio Features’). Ratio features were calculated for all features except for pH, H⁺, SC, water temperature, turbidity ($n=90$). The inclusion of features in the second and third categories was motivated by the observation that these two types of arithmetic combinations of geochemical parameters have been widely used by geoscientists in tracing the source of solutes

Table 3

Predicted likelihood of groundwater samples being impacted by anomalous methane for four scenarios: (1) top 100, (2) top 200, (3) top 500, and (4) top 1000 sub-models.

Dataset	Likelihood	Top 100	Top 200	Top 500	Top 1000
<i>Model Validation</i>					
Known	0%–20%	0	0	0	0
prob-	20%–40%	0	0	0	0
lem-	40%–60%	0	0	0	0
atic	60%–80%	0	0	0	0
sites	80%–100%	13	13	13	13
<i>Model Application</i>					
Shale	0%–20%	34	34	29	5
Net-	20%–40%	5	3	4	26
work	40%–60%	10	14	9	6
-	60%–80%	6	0	9	14
	80%–100%	9	13	13	13
<i>Fields</i>					
(n=34)	0%–20%	22	34	17	4
(n=64)	20%–40%	12	0	17	17
	40%–60%	0	0	0	13
	60%–80%	0	0	0	0
	80%–100%	0	0	0	0
Colorado	0%–20%	38	57	21	2
(n=58)	20%–40%	20	1	36	13
	40%–60%	0	0	1	43
	60%–80%	0	0	0	0
	80%–100%	0	0	0	0
New	0%–20%	4	4	3	2
York	20%–40%	0	0	1	2
(n=5)	40%–60%	1	1	0	0
	60%–80%	0	0	1	1 ^a
	80%–100%	0	0	0	0

^a Refer to the text for details. No oil or gas wells found within 5 km of this sample.

in groundwater because they can represent stoichiometric coefficients in the governing geochemical reactions (e.g., Bau et al., 2004; Brantley et al., 2014; Cantlay et al., 2020c, 2020b; 2020c; Tisherman and Bain, 2019). Furthermore, we reasoned that the stoichiometries of these geochemical reactions need not be restricted to one hydrocarbon basin alone, and thus might be more predictive across basins. Subtraction and multiplication of SGF were not considered because, unlike ratios, there are no known fundamental reasons why such functions should be predictive.

A machine learning model using only geochemical predictor features allows us to focus on assessing the interplay of geochemical parameters as well as their relative importance in determining whether the elevated [CH₄] present in groundwater samples is likely to represent anomalous CH₄. Therefore, no non-geochemical features (e.g., land use and bedrock geology) were considered in this study.

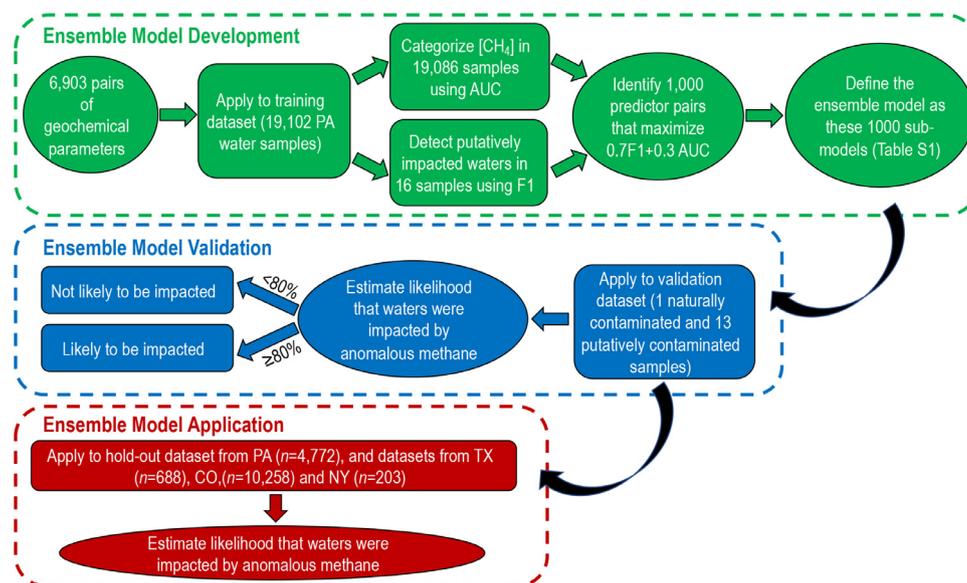


Fig. 2. Workflow of development, validation, and application phases of the ensemble model proposed in this study.

2.3. Machine learning-based ensemble model

Our workflow included three sequential phases: ensemble model development (which included training), validation, and application (Fig. 2). Taking two parameters from the 118 parameters at a time without repetition yields a total number of 6,903 pair combinations. We started with these 6,903 possible geochemical pairs that were each tested in a sub-model. The process of model development described in the next paragraphs identified the subset of 6,903 predictor pairs that were most successful in determining the likelihood of a groundwater sample being impacted by anomalous CH₄. The likelihood was calculated as the ratio of the number of sub-models flagging the CH₄ as not being naturally derived (and therefore, putatively, “anomalous”) divided by the total number of sub-models considered. The collection of sub-models is termed here the ensemble model.

