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Applicability of Aquifer Impact Models to Support Decisions at CO_2 Sequestration Sites

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Abstract

The National Risk Assessment Partnership has developed a suite of tools to assess and manage risk at CO_2 sequestration sites. This capability includes polynomial or look-up table based reduced-order models (ROMs) that predict the impact of CO_2 and brine leaks on overlying aquifers. The development of these computationally-efficient models and the underlying reactive transport simulations they emulate has been documented elsewhere (Carroll et al., 2014, Dai et al., 2014, Keating et al., 2015). In this paper, we seek to demonstrate applicability of ROM-based analysis by considering what types of decisions and aquifer types would benefit from the ROM analysis. We present four hypothetical examples where applying ROMs, in ensemble mode, could support decisions during a geologic CO_2 sequestration project. These decisions pertain to site selection, site characterization, monitoring network evaluation, and health impacts. In all cases, we consider potential brine/CO_2 leak rates at the base of the aquifer to be uncertain. We show that derived probabilities provide information relevant to the decision at hand.

Although the ROMs were developed using site-specific data from two aquifers (High Plains and Edwards), the models accept aquifer characteristics as variable inputs and so they may have more broad applicability. We conclude that pH and TDS predictions are the most transferable to other aquifers based on the analysis of the nine water quality metrics (pH, TDS, 4 trace metals, 3 organic compounds). Guidelines are presented for determining the aquifer types for which the ROMs should be applicable.

1. Introduction

Quite a few studies have been conducted over the past few years addressing the possible impact of fluids leaking from a CO_2 sequestration site into overlying aquifers. These include laboratory experiments (Little and Jackson, 2010, Karamalidis et al., 2012, Humez et al., 2013; Zheng et al., 2016, Bacon et al., 2015, Lawter et al., 2015, Wang et al., 2015), controlled release experiments (Spangler et al., 2010; Peter et al., 2012; Cahill et al., 2012; Trautz et al., 2013; Jones et al., 2014; Lassen et al., 2015; Yang et al., 2015), natural analog studies (Lewicki et al., 2006; Keating et al., 2009; Keating et al., 2014a); and numerical studies (Wang and Jaffe, 2004; Wilkin and Digiulio, 2010; Carroll et al., 2009; Siirila, et al. 2012; Carroll et al., 2014; Zheng et al., 2015). The understanding gained from these studies about the key physical and geochemical processes controlling CO_2/brine/shallow groundwater interactions has been integrated into a suite of science-based simulation tools developed by the DOE National Risk Assessment Partnership (NRAP; www.netldoe.gov/nrap). The primary intended use of these tools is probabilistic risk assessment for CO_2 sequestration (Viswanathan et al., 2008; Stauffer et al.,2011; Pawar et al., 2013); in these types of applications computational efficiency is extremely important because of the inherent uncertainty of subsurface and leakage parameters needed to be account for to assess the long-term performance of CO2 storage sites. For this reason, reduced-order models (ROM) were developed from a large ensemble of detailed reactive-transport simulations. The simulations, supporting datasets, and ROM derivation have been described in detail elsewhere (Carroll et al. 2014; Dai et al., 2014; Bacon et al., 2014; a., 2015) and will only be briefly summarized here.

Our primary goal in this paper is to examine a range of possible applications for the groundwater impact component of the risk assessment tool, to identify contexts in which useful and reliable information can be extracted, and to identify contexts in which existing tools should not be applied. These example applications are hypothetical and the specific conclusions drawn in each case cannot be generalized. However, the process we demonstrate for applying aquifer impact models to support decisions is novel and could be widely applicable at CO2 sequestration sites. A related goal of this study is to determine whether the existing aquifer impact models are sufficiently generic that they could be applied to new sequestration sites. Using previously published water quality data from a wide variety of drinking water aquifers (DeSimone, 2009) we propose guidelines for the transferability of existing NRAP models to new sites.

A large ensemble of detailed reactive-transport simulations were developed to predict the migration of CO_2 and brine within shallow aquifers, in response to a point source leak at the base of the aquifer. These ROMs couple hydrologic and geochemical uncertainty and predicted plume volumes ranging in size from 10^3 – 10^9 cubic meters. In this paper we do not address the accuracy of the underlying simulations. This is a complex topic in its own right, in part because simulations of CO_2-induced plumes of this size cannot be 'tested' or validated against field data in the classic sense. This is a consequence of the fact that, to our knowledge, large CO_2 plumes in shallow aquifers have only been observed at natural analogs (Evans et al., 2002; Frederico et al., 2004; Keating et al., 2009; Keating et al., 2014a), where many uncontrolled factors play an important role.

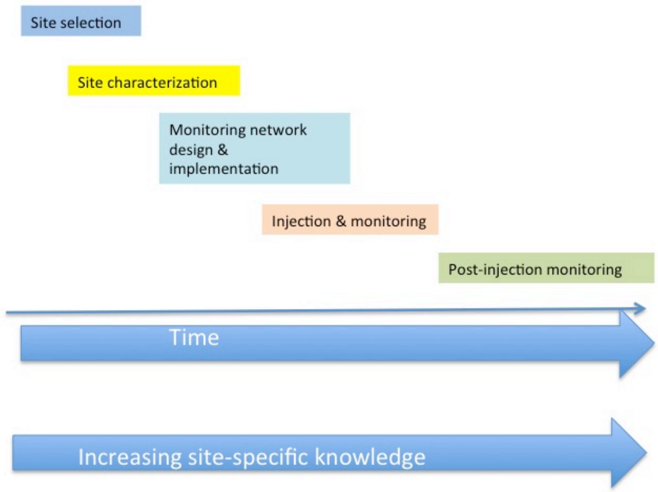

Figure 1. Time line of activities during a CO2 injection project

A conceptual lifespan of a CO_2 sequestration project is illustrated in Figure 1. In this paper, we propose four contexts where groundwater impact ROMs could be applied: 1) selecting between one or more potential sites by comparing aquifer vulnerability to leaks, 2) prioritizing characterization activities at a single site, 3) evaluation/design of a monitoring network for plume leakage detection, or 4) estimating possible impacts to human health. The first three examples correspond to the first three project stages shown in Figure 1. The last example, assessing potential impacts to human health, could be used as part of a comprehensive risk assessment that could occur early in the project and then be updated as injection proceeds. All of these example applications acknowledge uncertainty in both CO_2/brine leak rates and aquifer characteristics. This is important, given that uncertainty will exist at all stages of a project, and could be particularly large at early stages. .

2. Reduced Order Models

2.1. Development and Functionality

The NRAP aquifer impact ROMs predict the size of plumes in shallow aquifers caused by point-source CO_2 and/or brine leaks introduced at the base of the aquifer. A leak can be defined as one or more discreet point sources (e.g. leaky wellbores), or as continuous features such as a fractures or faults. The size of plumes were calculated using two alternative definitions of 'impact': one metric is defined as exceedance of a drinking water standard or maximum contaminant level (MCL), and the second metric is defined as being above and beyond the 'natural background variability' in the aquifer (Last et al., 2013). The latter definition is aligned with the proposed EPA Class VI Rule for CO_2 injection well permitting (http://water.epa.gov/type/groundwater/uic/wells sequestration.cfm) and is referred to as the 'no-impact' criterion in this paper. Nine water quality metrics are considered: pH, TDS, four trace metals (As, Ba, Cd, Pb), and three organic compounds (benzene, naphthalene, and phenol). Plume volumes are calculated for each water quality metric as the volume of aquifer that exceeds the 'impact' criterion for that metric. The presumption is that trace metals can be transported into the aquifer as dissolved ions in the brine and can also be released (or adsorbed) by aquifer minerals. An important mechanism for trace metal release in the aquifer is pH-depression caused by CO_2 dissolution into the groundwater.

Although the exact details of water quality changes due to CO_2 leakage will be site-specific, it is possible that aquifers with similar hydrologic and geochemical features will respond in similar ways. To begin to explore this issue, two sets of ROMs were developed for two very different classes of aquifers: confined alluvial sandstones and unconfined carbonates. Each set is comprised of 18 ROMs (9 water quality metrics, each measured according to one of the two threshold values described above). To represent the confined alluvium aquifer class a portion of the High Plains aquifer (Kansas/Nebraska, USA) was selected. For the carbonate class, an unconfined portion of the Edwards aquifer (Texas, USA) was selected. These two aquifers were chosen because there was ample site-specific information available for constructing reactive-transport simulations and also because these share characteristics of many other aquifers in the U.S. currently used for drinking water supply. Addressing the broader applicability of the resulting ROMs to other sites is one goal of this paper.

