

Relative Vulnerability of Public Supply Wells to VOC Contamination in Hydrologically Distinct Regional Aquifers

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Abstract

A process-based methodology was used to compare the vulnerability of public supply wells tapping seven study areas in four hydrologically distinct regional aquifers to volatile organic compound (VOC) contamination. This method considers (1) contributing areas and travel times of groundwater flowpaths converging at individual supply wells, (2) the oxic and/or anoxic conditions encountered along each flowpath, and (3) the combined effects of hydrodynamic dispersion and contaminant- and oxic/anoxic-specific biodegradation. Contributing areas and travel times were assessed using particle tracks generated from calibrated regional groundwater flow models. These results were then used to estimate VOC concentrations relative to an unspecified initial concentration (C/C_0) at individual public supply wells. The results show that the vulnerability of public supply wells to VOC contamination varies widely between different regional aquifers. Low-recharge rates, long travel times, and the predominantly oxic conditions characteristic of Basin and Range aquifers in the western United States leads to lower vulnerability to VOCs, particularly to petroleum hydrocarbons such as benzene and toluene. On the other hand, high recharge rates and short residence times characteristic of the glacial aquifers of the eastern United States leads to greater vulnerability to VOCs. These differences lead to distinct patterns of C/C_0 values estimated for public supply wells characteristic of each aquifer, information that can be used by resource managers to develop monitoring plans based on relative vulnerability, to locate new public supply wells, or to make land-use management decisions.

Introduction

Periodic monitoring of public supply wells for volatile organic compounds (VOCs) is an important strategy for avoiding public exposure to potentially toxic chemicals (Zogorski et al. 2006) and for assessing the vulnerability of particular aquifer systems to anthropogenic contamination (e.g., <http://www.waterboards.ca.gov/gama/>; Wright et al. 2004; Moran et al. 2003). Aquifer vulnerability can also be assessed using a variety of analytical tools including subjective rating, statistical, or process-based methods (Focazio et al. 2002). Each of these methods has advantages and disadvantages depending on the kinds and quality of available data. Process-based methods, which consider the physics of groundwater flow (Frind et al. 2006) and the biodegradability of individual anthropogenic contaminants (Schlosser et al. 2002), have the advantage that they can predict contaminant distributions in time and space for real or assumed contaminant source distributions. Frind et al. (2006) make

the useful distinction between *aquifer* vulnerability, which depends on groundwater travel times from land surface to the aquifer in general, and *well* vulnerability which depends on travel times to specific wells. In this paper, the range of computed travel times to specific wells are used to predict individual well vulnerability. These predictions, in turn, can be useful to resource managers responsible for locating public supply wells, for determining sampling frequency needed to screen for contaminants at existing wells, and for making land use decisions.

Process-based methods have the disadvantage that they make mathematical representations of complex hydrologic and biochemical systems which inevitably leads to simplification and uncertainty (National Research Council 1993; Starn et al. 2000). However, if these mathematical models are constrained with adequate hydrologic and geochemical data, and if contaminant source terms are applied in an internally consistent way, the resulting simulations can be used to *compare* the relative vulnerability of public supply wells located in different hydrologic systems. The purpose of this paper is to describe the results of a process-based methodology designed to compare the vulnerability to volatile organic carbon (VOC) contamination for public supply

wells located in seven different study areas of the United States.

Much of the literature describing aquifer vulnerability to anthropogenic contamination grew out of concerns about pesticide contamination of groundwater (Barbash and Resek 1996). A variety of process-based approaches for quantifying contaminant transport to groundwater systems have been used over the years (reviewed by Frind et al. 2006). These approaches are based on solutions of advection-dispersion equations for a variety of initial and boundary conditions (Jury et al. 1987; Meeks and Dean 1990; Rao and Alley 1993). In the case of pesticide transport to the water table, these solutions take the form of:

$$M(z)/M_o = e^{-\lambda z/RV} \quad (1)$$

where $M(z)$ is the mass of pesticide in the soil profile [ML^{-3}] at depth z [L], M_o is the mass of the chemical applied to the surface ($z = 0$), λ is the first-order decay coefficient (T^{-1}), R is a retardation factor (dimensionless), and V is the average-linear vertical soil-water velocity [LT^{-1}] (Schlosser et al. 2002). A variety of terms describing biodegradation can be added to this basic formulation depending on the compounds being considered and the goals of the modeling effort. The approach taken in this paper is consistent with this and is based on the observation that groundwater vulnerability (GWV) for any given aquifer is a function of the intrinsic susceptibility (IS) of a given aquifer, the contaminant mobility and persistence (CMP), and the chemical inputs (CI) being applied to the system (Focazio et al. 2002):

$$\text{GWV} = f(\text{IS}, \text{CMP}, \text{CI}) \quad (2)$$

Intrinsic susceptibility depends on physical aquifer properties (hydraulic conductivity, distributions of aquifer and aquitard materials, porosity, etc.) as well as temporally and spatially variable sources and sinks of water, and physical stresses (recharge rates, interactions with surface water, travel through the unsaturated zone, and pumpage from wells). The mobility and persistence of anthropogenic compounds are affected by hydrodynamic processes such as advection and dispersion, chemical processes such as sorption, dissolution/precipitation reactions, and biodegradation processes. Finally, chemical inputs are a function of human population distribution and land use patterns. If each of these conditions listed earlier can be described in a consistent manner, it becomes possible to compare the vulnerability to VOC contamination of different hydrologic systems. Furthermore, it becomes possible to evaluate how vulnerability varies spatially and temporally within individual hydrologic systems.