At the stage of ensemble model development (green in Fig. 2), sub-models using the full list of 118 geochemical features paired into 6,903 predictors were trained with 19,102 analyses referred to as training data (Table 1; Fig. 2). Each of the 6,903 sub-models (Fig. 2) considers only one pair of predictor features. In effect, each sub-model imitates the traditional procedure of using bivariate plots of geochemical variables to investigate the origin of dissolved CH₄ in groundwater [see, for example, Figure S10 in Woda et al. (2018)]. The performance of each sub-model was evaluated with respect to two tasks. First, it was evaluated for its ability to predict whether the [CH₄] is above or below the threshold identified as potentially problematic, 10 mg/L, in the 19,086 water samples (Task 1). Given that these samples were collected by professional consultants working for gas companies before drilling gas wells within a few kilometers of the water wells, the waters could be contaminated or uncontaminated by CH₄ from previous oil/gas activity, but we have no outside evidence of contamination. We hypothesized that successful sub-models would predict [CH₄] < 10 mg/L for samples reported to have [CH₄] ≥ 10 mg/L. We inferred these samples are impacted by anomalous CH₄. This approach is implicitly built on the assumption that natural high-[CH₄] waters are chemically distinct from anomalous high-[CH₄] waters. However, we acknowledge that our method will not detect anomalous methane in waters with very low values of [CH₄]. In Task 2, each sub-model was additionally evaluated to see if it successfully identified the CH₄ in 16 of the putatively contaminated training sam-

ples as anomalous (Task 2). The concentration of 10 mg/L was selected because it is a threshold above which immediate action is needed (Eltschlager et al., 2001; Wen et al., 2019b).

During ensemble model development (green in Fig. 2), a linear classifier – logistic regression (LR) – is used in the two tasks with 5-fold cross-validation. LR is generally used to solve binary classification problems. With LR, the relationship between predictor features and the prediction outcome can be described by a sigmoidal function as illustrated by Equation (1) in which x represents predictor features and y is the binary model output of 0 ([CH₄] < 10 mg/L) or 1 ([CH₄] ≥ 10 mg/L).

$$y = \frac{e^{wx+b}}{1 + e^{wx+b}} \quad (1)$$

In the training, the sub-model allows optimization of w and b to best predict the training data. Once w and b are optimized, each sub-model can be used in Task 1 to predict which groundwater samples are characterized by [CH₄] ≥ 10 mg/L. For this task, Area Under the Curve (AUC) is considered as the performance metric where a higher AUC value indicates higher accuracy of prediction. AUC, in particular, was chosen as the accuracy measure as it holistically evaluates the model performance in predicting both positive (i.e., high methane sample) and negative (i.e., low methane sample) results.

In Task 2 the sub-model was applied to 16 putatively contaminated samples. F1 score was calculated following Equation (2) as the performance metric:

$$F1 \text{ score} = \frac{2}{\text{recall}^{-1} + \text{precision}^{-1}} \quad (2)$$

Here *recall* is defined as the proportion of the 16 samples identified correctly while *precision* is the proportion of predicted anomalous CH₄ samples that are actually contaminated. F1 score was chosen to prioritize maximizing true positives (i.e., known problematic samples correctly identified) as it does not consider true negatives (i.e., known natural samples correctly identified).

Both Tasks 1 and 2 were used to identify the best sub-model to detect anomalous CH₄ in impacted waters. Samples reported to have high [CH₄] that were incorrectly classified as low [CH₄] samples by sub-models in Task 1 were inferred to have been impacted by anomalous CH₄. We chose sub-models with higher accuracy of prediction in Task 1 to yield a lower number of false positives. To

evaluate the performance of each sub-model for both Tasks 1 and 2, we defined a synthesized metric, namely, $0.7 \times \text{F1 score} + 0.3 \times \text{AUC}$. The selection of coefficients 0.7 and 0.3 is not entirely arbitrary. We assigned the higher weight (0.7) to F1 as that task is more critical. All sub-models (and the associated pair of features; $n=6,903$) were ranked by the final synthesized score. We also completed a sensitivity test of the coefficients (Table S1a and S1b) and determined that feature members in the top feature list (e.g., top 20) are mostly unchanged (e.g., SC, Na, Cl/SO₄), although the exact rank of features by frequency changes to a limited extent.