For each reactive-transport model, reaction networks were developed appropriate to the site-specific lithologies. In the unconfined alluvium aquifer model, based on datasets from the High Plains aquifer, a series of sorption reactions to goethite, and kaolinite, illite, and montmorillonite were applied. The adjustable parameters include the volume percent of each phase and the cation exchange capacity for the clay minerals (Swedlund et al., 2009; Dixit and Hering, 2003; Gu and Evans, 2007, 2008; Gu et al., 2010; Goldberg, 2002). The unconfined carbonate aquifer model, based on data from a portion of the Edwards aquifer, assumed that trace metal chemistry was controlled by surface complexation reaction with calcite (van Cappellen et al., 1993; Pokrovsky & Schott, 2002; Sø et al., 2008). The model has two types of surface sites, $>Ca^+$ and $>CO_3^-$, each with a density of 8.22 mol/m^2. Cations are assumed to sorb to the $>CO_3^-$ sites, and anions to the $>Ca^+$ sites.

It was assumed that the only source of organic compounds is the leaking brine. As shown in Figure 2, the inputs to the ROMs are time-varying CO_2 and brine leak rates and static aquifer characteristics (one example shown). The fidelity of the ROMs to the simulation dataset from which they were derived has been discussed in Bacon et al. (2014), Carroll et al., 2014 and Keating et al. (2015).

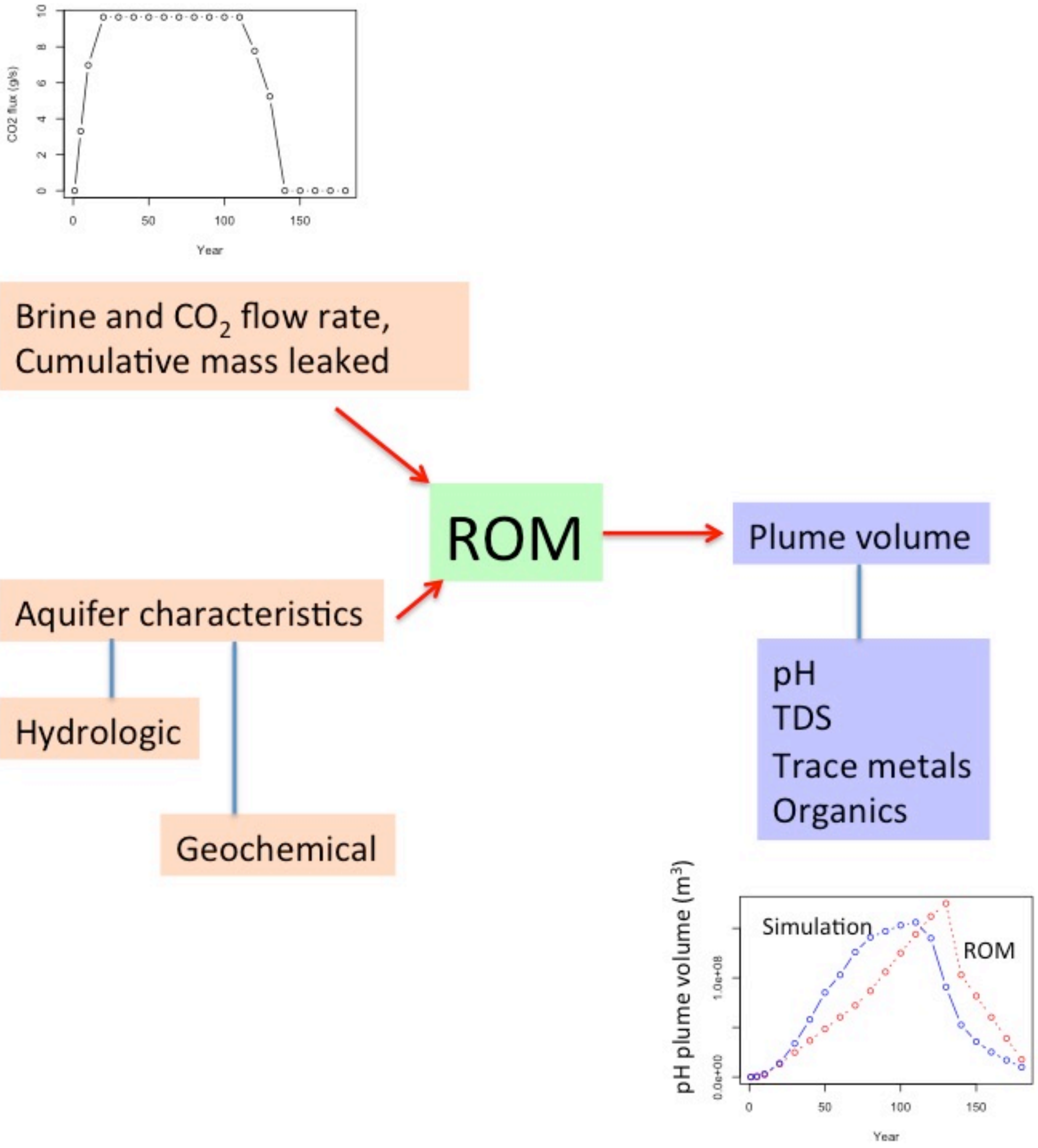

Figure 2. Reduced order model inputs and outputs

The ‘unconfined carbonate’ and ‘confined alluvium’ ROMs have 19 and 35 input parameters, respectively. Most of the parameters describe hydrogeologic and geochemical characteristics of the aquifer; a smaller number are related to the leaking CO_2/brine. The parameters and their acceptable input ranges are listed in Table 1.

2.2. Applicability to other aquifers

Part of the motivation for including adjustable input parameters was so that these ROMs could be applied to aquifers with different hydrogeologic or geochemical characteristics than the High Plains (HP) or Edwards aquifer (EA). For example, the carbonate ROM is designed to accept background hydrologic gradients ranging between .00028 and .02 m/m and aquifer thicknesses up to 500m, even though the unconfined portion of the Edwards aquifer has a very low background hydraulic gradient .000765 m/m and is approximately 150m thick. In principle, this generality could allow the ROM to be applied broadly to other aquifers. Many aquifers in the US have characteristics falling within the parameter ranges shown in Table 1. However, there are some aspects of the models from which the ROMs were derived that are intrinsic and non-adjustable. These less obvious factors should be considered when deciding whether to apply existing ROMs to a new site, or whether to build a new site-specific ROM. These include: background groundwater chemistry (both average values and variability), geochemical reactions affecting the transport of trace metals and organics, the type of permeability heterogeneity, and the nature of the upper boundary (closed or open). If an aquifer overlying a proposed CO_2 sequestration site was substantially different than the High Plains or Edwards Aquifer in one of these intrinsic characteristics, these ROMs should only be applied with caution or not at all. We discuss each of these factors in more detail below and conclude the section with recommendations for transferability of the aquifer impact models to new sites.

2.2.1. Background water chemistry

The reactive-transport simulations underlying the ROM development were designed so that simulated pre-leak groundwater chemistry matched background conditions reported for High Plains and the urban unconfined portion of the Edwards Aquifer (Carroll et al., 2014; Last et al., 2013). Other aquifers may have distinct pre-leak water quality parameters; at present there is no way to adjust for this fact using ROM input parameters. Additionally, the criterion for 'change beyond 95% threshold' was established using site-specific water quality data from the two sites (Last et al., 2013). Again, at present there is no way to adjust for this fact using ROM input parameters. If the 95% threshold of background water quality variability for a site is quite different than the High Plains and Edwards

Aquifer, then either the MCL threshold should be used or a site-specific ROM should be developed.

Data collected as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) can be used to provide some indication of how the water chemistry in the two NRAP aquifers compares to other major aquifers in the US. Water samples were collected during 1991–2004 from domestic wells (private wells used for household drinking water) for analysis of drinking-water contaminants, where contaminants are considered, as defined by the Safe Drinking Water Act, to be all substances in water. Physical properties and the concentrations of major ions, trace elements, nutrients, radon, and organic compounds (pesticides and volatile organic compounds) were measured in 2,167 wells. The wells were located within major hydrogeologic settings of 30 regionally extensive aquifers used for water supply in the United States. One sample was collected from each well prior to any in-home treatment. Concentrations were compared to water-quality benchmarks for human health, either U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) for public water supplies or USGS Health-Based Screening Levels (HBSLs) (DeSimone, 2009).

