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Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: A review and examples from principal aquifers in the United States

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SUMMARY

A detailed review was made of chemical indicators used to identify impacts from septic tanks on groundwater quality. Potential impacts from septic tank leachate on groundwater quality were assessed using the mass ratio of chloride–bromide (Cl/Br), concentrations of selected chemical constituents, and ancillary information (land use, census data, well depth, soil characteristics) for wells in principal aquifers of the United States. Chemical data were evaluated from 1848 domestic wells in 19 aquifers, 121 public-supply wells in 6 aquifers, and associated monitoring wells in four aquifers and their overlying hydrogeologic units. Based on previously reported Cl/Br ratios, statistical comparisons between targeted wells (where Cl/Br ratios range from 400 to 1100 and Cl concentrations range from 20 to 100 mg/L) and non-targeted wells indicated that shallow targeted monitoring and domestic wells (<20 m depth below land surface) had a significantly ($p < 0.05$) higher median percentage of houses with septic tanks (1990 census data) than non-targeted wells. Higher ($p = 0.08$) median nitrate–N concentration (3.1 mg/L) in oxic (dissolved oxygen concentrations >0.5 mg/L) shallow groundwater from target domestic wells, relative to non-target wells (1.5 mg/L), corresponded to significantly higher potassium, boron, chloride, dissolved organic carbon, and sulfate concentrations, which may also indicate the influence of septic-tank effluent. Impacts on groundwater quality from septic systems were most evident for the Eastern Glacial Deposits aquifer and the Northern High Plains aquifer that were associated with the number of housing units using septic tanks, high permeability of overlying sediments, mostly oxic conditions, and shallow wells. Overall, little or no influence from septic systems were found for water samples from the deeper public-supply wells.

The Cl/Br ratio is a useful first-level screening tool for assessing possible septic tank influence in water from shallow wells (<20 m) with the range of 400–1100. The use of this ratio would be enhanced with information on other chloride sources, temporal variability of chloride and bromide concentrations in shallow groundwater, knowledge of septic-system age and maintenance, and the use of multiple tracers (combination of additional chemical and microbiological indicators).

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1. Introduction

About one in four households in the United States uses an on-site waste-disposal system (typically a septic tank) or a small community cluster system to treat domestic wastewater. Septic-tank systems throughout the US process about 4 billion gallons per day of wastewater from an estimated 26 million homes and businesses and the resulting effluent is released to the subsurface (USEPA, 2002). About 10–20% of septic-tank systems fail annually (USEPA, 2002); although the actual rate can be quite variable from state to state (DeWalle, 1981; Gross and Thrasher, 1985; USEPA, 2002). The failure of septic-tank systems can increase the risk of contaminants entering the drinking water sources. Septic systems are sometimes located in close proximity to shallow domestic wells, increasing the probability of a direct connection between the septic system and the well, particularly in karst terrane (USEPA, 2002) and in crystalline-rock aquifers (Miller and Ortiz, 2007). Health concerns have arisen about groundwater quality in areas where septic tanks are poorly managed or where there are high densities of households with septic tanks (Ground Water Protection Council, 2007). High septic system densities were related to endemic diarrheal illness in Central Wisconsin (Borchardt et al.,

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2003b), and other studies have suggested a link between disease outbreaks and septic systems (e.g. Craun, 1979, 1984; Beller et al., 1997). DeBorde et al. (1998) found that seeded viruses are transported rapidly in a sand aquifer and long survival times resulted in the presence of viable seed virus for more than 9 months. Over the past several decades, studies repeatedly have shown that septic tanks contribute to degraded groundwater quality in shallow aquifers in urbanized areas (Katz et al., 1980; Harman et al., 1996; Andreasen and Fleck, 1997; Minnesota Pollution Control Agency, 1999; Jin et al., 2004; Francy et al., 2004; Gardner and Vogel, 2005; Panno et al., 2006, 2007; Landon et al., 2008; Brown et al., 2009). Shallow groundwater beneath septic systems has been shown to be elevated in nitrate, orthophosphate, chloride, sodium, calcium, potassium, dissolved organic carbon, and boron; depleted in dissolved oxygen, and depressed in pH (e.g. Peavy, 1978; Robertson et al., 1991, 1998; Panno et al., 2006, 2007). Also, elevated concentrations of trace metals (Fe, Al, Mn, Cr) can develop under anoxic conditions in plumes downgradient from septic systems (Robertson and Blowes, 1995). In karst aquifers and other highly vulnerable groundwater systems, such as fractured crystalline rock, enteric bacterial contamination from septic-tank systems has been documented (e.g. Panno et al., 2007; Harden et al., 2008). Recent studies have shown that short-circuiting of contaminated water from shallow aquifers or shallow zones within an aquifer can be withdrawn by a deep public-supply well (PSW) (Katz et al., 2007; Jurgens et al., 2008; Landon et al., 2009; Brown et al., 2009).

Over the past several decades, numerous studies have used a variety of chemical indicators to assess the influence of septic tanks on groundwater quality. For example, nitrate concentrations in community water system wells were related to the number of septic systems, unconfined formations, and rock type (Lichtenberg and Shapiro, 1997). Also, several studies have shown that the presence of nitrate in groundwater was correlated with septic tank numbers and density, and land use type (e.g. Katz et al., 1980; Perkins, 1984; Persky, 1986; Bicki and Brown, 1991; Hantzsche and Finnemore, 1992; Minnesota Pollution Control Agency, 1999; Gardner and Vogel, 2005). However, due to the non-conservative behavior of nitrate in suboxic or anoxic aquifers, several other studies have used conservative chemical constituents such as chloride and bromide ions to examine possible septic tank influence.

The focus of this paper is twofold: (1) to provide a review of Cl/Br ratios and other chemical indicators used to assess an influence from septic tanks on groundwater quality, and (2) to use Cl/Br ratios along with other chemical indicators and ancillary information to examine possible septic tank impacts on water quality in selected principal aquifers of the United States. Cl/Br ratios and other water quality data were analyzed for a large dataset containing a variety of well types (monitoring, domestic, and public supply) that represent different locations in the groundwater system (shallow or young versus deeper and possibly older waters) and different amounts of water withdrawals from principal aquifers in the United States. The ability to identify distinct chemical markers of septic-tank effluent (STE) in groundwater that can be analyzed relatively inexpensively and rapidly would have important human health and ecosystem implications for assessing impacts to groundwater quality.

1.1. Chloride to bromide mass ratio as an indicator of septic-tank effluent in groundwater

Chloride and bromide ions have been used to discriminate among various sources of anthropogenic and naturally occurring contaminants in groundwater. Both ions move conservatively in water, and have different abundances in natural fluids and solids (Davis et al., 1998). Even though chloride generally is 40–8000 times more abundant in nature than Br, chloride has a slightly lower aqueous solubility than bromide (Davis et al., 1998). As a result, plots of chloride concentrations and the mass (or molar) ratio of chloride to bromide (Cl/Br) have been used by several studies to distinguish pristine groundwater from wastewater sources and other anthropogenic and natural salinity sources such as road salt, seawater, and deep basin brines (Behl et al., 1987; Vengosh and Pankratov, 1998; Davis et al., 1998; Thomas, 2000; Dumouchelle, 2006; Panno et al., 2006; Landon et al., 2008; Alcalá and Custodio, 2008; Brown et al., 2009). Cl/Br mass ratios are presented in this paper; the Cl/Br molar ratio can be obtained by multiply mass ratio by 2.254.

Several studies have reported distinct ranges of Cl/Br ratios for various end members that control salinity processes in groundwater. Variations in Cl/Br ratios in rainfall and recharge waters have been extensively studied and are close to or below the Cl/Br ratio in seawater (290 ± 4). Alcalá and Custodio (2008) found that Cl/Br ratios in rainfall progressively decrease with distance from the coast (from about 290 to less than 130) based on samples from an extensive atmospheric deposition network and samples from 24 aquifers in Spain and Portugal. Cl/Br ratios in groundwater recharge also showed similar patterns in Spain and Portugal (Alcalá and Custodio, 2008) and for pristine groundwaters in the United States (Davis et al., 2004). However, Alcalá and Custodio (2008) found that salinity and Cl/Br ratios in groundwater were affected not only by variations in rainfall but by other factors such as orographic processes, proximity to urban and industrial areas, dissolution of evaporative rock outcroppings, mining facilities, Br-based pesticides (fumigants), and farm animal wastes (Hudak, 2003).

Cl/Br ratios in wastewater, such as septic-tank effluent and treated municipal wastewater, tend to have larger ranges due to variations in source water, salt intake, and other anthropogenic factors (Table 2). Thomas (2000) found that Cl/Br ratios above 400 were correlated with chemical constituents associated with human activities (higher nitrate concentrations, higher number of detections of volatile organic compounds, and pesticides). Vengosh and Pankratov (1998) used a higher range for the Cl/Br ratio (550–900) in sewage effluent to distinguish waters impacted by sewage from other anthropogenic sources with low Cl/Br ratios (such as street runoff, and agriculture return flow) and from natural contamination sources (such as salt water intrusion). Vengosh and Pankratov (1998) found that it was possible to detect and distinguish sewage contamination from marine ratios in groundwater when a sewage contribution of 5–15% is mixed with regional groundwater, particularly where the background bromide concentration in groundwater is low. Francy et al. (2004) found that detections of total coliforms or enteric viruses were statistically significant for Cl/Br ratios greater than 300 and were higher for groundwater samples from small public water supplies for residences served by septic systems than those served by sewer lines. They found that 88% of the total-coliform and virus-positive wells would have been properly identified using Cl/Br ratios as a screening technique for waters influenced by anthropogenic sources and susceptible to fecal contamination.