A significant source of uncertainty with this approach is assigning chemical inputs that are realistic for regional aquifer systems. Because of this, the approach taken in this study was to use constrained regional groundwater flow models that capture the hydrologic characteristics of each system, and to apply particle-tracking analysis (Pollock 1994) to estimate travel times and water volumes from recharge areas to public supply wells. Reduction/oxidation (redox)-specific contaminant biodegradation rates were then

superimposed on the particle-tracking analysis to provide a more realistic simulation of contaminant transport. Finally, rather than attempting to apply defined chemical inputs, a more general approach involving computing contaminant concentrations relative to an undefined initial concentration (C/C_o) was used. This approach precludes making well-specific predictions of contaminant concentrations, but it provides a framework for comparing the relative vulnerability of public supply wells located in different regional aquifer systems to VOC contamination.

Methods

Description of Regional Aquifers

The regional aquifer systems chosen for this study have all been studied previously by the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (<http://water.usgs.gov/nawqa/>, Figure 1). Each of these systems has been the subject of extensive groundwater chemistry data collection, including concentrations of VOCs and indicators of oxidation/reduction conditions. In addition, each of these systems has been simulated with numerical groundwater models constrained by hydrologic data (Paschke 2007) as part of the Transport of Anthropogenic and Natural Contaminants (TANC) program of NAWQA. The regional aquifers and the individual study areas are shown in Figure 1. These study areas include:

1. The Great Salt Lake Basin and Range aquifer of Utah (Stolp 2007).
2. The Spanish Springs Nevada Basin and Range aquifers (Schaefer et al. 2007).
3. The Eagle Valley Nevada Basin and Range aquifer (Schaefer et al. 2007).
4. The Central Valley aquifers of California (Philips et al. 2007).
5. The glacial White River-Little Miami River aquifer of Ohio (Sheets 2007).
6. The glacial aquifer of the Pomperaug River Basin of Connecticut (Lyford et al. 2007).
7. The Eastern High Plains aquifer of Nebraska (Landon and Turco 2007).

Because of their physical proximity, the Spanish Springs and Eagle Valley aquifers are considered together as well as individually. Taken together, these aquifer

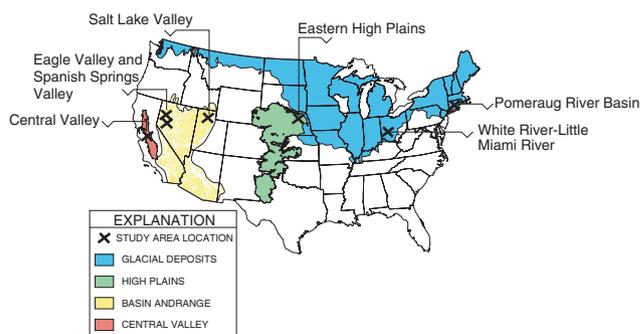


Figure 1. Locations of regional aquifers and individual study areas.

systems represent a wide variety of geological, climatic, and hydrological conditions which allow a broad comparison on how these conditions affect the relative vulnerability to VOC contamination of ground water being tapped by public supply wells.

Approach to Groundwater Flow Simulation and Particle-Tracking

Groundwater flow was simulated using the U.S. Geological Survey's modular finite-difference groundwater flow simulation code MODFLOW-2000 (Harbaugh et al. 2000). Models were calibrated following the guidelines of Hill (1998) using water-budget estimates and water-level data for the period 1997 to 2001. These steady-state models and the particle-tracking program MODPATH (Pollock 1994) were used to delineate areas contributing recharge and to compute advective travel times through the aquifers for individual public-supply wells within each study area. Model conceptualization, boundary conditions, calibration, and particle-tracking simulations for each regional study area have been previously described by Paschke (2007).

MODPATH uses the cell-by-cell flow values calculated by MODFLOW to calculate the groundwater flow velocity distribution throughout the system, which is then used to determine flow paths of water particles moving through the aquifer. Travel times along individual flow paths are computed by MODPATH using the magnitude of the cell-by-cell flows, effective porosity, and the model cell dimensions. Particle-tracking simulations are useful for outlining areas contributing recharge to a given pumping well. A summary description of the groundwater systems and their associated models considered in this study are given in Table 1.

Assessing Relative Vulnerability

The conceptualization of GWV used in this paper is illustrated in Figure 2. Each public supply well is assumed to draw water from recharge areas located at some distance from the well. It is assumed that contaminants are delivered to the water table at a given initial concentration (C_0) and move toward the well. Initially, contaminants are transported under oxic conditions, and the distance contaminants travel under oxic conditions is termed $Dist_{oxic}$. Similarly, the travel time of contaminants moving under oxic conditions is termed TT_{oxic} . For hydrologic systems that are uniformly oxic, the distance and time of travel can be described solely by $Dist_{oxic}$ and TT_{oxic} . Other hydrologic systems shift from oxic to anoxic conditions along individual flowpaths. The concentration of contaminants delivered to the boundary of oxic and anoxic conditions is termed C_{bound} and the distance and time of travel for contaminants under anoxic conditions are termed $Dist_{anoxic}$ and TT_{anoxic} respectively. Thus, computed C/C_0 values for systems that transition from oxic to anoxic include the effects of biodegradation under both sets of conditions.