In the phases of model validation and application, the prediction results for the best performing sub-models were used to estimate the likelihood of impact of groundwater samples by anomalous CH₄ (Fig. 2). This likelihood was defined as the percentage of considered sub-models that classified the sample as impacted by anomalous CH₄. We calculated four types of likelihood for each water sample using the best n sub-models where we explored $n = 100, 200, 500$ as well as 1,000. We ultimately chose $n = 1,000$ to be conservative. The selection of $n = 1,000$ is supported by the observation that (1) an ensemble model with fewer sub-models would be more likely to be biased towards a few geochemical parameters (e.g., the ensemble model for $n = 100$ was observed to be highly biased towards SC as discussed in the text below) and (2) an ensemble model with a larger number of sub-models (e.g., $n = 1,000$) was expected to assess water chemistry more holistically, improving model applicability and performance for new datasets with less likelihood of overfitting.

In this study, the ensemble model was trained and validated with hydrogeochemistry data in Pennsylvania (i.e., Marcellus shale) and then was tested in other natural gas production regions in Colorado, Texas, and New York. Differences in bedrock geology, regional hydrogeochemistry, topography, and land use between testing and training/validation datasets might in some cases hamper the applicability of the developed ensemble model. We strove to minimize this issue by considering interactions of ratios of concentrations of single geochemical features as these concentration ratios tend to yield less variability across different regions. As more hydrogeochemical data become available, in particular from presumably contaminated sites, the ensemble model can be further validated and even re-trained with new data.

3. Results and discussion

3.1. Model development

Two statistical methods – Pearson correlation and Spearman's rank correlation – were adopted to assess the pairwise correlation of the 15 single geochemical features in predicting the target feature, [CH₄]. The Pearson correlation is used to evaluate linear relationships between continuous variables that are assumed to obey normal distributions, while the Spearman's rank correlation is used to evaluate monotonic relationships between two continuous variables without the requirement that variables are normally distributed. Therefore, the Spearman's rank correlation identifies more pairs of features that report statistically significant correlations ($p < 0.05$) compared to the Pearson correlation (Fig. 3).

The pairwise correlations led us to note three groups for the fifteen single geochemical features: 1) salinity-related (Alk, Ba, Ca, Cl, Mg, Na, TDS, SC); 2) redox-sensitive (Fe, Mn, and SO₄); and (3) others (pH, Temp, Turbidity, and H⁺). These groupings are used to categorize the best-performing sub-models in subsequent discussions.

3.1.1. General observations

The synthesized scores of all sub-models ($n=6,903$) are listed and ranked in Table S1a. The best performing sub-model (synthe-

sized score = 0.9579, F1 = 0.9677, AUC = 0.9350) corresponds to the pair, 1/SC and Ca/Ba (Table S1a). From this observation we inferred that salinity is an effective tool to detect anomalous CH₄ samples (SC, Ca, and Ba are all salinity-related features). Previous studies (e.g., Brantley et al., 2014; Cantlay et al., 2020b; Tisherman and Bain, 2019; Wen et al., 2019b; Woda et al., 2020, 2018) have also identified other salinity-related parameters (Cl, Ca/Na, Mg/Na, Ca/Mg, and Ba/Cl) that are helpful in detecting anomalous CH₄ in groundwater samples or distinguishing chemical signatures of produced waters from shale gas development from other types of contamination. These same parameters, i.e., Cl, Ca/Na, Mg/Na, Ca/Mg, and Ba/Cl, show up in sub-models ranked as high as 8th, 13th, 19th, 82nd, and 191st (Table S1a), respectively. Furthermore, the frequency of inclusion of these features in the top 1000 sub-models are 87, 4, 2, 11, and 8, respectively (Table S1b and Fig. 4). In addition to the salinity-related parameters mentioned by previous authors, a few new ones were identified as important (i.e., high frequency) in the top 1,000 performance sub-models, e.g., Ca/TDS (49) and Ba/Alk (81) (Table S1b). These salinity-related features can effectively distinguish natural migration of thermogenic CH₄ from anomalous CH₄ presumably because CH₄ often migrates naturally with salt-containing Appalachian Basin brine into shallow groundwater (e.g., Warner et al., 2012; Wen et al., 2019b; Woda et al., 2018). Alkalinity may appear because it increases during sulfate reduction, one of the redox processes (see next paragraph) that sometimes couple to methane oxidation (Woda et al., 2018).

In addition to salinity, redox-sensitive features (e.g., Fe/SO₄, SO₄/Na) are also frequently found in the top performing sub-models (Table S1, and Fig. 4). For example, SO₄ and Fe concentrations have previously been used to detect anomalous CH₄ in groundwater (Wen et al., 2019b; Woda et al., 2020, 2018) and the frequency of SO₄-containing and Fe-containing features (e.g., Fe/SO₄) appearing in the top 100 sub-models are 17 and 10, respectively. It is worth noting that many SO₄- or Fe-containing features also incorporate salinity-related features, e.g., SO₄/Na and Fe/Ba. Redox features are expected because the presence of CH₄ creates an anoxic environment that in turn promotes reduction of redox-sensitive species such as sulfate (SO₄²⁻) to sulfide (S²⁻) and Fe(III) to Fe(II). The formation of sulfide leads to precipitation of metal sulfide and a decrease in SO₄ and Fe concentrations over time (Woda et al., 2020, 2018). Low concentrations of all of these redox-sensitive parameters are expected when the source of CH₄ is natural and the groundwater has had a relatively long time to reach thermodynamic equilibrium. In contrast, when anomalous CH₄ migrates into shallow, oxygenated groundwater, months can pass before the water reaches chemical equilibrium, allowing the co-existence of transiently high methane, sulfate, and iron in the same water samples that can be detected during the transient (Wen et al., 2019b; Woda et al., 2020, 2018).