Although the conservative characteristics of Cl/Br ratios have been demonstrated for tracing the origin of salinity in groundwater (e.g. Sophocleous et al., 1990; Starr and Glotfelty, 1990), other studies have shown that sorption of Br on clays and iron oxides in the soil can affect Cl/Br ratios in water (Fabryka-Martin et al., 1991; Whittemore and Davis, 1995). Other processes can modify the Cl/Br ratio in groundwater including decomposition of organic matter that can add Br to solution (Gerritse and George, 1988; Fabryka-Martin et al., 1991; Cartwright et al., 2004), seawater intrusion and upconing of brines (Wilson and Long, 1993; Davis et al., 1998), and fluids derived from evaporite mineral dissolution (Vengosh and Pankratov, 1998). There can also be large ranges of

Cl/Br ratios for wastewater (Davis et al., 1998; Dumouchelle, 2006) that may overlap somewhat with Cl/Br ratios from other sources (Vengosh and Pankratov, 1998). Mixing of groundwater possibly affected by wastewater with water affected by other sources such as road salt (Brown et al., 2009) or halite (Cartwright et al., 2004) can result in high Cl/Br ratios. Mixtures with oil-field brines (Cl/Br 110–400) would also result in lower Cl/Br ratios but high Cl concentrations (Eberts et al., 1990; Thomas, 2000; Jagucki and Darner, 2001).

1.2. Review of potential markers of septic-tank effluent in groundwater

A variety of inorganic and organic chemical indicators have been used to evaluate impacts from septic tanks on shallow groundwater quality, mostly at a site-specific scale. The sodium to potassium (Na/K) ratio was useful in discriminating septic waste from other animal-derived nitrogen sources where Spruill et al. (2002) found that Na/K ratios in groundwater contaminated by septic wastes were significantly higher than groundwater contaminated by poultry wastes, land spraying of hog wastes, and fertilizers used on cropland or golf courses. Nishikawa et al. (2003) used nitrate/chloride ratios to determine that STE accounted for the increase in nitrate concentrations in an area where imported water was artificially recharged to groundwater. Other studies have used multiple indicators, such as a combination of nitrate isotope data ($\delta^{15}N$ and $\delta^{18}O$ of nitrate) (Aravena et al., 1993; Khayat et al., 2006), dissolved gases (N_2 and Ar), and organic wastewater compounds (Seiler, 2005). Landon et al. (2008) found that elevated concentrations of chloride (>30 mg/L), sulfate (90–220 mg/L), and boron (>50 μg/L) in water from wells in a shallow unconfined aquifer were associated with initial $\delta^{15}N$–nitrate values greater than 8.6‰ and likely related to many upgradient septic-tank systems. Chemicals present in laundry detergents, such as boron and optical brighteners, also are indicative of the effects of STE on groundwater quality (Alhajjar et al., 1990; Barringer et al., 2006; Panno et al., 2007). Other potential indicators of groundwater contamination from septic-tank systems include pharmaceutical compounds, pesticides, and chemicals in personal-care and household-cleaning products (Godfrey et al., 2007; Miller and Ortiz, 2007; Carrara et al., 2008).

In a study of volatile organic compounds (VOCs) in principal aquifers of the United States (1631 wells from primarily rural domestic supplies sampled between 1996 and 2002), Squillace and Moran (2007) found a positive correlation between septic-system density (in a 500-m radius buffer area around each well) and five VOCs [chloroform, methylene chloride, 1,1,1-trichlorethane (TCA), trichloroethene (TCE), and perchloroethene (PCE)]. They also found an association between septic tanks and chloroform, TCE, and PCE in samples from public water supplies. Chloroform can be formed in septic systems if household bleach (sodium hypochlorite) is present. Shock chlorination (bleach used to disinfect a private well contaminated by bacteria) is another source of free chlorine, which can react with naturally occurring organic material in groundwater to produce chloroform (Moran et al., 2004). Triclosan, an antimicrobial agent used in household dishwashing soaps, also reacts with chlorinated water to produce chloroform (Rule et al., 2005). Elevated chloroform concentrations in water mains and sewer lines also were used as a marker for leakage from these sources in a study of groundwater quality in the United Kingdom (Burston et al., 1993).

Mixing of septic-tank effluent with groundwater can reduce concentrations of constituents by dilution, but plumes from septic systems that contain elevated mobile solutes (e.g. Cl, Na, nitrate) have been delineated over considerable downgradient distances (more than 130 m) (Robertson et al., 1991). However, a limitation with using most of the aforementioned chemical markers for evaluating impacts from septic systems on regional scales and on deep groundwater is their non-conservative movement in the subsurface. In most cases, the concentrations of these markers in the unsaturated zone and in groundwater typically are affected by various biogeochemical processes, including mineral dissolution and precipitation, ion exchange, sorption, and microbial degradation. Also, given the chemical variability of STE from one household to another and seasonally due to differences in recharge rates (e.g. Robertson et al., 1991; Barringer et al., 2006), and differences in redox conditions (Robertson and Blowes, 1995), an "ideal" chemical marker of STE would need to be conservative as it moves through the unsaturated zone and in groundwater, which then could be used to investigate effects on groundwater quality from septic tanks at regional scales and in deeper parts of aquifers.

Chloride concentrations were elevated in water samples when an enteric virus was present in household wells in a rural subdivision served by septic-tank systems (Borchardt et al., 2003a), but chloride had a fairly low predictive power (15%) as an overall indicator of viruses in well water. Studies have shown that enterovirus contamination may be transient, as few wells test positive for sequential samples (Borchardt et al., 2003a; Francy et al., 2004).

2. Methods

2.1. Sources of water-chemistry data

The water-chemistry data analyzed in this paper includes water samples collected from public-supply, monitoring, and domestic wells during 1993–2005 as part of numerous studies of the US Geological Survey's (USGS) National Water Quality Assessment (NAWQA) Program (USGS, 2006a). These data included water samples from 1848 domestic wells in 19 principal aquifers, (Fig. 1); 121 public-supply wells (PSWs) in seven principal aquifers (Fig. 1). Monitoring wells (123) were located in modeled contributing recharge areas to a studied PSW in each of four principal aquifers (Fig. 1) and in overlying hydrogeologic units (Table 1).

Detailed hydrogeologic and water-quality information are available for the monitoring and PSWs (Delzer and Hamilton, 2007; Katz et al., 2007; Jurgens et al., 2008; Landon et al., 2008; Brown et al., 2009), and for the domestic wells (DeSimone, 2009). Chemical data for water samples from the three well types included major ions, boron, bromide, dissolved organic carbon (DOC), nutrients (N and P species) and selected VOCs (including chloroform, tetrachloroethene, trichloroethene, methylene chloride, and trichloroethane). Water samples from monitoring wells were analyzed for nitrogen isotopes of nitrate in addition to the aforementioned constituents. Water samples were collected using USGS protocols designed to collect representative groundwater samples (Koterba et al., 1995; USGS, 2006b; Moran et al., 2006). Water samples were collected directly from PSWs and domestic wells before any water treatment and, in most instances, before any pressure or holding tanks (Carter et al., 2007; DeSimone, 2009). Chemical data from the different studies are directly comparable as they were collected using consistent field methods, laboratory analytical procedures, and quality assurance techniques (USGS, 2006b). Cl and Br in filtered (0.45 μm) water samples were analyzed using ion chromatography methods (Fishman and Friedman, 1989), with method reporting levels of 0.12 and 0.02 mg/L, respectively. Median recoveries for instrument spikes were 99% for both Cl and Br during the period January 2002 through December 2007. Percent recoveries for Cl and Br in instrument spikes ranged from 75–121 for the 95% confidence interval (2σ) with a median of 99.