Measurements of pH, TDS and selected trace metals and organic compounds for 8 aquifers were compared to the High Plains and Edwards aquifers considered in the NRAP studies. The pH, TDS, and relevant trace metal data are presented in Figures 3 – 5. Abbreviations for the aquifer names are listed in **Table 3**. In general, if an aquifer's median and 90th percentile values (10th percentile for pH) reported in DeSimone (2009) are similar to the EA or HP sites then the no-impact threshold ROMs might be applicable. Alternatively, if the 90th percentile values are quite different than the EA or HP sites, then only the MCL-based ROMs should be considered.

The aquifers have median pH values ranging from 6.8 to 8.1 (Figure 3). Most have median values within 0.5 pH units of either the HP or EA sites. Two aquifers (CL and NEx) have substantially lower 10th percentiles than either the EA or HP sites and thus would be poor candidates to apply the existing no-impact threshold ROMs. Likewise, many of the aquifers have similar median TDS values to the HP and EA sites, although one aquifer (LT) has much higher TDS and so the existing ROMs that predict the size of TDS plumes would clearly not be applicable at that site. There are significant differences in background levels of trace metals amongst all the aquifer (see Figure 4, note log scale of vertical axis). For this reason, the 'no-impact' trace metal ROMs are probably the least transferrable of any of the existing ROMs.

Although the MCL-based ROMs are likely to be more widely transferrable to other sites, it is interesting to note that several of the aquifers have 90th percentile values in violation of drinking water standards for pH, TDS, and arsenic. With regard to pH, two aquifers have 10th percentile values that are less than the regulatory limit of 6.5: the Coastal Lowlands sand aquifer (5.1) and New England crystalline-rock aquifer (5.9). For TDS, one aquifer (LT) has a median TDS value exceeding the secondary regulatory limit of 500 mg/L (Figure 4). Many have 90th percentile values above the TDS limit, with some above 1000 mg/L (High Plains, Basin and Range, Lower Tertiary). All of the aquifers have median arsenic concentrations less than the regulatory limit of 10 µg/L (Figure 5), but many have 90th percentile values above the regulatory limit (Basin and Range sand and gravel, Central glacial sand and gravel, Mississippian sandstone and carbonate, Snake River Plain basaltic and New England crystalline).

Background concentrations of barium, cadmium, lead, and all three organics compounds tend to be quite low in all the aquifers. All of the aquifers have median and 90th percentile barium concentrations below the regulatory limit of 2000 µg/L (most aquifers have undetectable levels of cadmium so these data were not plotted and so the 90th percentile values are set to the detection limit). All of the aquifers have very low median concentrations of lead and most have 90th percentile concentrations of less than 1 µg/L, well below the regulatory limit of 15 µg/L.

Only summary data for benzene, naphthalene and phenol were provided in DeSimone (2009). Benzene was detected (> 0.2 µg/L) in 2 out of 1,948 samples. Naphthalene was detected (> 0.2 µg/L) in 2 out of 1,928 samples. Phenol was not detected (> 0.2 µg/L) in any of the 919 samples. This indicates that these organic compounds are not normally present in drinking water aquifers, except due to contamination.

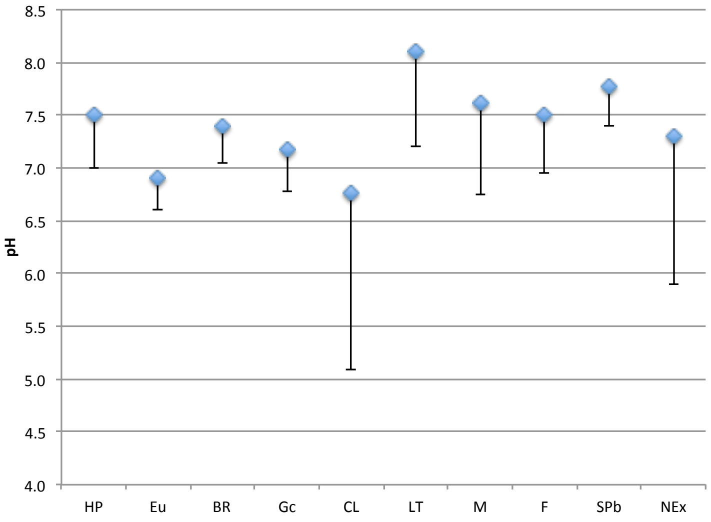

Figure 3. Comparison of background values of pH for the High Plains aquifer and shallow, urban unconfined portion of the Edwards aquifer used in NRAP studies

with ranges for various aquifer types in the United States. Symbols represent median value and error bars the 10th percentile. See Table 3 for Aquifer names.

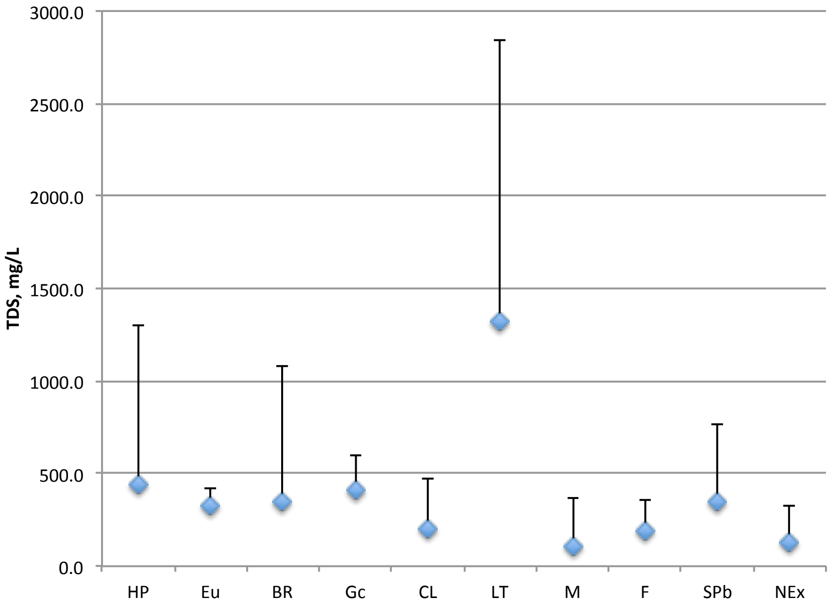

Figure 4. Comparison of background values of TDS for the High Plains aquifer and shallow, urban unconfined portion of the Edwards aquifer used in NRAP studies with ranges for various aquifer types in the United States. Symbols represent median value and error bars the 90th percentile. See Table 3 for Aquifer names.

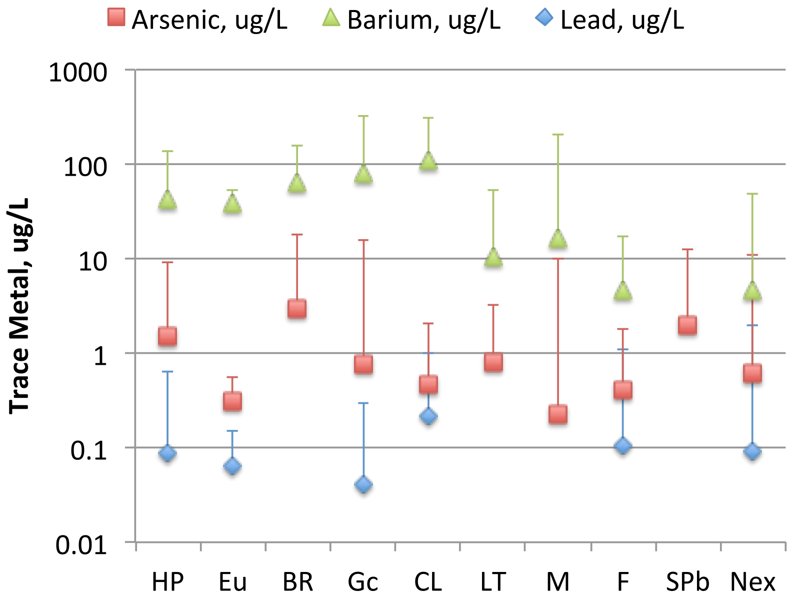

Figure 5. Comparison of background values of arsenic, barium and lead for the High Plains aquifer and shallow, urban unconfined portion of the Edwards aquifer used in NRAP studies with ranges for various aquifer types in the United States.

Symbols represent median value and error bars the 90th percentile. See Table 3 for Aquifer names.