As contaminants are transported along aquifer flowpaths, they are subject to natural attenuation processes that include hydrodynamic dispersion and biodegradation. For the VOC compounds considered in this paper, it is assumed that contaminant concentrations are not affected by sorption

processes, and this assumption will tend to over-predict the delivery of VOCs to individual public supply wells. The sum of these dispersing and biodegrading processes has been termed the natural attenuation capacity (NAC), and the ratio of initial (and constant) contaminant concentrations (C_0) in a source area to contaminant concentrations at any point in the flow system ($C(x)$) is given by the equation (Chapelle and Bradley 1998):

$$C(x) / C_0 = \exp\left(-\left[\frac{-v + \sqrt{v^2 + 4Dk}}{2D}\right]x\right) = \exp(-NAC)x \quad (3)$$

where D = coefficient of hydrodynamic dispersion (m^2/d)

v = velocity of groundwater flow (m/d)

k = first-order biodegradation rate constant (d^{-1})

x = distance along the flowpath (m)

Note that the form of this equation is identical to that of Equation 1, reflecting the underlying assumption that the standard one-dimensional advective-dispersion equation, which includes consideration of longitudinal (but not transverse) dispersion, describes solute transport in groundwater systems. It has been shown that transverse dispersion increases the attenuation of contaminants in porous media (Frind et al. 1987; Frind and Hokkanen 1987) and so considering only longitudinal dispersion may tend to over-predict VOC transport to individual wells. Because rates of biodegradation for VOCs vary under different redox conditions (Bradley 2003), groundwater velocity (v_{oxic}) is computed for the oxic portion of the aquifer:

$$v_{oxic} = Dist_{oxic} / TT_{oxic} \quad (4)$$

From this, contaminant concentration changes are computed for the oxic portion of the flowpath to give C_{bound} :

$$C_{bound} = C_0 \exp(-NAC_{oxic}) Dist_{oxic} \quad (5)$$

For systems that exhibit anoxic conditions, groundwater velocity and final contaminant concentrations at the public supply well are then computed from C_{bound} and the anoxic NAC:

$$v_{anoxic} = Dist_{anoxic} / TT_{anoxic} \quad (6)$$

$$C_{final} = C_{bound} \exp(-NAC_{anoxic}) Dist_{anoxic} \quad (7)$$

The conceptual diagram shown in Figure 2 shows a single flowpath with different distances of transport under either oxic or anoxic conditions. In the model simulations made for this study, however, particle tracks for hundreds of flowpaths converging on each public supply well were simulated. The C/C_0 value for each well was computed as the average C/C_0 value of each flowpath converging on that well weighted by the volume of recharge represented by each particle. For comparing C/C_0 values between different study areas, the 90th percentile of the C/C_0 values obtained from the simulated wells in each study area were used.

Table 1
Summary Table Describing the Aquifer Systems Considered in this Paper and the Models Used to Simulate Them

Climate	Predominant Aquifer PA and Lithology	Predominant Redox Conditions	Range of Aquifer Transmissivity (m ² /d) or Hydraulic Conductivity (m/d)	Modeled Area (km ²)	Spatial Discretization	Period of Steady-State Simulation	Calibration (RMSE of Measured vs. Simulated Water Levels)	Water Budget (m ³ /d)		
								Diffuse Inflow (Recharge)	Diffuse Outflow (Discharge)	
Great Salt Lake Basin and Range, Utah										
Arid to semi-arid	Basin and Range. Unconsolidated fluvial gravel, sand, silt	Predominantly anoxic with approximately 40% of aquifer volume oxic	Transmissivity range 93 to 2790	1152	94 rows 62 columns 7 layers	1997–2001	RMSE ~ 6%	1,009,863	509,863	500,000
Eagle Valley and Spanish Springs Valley Basin and Range, Nevada										
Arid to semi-arid	Basin and Range. Unconsolidated fluvial gravel, sand, silt	Predominantly oxic with approximately 28% of aquifer volume anoxic	Transmissivity range 1 to 11,600	70	186 rows 130 columns 2 layers	1997–2001	RMSE ~ 6%	15,000	9800	5200
Central Valley, California										
Arid to semi-arid	Basin and Range. Unconsolidated fluvial gravel, sand, silt, clay	Predominantly oxic with approximately 17% of aquifer volume anoxic	Horizontal hydraulic conductivity range 5 to 250	3354	153 rows 137 columns 16 layers	2000	RMSE ~ 10%	5,456,000	2,501,000	2,955,000
Pomperaug River Basin Glacial Aquifer, Connecticut										
Temperate	Glacial aquifer. Fluvial Valley-fill sands and gravels and tills	Predominantly anoxic with approximately 47% of aquifer volume oxic	Horizontal hydraulic conductivity range 1.5 to 76	128	183 rows 184 columns 2 layers	1991–2002	RMSE ~ 11%	132,900	125,800	7100
White River-Great and Little Miami River Glacial Aquifer, Ohio										
Temperate	Glacial/Fluvial Valley-fill sands and gravels and tills	Predominantly anoxic with approximately 32% of aquifer volume oxic	Horizontal hydraulic conductivity range 1 to 3900	620	230 rows 370 columns 3 layers	1997–2001	RMSE ~ 5%	1,005,000	467,000	538,000
Eastern Regional High Plains Ground Water Aquifer, Nebraska										
Dry continental	Fluvial gravels, sands and silt	Predominantly anoxic with approximately 32% of aquifer volume oxic	Horizontal hydraulic conductivity range 41 to 122	41	200 rows 300 columns 6 layers	1997–2001	RMSE ~ 5%	499,518	320,205	179,313

RMSE = root mean square error.