3.1.2. Specific observations

Best performing features are summarized for the top 100, 200, 500, and 1,000 models in Fig. 4 and the likelihood of the presence of anomalous CH₄ in groundwater is calculated for all of these four top lists in the following sections. It is clear that in the first two lists (i.e., top 100, 200), the frequency of SC-containing features (SC and 1/SC) dominate over the other top features. So, if the likelihood of groundwater samples being impacted by anomalous CH₄ is calculated from an ensemble model considering only the top 100 (or 200) features, the calculated likelihood will be largely biased towards SC. Two more features (Na and Cl) are reported with high frequency in the top 500 list, but the calculated likelihood of groundwater samples being impacted by anomalous CH₄ still depends strongly on the salinity features SC, Na, and Cl. To holistically assess groundwater chemistry and to be more conservative,

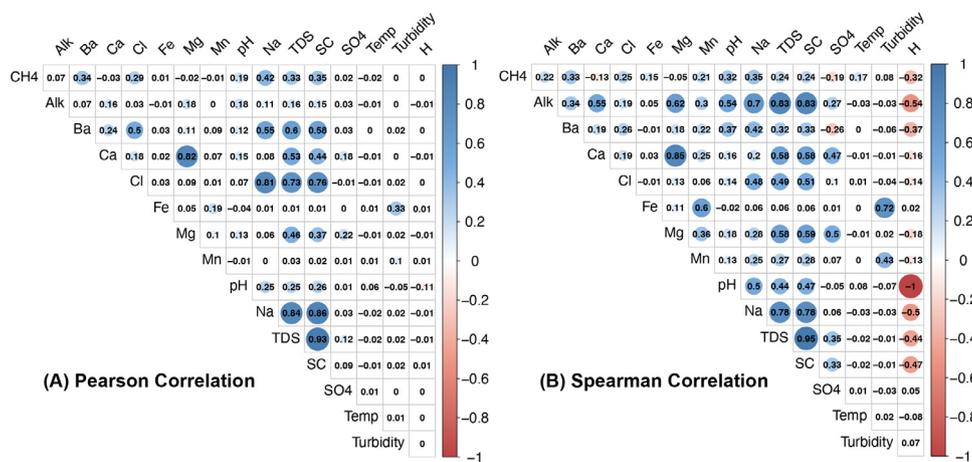


Fig. 3. Correlation matrices for the 15 single geochemical features and the target feature (i.e., CH₄) determined for the training data derived from the Shale Network database ($n = 11,875$; Table 1) for: (A) Pearson correlation and (B) Spearman's rank correlation. The pairwise correlation coefficient is indicated in the corresponding cell. A statistically significant correlation is highlighted by either blue (positive) or red (negative) colors.

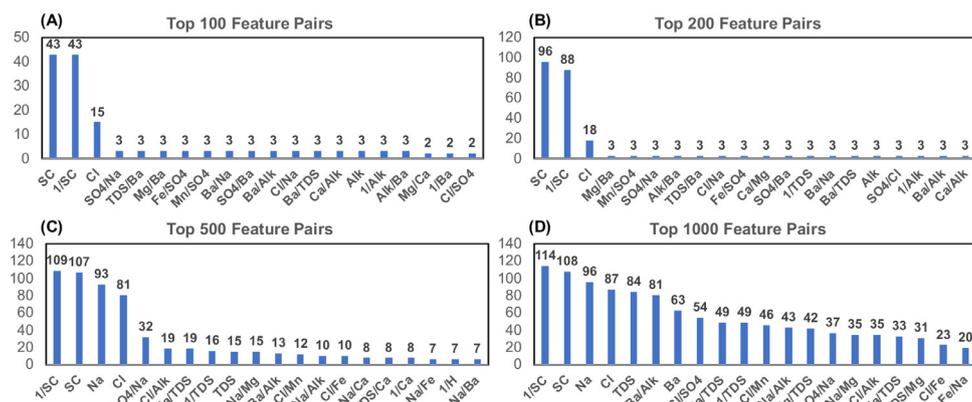


Fig. 4. Frequency of the top 20 features in the best-performing models with respect to both the categorization of methane concentration and the detection of putatively contaminated samples in the model development. Feature frequency is shown for (A) top 100 models; (B) top 200 models; (C) top 500 models; and (D) top 1,000 models. The y-axis summarizes the frequency of each feature.

we focus the most extensive discussion mainly about the results based on the list for the top 1,000 (the “top 1,000 model”, Fig. 4).