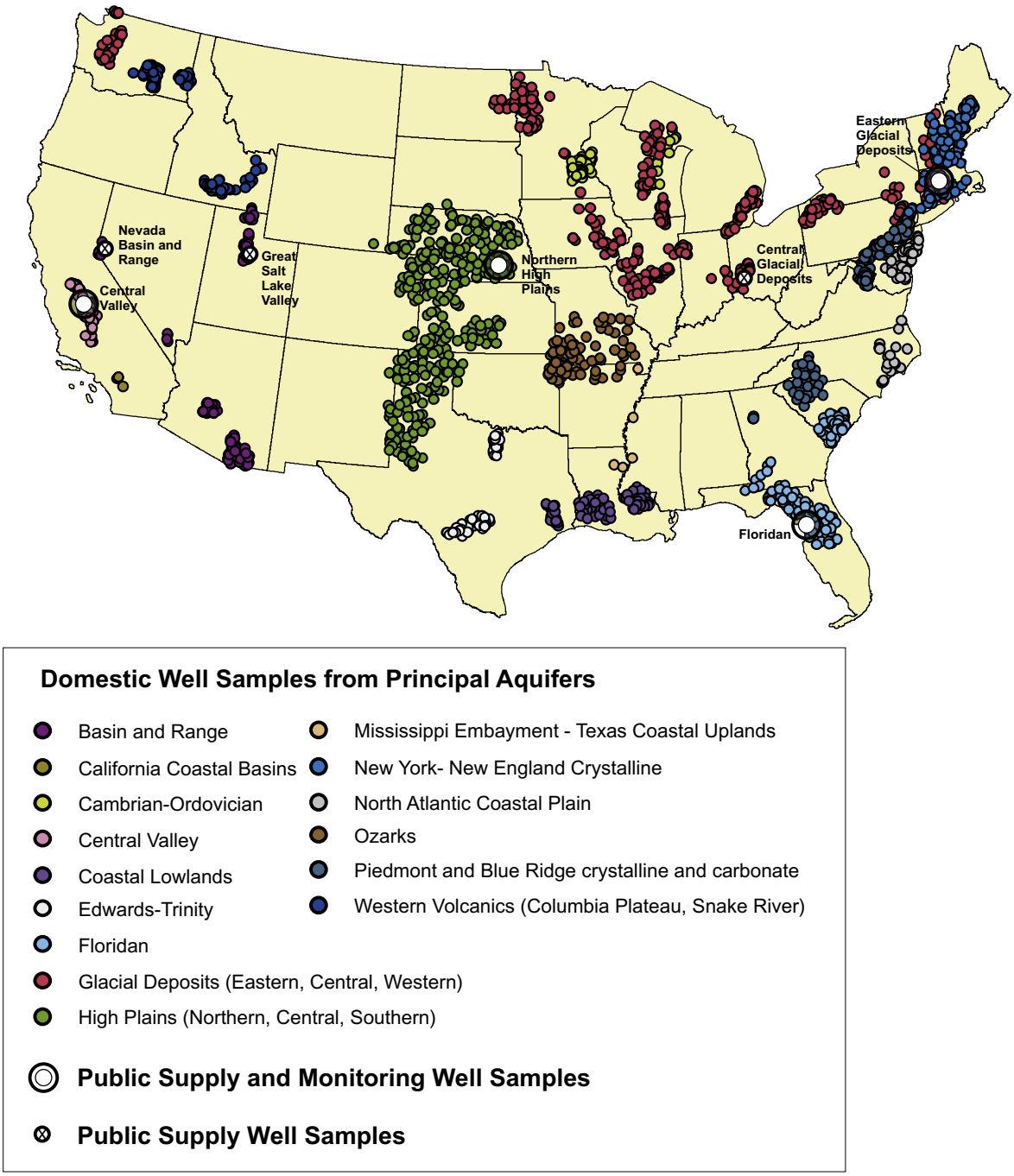

Fig. 1. Map showing location of domestic wells sampled in 19 principal aquifers in the United States and general location of sampled public-supply wells and monitoring wells in four principal aquifers.

2.2. Ancillary data and statistical analyses

Cl/Br ratios and other chemical data for water from each well were evaluated statistically with selected hydrogeologic and anthropogenic variables for a circular area (500-m radius buffer) around each well site. These factors, which can affect the sources, movement, and fate of various chemical constituents and microorganisms in the subsurface, consisted of land use characteristics, census data such as the percent of households served by septic tanks, the number of underground storage tanks present, well characteristics, aquifer properties, and soil characteristics. The use of a circular area (500-m radius circle) around each well is based on previous investigations that found significant correlations between groundwater quality and a variety of hydrogeologic and anthropogenic factors within circular buffer areas (Nolan and Hitt, 2006; Squillace and Moran, 2006; Moran et al., 2007; Lindsey et al., 2009). Sources of ancillary data along with some of their limitations and assumptions are discussed in more detail by previous studies (e.g. Squillace et al., 2004; Moran et al., 2006; Squillace and Moran, 2006; DeSimone, 2009). In addition, ancillary information was compared with Cl/Br ratios in a simulated area contributing recharge (ACR) (Reilly and Pollock, 1993) for each public-supply well that was delineated using regional scale groundwater flow models and particle tracking (Paschke, 2007). The particle tracking approach included a grid-refinement program so that particle movement to the PSW was adequately represented

Table 1
Number of domestic, public supply, and monitoring wells in the 19 studied principal aquifers.

Principal aquifer	Domestic wells	Public-supply wells	Monitoring wells
Basin and Range	127	46: (31 GRSL; 15 NVBR)	
California Coastal Basins	5		
Cambrian–Ordivician	71		
Central Valley	77	15	23
Coastal Lowlands	73		
Edwards–Trinity	67		
Floridan	97	30	28: (13 Floridan, 11 surficial aquifer system, 4 intermediate confining unit)
Glacial Deposits-Central	292	13	
Glacial Deposits-Eastern	72	9	36
Glacial Deposits-Western	54		
High Plains-Central	89		
High Plains-Northern	166	8	36
High Plains- Southern	46		
Mississippi Embayment–Texas Coastal	5		
NY–New England Crystalline	113		
North Atlantic Coastal Plain	65		
Ozark Plateaus	107		
Piedmont/Blue Ridge	183		
Western Volcanics	139		

Note: GRSL, Great Salt Lake aquifer; NVBR, Nevada Basir and Range aquifer.

in models otherwise constructed to describe flow at a regional scale (Paschke, 2007). This additional ancillary information also included parameters such as travel times through various aquifer zones, percentage of well flow through various oxidation–reduction (redox) conditions and beneath different land uses for the zone of contribution (ZOC) (Morrissey, 1989), the number of underground storage tanks, and nitrogen in fertilizer applied in the ACR. Having ancillary data for both circular areas around each PSW and for modeled ACRs allows for a comparison of datasets regarding assessments of potential water-quality degradation.

Nonparametric statistical techniques (Spearman's correlation test) are used to determine relations among chemical constituents and ancillary data. Descriptive and nonparametric statistical tests (Wilcoxon rank-sum, Kruskall-Wallis, Chi-square) are used to summarize and compare chemical data between targeted (Cl/Br ratio range, 400–1100; Cl concentration range, 20–100 mg/L) (see below) and non-targeted well groups (SAS Institute, Inc., 1989a,b; Helsel and Hirsch, 1992).

2.3. Targeted Cl/Br ratios and chloride concentrations

Based on previous studies, the potential influence of wastewater from septic tanks on groundwater quality is assessed in this study by comparing a targeted group of wells that have a septic tank influence with a non-targeted group of wells that do not. These two groups were defined using Cl/Br mass ratios and chloride concentrations. The targeted well group had Cl/Br ratios in the range of 400–1100 and chloride concentrations in the range of 20–100 mg/L; the non-targeted group had Cl/Br ratios and Cl concentrations outside of these ranges. These ranges incorporate data from previous studies that have used Cl/Br ratios to distinguish wastewater (septic-tank) sources from other potential sources of Cl and Br in groundwater (Table 2). These ranges for Cl/Br ratios and Cl concentrations also are consistent with data from a recent study of the attenuation of nutrients, other chemical species, and microorganisms in the subsurface beneath three septic-tank drainfields in northern Florida (Katz et al., 2010), in which the median Cl/Br ratio in STE was 694 ($N = 9$ range 540–1150), which is similar to the median value (769; $N = 29$) reported by Panno et al. (2006) for STE. The range and median of Cl/Br ratios are smaller and lower for well water samples collected at the water table (335–805; median 518) beneath the drainfields (Katz et al., 2010), but the median still falls within the 400–1100 range. Lower Cl/Br ratios in groundwater beneath the septic tanks may result from release of Br from clays, as the Br concentrations in the groundwater samples generally are higher than those in the STE and were higher at the site with higher content of clay material (Katz et al., 2010). Higher bromide concentrations (and correspondingly lower Cl/Br ratios) may also originate from decomposition of organic matter (Gerritse and George, 1988; Seaman et al., 1996).

In addition to delineating a targeted range of Cl/Br ratios and chloride concentrations, binary mixing curves were developed to show how the Cl/Br ratio of dilute groundwater changes with the addition of increasing amounts of Cl from different sources (domestic wastewater, halite (road salt), and seawater. The septic tank end-member has a Cl/Br ratio of 769 and a Cl concentration of 91 mg/L (Panno et al., 2006). The seawater end member has a Cl/Br ratio of 67.2, based on chloride and bromide concentrations of about 19,500 and 290 mg/L, respectively (Davis et al., 1998). The Cl/Br ratio of 6770 for road salt (halite) is based on chloride and bromide concentrations of about 10,000 and 1.48 mg/L, respectively (Granato, 1996). The high Cl/Br ratio in halite results from the depletion of bromide in halite (about a factor of 20–30 relative to Cl) because of its larger size (Schoonen et al., 1995). Water-softener backwash is another source of halite that could be introduced to groundwater from disposal into septic tanks, dry-wells, storm-sewers, or ditches (Thomas, 2000). The primary source of chloride and bromide in pristine groundwater is atmospheric deposition, which has Cl/Br ratios in the range of 50–100. Near the coast, Cl/Br ratios are closer to seawater (about 290), and they decrease to 20–56 in the midwestern US (Panno et al., 2006). Cl/Br end-member values used in this study for different sources are similar to those used to develop binary mixing curves in other studies (e.g. Davis et al., 1998; Thomas, 2000; Jagucki and Darner, 2001; Francy et al., 2004; Brown et al., 2009).

3. Results and discussion

3.1. Public-supply wells (PSWs)

The first part of this section examines Cl/Br ratios in water samples from the dataset of 121 PSWs (Table 1) relative to other chemical indicators and relative to ancillary information for two areas around wells (circular areas and modeled areas contributing recharge (ACR) for each PSW). The second part of this section presents detailed chemical information for shallow monitoring wells that are located within a modeled ACR for an intensively studied PSW in four aquifers: the Eastern Glacial Deposits, Central Valley, Floridan, and Northern High Plains aquifers. Most PSWs sampled in all six principal aquifers are deep (Fig. 2) (median depths below land surface >80 m), with the exception of the Eastern and Central Glacial Deposits aquifers that have median well depths of 14 m and 37 m, respectively.