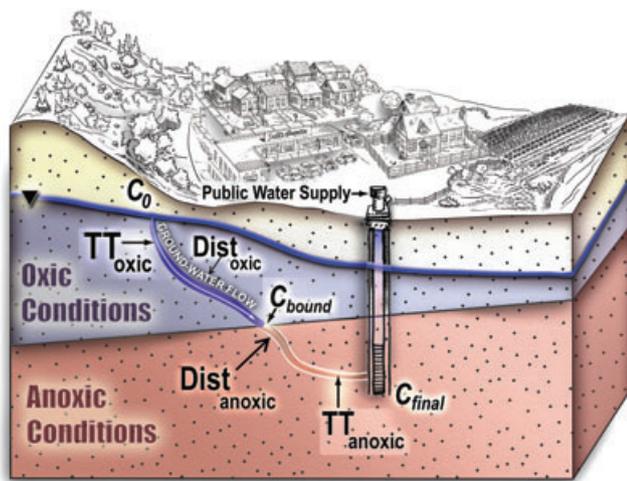


Figure 2. Diagram illustrating the conceptualization of vulnerability to contamination used in this paper.

Treatment of Biodegradation Rates

Rates of biodegradation are contaminant-specific, concentration-dependent, and affected by ambient redox conditions (Howard et al. 1991). Benzene and toluene, which act as electron donors in microbial metabolism, exhibit rapid biodegradation ($k \sim 1.0$ to $0.1/d$) under oxic conditions (Howard et al. 1991; Suarez and Rifai 1999), somewhat lower rates ($k \sim 0.01/d$) under iron and sulfate-reducing conditions (Kazumi et al. 1997; Weiner and Lovely 1998; U.S. Environmental Protection Agency [U.S. EPA] 1999), and even lower rates ($k \sim 0.001/d$) under methanogenic conditions (Chapelle et al. 1996). Toluene is consistently observed to degrade somewhat faster than benzene under all redox conditions (Suarez and Rifai 1999). Perchloroethene (PCE) and trichloroethene (TCE), which act as electron acceptors in microbial metabolism, exhibit low-biodegradation rates ($k \sim 0.00001/d$) under oxic conditions, slow biodegradation rates ($k \sim 0.01/d$) under iron and sulfate-reducing conditions, and moderately fast rate constants ($\sim 0.05/d$) under methanogenic conditions (U.S. EPA 1999). PCE is observed to degrade somewhat faster under anoxic conditions than TCE. Chloroform, which can act either as an electron donor or acceptor, has been observed to degrade relatively slowly ($\sim 0.0005/d$) under oxic and anoxic conditions in groundwater sediments (Landmeyer et al. 2000). Similarly, methyl *tert* butyl ether

(MTBE), which acts predominantly as an electron donor in microbial metabolism, is observed to be relatively recalcitrant in anoxic groundwater systems ($k \sim 0.0001/d$) but is observed to be more biodegradable under oxic conditions (Landmeyer et al. 2001). In summary, biodegradation rate constants for the VOC compounds considered in this study are observed to vary considerably for different redox and hydrologic conditions (Howard et al. 1991; U.S. EPA, 1999; Suarez and Rifai 1999).

Given the observed variability of redox-specific biodegradation rates, and given that this study did not attempt to resolve anoxic conditions into specific electron-accepting processes, a range-of-values approach was taken to assign biodegradation rate constants. Under either oxic or anoxic conditions biodegradation rates for particular contaminants can range from low to fast. Assuming rates range from low (l, $k = 0.00001/d$), resistant (r, $k = 0.0001/d$), slow (s, $k = 0.001/d$), moderately fast (m, $k = 0.01/d$), or fast (f, $k = 0.1/d$), a matrix of possible biodegradation rates can be generated for both oxic and anoxic conditions (Table 2). This approach has the advantage of considering virtually the entire range of biodegradation rates that are plausible under oxic and anoxic conditions. The approach has the disadvantage of not directly assigning compound- and redox-specific biodegradation rates making the model results more difficult to interpret. To minimize this disadvantage, approximate compound- and redox-specific biodegradation rates from the literature can be superimposed on the model-generated results in order to provide context for interpretation. Based on the literature cited above, estimates of the oxic/anoxic biodegradation rate constants for the VOCs considered in this study are PCE (lm), TCE (ls), benzene (mr), toluene (ms), MTBE (sl), and chloroform (rs) (Table 2). These values are used only for illustrative purposes in order to provide a frame of reference for interpreting model results obtained with the range-of-values approach.