2.2.2. Geochemical reaction network.

The most important reactions to consider when predicting the impact of CO_2/brine on pH and TDS in aquifers containing even small amounts of calcite are aqueous bicarbonate speciation reactions and calcite precipitation/dissolution. This is primarily because these reactions control pH buffering. Also, if the threshold for TDS is relatively low, as it is for the Edwards Aquifer, even small amounts of calcite dissolution can cause TDS to rise above the impact threshold. Since both sets of the NRAP ROMs include aqueous bicarbonate speciation reactions and calcite precipitation/ dissolution, the reaction network limitation should not limit broad applicability of the pH and TDS ROMs to other aquifers. The trace metals and organics ROMs, however, should only be applied to aquifers that have similar mineralogy and redox conditions.

2.2.3. Permeability heterogeneity and confinement

Both sets of the NRAP ROMs were based on geostatistical models of heterogeneity that are widely used for many types of aquifers (for examples, see Koltermann and Gorelick, 1996). These models can be adapted to new aquifers by adjusting the appropriate ROM input parameters (e.g. correlation length). The alluvium ROM utilized a two-facies (sand/clay) indicator model that is appropriate for alluvial/sedimentary aquifers. The gaussian model used for the carbonate ROM is not specific to any one type of lithology, however, it would be inappropriate for aquifers with large-scale, coherent structures such as faults, channels, and dissolution networks. If the aquifer has specific and important structural features at scales similar to expected plume sizes, and spatially-explicit plume predictions are desired, a site-specific model will have to be constructed.

2.2.4. Recommendations

The pH and TDS ROMs should be applicable to aquifers that satisfy the following criteria. First, their hydrologic characteristics should fit within the parameter ranges listed in Table 1. Second, there should be at least minor (secondary) calcite present in the aquifer. We expect that most aquifers will meet these two criteria.

For no-impact ROMs, a third criterion would be that the initial chemistry and threshold values defining 'impact' be similar to the values listed in Table 2. We expect this to be a relatively difficult criterion to meet. Nevertheless, depending on the specific differences between the new aquifer and the values in Table 2 the no-impact ROMs may be useful as conservative or 'worst case' estimates. A more suitable metric, especially in the absence of suitable characterization of the ground water chemistry, would be to use the MCL thresholds. The MCL thresholds are tied to health impacts and are independent of aquifer specifics.

For pH and TDS, we offer the following guidelines for which of the two sets of ROMs to apply. The confined alluvium ROMs are appropriate if the two-facies type of lithology is thought to control heterogeneity, and aquifer thickness and background hydrologic gradients are similar to the High Plains aquifer (Carroll et al., 2014; Table 1). The unconfined carbonate ROMs are preferable if a Gaussian model of heterogeneity is appropriate for a site, or if the lateral background gradient and/or aquifer thickness differs substantially from the confined alluvium model (240m, .003 m/m).

The trace metal ROMs will be applicable under a more limited set of circumstances. The first criterion is that there be significant amounts of trace metals either in aquifer minerals or surface sites or in the reservoir brine. The second criterion is that the mineralogy and redox conditions of the aquifer be similar to either the High Plains or Edwards aquifer.

The organic ROMs will be applicable only if these organics are present in the reservoir brine.

3. Potential contexts for ROM Application

This section presents conceptual examples of four project activities that could be supported by a ROM-based analysis. The first example is site selection. This activity would benefit from applying the ROMs to each site under consideration, to get a general understanding of the relative vulnerability of the overlying aquifers to potential CO_2 leaks. Once a site has been selected, site-characterization activities would begin. As shown in the second example, a site characterization program could benefit from applying the ROMs to determine which type of data collection would be the most beneficial to risk reduction. As the project matures and more data is collected, this process could be repeated to refine risk estimates and prioritize further data collection. The third example relates to monitoring groundwater for leak detection. At all stages in the project (before, during, and post-injection) ROM application could be used to evaluate the effectiveness of a well network for leak detection. The final example discusses the relationship between aquifer impacts and risks to human health.

In each of these examples for the purpose of simplicity we use a simple heuristic model for point source CO_2/brine leakage at the base of the aquifer, coupled to one or both sets of the NRAP Aquifer Impact ROMs. In a real project, these ROMs might be applicable to the new site(s), or alternatively new site-specific ROMs would need to be developed (see Section 2.2 for guidelines). A more comprehensive risk assessment considering all parts of the system (reservoir, leakage pathways, receptors) could be conducted using the NRAP Integrated Assessment Model (Pawar et al, 2014; https://edx.netl.doe.gov/nrap), which includes these Aquifer Impact ROMs as one of many components.

In the first three examples, we apply the set of ROMs that define an impact plume as the volume of water with a concentration change outside the range of natural background variability. This is the most stringent definition of 'impact', aligns with current EPA guidelines for Class VI well permitting, but does not necessarily imply risk to human health. In the fourth example, we apply the set of ROMs that define impact plume as the volume of water in exceedance of an MCL (maximum contaminant level). This definition of impact is directly related to drinking water safety and possible human health impacts.

Example1: Site Selection

A CO_2 sequestration site will have to meet a large number of criteria. From a risk perspective, one key criterion will be evidence of robust seals above the reservoir and thus very low probability of a CO_2 leak. Even if this criterion is met, however, a site might be even more attractive if it could be shown that the water quality in overlying aquifers would be resilient to leaks if they were to occur. In other words, perhaps leaks will have low probability *and* low consequence on groundwater quality. In this example, we envision a situation where two sites are being considered, each with a shallow aquifer above the reservoir. The following question is asked: which aquifer would be more impacted by a CO_2 leak?

The size of the pH 'impact' plume is a good proxy for aquifer vulnerability to CO_2 leaks. This is because pH change may, in some aquifer types, cause the release of toxic trace metals into groundwater. For the purpose of illustration, we conducted a Monte Carlo analysis of a large number of leakage scenarios using the two sets of NRAP aquifer ROMs. The distribution of CO_2 leak magnitudes considered is shown in Figure 6a. Each ROM was parameterized using a single set of 'best guess' aquifer parameters, derived from published reports on the High Plains aquifer and an unconfined portion of the Edward's aquifer (See values listed in Column 'Ex1' in Table 1). We use the 95% threshold criterion to define pH 'impact', following the

EPA Class VI guidance. It is important to note that when using this criterion, even if two aquifers have the identical geochemical response to a CO_2 leak, the aquifer with lower background variability may contain a larger pH 'impact' plume.

The resulting cumulative distribution functions of pH plumes for the two sites (all times) are shown in Figure 6.

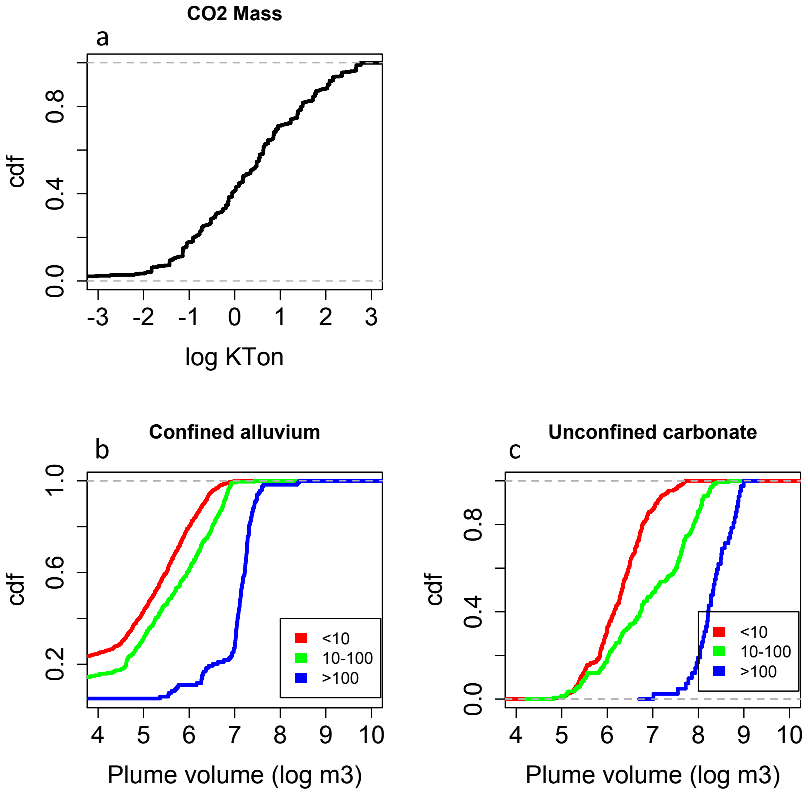

Figure 6 Variation in pH plume volumes resulting from uncertainty in CO2 leakage scenarios. a) CO2 Mass leaked b) High Plains aquifer ROM variation, binned by CO2 mass, c) Edwards aquifer ROM variation, binned by CO2 mass.