3.1.1. 500-m radius circular areas around each PSW

Differences in Cl/Br ratio between targeted (Cl/Br ratio, 400–1100; Cl concentrations, 20–100 mg/L) and non-targeted PSW groups were not consistent with the percentage of households on septic-tank systems—the percentage was significantly higher for

Table 2
Ranges of Cl/Br ratios, chloride and bromide concentrations for selected sources of chloride and bromide in ground water. Concentrations are in milligrams per liter. NA, no data available.

Source	Cl	Br	Cl/Br mass ratio	Cl/Br molar ratio	References
Sewage or septic-tank effluent					
Sewage samples from US, England	NA	NA	300–600	676–1350	Davis et al. (1998)
(Israel)	260–396	0.4–0.9	410–873	924–1970	Vengosh and Pankratov (1998)
Septic-tank effluent	69	NA	450	1010	Thomas (2000), Jagucki and Darner (2001)
Septic-tank effluent, median values; midwestem US	91	0.118	769	1730	Panno et al. (2006)
Pomperaug leachfield median	62.7	0.053	852	1920	Brown et al. (2009)
	NA	NA	275–531	620–1200	Behl et al. (1987)
Septic-tank effluent-tile drainfield (HSTS-MD-18)			1167	2630	Dumouchelle (2006)
Septic-tank effluent-(HSTS-MD-19)			513	1155	Dumouchelle (2006)
Septic-tank effluent-median of 9 samples	35.0 (20–136)	0.050 (0.02–0.25)	694 (544–1150)	1564 1230–2590	Katz et al. (2010)
Road salt or halite					
Road salt analysis	10,000	1.5	6667	15,000	Granato (1996)
Highway runoff	80,000		3300	7440	Granato (1996)
First flush winter storm	17,000		58,621	132,000	Granato (1996)
Road salt			1000–10,000	2250–22,500	Davis et al. (1998)
Analysis of road salt (Long Island)	10,000	1.76	5690	12,800	Schoonen et al. (1995)
Seawater					
	19,000–20,000		288–292	649–658	Davis et al. (1998)
	19,000	65	292	658	Hem (1992)
	18,800	67	281	633	Krauskopf (1979)
Basin brines					
	64,600	ND	406	915	Panno et al. (2006)
	75,800–251,000	315–4210	110–213	248–480	Wilson and Long (1993)
			200–400	450–900	Davis et al. (1998)
Atmospheric deposition					
Inland US			50–120	113–270	Davis et al. (1998)
Near coast, US			130–180	293–406	Davis et al. (1998)
Midwestern US; median of 4 samples;	0.2	0.0045	47	106	Panno et al. (2006)
High altitude continental, Spain, Portugal			89–244	200–550	Alcalá and Custodio (2008)
Inland areas, Spain, Portugal			133–288	300–650	Alcalá and Custodio (2008)
Coastal areas, Spain, Portugal			222–315	500–710	Alcalá and Custodio (2008)
Dry deposition, Spain, Portugal			75–634	169–1430	Alcalá and Custodio (2008)
Volcanic contribution of halides					
			330–490	750–1100	Alcalá and Custodio (2008)
Landfill leachate					
Median of samples from 7 Illinois landfills	1284	7.81	193	435	Panno et al. (2006)
Garbage and solid waste leachate			330–440	750–1000	Alcalá and Custodio (2008)
Animal waste					
Hog and horse waste; median of 4 samples	847	0.572	1245–1654	2810–3730	Panno et al. (2006)
Goats, cattle, horses:medians of 5 samples of each			58; 86; 146	131;94;329	Hudak (2003)

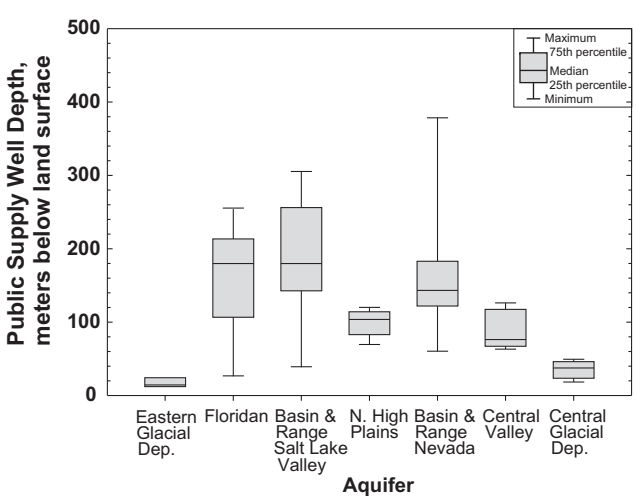

Fig. 2. Boxplot showing depth distribution for public-supply wells in selected principal aquifers.

the non-target well group than the target group (Table 3) (Table S1 in the Supplementary Information). In the targeted well group there was a significant correlation between this variable and the percent cropland indicating that septic tanks were more prevalent in agricultural areas. No significant correlations were found between percent households with septic tanks and percent agricultural land for the non-targeted well group. There were no significant differences between nitrate–N concentrations in water from 21 targeted PSWs compared to 63 non-targeted PSWs. Similarly no significant difference was found for nitrate–N between the two groups when only oxic waters ($O_2 \geqslant 0.5$ mg/L) were compared. There were no significant differences between concentrations of the five selected VOCs between the targeted and non-targeted groups of wells when non-detects were removed from the dataset (Table S1 in the Supplementary Information).

Several PSWs in the Basin and Range aquifer in Utah (Great Salt Lake aquifer) and the Glacial Deposits aquifer in the central US have Cl/Br ratios in the targeted range (Fig. 3). The targeted well group in the Great Salt Lake aquifer did have a significantly higher percentage of houses on septic tanks ($p < 0.05$) than non-target wells. However, no differences in nitrate–N or other chemical

Table 3
Comparison of wells with Cl/Br mass ratios and chloride concentrations within and outside the targeted area of possible septic tank influence.

	All domestic wells: 500-m radius circular area around well	Shallow domestic and Monitor Wells (⩽20 m depth); 500-m radius circular area around well	Public-supply wells: 500-m radius circular area around well	Public-supply wells; modeled areas contributing recharge
Median percentage or number of houses served by septic systems	No statistically significant difference between well groups	No statistically significant difference between well groups	SIGNIFICANTLY HIGHER for wells with Cl/Br and Cl outside of targeted ranges	SLIGHTLY HIGHER for wells with Cl/Br and Cl within targeted ranges, NOT SIGNIFICANTLY
Well depth	SIGNIFICANTLY LOWER for wells with Cl/Br and Cl in targeted ranges	Not Applicable	No statistically significant difference between well groups	No statistically significant difference between well groups
Minimum and median simulated travel times	Not Applicable	Not Applicable	Not Applicable	SIGNIFICANTLY LOWER for wells with Cl/Br and Cl within targeted ranges

constituents were found between the two groups for both aquifers; unfortunately, there was a small number of wells for comparison between the two groups (Table 1). Other recent studies in the valley fill aquifer in Utah have shown that nitrate contamination of groundwater originates from multiple sources including fertilizer, septic tanks, and feedlots (Wallace, 2007, 2008). There were no differences in the percentage of houses on septic tanks and other variables between target and non-target PSWs in the Central Glacial Deposits aquifer. However, in a groundwater quality study of the Central Glacial Deposits aquifer in a suburban area near Detroit, Michigan, Thomas (2000) found that Cl/Br ratios above 400 were useful in attributing elevated salinities to septic-system effluent (particularly water-softener backwash) and infiltration of storm-water runoff from paved surfaces.

3.1.2. Area contributing recharge (ACR) and zone of contribution (ZOC) for each PSW

Similar to the lack of differences between targeted and non-targeted well groups for ancillary data within a circular area around each PSW, there were few differences between target and non-target PSWs for data within modeled ACRs. Based on 21 wells in the target group and 62 non-target wells, the number (and percent) of houses served by septic tanks was slightly higher (but not statistically significant) for the targeted well group compared to the non-target group (Table S2 in the Supplementary Information). There was no significant difference in nitrate–N concentrations between the groups, although there was a significantly higher percentage of agricultural land use in the ACR for the non-target well group. The slightly higher median nitrate–N concentration in the non-target group could be related to the significantly higher contributions of nitrogen from fertilizers in the ACR for the non-targeted group compared to the target well group. No significant differences were found for well depth, dissolved oxygen, soil permeability. It is worth noting that the target well group has significantly shorter travel times in the modeled ZOC than those for the non-target well group ($p < 0.05$) (Table 3), suggesting that water from PSWs with Cl/Br ratios in the targeted range may be indicative of wells that contain younger water and hence are more vulnerable to contamination.

The most shallow PSWs (⩽26 m depth below land surface (bls)) in the target group were in the Glacial Deposit aquifers in the central and eastern US. Water from these wells generally had nitrate–N concentrations >1.5 mg/L (for oxic conditions) with median travel times <7 years. For shallow non-target PSWs, nitrate–N concentrations were lower (median 0.6 mg/L), and median travel times generally were also less than 7 years (but as high as 26 years). Non-target shallow wells also were in Glacial aquifers in the central and eastern US.