3.2. Model validation

After training with the use of putatively contaminated sample data ($n = 16$), the top 1,000 sub-models were validated against another groundwater quality dataset of 14 high-[CH₄] groundwater samples from northeastern or central PA. All were reported with [CH₄] ≥ 10 mg/L. Of these, 13 were reported for 4 sites putatively impacted by anomalous CH₄ (Llewellyn et al., 2015; Wen et al., 2019b; Woda et al., 2018). The likelihood of contamination was $>90\%$ for each of these 13 validation samples (Tables 3 and S2) by the ensemble model using the top 1,000 sub-models. This suggests that the ensemble model has high sensitivity (i.e., high recall rate), i.e., the model is very effective in detecting anomalous CH₄ in groundwater samples (true positives). The 14th sample that we used for validation was groundwater from Salt Spring State Park in northern PA. That spring sample is known to contain naturally occurring CH₄ with [CH₄] > 10 mg/L (‘Salt Spring State Park’ in Table S2). The predicted likelihood that this groundwater sample is impacted by anomalous CH₄ is 14%, which means that the ensemble model predicts that this sample is likely not contaminated by anomalous CH₄ (i.e., a true negative). Thus, the proposed ensemble model is also very effective in distinguishing whether high [CH₄] in groundwater is naturally occurring (e.g., $<20\%$ likelihood) or anomalous (e.g., $>90\%$ likelihood).

3.3. Model application

We now apply this ensemble model to the hold-out Pennsylvania data (data not incorporated in the training dataset) as well as groundwater data from other states (Fig. 5) to seek to detect anomalous CH₄ in other groundwater samples as a way to explore our two hypotheses and to compare to previous research (Christian et al., 2016; Darvari et al., 2017; Nicot et al., 2017a, 2017b, 2017c; Sherwood et al., 2016; Wen et al., 2019b, 2018).

3.3.1. Pennsylvania hold-out data

A total of 4,772 groundwater samples from the Shale Network database are in the Pennsylvania hold-out dataset. Among these, only 64 show both [CH₄] ≥ 10 mg/L as well as measurements for all the single predictor features. These 64 groundwater samples are all located in northeastern PA (Figs. 5 and 6; Table S3). The top 1,000 model predicts that 29 of these 64 groundwater samples show a $\geq 50\%$ likelihood and, of these, 13 show $\geq 80\%$ likelihood of being impacted by anomalous CH₄ (Figs. 5 and 6; Table S3).

To assess the efficacy of the ensemble model for Pennsylvania, we compare the machine learning results to the results based on a more simplified and streamlined approach by Wen et al. (2019b). Based on six selected geochemical parameters (CH₄, Cl, Ca, Na, Fe, and sulfate concentration), Wen et al. (2019b) categorized groundwater samples into five geochemical types. Their type 4 and 5 waters were considered to be the most likely to be impacted by anomalous CH₄: their characteristics include Ca/Na mass ratio ≥ 0.52 ,

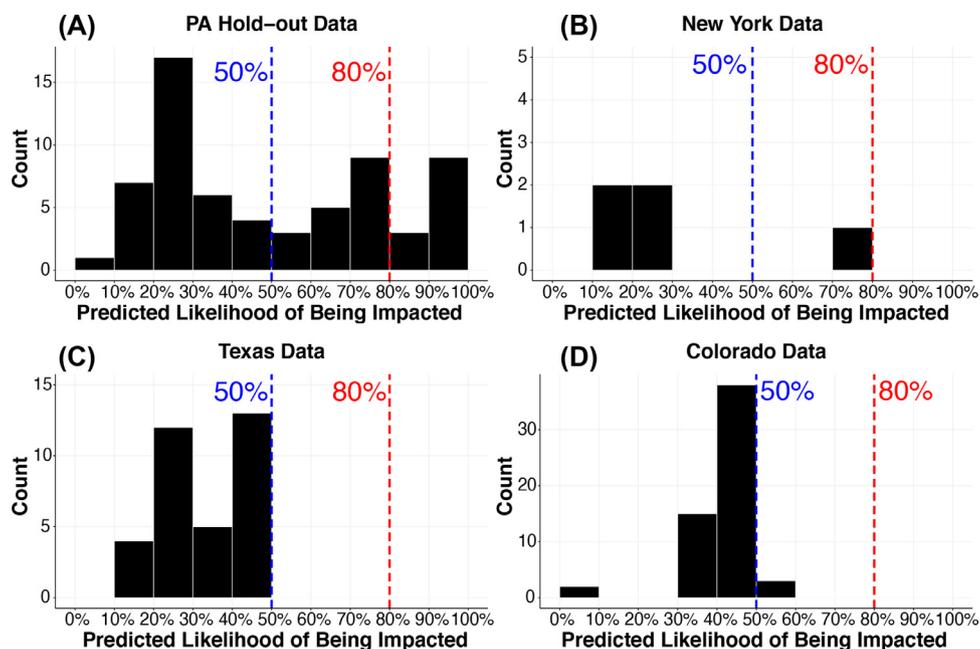


Fig. 5. Distribution of predicted likelihood of being impacted by anomalous methane for high methane samples (≥ 10 mg/L) across the U.S. by considering the top 1000 sub-models: (A) Pennsylvania hold-out data, (B) New York data, (C) Texas data, and (D) Colorado data.