The results were binned into three categories of leaks: < 10 Mton, 10 – 100 Mton, and > 100 Mton. The 'confined alluvium' aquifer ROM predicts a fairly narrow range of plume sizes. For small leaks (< 10 kTon) the plumes are very small (95% < 3 x 10^6 m^3). There are relatively small differences between plumes for different leak magnitudes. The 'unconfined carbonate' ROM predicts more variability and larger differences between various leak magnitudes. All other things being equal, it could be said that of these two sites, the unconfined carbonate aquifer is potentially more vulnerable to CO_2 leaks. The reasons for this are complex. Neither of the two most obvious differences between the sites (lithology and degree of confinement) can explain the difference. Lithology is not producing the difference because both aquifers include sufficient calcite to buffer pH changes. As noted in Bacon et al. (2014) the unconfined character of the aquifer tends to *reduce* plume size, not increase it. Therefore, degree of confinement is not a plausible mechanism to explain the differences. Differences between the initial conditions and impact thresholds for pH at the two sites (Table 2) may be the cause of the apparent vulnerability of the 'unconfined carbonate' aquifer. The change in [H+] required to satisfy the 'pH impact' threshold for the 'confined alluvium' aquifer is approximately twice that for the 'unconfined carbonate'. In other words, the volume of water considered to be measurably impacted could be controlled more by background variability than by aquifer hydrology or lithology.

3.1. Example 2: Prioritizing site characterization studies

After a site has been selected it may be necessary to conduct a quantitative probabilistic risk assessment (RA). If the preliminary risk assessment reveals unacceptably high uncertainty, characterization activities may be proposed to reduce uncertainty. Site characterization can be very expensive and so establishing priorities will be essential. One approach to establishing priorities would be to conduct a sensitivity analyses, using ROMs, to determine which input parameters have the most effect on CO_2 impacts. The most sensitive parameters would become high priority for site-characterization. This method would not consider other risks related to the sequestration reservoir, atmosphere, or economic risks. Those types of analyses could only be accomplished using a higher level RA model (e.g. Pawar et al., 2013).

We conducted a global sensitivity study on the two sets of aquifer ROMs using the "extended-FAST" method (Saltelli et al., 1999) as implemented in the R Code, Sensitivity Package (Pujol et al., 2015). This method allows the estimation of first order and total Sobol indices for each model parameter. These indices are defined as the proportion of total variance that any one parameter explains. For the unconfined carbonate ROM, the analysis varied all 19 parameters and required 19,000 model runs. This was easily achieved within a few seconds, due to the computational efficiency of the ROMs. The confined alluvium ROM analysis required 35,000 model runs. Importantly, in this example we simultaneously consider uncertainty in both leakage rates and in aquifer characteristics, rather than analyzing these two types of uncertainty separately. This approach should reveal which type of uncertainty reduction would most effectively reduce risk.

Here we present results for the pH and TDS ROMs. For the unconfined carbonate aquifer pH plume ROM (Figure 7) there is virtually no sensitivity to any aquifer-specific parameter.

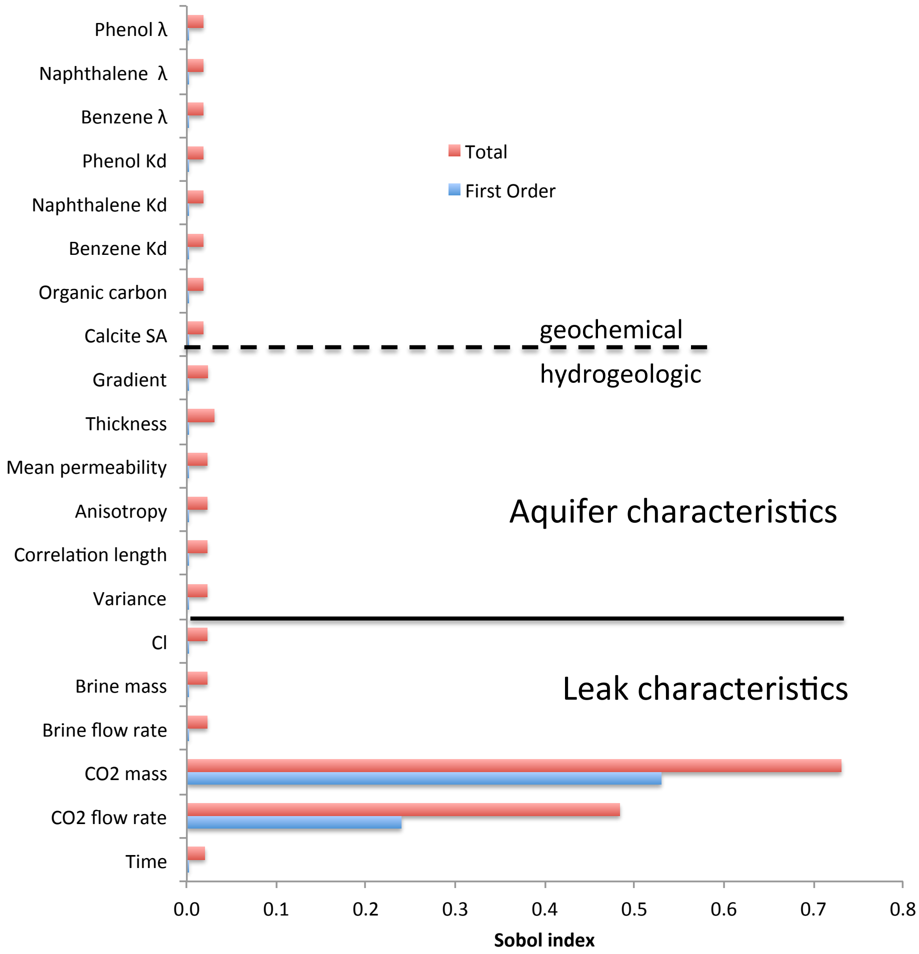

Figure 7. Sensitivity results for unconfined carbonate, pH plumes

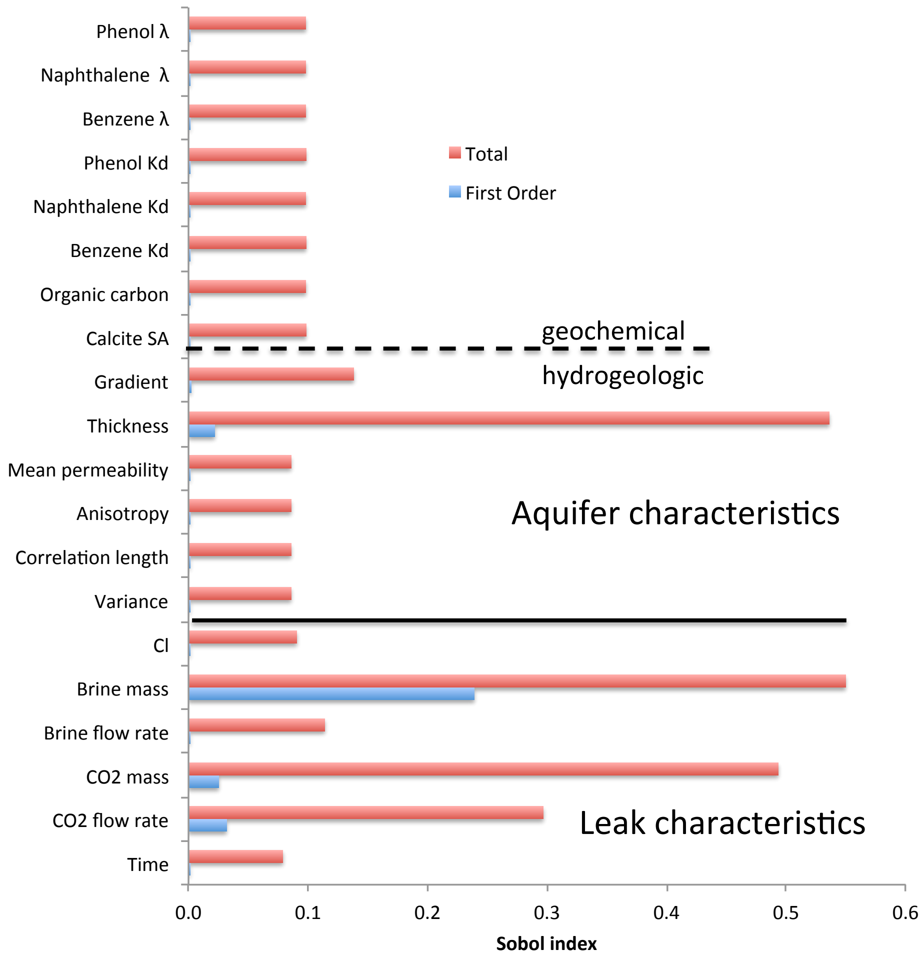

Figure 8. Sensitivity results for unconfined carbonate, TDS plumes

Sensitivities are dominated by CO_2 leak rates. The TDS ROM (Figure 8) shows similar behavior, although one aquifer-specific parameter (thickness) does show a significant impact. The implication here is that focusing on improved estimates of potential leak scenarios at a site will have more benefit to uncertainty reduction than collecting data on aquifer hydrology or geochemistry.