3.1.3. Monitoring wells within the area contributing recharge to a PSW

Water from shallow monitoring wells are often the most likely to reveal impacts from septic-tank systems. Thomas (2000) found that shallow wells (<15 m depth) in Glacial Deposits aquifer in the Midwest US (Detroit area) had higher median nitrate, dissolved

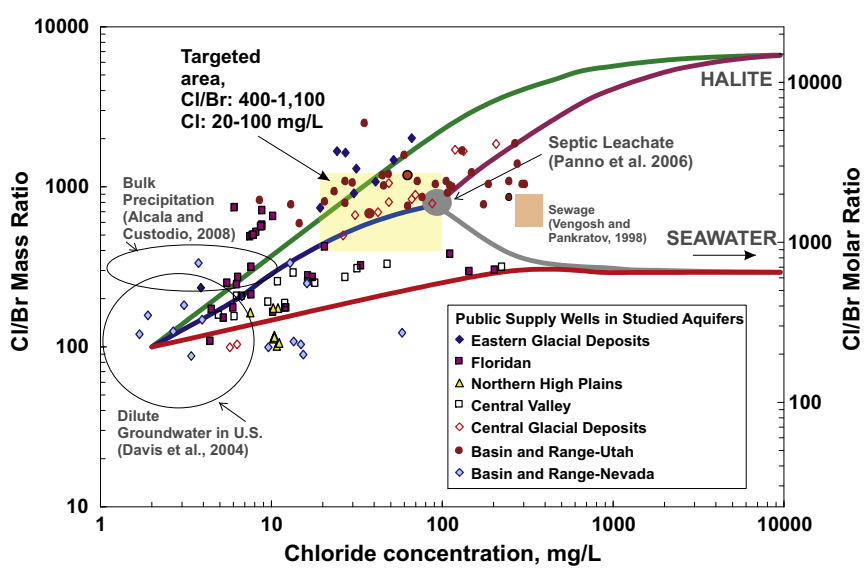

Fig. 3. Plot of Cl/Br ratios versus chloride concentrations in water samples from public-supply wells. Also shown are binary mixing lines between dilute groundwater and halite, septic leachate, and seawater; and between septic leachate and halite and seawater.

solids, and chloride concentrations than deep wells (⩾15 m) and this could be attributed to influence from septic tanks and storm-water runoff. Mullaney and Grady (1997) found elevated concentrations of nitrate and VOCs in wells up to 20 m below the water table that were attributed to several anthropogenic sources. Four aquifers (Eastern Glacial Deposit, Central Valley, Upper Floridan, and Northern High Plains) contain several shallow monitoring wells that are located within a modeled ACR for an intensively studied PSW.

In two of the study areas, the Eastern Glacial Deposits and the Northern High Plains aquifer, water-chemistry data from shallow monitoring wells (<20 m) indicated a septic tank source. Depths of shallow monitoring wells in the Eastern Glacial Deposits aquifer (Woodbury, Connecticut, study area) range from 4.0 to 11.2 m bls. These wells, located downgradient from residences with septic-tank systems (Brown et al., 2009), yielded water samples with Cl/Br ratios that ranged from 521 to 3150, with a median Cl/Br ratio of about 920 and a median Cl concentration of 54 mg/L. However, water from one well (CT-WY85) in this study area with the highest Cl/Br ratio (3150) and elevated Cl concentrations (200–400 mg/L) likely indicates impacts from halite on nearby roads (Fig. 4) (Brown et al., 2009). The median nitrate–N concentration in water from wells near septic-tank systems was 10 mg/L in the mostly oxic glacial aquifer, but nitrate–N concentrations were much lower (near the method reporting level, 0.06 mg/L) in water samples from wells under anoxic conditions (e.g. well WY85) where denitrification likely occurred (Brown et al., 2009). Other wells not directly downgradient from septic-tank systems but possibly affected by septic-system leachate have Cl/Br ratios of 644–957 (well WY76) and 1158 (well WY73), and Cl concentrations from 29–37 mg/L. These shallow wells ranged in depth from 4.3 to 10.7 m bls, and yielded water samples with elevated concentrations of nitrate–N, dissolved organic carbon, chloride, and boron. Boron is a component of many detergents and typically found in wastewater, although variations in detergent composition mean that this will not always be the case (Barrett et al., 1999). Elevated concentrations of these chemical constituents are consistent with a septic tank influence for these wells. Other evidence for a septic tank influence was elevated dissolved organic carbon (DOC) concentrations. The median DOC concentration was 0.8 mg/L in water from wells downgradient from septic-tank drainfields. However, not all these wells had elevated DOC concentrations. In some areas, rapid oxidation of DOC into CO_2 may account for the lower DOC concentrations (Brown et al., 2009). With the exception of one sample (Cl/Br = 1255), Cl/Br ratios (789–1070) (Fig. 5) and Cl concentrations (30–34 mg/L) for the shallow PSW (well CT-WY23, depth 16 m bls) plot in the target area for septic tank influence. Water from the PSW also contains elevated nitrate–N concentrations (1.8–1.9 mg/L) and delta ^{15}N–NO_3 values (8.0–8.5‰) that are consistent with an organic nitrogen source.

Water samples from several monitoring wells in the Northern High Plains aquifer (wells OFPS-38 and UWT2–23) have Cl/Br ratios and Cl concentrations that plot within or close to the targeted area for groundwater affected by septic leachate (Fig. 4). In the York, Nebraska, study area in the Northern High Plains aquifer, water from monitoring wells in shallow unconfined urban areas with houses using septic tanks had relatively high chloride concentrations (33–187 mg/L) but had low Cl/Br ratios that ranged from

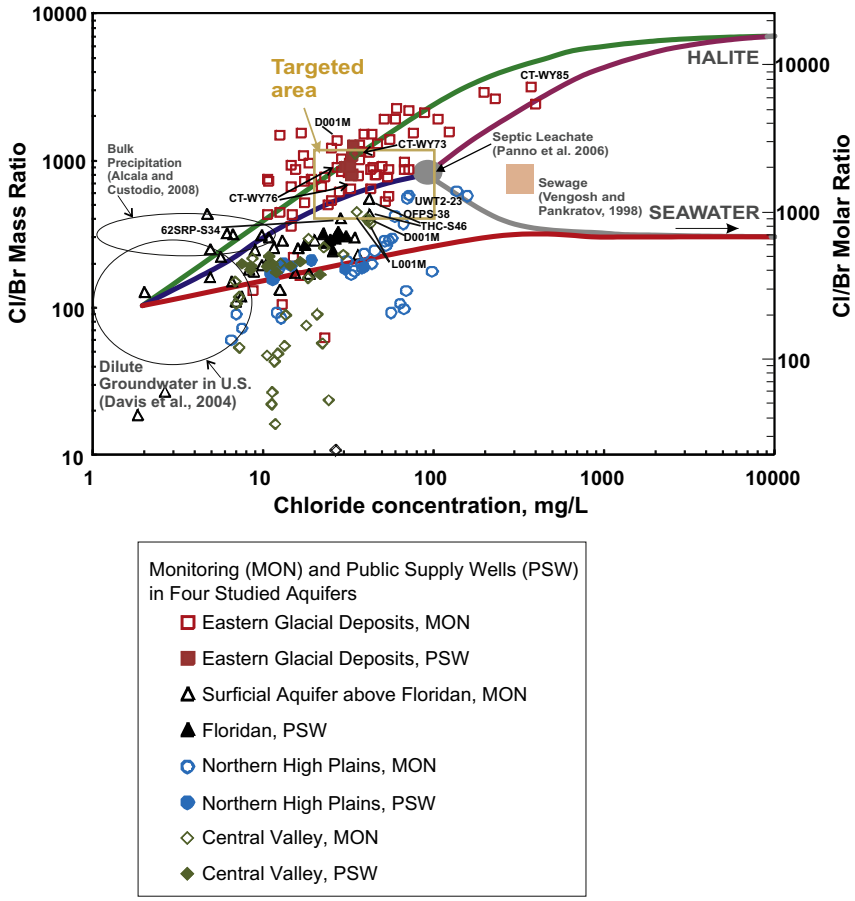

Fig. 4. Plot of Cl/Br versus chloride concentrations for public-supply wells and monitoring wells (<20 m depth) in modeled contributing recharge areas to studied public-supply wells in four aquifers. Also shown are binary mixing lines between dilute groundwater and halite, septic leachate, and seawater; and between septic leachate and halite and seawater.

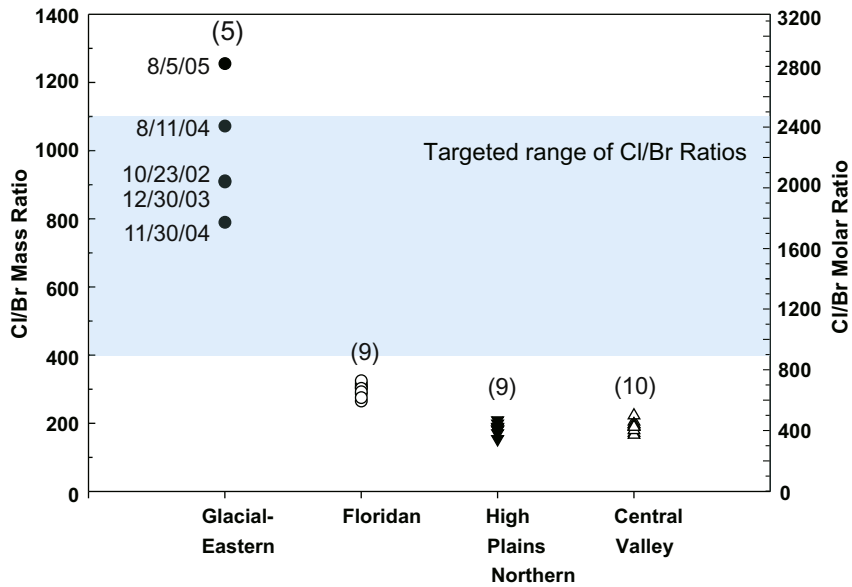

Fig. 5. Plot showing fluctuations in Cl/Br ratios in water samples from a public-supply well in four aquifers. Water samples from 2002 to 2005. Number of samples in parentheses.