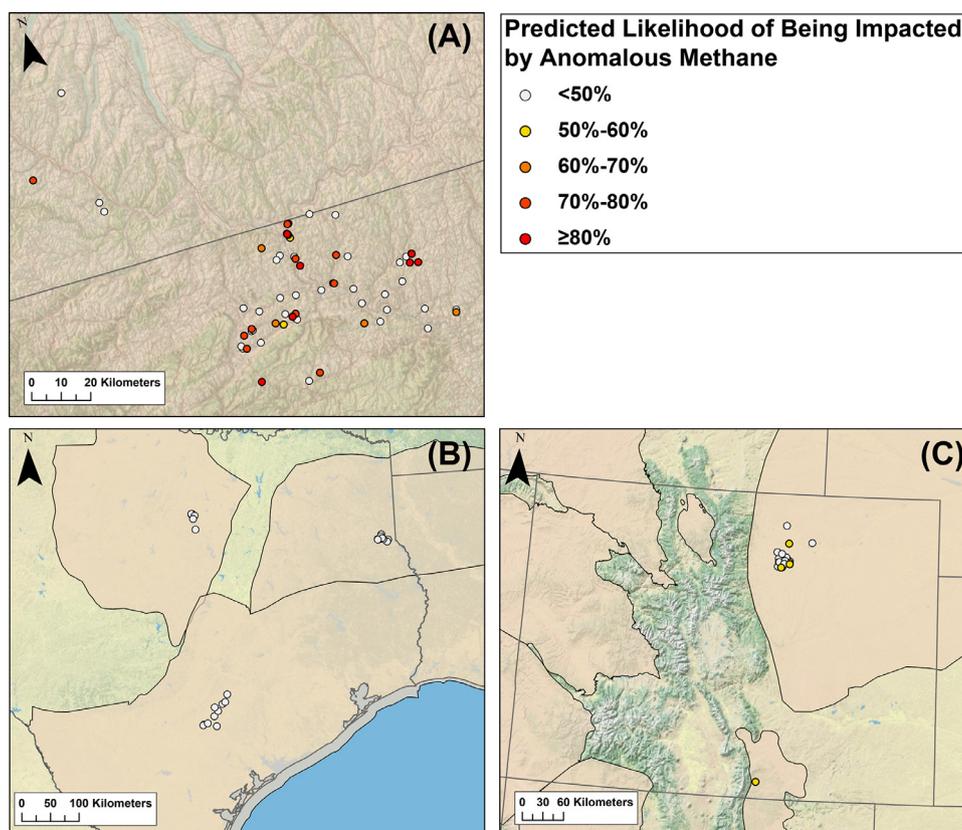


Fig. 6. Maps showing locations and the range of predicted likelihood of being impacted by anomalous methane for high methane samples (≥ 10 mg/L) across the U.S. by considering the top 1000 sub-models: (A) Pennsylvania and New York, (B) Texas, and (C) Colorado.

Cl ≤ 30 mg/L, $[\text{CH}_4] \geq 10$ mg/L, and dis-equilibrated Fe concentrations (≥ 0.3 mg/L) and/or dis-equilibrated sulfate concentration (≥ 6 mg/L). Using this simplified workflow from Wen et al. (2019b), we identified a total of 17 samples of types 4 or 5 in the hold-out PA dataset. Ten of these 17 samples were used to train the ensemble model and five were not considered by the en-

semble model because they lacked values for all of the 15 single geochemical features. The remaining two analyses (sample IDs are “PADEP_Predrill_CHK_827” and “PADEP_Predrill_Bradford-Burlington_T_005-well”; Table S3) were detected accurately (true positives) by the top 1,000 model as showing a high likelihood (i.e., $\geq 50\%$) of impact by anomalous CH_4 .

In addition to the two samples detected by both the ensemble model in this study as well as by Wen et al. (2019b), the ensemble model also identified 27 other samples with a predicted likelihood of $\geq 50\%$ (12 samples $\geq 80\%$) of anomalous CH_4 . The workflow of Wen et al. (2019b) did not detect these 27 samples as impacted by anomalous methane because $\text{Cl} > 30$ mg/L or sulfate < 6 mg/L. If the new ensemble model approach is correct, these samples are impacted by anomalous methane and were false negatives in the previous study. Lending credence to the conclusion that these sites were impacted by anomalous methane is the observation that all but 11 of these 27 samples were from four areas that lie near locations with known contamination as reported in the literature (Llewellyn et al., 2015; Wen et al., 2019b, 2018) (Figs. 5 and 6; Table S3). The last eleven putatively-false-negatives are not close to any sites previously identified as problematic. Given that all the other 16 sites show some history of local contamination, we conclude that all these putatively-false-negatives were impacted by recent intrusion of anomalous methane (which might be caused by nearby shale gas drilling) at the time of sampling, and should have received in-depth analysis to determine the source and mechanism of the elevated $[\text{CH}_4]$.

