

# Derivation of groundwater threshold values for analysis of impacts predicted at potential carbon sequestration sites



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## ABSTRACT

The U.S. Department of Energy's (DOE's) National Risk Assessment Partnership (NRAP) Project is developing reduced-order models to evaluate potential impacts to groundwater quality due to carbon dioxide (CO<sub>2</sub>) or brine leakage, should it occur from deep CO<sub>2</sub> storage reservoirs. These efforts targeted two classes of aquifer—an unconfined fractured carbonate aquifer based on the Edwards Aquifer in Texas, and a confined alluvium aquifer based on the High Plains Aquifer in Kansas. Hypothetical leakage scenarios focus on wellbores as the most likely conduits from the storage reservoir to an underground source of drinking water (USDW). To facilitate evaluation of potential degradation of the USDWs, threshold values, below which there would be no predicted impacts, were determined for each of these two aquifer systems. These threshold values were calculated using an interwell approach for determining background groundwater concentrations that is an adaptation of methods described in the U.S. Environmental Protection Agency's *Unified Guidance for Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities*. Results demonstrate the importance of establishing baseline groundwater quality conditions that capture the spatial and temporal variability of the USDWs prior to CO<sub>2</sub> injection and storage.

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## 1. Introduction

Geologic storage of carbon dioxide (CO<sub>2</sub>) is a promising tool in the strategy for reducing atmospheric emissions of CO<sub>2</sub>, thereby mitigating climate change (Hepple and Benson, 2005; IPCC, 2005; NETL, 2012). All signs continue to point to the necessity and viability of carbon capture and storage (CCS) as a CO<sub>2</sub> abatement technology (IEA, 2014). Long-term storage of CO<sub>2</sub> in deep geologic formations requires careful assessment of the reservoir integrity, potential leakage pathways, and consideration of potential impacts on the atmosphere and shallow groundwater (Herzog et al., 2003; Benson and Cole, 2008; Bielicki et al., 2014).

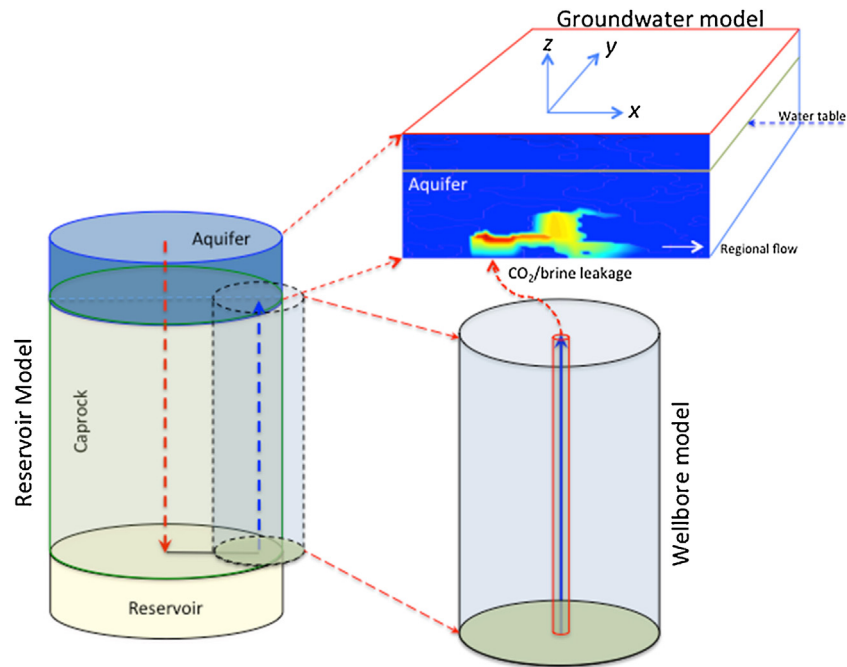
The U.S. Department of Energy's (DOE) Office of Fossil Energy established the National Risk Assessment Partnership (NRAP) Project aimed at developing a defensible, science-based quantitative methodology for determining risk profiles at CO<sub>2</sub> storage sites. As part of this effort, scientists from Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), Pacific

Northwest National Laboratory (PNNL), and the National Energy Technology Laboratory (NETL) are developing reduced-order models (ROMs) to evaluate the potential for aquifer impacts should CO<sub>2</sub> or brine leak from deep subsurface storage reservoirs. This methodology uses detailed physics and chemistry simulation results to train more computationally efficient ROMs. These ROMs can be used to help regulators and operators understand the potential sizes and longevity of contaminant plumes that could result from leakage of brine and/or CO<sub>2</sub> from a storage reservoir into underground sources of drinking water (USDW) (Carroll et al., 2014).