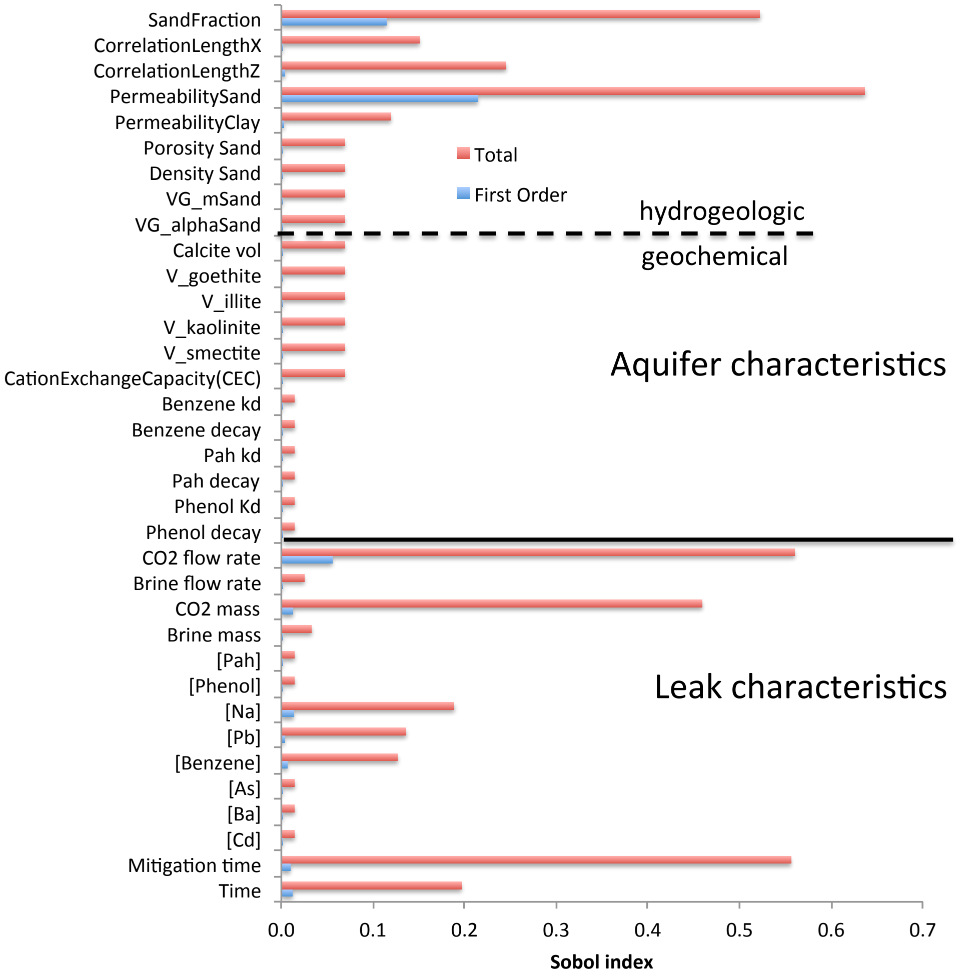

Figure 9. Sensitivity results for confined sandstone, pH plumes

The sensitivity analysis shows slightly different results for the confined alluvial ROM (Figure 9 and Figure 10). Again, sensitivities to leak rate are quite large, but some hydrologic parameters for the aquifer are important, too. Like the unconfined carbonate aquifer ROM, this ROM shows very low sensitivity to geochemical parameters. The parameter 'time' shows fairly large total sensitivity (red bar) but very low first-order sensitivity (blue bar). This sensitivity may be due to the co-variation of time and flow rates in the leakage scenarios used to build the simulations and the ROMs.

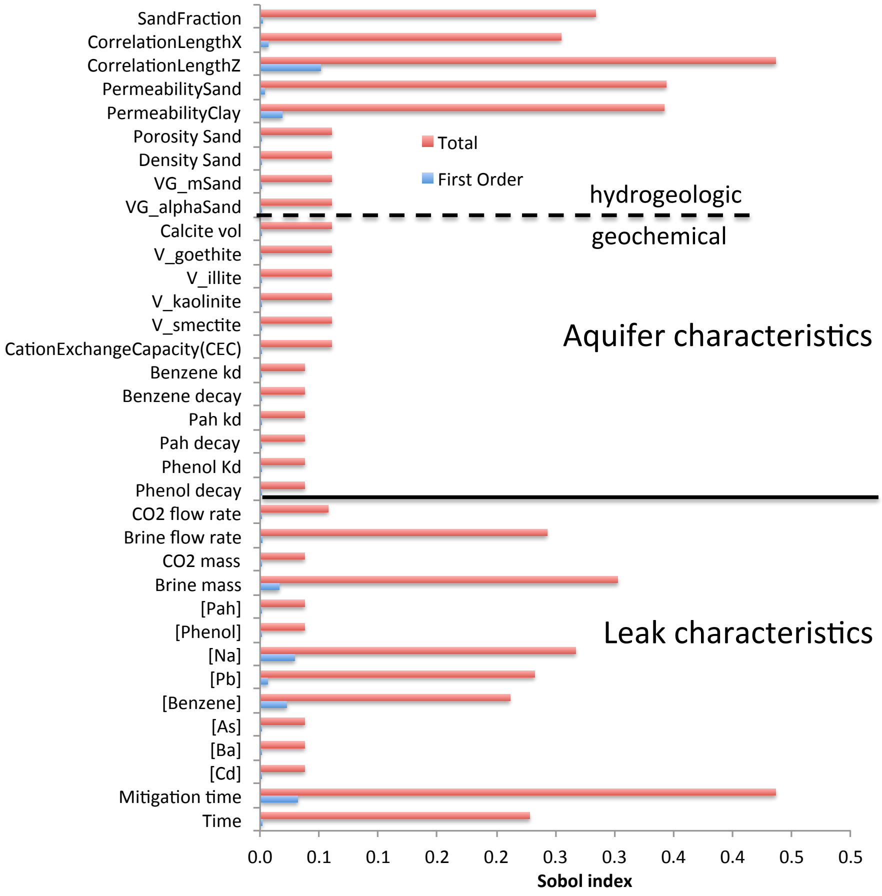

Figure 10. Sensitivity results for confined sandstone, TDS plumes

If a much smaller range of leak rates had been considered, it is possible that the aquifer parameters would have made a larger impact. To explore this issue, we repeated the sensitivity analysis for the unconfined carbonate, holding all leak rate parameters constant and varying only the aquifer parameters. In this case, one aquifer parameter (hydraulic gradient) dominated the sensitivity. This particular result is not transferrable; each site would have its own range of uncertainty for each aquifer parameter and hence a unique sensitivity analysis result. This process, however, should be broadly applicable.