Assumptions and Limitations

The approach taken in this paper has inherent assumptions which can lead to limitations in how the approach might be applied elsewhere and interpretations made. Although more rigorous numerical simulations might do a better job of including more relevant processes, the approach presented here was intended to be kept relatively simple so it can be easily applied in multiple study areas. The C/C_0

Table 2
Classes of Contaminant Biodegradation Rates under Oxic and Anoxic Conditions

		Oxic Conditions				
		Lowest (0.00001) ¹	Resistant (0.0002)	Slow (0.001)	Modfast (0.01)	Fast (0.1)
Anoxic Conditions	Lowest (0.00001)	ll	rl	Sl	ml	fl
	Resistant (0.0001)	lr	rr	Sr	mr	fr
	Slow (0.001)	ls	rs	Ss	ms	fs
	Modfast (0.01)	lm	rm	Sm	mm	fm
	Fast (0.1)	lf	rf	Sf	mf	ff

¹Biodegradation rate constants in units of day⁻¹.

values, while seeking to include relevant processes, are intended to be used as a measure of some component of the vulnerability of wells to contamination.

One assumption is that transverse dispersion is not considered due to using the particle tracking results as the starting point of the analysis. In reality, most VOC contamination enters aquifers as plumes and the transverse dispersion is generally an important consideration in the attenuation and spreading of the contaminant. In this analysis, since the results are in terms of the initial concentration, the source is uniform and concentration gradients in the transverse directions would generally be small except for areas where flowlines are converging such that water with different travel times are in close proximity. Nevertheless, not considering transverse dispersion in the analysis will tend to overestimate C/C_0 values at given wells. Another assumption in the approach is the use of a constant velocity within a given redox zone for each flow path. Although the velocity would vary along a given flowpath the overall travel time is still captured and the longitudinal dispersion should account for some of the velocity variation that is neglected. Because many particles are used for each well, each with its own velocity for each redox zone encountered, many different velocities are still represented in the overall movement of the water to the well.

Results and Discussion

The hydrologic differences between the regional aquifers considered in this study (Table 1) lead to significant differences in groundwater recharge rates, residence times, and redox conditions. These differences are reflected by the simulated median travel times of ground water reaching public supply wells (Figure 3). The Spanish Springs Valley Basin and Range aquifer of Nevada had the longest simulated travel times followed by the Basin and Range Utah and High Plains, Nebraska aquifers. In contrast, the glacial aquifers of Connecticut and Ohio are characterized by relatively

thin, high-recharge aquifers that exhibit proportionally shorter flowpaths and travel times. In general, public supply wells tapping the relatively thick, low-recharge aquifers characteristic of the western United States have longer flowpaths and greater travel times than the glacial aquifers of the eastern United States. Based solely on these model-estimated travel times (Figure 3), it would be expected that the intrinsic susceptibility (Equation 2) to anthropogenic contamination will be greater for the Connecticut and Ohio glacial aquifers than for the Basin and Range aquifers of Nevada, California, and Utah.

If, in addition to intrinsic susceptibility, consideration of redox-dependent biodegradation is added to the analysis, differences in vulnerability between regional aquifers become even more evident. Figure 4 shows computed C/C_0 values at simulated public supply wells in each study area plotted as a function of oxic and anoxic biodegradation rate constants (Table 2). Because of their physical proximity, the Spanish Springs and Eagle Valley systems were considered together and are referred to as the Nevada Basin and Range system. The color gradation for the computed C/C_0 values (Figure 4) ranges from red, which denotes less biodegradation ($C/C_0 > 10^{-5}$), to blue, which denotes extensive biodegradation ($C/C_0 < 10^{-8}$). For each study area, the 90th percentile C/C_0 values are plotted for each combination of biodegradation rates. Using the 90th percentile means that the comparison is based on an almost worst case for each system. Superimposed on these plots are approximate compound- and redox-specific biodegradation rate constants for PCE, TCE, MTBE, benzene, toluene, and chloroform to provide context for interpretation. These simulations indicate that VOC compounds plotting in the red portions of Figure 4 are more likely to be detected in public supply wells than those that plot in the blue areas. They also suggest that the petroleum hydrocarbons benzene, toluene, and MTBE, which degrade relatively rapidly under both oxic and anoxic conditions, are less likely to be detected than the chlorinated VOCs chloroform, PCE, and TCE.

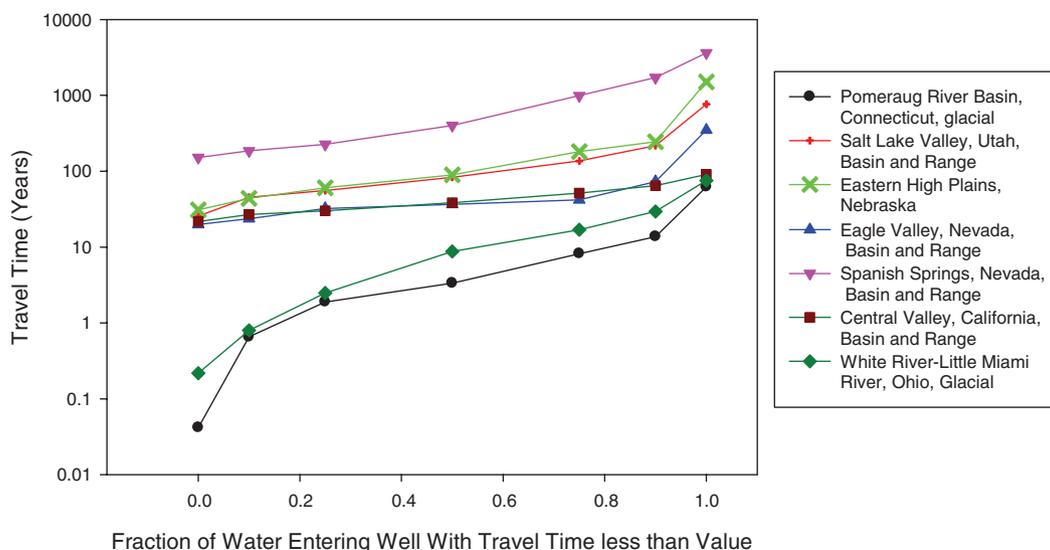


Figure 3. A comparison of the median distribution of travel times for ground water arriving at public supply wells in different regional aquifers.

