

A redox aqueous geochemistry approach to predict methane occurrence in shallow aquifers in Alberta, Canada

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Introduction

A major scientific challenge and an indispensable prerequisite for environmental impact assessment in the context of petroleum development in low permeability reservoirs is a reliable determination of the baseline conditions against which potential environmental impacts on shallow freshwater resources can be accurately and quantitatively tested. A major goal of such surveys is to determine the occurrence of methane and its spatial distribution in shallow groundwater to establish a baseline prior to resource development against which alleged fugitive gas migration impacts potentially associated with resource development can be evaluated. To achieve this, many jurisdictions with petroleum development in low permeability reservoirs have initiated baseline groundwater testing programs that require the analysis of numerous water quality parameters and the concentration and carbon isotope ratios of dissolved methane or of methane in free gas obtained from the groundwater. While such baseline groundwater data sets containing gas composition results are emerging, many jurisdictions have also compiled groundwater quality data for many years or even decades for thousands of landowner wells, but these water quality data sets do not usually include gas concentration results. The objective of this study was to test whether an aqueous geochemistry approach based on assessment of redox states for such large water quality data sets can predict the occurrence of methane in shallow aquifers with reasonable certainty.

Theory and Methods

To test whether an aqueous geochemistry approach based on assessment of redox states can predict the occurrence of methane in shallow groundwater we used data from Alberta's Baseline Water Well Testing program (BWWT). For more than 750 BWWT groundwater samples, we evaluated dissolved aqueous geochemistry species to determine the redox state of the groundwater. This methodology is based on the redox ladder concept. As groundwater evolves from highly oxidized to highly reducing conditions, it undergoes a sequence of redox reactions including O₂ consumption, denitrification, Mn(IV) and Fe(III) reduction, and bacterial sulfate reduction, followed by methanogenesis. Only if groundwater is in the methanic redox state is the in-situ formation of methane in the aquifer feasible. Hence, the groundwater samples were classified into redox categories dependent on the concentrations of terminal electron acceptors (TEAPs) such as O₂, NO₃, Mn, Fe and SO₄ participating in redox reactions with the goal to identify the number of groundwater samples with methanic redox conditions where the in-situ formation of methane in aquifers is feasible. Subsequently, we evaluated the gas composition data for free gas samples for the same BWWT groundwater wells and tested in how many cases predicted methane occurrences based on the redox aqueous geochemistry approach were coupled with free gas samples that had elevated methane concentrations.

Results and Discussion

A BWWT dataset composed of 762 high quality groundwater samples coupled with free gas occurrence was evaluated using the redox aqueous geochemistry approach (Fig. 1).