Although the streamlined workflow from Wen et al. (2019b) is easy to implement and effective in detecting anomalous methane samples, it is limited in the number of geochemical parameters considered and it likely returned at least 27 false negatives for the PA hold-out dataset. In contrast, our ensemble model evaluates a fuller set of groundwater chemistry data and can identify waters that are contaminated that were missed by the streamlined workflow of Wen et al. (2019b).

3.3.2. New York

Although New York is almost geologically identical to Pennsylvania in the counties considered here, it is not producing shale gas because high-volume hydraulic fracturing with horizontal drilling is banned. Instead, conventional oil and gas drilling has long been important in the state. Brantley et al. (2014) summarized reports from the PA regulator showing that the reporting rate of problems of anomalous CH_4 from conventional oil and gas well development in PA was much smaller than that observed for shale gas development after 2004. We thus hypothesized that we would see a very low rate of anomalous CH_4 in the small dataset of groundwater quality available for the region of oil and gas production in New York (Christian et al., 2016). This hypothesis is especially compelling because geologically, northern PA is very similar to NY, but the laws are different, and the use of high-volume high-pressure hydraulic fracturing in NY unconventional reservoirs is not allowed. Therefore, unlike PA samples, all of the New York samples were collected in advance of high-volume hydraulic fracturing but might postdate some of the nearby conventional drilling.

In the New York dataset of 203 groundwater samples, only five are reported with high $[\text{CH}_4]$ (≥ 10 mg/L). Four of these five samples are predicted by the top 1,000 ensemble model as low likelihood (i.e., $< 30\%$) of containing anomalous methane (Tables 3 and S4; Figs. 5 and 6). However, one ("ST35B"), with a $[\text{CH}_4]$ of 13.8 mg/L, yields a 71% likelihood of impact by anomalous CH_4 (Table S4 and Figs. 5 and 6). Sample ST35B was identified in the ensemble model because it has a very low $[\text{Cl}]$ of 4.1 mg/L, but relatively high $[\text{sulfate}]$ and $[\text{Fe}]$ of 8.99 and 0.42 mg/L, respectively. It is thus also detected as a contaminated sample by the streamlined test of Wen et al. (2019b) and is likely, based on these tests, to contain CH_4 that has infiltrated the groundwater recently.

Although this sample appears to have been infiltrated with CH_4 recently, other lines of evidence suggest that the migration was not caused by oil or gas development. For example, the distance between site ST35B (sampled in 2013) and the nearest oil or gas well (drilled prior to 1980) is ~ 6 km. The large distance and long pe-

riod of time between gas well drilling and water sample collection render the source of methane in water wells unlikely to have originated from the gas wells. But this water well is drilled into the very gas-rich Canadaway Formation near a large number of faults and lineaments, and may nonetheless have been affected by recent migration of naturally occurring CH_4 to the water well. Consistent with this conclusion, Christian et al. (2016) pointed out that values of $[\text{CH}_4]$ in the NY groundwater data (including, implicitly, ST35B) do not statistically vary with proximity to gas wells or faults. They argued that elevated $[\text{CH}_4]$ in the NY samples is most likely of natural origin. This conclusion was based on the observation that high $[\text{CH}_4]$ is often associated with Na-rich waters in valleys in NY that are impacted by natural brines (Christian et al., 2016). However, while ST35B had a high $[\text{Na}]$ (30.1 mg/L), it had very low $[\text{Cl}]$ (4.1 mg/L). Therefore, the high Na in that sample did not derive from contamination by NaCl-rich brine (and was not flagged as such by the ensemble model). On the other hand, water from ST35B was reported to smell like 'rotten egg' (i.e., H_2S) and is locally associated with brownish red stains (pers. comm., Laura Lautz), perhaps pointing to ongoing sulfate reduction coupled with methane oxidation (Wen et al., 2019b; Woda et al., 2020, 2018). Our prediction that ST35B contains anomalous methane might be a false positive: in particular, it could be water that was recently impacted by natural CH_4 rather than CH_4 migrated from hydrocarbon development activities. In future predictions with the ensemble model, a filter for proximity to oil/gas wells should be included (e.g., waters sampled within 5 km).