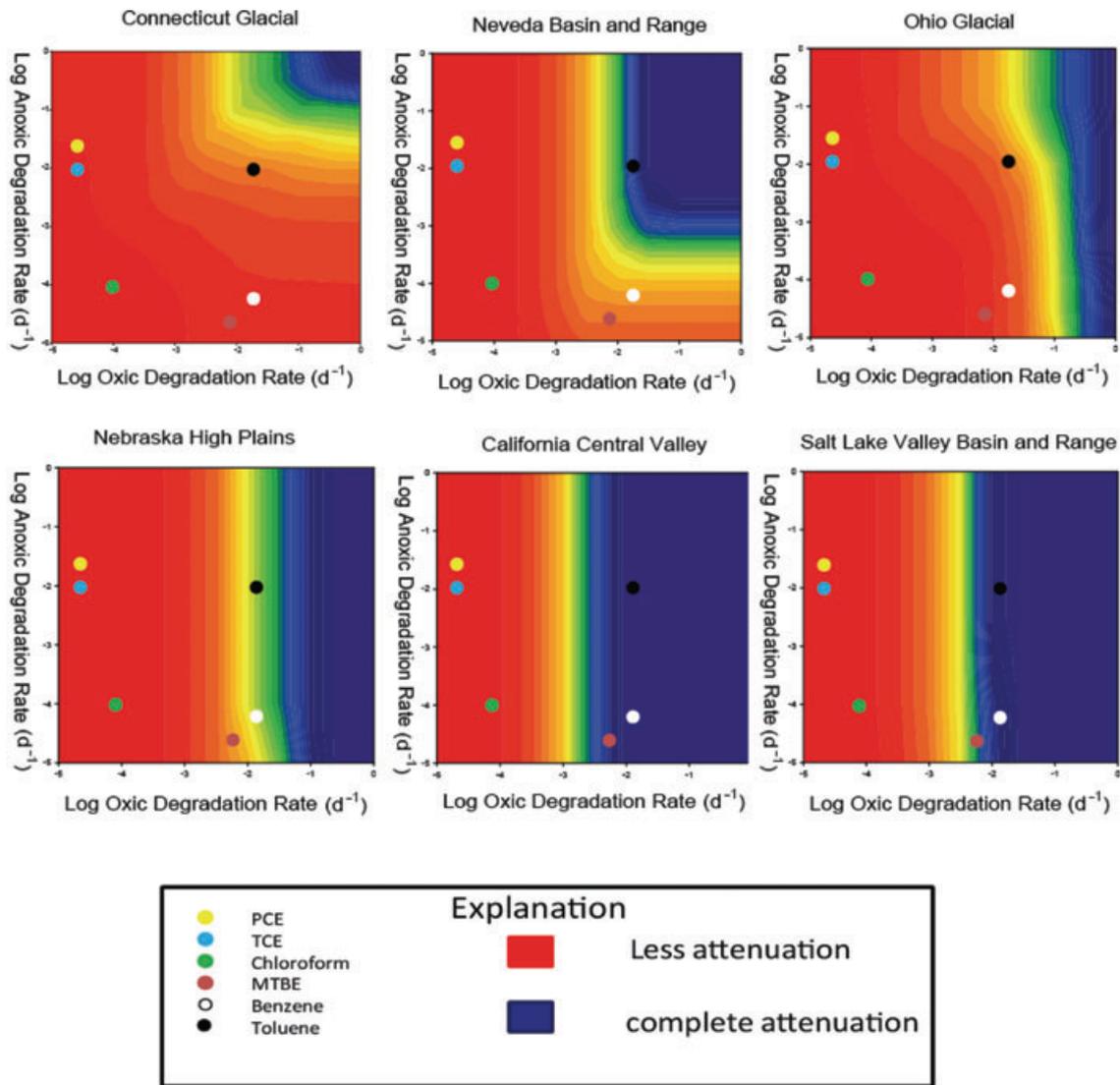


Figure 4. Comparison of the 90th percentile C/C_0 values of six regional aquifers for selected volatile organic carbon compounds.

Box plots of C/C_0 values computed at individual public supply wells and shown as a function of biodegradation redox class are shown in Figure 5. Once again, the Spanish Springs and Eagle Valley systems were considered together. This method of visualization illustrates the variability of computed C/C_0 values within a study area for the number of public supply wells considered in the analysis. The red dots denote the median C/C_0 value for each redox class and the width of the boxes indicates the variability of the computed C/C_0 values. The black dots were considered statistical outliers by the graphing software package used in this analysis (Spotfire S+, TIBCO Inc., Seattle, Washington), and are an additional indication of the variability associated with each regional aquifer. The number of public supply wells included in the analysis (n) is also indicated for each aquifer on Figure 5. These results illustrate that for the glacial aquifers of Connecticut and Ohio, median C/C_0 are relatively high ($>10^{-5}$) even if the most rapid biodegradation rates (redox classes mm to ff) were assumed to apply. In contrast, the High Plains and Basin and Range aquifers show low ($<10^{-8}$) C/C_0 values for these same rapid biodegradation rates (redox classes mm to ff).