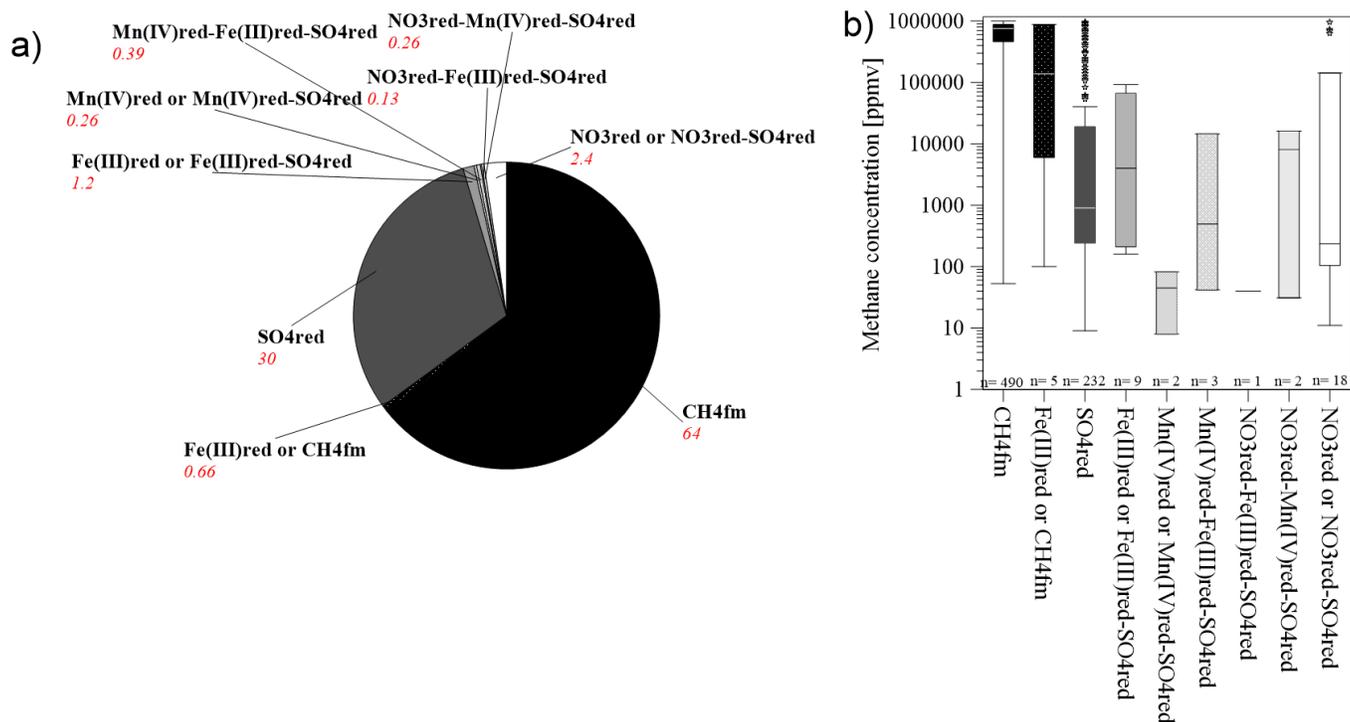


Figure 1: Assignment of redox categories applied to groundwater samples from the BWWT database a) percentages (red label) of the redox categories represented in a pie chart, b) Box-Whisker plot of the distribution of methane concentrations in free gas samples in each redox category with n representing the number of samples in each redox category.

The results indicate that 64 % of the groundwater samples (n=490) belong to the methanic zone where NO_3 and SO_4 have low to negligible concentrations (labeled CH4fm, Fig. 1a). Only 0.7% (n=5) of the samples belong to the redox zone where Fe(II) is present indicating the occurrence of Fe(III)-reduction and/or a mixed redox zone where methanogenesis occurs as well as Fe-reduction (labeled Fe(III)red or CH4fm). Circa 30% of the groundwater samples (n=232) belong to a redox zone with elevated sulfate concentrations and evidence that bacterial sulfate reduction is ongoing (labeled SO4red). The remaining <6% of samples belong to mixed redox zones where Mn(IV) reduction process (labeled Mn(IV)red or Mn(IV)red-SO4red) or coupled Mn(IV) and Fe(III) reduction processes (labeled Mn(IV)red-/Fe(III)red-SO4red) are ongoing as evidenced by the presence of dissolved constituents such as Mn, Fe and SO_4 or mixed redox zones were observed that included NO_3 , Mn(IV) and Fe(III) reduction (NO3red-Mn(IV)red-SO4red, NO3red-Fe(III)red-SO4red) (Fig. 1a). Subsequently, the assigned groundwater redox classes were compared to the methane concentrations in free gas samples from the BWWT dataset (Fig. 1b). Samples containing elevated concentrations of methane (>15,000 ppmv) were associated with redox zones CH4fm and Fe(III)red or CH4fm suggesting that methanogenesis can occur in-situ in the aquifer. Free gas samples with methane concentrations <15,000 ppmv were predominantly associated with SO4red, and other mixed redox process classes (Fig. 1b). Comparison of aqueous and gas geochemistry datasets revealed that the redox aqueous geochemistry assignment correctly predicts that methane occurrence is feasible in 457 of 527 groundwater samples (87%) where elevated methane

concentration >15,000 ppmv were observed in free gas samples (Table 1, orange box). In addition, the redox aqueous geochemistry assignment also correctly predicts that methane does not occur in significant quantities (methane concentration in free gas <15,000 ppmv) in 197 of 235 groundwater samples (84%) that belong to non-methanic groundwater redox classes (Table 1, green box). The combined performance of the redox aqueous geochemistry approach correctly predicts in >85 % of all cases baseline methane occurrence in the aquifers.

		Redox class [abbreviation]	Observed events			
			CH ₄ > 15,000 ppmv		CH ₄ < 15,000 ppmv	
			n	%	n	%
Predicted events	Methanic zones	CH ₄ fm	457	86.7	38	16.2
		Fe(III)red or CH ₄ fm				
	Non-methanic zones	SO ₄ red	70	13.3	197	83.8
		Fe(III)red-SO ₄ red				
		Mn(IV)red-SO ₄ red				
		Mn(IV)red-Fe(III)red-SO ₄ red				
		NO ₃ red-Mn(IV)red-SO ₄ red				
	NO ₃ red -SO ₄ red					
	Total		527	100.0	235	100.0

Table 1: Overview of the metrics of performance of the redox aqueous geochemistry approach: predicted versus observed occurrence of methane in groundwater.

Conclusion

The presented redox aqueous geochemistry approach for evaluating potential methane occurrence in groundwater correctly predicts methane presence (>15,000 ppmv) and absence (<15,000 ppmv) in >85% of groundwater samples from the BWWT program, for which free gas samples were available for verification of the prediction accuracy. The excellent agreement between observed and predicted methane occurrence provides a sufficient confidence level for applying the redox aqueous geochemistry approach to forecast methane occurrence in shallow groundwater for the much larger Alberta Health Services (AHS) groundwater chemistry dataset (n>60,000 groundwater samples), for which gas data are not available.

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