Hypothetical leakage scenarios have focused on wellbores as the most likely conduits from the storage reservoir to the USDW (Fig. 1). To compare potential groundwater impacts, simulation results are used to calculate the volume of aquifer exceeding some groundwater quality threshold concentration. Initially, threshold values were based on the U.S. Environmental Protection Agency (EPA) national primary and secondary drinking water limits. However, feedback received from the NRAP Stakeholder Group indicated that additional threshold values were needed that could differentiate areas of no degradation (i.e. no impact) from those areas that reflect some degree of change from background groundwater quality levels suggesting potential impacts. Experimental and numerical simulation results (Wang et al., 2015; Lawter et al., 2015; Bacon et al., 2015; Zheng et al., 2015) indicate that although CO<sub>2</sub> and brine leakage

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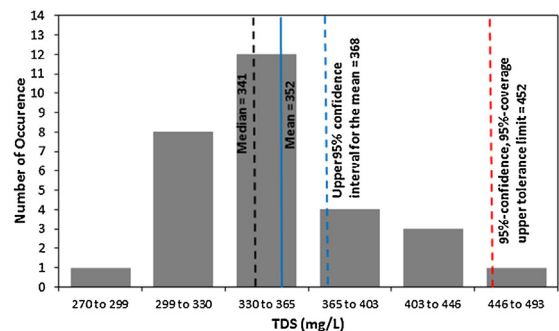
**Fig. 1.** Conceptual model for simulating potential impacts to an underground source of drinking water (USDW) due to leakage of CO<sub>2</sub> and/or brine from a carbon sequestration reservoir (from Carroll et al., 2014).

may cause decreases in pH and increases in TDS concentrations beyond regulatory limits in the USDW, the release of trace elements (e.g., As, Cd, Cu, Cr, Pb, Mo, Zn) are not expected to significantly degrade groundwater quality.

In this study, we examined various methodologies for determining natural background concentrations and statistical protocols for determining threshold values that would indicate a significant change from the background concentrations. We evaluated the statistical variability of background groundwater concentrations in underground sources of drinking water (USDW) for two classes of USDWs—an unconfined fractured carbonate aquifer based on the Edwards Aquifer in Texas, and a confined alluvium aquifer based on the High Plains Aquifer in Kansas (Carroll et al., 2014). Of particular interest were the constituents As, Ba, Cd, Cr, Fe, Mn, Pb, pH, TDS, and selected organic elements (benzene, ethylbenzene, naphthalene, toluene, m- & p-xylene, o-xylene, and phenol). Using these case studies, we evaluated various statistical approaches and converged on a proposed methodology for determining site-specific threshold values that could be used to quantify simulated changes in groundwater chemistry due to CO<sub>2</sub> or brine leakage from geologic carbon sequestration reservoirs. Our approach generally follows the “interwell” approach recommended for determining background groundwater concentrations (EPA, 2009), and using tolerance limits to define threshold values (TVs) representing a significant change over background. There are, however, a number of issues that need to be addressed, including: the potential for these threshold values to actually exceed regulatory limits; the treatment outliers; and the availability of sufficient data to provide reliable statistical results.

## 2. Background

Although not specifically required by the EPA (unlike surface water under the Clean Water Act), the majority of States have established some form of ground-water anti-degradation (or non-degradation) requirements. As a general rule these anti-pollution requirements (not cleanup requirements) are designed to prevent degradation of ground water (e.g. reduced quality from



**Fig. 2.** Example of a background upper tolerance limit that approximates the upper 95th percentile of a background distribution of a contaminant of interest.

background conditions), by prohibiting or limiting discharges that potentially degrade the ground water; or by requiring maintenance of the ground-water quality consistent with current uses. Often these nondegradation limits are set at definite concentrations (trigger/threshold levels) or at a percentage of the lowest applicable water-quality standard to be measured at the end of a mixing/dilution zone.<sup>1</sup>

Background groundwater concentrations are generally considered to be naturally occurring concentrations that are indicative of minimal influence by human (anthropogenic) sources (USGS—Water Basics Glossary). This is similar to the definition of “Natural Background Levels” used by the Groundwater Daughter Directive (GWDD) adopted by the European Union (EU). Where both natural (geogenic) and anthropogenic sources have contributed to chemical concentrations in the groundwater, the use of the term “baseline concentrations” might be a more appropriate term. The Resource Conservation and Recovery Act (RCRA) uses groundwater concentrations from wells upgradient of a

<sup>1</sup> Montana Water Quality Information, Nondegradation Determinations & Mixing Zones. Available at <http://deq.mt.gov/wqinfo/nondeg/default.mcpx>; accessed 2014-09-09.

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