A Fisher exact test was used to test our original hypothesis, i.e., to test if the frequency of detection of CH_4 -impacted groundwater samples ($\geq 50\%$ likely to be impacted by anomalous methane) differ between PA (i.e., 42/2,983) and NY (i.e., 1/78). Whether we assume that ST35B is an example of anomalous methane caused by oil/gas development or not, the Fisher test results show no statistically significant difference between PA and NY at a confidence level of 95% ($p > 0.05$). Thus, we must reject the hypothesis in that the ensemble model reveals similar frequencies of putative contamination by anomalous methane in the part of the Marcellus shale play utilizing horizontal drilling + hydraulic fracturing as compared to the part with conventional resource development.

3.3.3. Texas and Colorado

We also compiled groundwater quality data from Texas to test the hypothesis that the frequency of identification of anomalous methane in groundwater wells is higher in PA than in other shale plays/states. A total of 688 groundwater samples are included in the compiled Texas data, which cover three major shale gas plays in Texas: Barnett Shale, Eagle Ford Shale, and Haynesville Shale. Among these samples, $[\text{CH}_4]$ is ≥ 10 mg/L in 34 groundwater samples (Table S5 and Figs. 5 and 6). Of these 34 samples, none were identified to have a likelihood of anomalous $\text{CH}_4 \geq 50\%$. This is consistent with the findings from previous investigations of the sources of CH_4 in these three shale plays (Darvari et al., 2017; Nicot et al., 2017a, 2017b, 2017c), i.e., no CH_4 in these shallow water wells is associated with recent development of nearby shale gas production.

The ensemble model was also applied to a large groundwater quality dataset of 10,258 water samples collected across Colorado mainly within the Denver-Julesburg, Raton, San Juan, and Uinta-Piceance basins (Fig. 1). Of these samples, high $[\text{CH}_4]$ (≥ 10 mg/L) samples ($n=58$) with complete measurements for all required single geochemical features exist only in the Denver-Julesburg Basin and Raton Basin (Fig. 1). These 58 samples were collected from 29 sites (Table S6), of which only four samples from four sites (i.e., 705739, 755481, 752672, 750143) are associated by the ensemble model with a likelihood $\geq 50\%$ for anomalous methane. Three of the sites are in the Denver-Julesburg Basin and one in the Raton

Basin. All other samples/sites with high $[\text{CH}_4]$ are calculated to be <50% likely to have been impacted by anomalous CH_4 . A detailed discussion of the results of model application to Colorado dataset is included in the supporting information.

With these data, we test our second hypothesis, namely that the frequency of detection of anomalous methane in the Marcellus shale play is higher than in Texas + Colorado. Treating the Colorado and Texas measurements as one dataset, the combined frequency of detection of groundwater samples showing $\geq 50\%$ likelihood is 4/795, statistically lower than the rate in Pennsylvania (i.e., 42/2,983) at a confidence level of 95% ($p=0.04$) using the Fisher exact test. This finding supports our second hypothesis that the frequency of detection in the Marcellus shale play is higher than in Texas and Colorado. To explain this result, we point to Hammond et al. (2020) which suggested that most of the anomalous CH_4 released from gas wells in the US occurs because primary cementation is not completed along the full lengths of production casings from the target shale to intermediate casings (or to surface casings, if intermediate casings are not used). The higher frequency in the Marcellus play could therefore derive from differences in casings and cementation or differences in gas contents at intermediate depths for boreholes in that play as compared to other plays.

4. Conclusion

We presented a machine learning ensemble model that shows that salinity-related and redox-related measurements are effective geochemical features that can detect anomalous methane in groundwater. One problem with the application of the model to date is that we cannot exclude the possibility that differences in sample sizes contributed to differences in detection frequencies. Clearly, larger datasets for all shale gas plays could be used to eliminate this problem. Furthermore, a machine learning model that incorporated additional geochemical measurements such as isotopes would presumably be even more adept at finding evidence of anomalous CH_4 .

For the regions we studied (PA, TX, CO, NY), the frequency of reported water samples with $[\text{CH}_4] \geq 10$ mg/L, the level often considered to be dangerous, was 2.1%, 5.8%, 7.4%, and 3.4%. In contrast, the frequency of identification of anomalous methane by the ensemble machine learning model was 1.4%, 0%, 0.9%, 1.3% (with ST35B) and 0% (without ST35B). These values were determined by application of the ensemble model where we detected 42/2,983, 0/338, 4/457, and 1/78 (or 0/77) of the water samples were $\geq 50\%$ likely to be impacted by newly migrated natural gas in these states, respectively. One NY sample, flagged as likely to have newly migrated methane, was sampled ~6 km from the nearest oil/gas well, and thus may be contaminated by new methane from a different source. Fisher exact tests show statistically significant differences between the results for PA versus TX+CO (i.e., with evidence for a higher frequency of migrated methane sites in PA) but show no statistically significant difference within the Marcellus shale play between regions using versus not using high-pressure high-volume hydraulic fracturing. The new machine learning tool appears to be useful in detecting anomalous methane in multiple shale plays. Future work should include additional training and validation of data-driven models as new data from presumably impacted sites in shale plays other than the Marcellus become available.

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.

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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.2021.117236.

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