3.2. Example 3: Evaluation and design of a monitoring network for plume detection

Design of cost-effective monitoring strategies in the shallow aquifer will require at least approximate predictions of groundwater impacts for a variety of leakage scenarios. Point-measurement-based monitoring strategies will only be able to detect CO2 and/or brine plumes larger than average well spacing. Questions such as ‘What is the smallest leak that this monitoring network will be able to detect?’ and ‘What is the expected detection efficiency of this network ?’ are likely to be

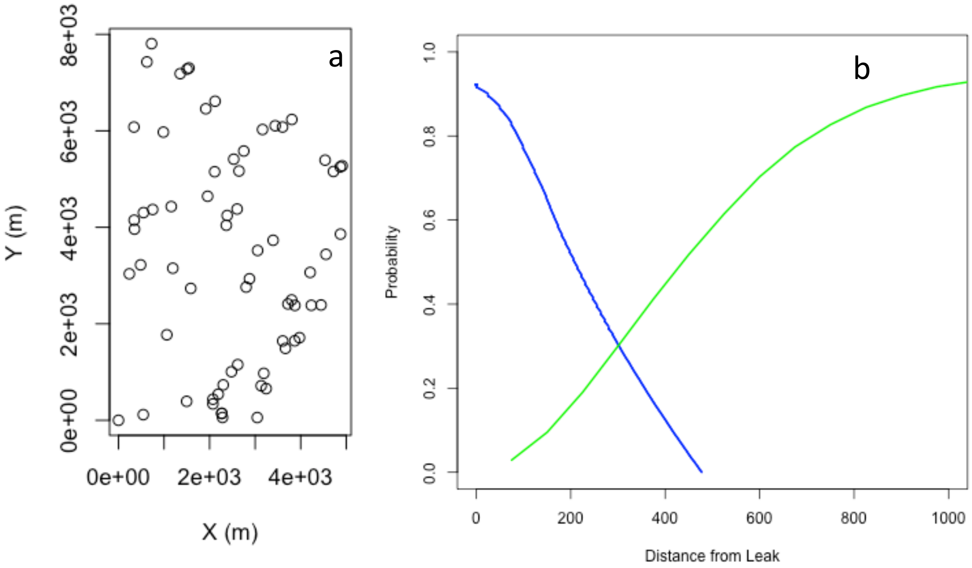

Figure 11. Probability of detection calculation for a) well network (see Carroll et al., 2014) b) for a random point-source leak, where the probability at least one well

will be present a given distance from the leak (green line), and the probability there will be a detectable pH plume a given distance from the leak (blue line).

asked. Here we discuss the applicability of ROMs to these types of questions.

Of the nine water quality parameters the NRAP ROMs predict, we expect pH and TDS to be the most useful for plume detection for the following reasons. In the case of CO_2 leak detection, the pH plume will be equal to or larger than any CO_2-induced trace element plumes, and therefore easier to detect. Also pH monitoring will be less costly than trace element monitoring. Similarly in the case of brine leak detection, non-reactive major elements in the brine should be more easily detected at less cost than reactive trace elements or organics.

By varying all the leakage parameters for the unconfined carbonate aquifer ROM randomly we obtain a cumulative distribution function of plume length (blue line in Figure 11b). For a given a monitoring well network, an approximation to detection probability can be calculated easily(for details see Keating et al., 2014b). The blue line in Figure 11b can be interpreted as the probability a detectible pH change will occur, as a function of distance from the leak source. If a specific monitoring well network is proposed (e.g. Figure 11a), the probability a well will be encountered a given radial distance from any random location within the site (green line in Figure 11b). For this example, the proposed monitoring network has a very low probability of detection. To have at least a 50% chance of encountering the plume, the well would need to be within ~200 m of the leak. For the well network considered here, there is a very low chance of a well being present at that distance (< 20 %).

3.3. Example 4: Evaluating potential for health impacts from arsenic

The U.S. Environmental Protection Agency has set a maximum contaminant level (MCL) for arsenic in groundwater at 10 µg/L. Possible long term health consequences of drinking water in excess of the MCL include skin damage, circulatory system problems, and increased cancer risk (U.S. EPA, 2015). For these reasons it is important to understand the likelihood that As concentrations would exceed the MCL if CO_2 or brine would leak into a USDW. The chemistry controlling arsenic concentrations in both the alluvial and unconfined aquifer models is described in section 2.1. Figures 12 and 13 show the leakage scenarios and the aquifer response in terms of the effected pH, TDS, and As plume volumes over time. Both the CO_2 and brine fluxes achieve a maximum value within the first 50 years or so, and then drop back to much lower steady-state fluxes for the remained of the 200 year emulation. The leakage profiles attempt to capture the concept that risk to leakage is greatest during the injection phase when pressures are high. CO_2

maintains maximum fluxes for longer periods due to its buoyancy even in the absence of elevated pressure.

Arsenic plume volumes do not equate with the size of the pH or TDS plumes. Maximum As plumes are 10 and 100,000 times smaller than the pH plumes for the alluvium and carbonate aquifers, at least measured against a MCL threshold. Although smaller, the duration of the As plume should be similar to the pH plume for the alluvium aquifer, because the sorption reactions depend on solution pH. This is not the case for carbonate aquifer, where the arsenic plume falls below the threshold and the pH plume continues to rise. This difference most likely reflects more acid conditions at early time periods, a greater amount of calcite dissolution, and less arsenic uptake on the calcite surfaces for the carbonate aquifer system.

At a specific site, the predictions of volumes of water exceeding the As MCL threshold shown in Figure 13 could be compared to the density of drinking water receptors to calculate the probability of exposure. Also, the timing of water quality changes predicted by the models could be used to inform mitigation plans.

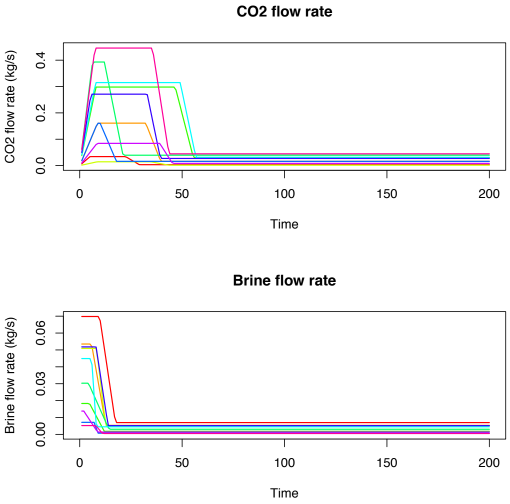

Figure 12. Selected CO_2 and brine leakage rates into the aquifer.

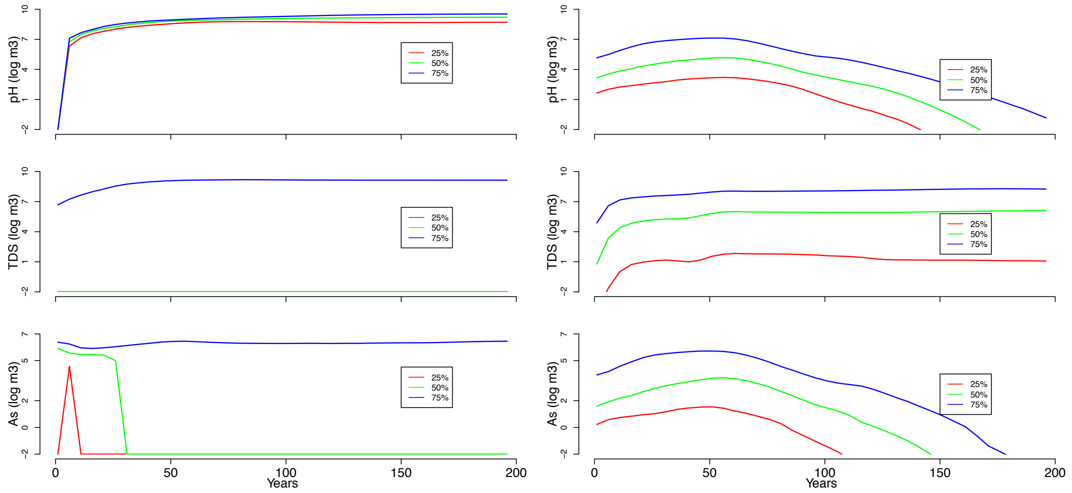

Figure 13. Groundwater volume (log m^3) impacted by changes in pH, TDS and arsenic beyond the MCL thresholds for the a) carbonate aquifer and b) alluvium aquifer. The three lines indicate the 25,50, and 75th percentiles derived from the Monte Carlo analysis.

4. Conclusions

The aquifer impact ROMs developed by NRAP (Carroll et al., 2014, Bacon et al., 2014) are computationally efficient and thus well-suited to uncertainty analysis and risk assessment. Here we have shown that these ROMs, or similar models that could be developed for new sites, could be useful in supporting several types of decisions throughout the stages of a CO_2 sequestration project. We have presented a process that could be followed to utilize the ROMs to support site screening, to prioritize site characterization activities, to evaluate plume detectability by groundwater monitoring, and to estimate impacts on human health. Although the specific conclusions would vary from site to site, the process we illustrated using these examples could, in principal, be applied to any new site. In each of these examples, it is assumed that potential leak rates into the aquifer are highly uncertain, which is a conservative assumption. In none of these cases would the ROM-based analysis alone be sufficient to make these complex decisions. Nevertheless, these types of analyses could provide useful information that would be difficult to obtain with any other methods.