The veracity of the modeling results was examined by comparing computed C/C_0 values to actual measured concentrations of VOCs in water produced from the public-supply wells considered in this study. In all, 84 wells from these study areas had water-quality data that could be compared to computed C/C_0 values. The detection frequencies were 50% for chloroform (42/84), 24% for PCE (20/84), 16% for TCE (13/84), and 4% for MTBE (3/84). Benzene and toluene were not detected in any of the sampled wells. For each of the four VOCs that were detected, the modeled C/C_0 values were split into two groups. One group was for wells in which the VOC was detected, and the other group was for wells in which the VOC was not detected. For each VOC, the mean computed C/C_0 values were significantly higher for the wells with detections than for the wells without detections (Figure 6). Statistical tests (Student's t -test) performed on the base-10 logarithms for the C/C_0 values showed that the detect groups means were higher than the non-detect groups at the following significance levels PCE ($p = 0.09$), TCE ($p = 0.004$), MTBE ($p < 0.0001$), chloroform ($p = 0.007$). This, in turn, indicates that the methodology used in this study to determine relative vulnerability

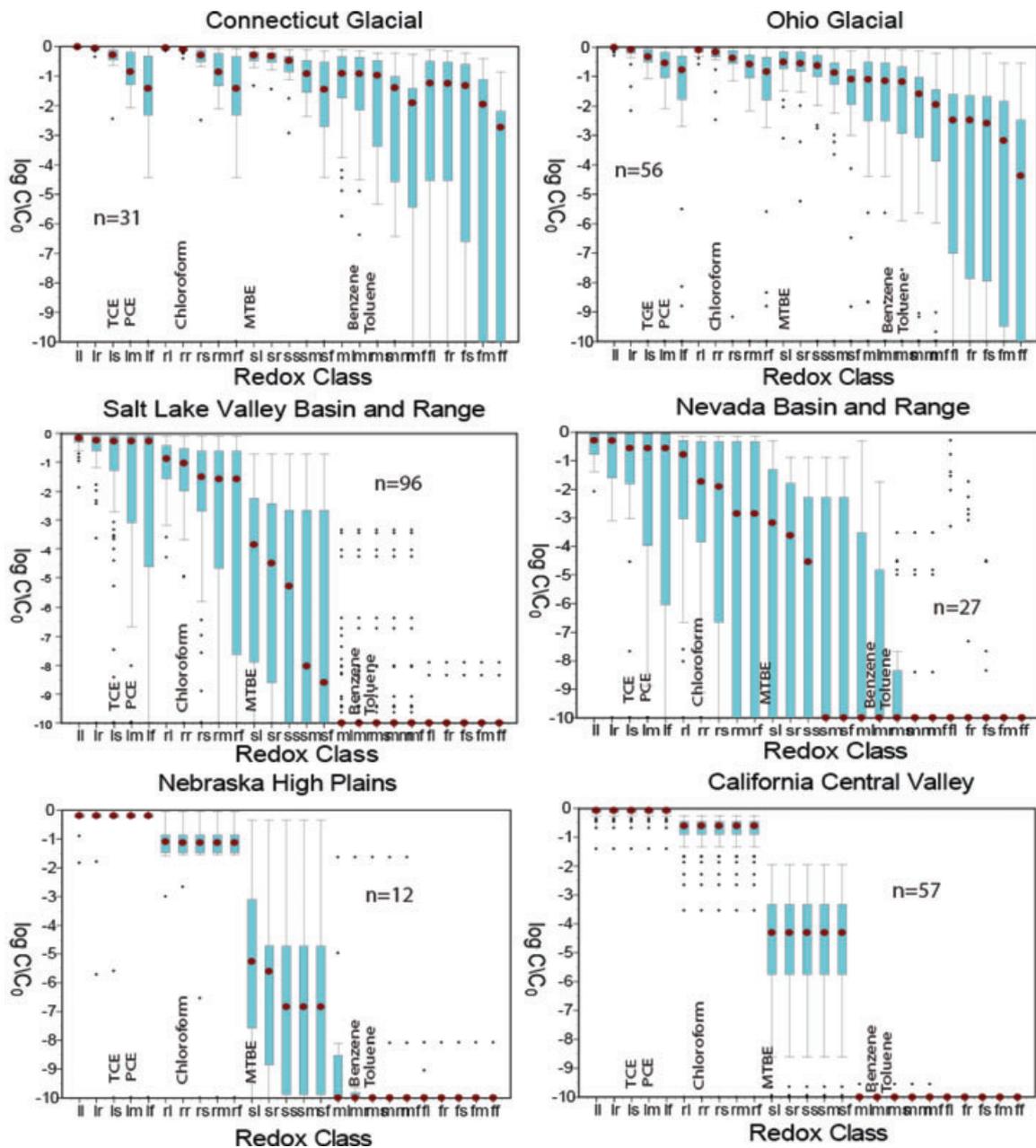


Figure 5. Box plots showing variation of computed C/C_0 values plotted vs. degradation rate classes for the different study areas.

to VOC contamination (C/C_0) is roughly consistent with observed VOC detections at public supply wells in these aquifer systems.