96 to 778. Based on associations of boron, chloride, initial δ^{15}N–nitrate, potassium, orthophosphate, and sulfate concentrations, Landon et al. (2008) inferred a septic tank influence for these wells. Water from well UWT2–23 (Cl/Br = 572–617) was considered to be a septic impacted end-member based on chloride and potassium concentrations, and boron concentrations were higher than values in agricultural shallow unconfined wells but overlapped with values in unmixed confined wells (Landon et al., 2008). Septic systems primarily located near upgradient margins (west) of York likely would be points of focused recharge to the aquifer, as there is less estimated recharge beneath the York urban area than in the upgradient agricultural area (Landon et al., 2008). Based on nine water samples collected during 2002–2005, the studied PSW had Cl/Br ratios (154–208) and Cl concentrations (11–39 mg/L) that plot below the target area (Fig. 4). Although this PSW is vulnerable to contamination from the overlying shallow unconfined aquifer due to downward leakage through well bores or wells that penetrated overlying upper and lower confining units (Landon et al., 2008), influence from septic tanks appears to be minimal.

Water from two shallow monitoring wells in the Upper Floridan aquifer (well depth, 10.4 m) in the surficial aquifer system (wells 62SRP-S34 and THC-S46) overlying the Upper Floridan aquifer, had a Cl/Br ratios of 402–548 and a chloride concentrations of 29–43 mg/L (Fig. 4). Although this area is sewered, leakage from sewer lines may have affected the groundwater quality at this site. The young age of water from well THC-S46 [(<8 yrs, assuming piston flow (Katz et al., 2007)] is not consistent with a septic tank source, as sewers were installed more than 30 years ago. However, a sewage-related source at well 62SRP-S34 is consistent with elevated concentrations of potassium (2.1 mg/L), nitrate–N (3.2 mg/L), and dissolved organic carbon (13.8 mg/L). A dissolved oxygen concentration of 6.8 mg/L in the sample likely indicates rapid movement of water from the surface to the water table. Unfortunately, there were no analyses for boron or nitrogen isotopes for water samples from this well, which could help identify a human wastewater source. Low Cl/Br ratios for the Floridan PSW (242–325) and Cl concentrations (18–31 mg/L) plot outside the targeted group (Fig. 4). Mixing of water from the surficial and Floridan aquifer systems have resulted in elevated nitrate–N concentrations (0.7–3.6 mg/L) in the PSW; however, denitrification likely occurs in the anoxic Floridan aquifer system in this area (Katz et al., 2007).

Low Cl/Br ratios and Cl concentrations for most monitoring wells and the PSW for the study area in the Central Valley aquifer plot below the targeted area for septic tank influence (Fig. 4). However, two shallow wells (D001 M, 11 m depth; L001 M, 12.5 m depth) have Cl/Br ratios of 400–1100 and 368–441, respectively, along with elevated nitrate–N concentrations (6.5–8.6 mg/L) and (8.3–11 mg/L), which may indicate a septic tank influence in this oxic groundwater system. Agricultural activities likely have influenced the groundwater chemistry in this area as indicated by elevated nitrate–N concentrations in water from the PSW (1.9–9.7 mg/L) and in several shallow monitoring wells in this study area (Jurgens et al., 2008).

Nitrate and nitrate isotope data were not always consistent with Cl/Br ratios as indicators of the possible impact of septic tanks on groundwater quality in the four aquifers. For example, water from monitoring wells in the Eastern Glacial Deposits and High Plains aquifers generally had the highest δ^{15}N–NO_3 values (>15‰), which tended to be associated with low nitrate–N concentrations (<0.1 mg/L) (Fig. 6) and likely indicative of denitrification rather than an organic N source. Some δ^{15}N–NO_3 values (>10‰) in monitoring wells also were associated with higher nitrate–N concentrations (>2.0 mg/L), which likely indicate a wastewater N source. However, water from these wells had a wide range of Cl/Br ratios (Fig. 6). Water from only two targeted wells (Cl/Br 400–1100 and Cl concentrations 20–100 mg/L) in each aquifer have δ^{15}N–NO_3 values that may indicate a wastewater source (>10‰). Some wells downgradient from septic-tank drainfields in the Eastern Glacial Deposits aquifer had high δ^{15}N–NO_3 values (>9‰) that were consistent with a septic-system leachate source of nitrate; however, the use of nitrogen and oxygen isotopes of nitrate to differentiate nitrate sources may have been affected by gas stripping, sporadic fertilizer use, and poor well yields (Brown et al., 2009). Other processes, such as mixing of waters from various aquifer zones, and variable redox conditions (denitrification) limit the use of nitrate and nitrogen isotopes to determine possible impacts from septic-tank systems.

3.2. Domestic wells

This section provides an examination of Cl/Br ratios in water samples from the entire domestic well dataset (1848 wells in 19

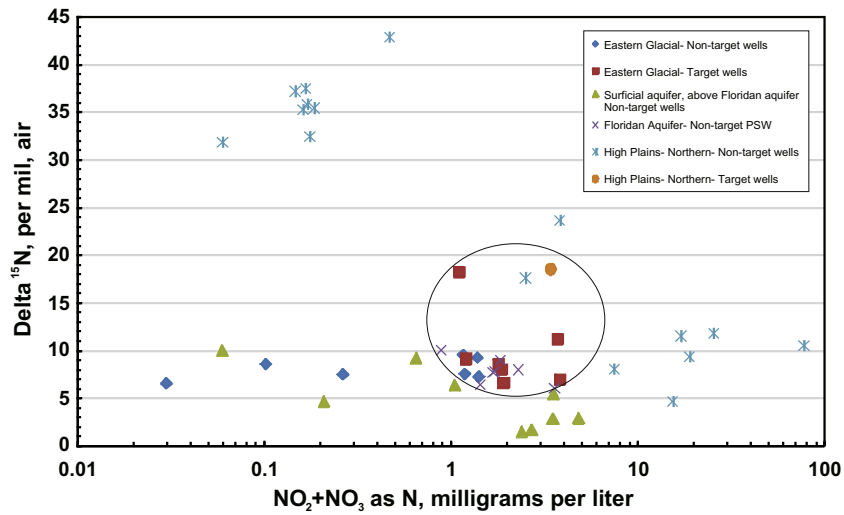

Fig. 6. Plot of delta $^{15}N–NO_3$ and nitrate–N concentrations for targeted and non-targeted shallow (<20 m depth) monitoring wells (based on Cl/Br ratios, see text for more explanation) in modeled contributing recharge areas to studied public-supply wells in four aquifers. The circular area represents a likely wastewater source based on delta $^{15}N–NO_3$ and nitrate–N concentrations.

principal aquifers; Table 1). Subsets of this database were examined for each aquifer and for shallow wells (<20 m depth). The ratios of Cl/Br are compared to other chemical indicators and ancillary information within circular areas around each domestic well.

The percentage of households served by septic tanks for domestic wells was similar among the 19 aquifers (Fig. 7a), and well depths generally were similar and deep (Fig. 7b), but there were some notable differences for the entire dataset between the 138 targeted wells (Cl/Br ratios, 400–1100; Cl concentrations, 20–100 mg/L) and the 1193 non-targeted wells (Table S3 in the Supplementary information). Nitrate–N concentrations were significantly higher in water from targeted wells than non-target wells and among all redox conditions in the targeted well group. The targeted well group had statistically significantly shallower depths below the water table than wells in the non-targeted group (Table 3), which may indicate a greater vulnerability to contamination than deeper wells in the non-target group. There also was a significant correlation between nitrate–N concentrations and soil drainage characteristics (higher nitrate concentrations in more well-drained soils), but no correlation between nitrate–N and percent agricultural land for the targeted wells. In contrast, nitrate–N concentrations were significantly correlated with the percentage of cropland, soil drainage characteristics, and chloride concentrations for the non-target well group. When only samples with oxic conditions ($O_2 \geqslant 0.5$ mg/L) were included, nitrate–N concentrations also were significantly higher for water in the targeted group, and there was no correlation between nitrate–N concentration and percent agricultural land use or the percentage of households on septic tanks. There was a significant correlation between chloride concentrations and potassium, sulfate, and boron concentrations for the non-target group of wells (possible influence from agricultural land use), but only potassium and chloride were correlated with one another for the target group of wells. When non-detects were removed from the dataset for chloroform, TCE, PCE, TCA, and methylene chloride, there were no significant differences in concentrations between the targeted and non-targeted groups. However, the median, mean, and maximum chloroform and trichloroethane (TCA) concentrations were higher in the targeted group than the non-targeted group when non-detects were removed (Table S3 in the Supplementary information). In contrast, the median, mean, and maximum concentrations of PCE, TCE, and methylene chloride were higher in the non-targeted group than for the targeted group of wells when non-detects were removed.