The NRAP ROMs are capable of predicting groundwater impacts as defined by a number of water quality metrics (pH, TDS, trace metals, and organic compounds). In this study we have developed criteria that should be applied when deciding whether or not existing ROMs might be applicable to a new site, and, if so, which water quality metrics might be most useful. For applications related to leakage detection and monitoring, the pH and TDS ROMs should be the most useful. In these cases, the 'no impact' threshold should be used, since it is specifically targeted at questions of detectability given natural variability in water quality. Risk assessment and site selection applications, on the other hand, may benefit from analyses using all the water quality metrics. For those applications, either the 'no impact' threshold or the MCL threshold would be useful.

Data from two specific aquifers were used to inform development of the two sets of NRAP groundwater impacts ROMs. However, the ROMs allow input variables to vary over wide ranges and so, in principle, they could be applied to other aquifers by adjusting input parameters appropriately. Two aspects that should be considered when deciding if these ROMs could be applied to a new site include 1) similarity of the new site to the aquifers used to develop the NRAP ROMs, and 2) level of accuracy expected from the ROM. In early stages of a project when site-specific data is sparse the expected level of accuracy should be low to moderate. Even under these conditions, an uncertainty and sensitivity analysis using one of these ROMs could help to inform data collection and monitoring design decisions.

Of all the water quality metrics, we expect the trace metal ROMs to be the most site specific and difficult to apply at new sites using input parameter adjustments. Only if the mineralogy / geochemistry at a new site is similar to that of the High Plains aquifer or the Edwards aquifer could these trace metal ROMs be applied. The pH and TDS ROMs are, in a sense, more generic and could be used at new sites under some circumstances. Aquifers (whether carbonate or sedimentary) with at least some calcite present should respond to leaks in similar ways as these ROMs predict. However, the background water chemistry at the site (mean and variability) should be carefully compared to the values used to develop the NRAP ROMs (Table 1, Figures 3 and 4). All other factors being equal, a site with larger background variability than the values assumed for the two sites studied by NRAP will have smaller impact plumes than the NRAP ROMs predict.

There will certainly be cases where the existing NRAP ROMs will have no applicability. One example would be an aquifer that contains no soluble minerals such as calcite to buffer the impact of CO_2. In these cases, new simulations will need to be developed and, if probabilistic risk assessment is required then perhaps efficient ROMs will be derived. The methods presented in this paper and elsewhere (Carroll, 2014; Bacon, 2014, Dai, 2014) should provide a useful roadmap for the process.

5. Acknowledgements

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Table 1. ROM input parameters and their ranges. The values used for Example 1 are shown in the column labeled 'Ex 1'.

Confined/alluvium ROM

Parameter	Min	Max	Ex 1	Units
Aquifer parameters: hydrogologic				
Sand fraction	0.35	0.65	0.5	-

Permeability correlation length (x)	200	2500	1000	m
Permeability correlation length (y)	0.5	25	12.75	m
Mean permeability (sand)	-14	-10	-12	log (m^2)
Mean permeability (clay)	-18	-15	-16.5	log (m^2)
Porosity (sand)	0.25	0.5	0.375	-
Density (sand)	1500	2500	2000	kg/m^3
Van Genuchten parameter (m) (sand)	0.52	0.79	0.655	-
Van Genuchten parameter (α) (sand)	-4.69	-3.81	-4.25	-
Aquifer parameters: geochemical				
Volume fraction - calcite	0	0.2	0.1	-
Volume fraction - goethite	0	0.2	0.1	-
Volume fraction - illite	0	0.3	0.15	-
Volume fraction - kaolinite	0	0.2	0.1	-
Volume fraction - smectite	0	0.5	0.25	-
Cation Exchange Capacity	0.1	40	20.05	meq/100g
Benzene Kd	-4.5	0.69	-1.905	log(L/kg)
Benzene decay constant	-100	-6.1	-3.05	log(1/s)
PAH Kd	-3.1	1.98	-0.56	log(L/kg)
PAH decay constant	-10	-6.45	-3.225	log (1/s)
Phenol Kd	-6	0.15	-2.925	log(L/kg)
Phenol decay constant	-10	-5.63	-2.815	log(1/s)

Leak parameters: rates				
Mitigation time	1	200	200	yr
CO_2 leak rate	0	500	0 - 480	g/s
Brine leak rate	0	75	35	g/s
Cumulative CO_2 mass leaked	-3.7	3.1	-3 – 2.8	log(kTon)
Cumulative Brine leaked	-1.5	2.1	0.3	log(kTon)
Time	0	200	0-200	yr
Leak parameters: brine composition				
[Na]	-3	1	-1.0	log (Molality)
[Pb]	-8.5	-5	-7.02	log (Molality)
[Benzene]	-8.8927	-3.2	-6.82	log(Molality)
[As]	-7.98	-4.9	-6.76	log(Molality)
[Ba]	-5.1	-2.3	-3.91	log(Molality)
[Cd]	-8.87	-6.43	-7.76	log(Molality)

[PAH]	-10	-4.1	-7.2	log(Molality)
[Phenol]	-10	-3.7	-7.06	log(Molality)

Unconfined carbonate ROM

Parameter	**Min**	**Max**	**Ex 1**	**Unit**
Aquifer parameters: hydrologic				
Permeability variance	0.017	1.89	1	-
CorrelationLength	1	3.95	1	km
Kx/Kz	1.1	49.1	10	-
Mean permeability	−13.8	−10.6	1	log (m^2)
Aquifer thickness	100	500	240	m
Horizontal hydraulic gradient	2.88E-4	1.89E-2	.003	-
Aquifer parameters: geochemical				
Calcite surface area	0	0.01	.005	m^2/g
Organic carbon volume fraction	0	0.01	.005	-
Benzene Kd	1.49	1.73	1.6	log (Koc)
Benzene decay	0.15	2.84	1.49	log (day)
PAH kd	2.78	3.18	2.98	log (Koc)
PAH decay constant	-0.85	2.04	.595	log (day)
Phenol kd	1.21	1.48	1.34	log (Koc)
Phenol decay constant	-1.22	2.06	0.42	log (day)
Leak parameters				
CO_2 leak rate	0	500	0 - 480	g/s
Brine leak rate	0	75	35	g/s
Cumulative CO_2 mass leaked	0	500	-3 – 2.8	kTon
Cumulative Brine leaked	0	100	0.3	kTon
Time[1]	0	200	0-200	yr
[Cl][1]	-3	1	-1	log (Molality)

[1] Only used for chemical scaling factor

Table 2. Initial aquifer concentrations used in the simulations, no-impact and MCL (EPA, 2009) thresholds (Carroll et al., 2014 and references therein)

Analyte	**Unconfined Carbonate Aquifer (Edwards)**		**Confined Unconsolidated Sands Aquifer (High Plains)**		**U.S. EPA Regulatory Standard**
	Initial Model	**No-Impact Threshold**	**Initial Model**	**No-Impact Threshold**	**MCL Threshold**
pH	6.9	6.6	7.6	6.625^{d}	6.5
Total Dissolved Solids	330	420 mg L^{-1}	570 mg L^{-1}	1300 mg L^{-1e}	500 mg L^{-1}
Arsenic	0.31	0.55 µg L^{-1}	1.5 µg L^{-1}	9.3 µg L^{-1}	10 µg L^{-1}
Cadmium	0.00	0.04 µg L^{-1}	0.059 µg L^{-1}	0.25 µg L^{-1}	5 µg L^{-1}
Lead	0.06	0.15 µg L^{-1}	.086 µg L^{-1}	0.63 µg L^{-1}	15 µg L^{-1}

Table 3. Aquifer name abbreviations

Abbreviation	**Description**
HP	NRAP High Plains sand and gravel aquifer
Eu	NRAP Edwards shallow, urban carbonate-rock aquifer
BR	Basin and Range basin-fill sand and gravel aquifers
Gc	Central glacial sand and gravel aquifers
CL	Coastal lowlands sand aquifer system
LT	Lower Tertiary and Upper Cretaceous sandstone aquifers
M	Mississippian sandstone and carbonate-rock aquifers
F	Floridan carbonate-rock aquifer system
SPb	Snake River Plain basaltic-rock aquifers
NEx	New England crystalline-rock aquifers