The results suggest that the vulnerability of different aquifer systems to VOC contamination varies considerably. For the glacial aquifers of Connecticut and Ohio, median C/C_0 values for the entire range of redox classes considered are typically greater than 10^{-5} (Figure 5). Assuming maximum C_0 values for a given VOC on the order of $10^5 \mu\text{g/L}$ (i.e., a gasoline or solvent spill), VOC detections of greater than $1 \mu\text{g/L}$ are possible throughout the entire Connecticut and Ohio glacial systems (Figure 4). In contrast, the Basin and Range aquifers of Utah and Nevada, the High Plains aquifer of Nebraska and the Central Valley of California exhibit substantially lower C/C_0 values (on the order of 10^{-10}) for the faster degradation rate classes (Figure 5). Anoxic zones

are either less in evidence in the western aquifers (Table 1) or the travel times to them are so great that C/C_0 values are already small before reaching the anoxic zones. This finding suggests that VOC detections are not likely in substantial portions of these western aquifers.

The results also suggest the kinds of VOCs most likely to be detected in these regional aquifers. Because petroleum hydrocarbons biodegrade to some extent under both oxic and anoxic conditions, detections of benzene and toluene are less likely than the chlorinated hydrocarbons chloroform, PCE, and TCE which biodegrade primarily under anoxic conditions (Figures 4 and 5). The lack of benzene and toluene detections in public supply wells was observed in this study and is consistent with the behavior implied by the plots shown in Figures 4 and 5. The lack of measurable benzene concentrations in western aquifers has

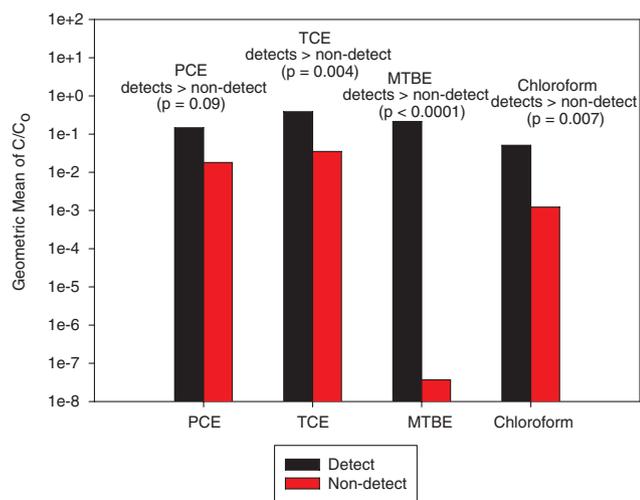


Figure 6. Graph showing a comparison of computed geometric mean C/C_0 values for wells with and without detection of four different VOCs in all study areas.

been previously noted in water-quality monitoring studies (Hadley and Armstrong 1991). Considering that petroleum products are by far the most widely used potential source of VOCs to ground water, the relative lack of benzene and toluene detections is remarkable and can be directly attributed to their relative susceptibility to biodegradation processes (Figures 4 and 5). MTBE is observed to biodegrade more slowly than benzene and toluene for a wide range of redox conditions (Landmeyer et al. 2001) and thus would be expected to be detected more frequently (Figure 6). This is consistent with the finding that MTBE is commonly detected in groundwater (Zogorski et al. 2006). While the detection frequencies of VOCs appear qualitatively consistent with their postulated biodegradation characteristics, the absence of information concerning chemical inputs for these systems precludes a more quantitative analysis.

The methodology described in this paper was designed specifically to compare the vulnerability to VOC contamination in public supply wells located in different hydrologic systems of the United States. We wish to note, however, that this method can potentially be applied to any aquifer system for which calibrated groundwater flow models are available. In addition to comparing the relative vulnerability of different hydrologic systems, it may also be feasible to compare the relative vulnerability of individual public supply wells in a given hydrologic system as suggested by Frind et al. (2006). This, in turn, may allow resource managers to optimize the spatial and temporal design of ongoing water-quality monitoring programs, to assist in the location of new public supply wells, or to make land-management decisions.

Conclusions

This paper describes an internally consistent, process-based methodology for comparing the relative vulnerability of public supply wells to VOC contamination in geographically and hydrologically distinct aquifer systems. This methodology uses calibrated groundwater models to simulate water flow, particle track analyses to delineate contributing

areas and travel times to individual public supply wells, and a range-of-values approach for applying redox-specific biodegradation rates for individual VOCs. The results suggest that (1) higher recharge rates, shorter travel times, and more widespread anoxic conditions characteristic of eastern glacial regional aquifers increase overall vulnerability to VOC contamination, that (2) lower recharge rates, longer travel times, and more oxic conditions characteristic of western Basin and Range regional aquifers decrease overall vulnerability to VOC contamination, and (3) the relatively rapid oxic and anoxic biodegradation rates for the petroleum hydrocarbons benzene, toluene, and to a lesser extent MTBE, tends to decrease their detection frequencies relative to chlorinated hydrocarbons such as chloroform, PCE, and TCE.

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