3.2.1. Comparisons of target and non-target domestic wells for each principal aquifer

When target and non-target groups of domestic wells were compared for each aquifer, there were significantly higher nitrate–N concentrations for target wells only for three of the 19 aquifers (New York–New England crystalline, the North Atlantic Coastal Plain and the Blue Ridge crystalline and carbonates). However, the percentage of households on septic systems was not significantly different with the exception of the Northern High Plains aquifer. Median values for the percentage of households in circular areas around each well that were served with septic tanks were greater than 75%, with the exception of California Coastal Basins aquifer where the median value was 65%. Most of the circular areas around domestic wells in these aquifers are dominated by agricultural land use. There were significantly higher percentages of cropland for the targeted well group compared to the non-targeted well group in seven aquifers (Basin and Range, Cambrian–Ordovician, Central Valley, Northern High Plains, North Atlantic Coastal Plain and the Piedmont-Blue Ridge crystalline and carbonates, and the Western Volcanics). Boron concentrations were significantly higher in the targeted well group than the non-targeted group in the Coastal Lowlands and Central Valley aquifers, but only three wells had boron concentration data in the target group for the Coastal Lowlands aquifer. Significant correlations between boron, nitrate, and chloride were found only for the targeted well group in the Cambrian–Ordovician aquifer; there was a significant correlation between boron and sulfate for the targeted well group in the Central Valley and Eastern Glacial Deposits aquifers. Boron and nitrate concentrations were inversely correlated in the Piedmont-Blue Ridge aquifer. There were no significant differences in VOC concentrations between the target and non-target group wells in any aquifers. However, when non-detects were removed from the dataset, there were higher mean and median chloroform, trichloroethane, trichloroethene, and PCE concentrations in the targeted well group compared to the non-target well group (Table S4 in the Supplementary Information).

3.2.2. Subset of shallow domestic wells

Similar statistical comparisons were made between targeted and non-targeted well groups for a subset containing shallow domestic wells (depths $\leqslant 20$ m) to test if water from shallow wells is more likely to show chemical differences related to STE

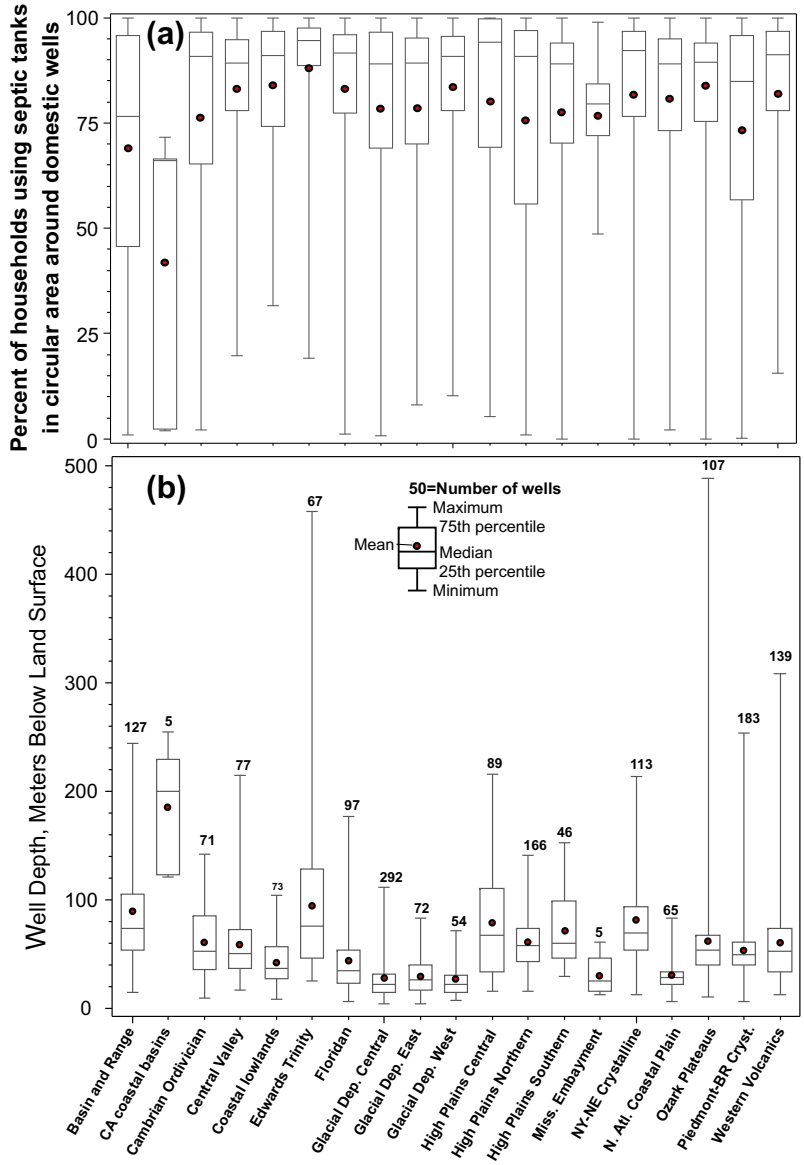

Fig. 7. Boxplots showing (a) the percent of households with a septic tank (based on 1990 census data) within a circular area (500-m radius) around each domestic well, (b) depth distribution of domestic wells in the 19 studied principal aquifers.

than deeper wells (Table S5 in the Supplementary Information). There were 27 wells in the targeted well group (Cl/Br ratios of 400–1100; Cl concentrations 20–100 mg/L) and 148 wells outside this range (non-targeted well group). The median nitrate–N concentration in the targeted well group (1.1 mg/L) was slightly higher than the median concentration for the non-targeted well group (0.69 mg/L) (but not statistically significant). However, significantly higher potassium, boron, chloride, dissolved organic carbon, and sulfate concentrations were found in the targeted well group. Also, the percentage of houses on septic systems was higher for the targeted well group ($p = 0.12$) (Table 3). When only oxic water samples from the shallow subset were included in the analysis ($O_2 \geqslant 0.5$ mg/L), nitrate–N concentrations were significantly higher ($p = 0.08$) for the targeted well group compared to the non-targeted well group. The median nitrate–N concentration was 3.1 mg/L for the targeted wells compared to 1.5 mg/L for the non-targeted well group. This difference in nitrate concentrations could be related to differences in agricultural land use because the percentage of cropland (within the 500-m circular area around each well) was significantly higher for the targeted well group (median 69%) compared to the non-targeted well group (median 44%). However, the significantly higher concentrations of potassium, boron, chloride, dissolved organic carbon, and sulfate for the targeted shallow wells, are consistent with a STE source.

Generally, there were insufficient data to compare shallow targeted and non-targeted wells in each aquifer individually; although, the Central Glacial Deposits aquifer had 21 targeted wells and 62 non-targeted wells in the shallow subset (Table S5 in the Supplementary Information). No statistically significant differences between targeted and non-targeted well groups were found for nitrate–N, sulfate, dissolved oxygen, and boron concentrations; and likewise no differences were found for the percentage of houses served by septic tanks, cropland percentage, and well depth. There also were no statistical differences in detection frequencies between the target and non-target shallow well groups for chloroform, PCE, TCE, methylene chloride, or trichloroethane.

3.3. Additional information needs to assess impacts from septic systems

Not surprisingly, water from shallow domestic and monitoring wells (<20 m depth, below land surface) had more chemical indicators of a potential impact from septic systems (Table 3). Although the median percentage of houses served by septic tanks was slightly higher (although not statistically significant) for the targeted shallow domestic wells than for the non-targeted group of domestic wells, the difference in septic tank density between the two groups (albeit small) is not predictive of groundwater impacts from STE. The only housing information on sewage disposal methods that was available for this study was from the 1990 census data. Additional information that would be more useful for assessing potential impacts from septic systems in future studies could include septic-system age, maintenance records, and failure rates. In a study of effects of septic-tank systems on water quality in alluvial, crystalline-rock, sedimentary-rock and volcanic-rock aquifers in Park County, Colorado, Miller and Ortiz (2007) found significantly higher nitrate–N concentrations in water from domestic wells in areas with older septic tanks (installed in the 1970s) compared to those installed in the 1980s, and the overall highest and lowest nitrate concentrations were found in wells with septic tanks installed before 1980 and after 1999, respectively. In areas of intensive agricultural activities, it would be desirable to have information about the types of pesticides applied to cropland, as low Cl/Br ratios in atmospheric aerosols have been attributed to the release of Br-rich volatile compounds used as soil fumigants (Alcalá and Custodio, 2008).

The main advantage to using chloride and bromide as indicators of potential impacts from septic systems is that they are relatively conservative in solution, whereas nitrate and other anthropogenic contaminants (e.g. VOCs, pesticides) are affected by changes in redox conditions. Multiple chemical indicators can help to reduce the ambiguity in source identification. For example, the significantly higher potassium, boron, dissolved organic carbon, and sulfate concentrations that were found in the targeted domestic well group, were consistent with the higher percentage of houses using septic systems. Additional chemical and source information that also would be useful to increase the viability of this technique as a screening tool include: (1) temporal variability of Cl and Br concentrations in shallow groundwater near septic systems, (2) sources of natural and anthropogenic chloride in the study area (halite, brines, water softeners), (3) distance of well to nearest upgradient septic tank(s), and (4) microbiological indicators. These factors are discussed in more detail below.

Cl and Br concentrations in groundwater near septic systems vary temporally, however, Cl/Br ratios remained within or near the targeted range (400–1100). In water from three wells showing probable impacts from septic-system leachate in the Eastern Glacial Deposits aquifer, Cl/Br ratios varied from 644–957 (well WY-76), 794–1145 (well WY-74), and 521–1568 (well WY-71). Only one of four samples collected during November 2003–June 2005 from wells WY-74 and WY-71 was outside the target range (Fig. 8) and there was no apparent seasonal effect. In fact, Cl/Br ratios in three or more water samples from the PSW in the Eastern Glacial Deposits aquifer and from 16 other monitoring wells in the Eastern Glacial Deposits, surficial (above the Floridan), High Plains, and Central Valley aquifers vary but remain either in or outside of the target range (Fig. 8). Unfortunately, information was not available for hydrologic conditions (e.g. recharge, rainfall, water table elevation relative to past levels) at the time of sample collection, all factors that could affect the transport and concentrations of chloride, bromide, and other water-quality constituents. The addition of road salt in the area of the Eastern Glacial Deposits aquifer likely impacted (increased) the Cl/Br ratio in groundwater. Furthermore, the influx of Na from halite road salt can release exchangeable cations from soils, which resulted in increased concentrations of Ca, Mg, and K in groundwater samples especially during winter months (Brown et al., 2009). The use of water-softener salts (Thomas, 2000; Panno et al., 2006) can also modify the Cl/Br ratio in septic-system effluent. Depending upon when groundwater samples are collected relative to the use of water softeners, sodium and chloride concentrations can be as much as 100 times greater than during times of no water softener use in normal septic tank operation (Panno et al., 2007). Other chemical and microbiological indicators can also vary seasonally, as was found in a septic system study in southeastern Florida, where groundwater samples collected during the wet season contained twice as many fecal coliforms and higher concentrations of nitrate and phosphate than samples from the dry season (Arnade, 1999).

Redox conditions can vary seasonally near septic systems, although this would have little effect on Cl/Br ratios. Reducing conditions can persist during high water-table levels and oxidizing conditions in lower water-level periods (Robertson and Blowes, 1995; Arnade, 1999). Localized reducing conditions within

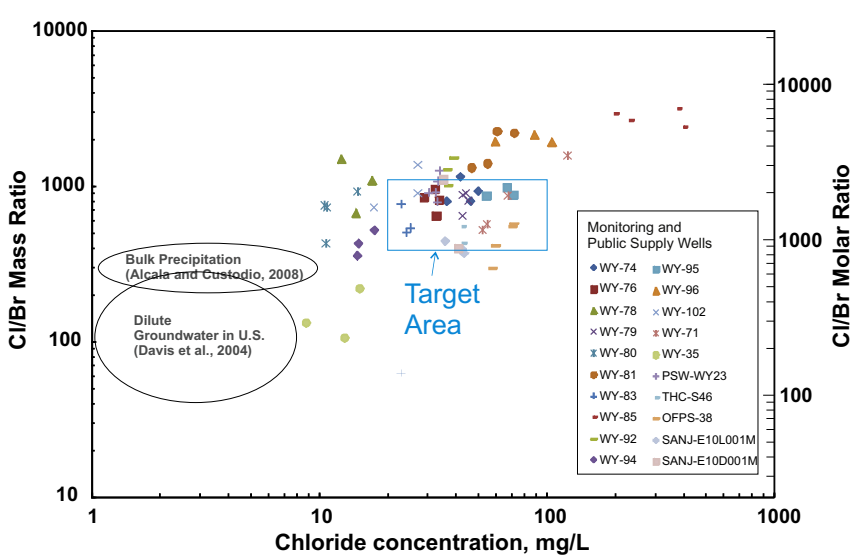

Fig. 8. Temporal variability of Cl/Br ratios in shallow monitoring wells (<20 m) and a public-supply well with three or more water samples.

oxic–suboxic aquifer sediments likely accounted for differences in sulfate concentrations beneath septic systems, which also affected mercury transport in groundwater (Barringer et al., 2006). Several studies have documented substantial attenuation of nitrate beneath septic systems resulting from denitrification (Postma et al., 1992; Robertson and Cherry, 1992; Harman et al., 1996; Aravena and Robertson, 1998). Therefore, other indicators not sensitive to changing redox conditions would be more useful than nitrogen species to track the movement of STE, such as boron isotopes and coliphages (Verstraeten et al., 2005).

Data were not available in this study to evaluate the effect of distance of a well from the nearest upgradient septic tank on groundwater quality. However, most domestic wells are intentionally located upgradient from the household septic tank, and at a specified minimum distance or depth to minimize potential groundwater-quality problems. Most studied domestic wells extended far below the water table, which likely minimized any impacts from septic-tank systems. Arnade (1999) found a statistically significant inverse correlation between the distance of wells from a septic system and coliform, nitrate, and phosphate concentrations in southeastern Florida, where the depth to the water table was <1 m.

In areas where there is a low density of households on septic-tank systems, groundwater contamination from septic leachate would be difficult to detect, as plumes from septic tanks tend to be highly variable in length and shape related to differences in groundwater velocity, aquifer lithology and mineralogy, and redox conditions (e.g. Tinker, 1991; Robertson et al., 1998). For seven septic-tank systems studied in Minnesota, the average plume length was 25 m, but ranged from 10 to more than 100 m depending on the chemical constituent evaluated (Minnesota Pollution Control Agency, 1999). Plumes from small septic systems tend to be narrow (10–20 m) and shallow in sand aquifers (Robertson et al., 1991). Contaminants tend to disperse on the outside edges of the plume, but vertical and lateral (transverse) dispersion of the plume tend to be small, about 1% and 10%, respectively (Robertson et al., 1991; Harman et al., 1996). In these areas, any effects of STE on groundwater quality would only be observed if an old system had been leaking for a long time (Harman et al., 1996) and if downgradient wells intercept the plume of septic-tank effluent (Ptacek, 1998). Chloride and boron concentrations were significantly higher in groundwater samples collected from domestic wells located in areas with average lot sizes less than 0.4 hectare than in areas with average lot sizes greater than or equal to 0.4 hectare (Miller and Ortiz, 2007). Their study collected water samples from 224 domestic wells that ranged in depth from 5.5 to 229 m below land surface. Water from domestic wells in the volcanic-rock aquifer had significantly higher potassium, chloride, and boron concentrations in areas with average subdivision lot sizes of less than 0.4 ha compared to areas with average subdivision lot sizes greater than 2 ha.

The ranges used in this study for Cl/Br ratios (400–1100) and chloride concentrations (20–100 mg/L) are consistent with previous and ongoing studies of septic system impacts on groundwater quality; however, Cl/Br ratios outside of the target range used in this study have been reported for well water samples known to be affected by STE (e.g. Panno et al., 2006; Landon et al., 2008; Brown et al., 2009). To enhance the use of Cl/Br ratios as a screening tool, additional chemical and/or microbiological data would be desirable. Miller and Ortiz (2007) found that the co-occurrence of multiple constituents (bacteria, wastewater compounds, and elevated concentrations of nitrate, chloride, or boron) provided strong evidence of contamination from STE in a volcanic-rock aquifer. Francy et al. (2004) found that the presence of viruses or bacteria indicators was related to subdivisions served by septic tanks compared to those served by sewer lines.

New markers and various combinations of markers of STE in groundwater continue to be sought. As shown in this and numerous previous studies, the use of multiple constituents (indicators) associated with wastewater provides more certainty in attributing groundwater contamination to septic tanks. Miller and Ortiz (2007) reported that chloride and boron concentrations were significantly higher in wells with detections of organic wastewater compounds (OWCs) than in wells with no detections of OWCs. Verstraeten et al. (2005) used several tracers including nitrogen and boron isotopes, DOC, coliphages, and nitrogen species and found that sand point domestic wells within 30 m of a septic system and <14 m deep in a shallow aquifer were the most vulnerable to contamination from septic effluent. Caffeine and other prescription and nonprescription drugs also have been reliable indicators of wastewater contamination (Seiler et al., 1999; Godfrey et al., 2007; Carrara et al., 2008).

After an extensive review of potential markers of leakage from sewer lines into urban groundwater, Barrett et al. (1999) concluded that a multi-component approach is needed. They found that a combination of microbiological indicators and nitrogen isotopes were the most useful markers of sewage, but not absolute indicators because of microbial die-off and the mixing and fractionation processes associated with nitrogen isotopes in the subsurface. Barrett et al. (1999) also found that d-limonene, an ingredient in some detergents, was found in samples where microbial indicators and nitrogen isotopes indicated that sewage contamination was likely. Cronin et al. (2006) also concluded that several varied indicators were more useful than a single parameter in assessing sewer leakage impacts; for example, the correlation among sulfite reducing clostridia, fecal streptococci, and boron indicated that groundwater quality was impacted by sewer leakage. Other organic chemicals have recently been suggested as markers of raw sewage: aminopropanone (a species found in human urine) has been identified in contaminated coastal waters (Fitzsimmons et al., 1995; Barrett et al., 1999) and EDTA (ethylenediaminetetraacetic acid, a sequestering agent in washing products) was also proposed as a possible sewage marker due to its relative stability (Barrett et al., 1999).

4. Conclusions

This study found that Cl/Br ratios were useful in elucidating potential impacts from septic-tank systems on groundwater quality and most applicable in shallow monitoring wells and shallow domestic wells. The relatively inexpensive analyses of bromide and chloride (Cl/Br ratio) has the potential for screening domestic and public-supply wells (PSWs) for possible contamination from septic tanks if used in conjunction with other indicators and ancillary information. The co-occurrence of multiple chemical indicators (for example, boron, Cl/Br ratios, sulfate, DOC, nitrate in oxic systems, organic wastewater compounds) would help to increase the certainty in discriminating between STE and other sources of groundwater contamination, such as road salt, seawater, brines, and fertilizers.

Little or no effects from septic tanks were observed for the generally deep public-supply wells in this study. Although, when travel time information for the modeled zone of contribution to each PSW was considered, the targeted Cl/Br ratio group had significantly lower travel times than the non-target well group. This finding indicates that water from PSWs with Cl/Br ratios in the targeted range withdraw younger water and hence could be more vulnerable to contamination. Also, the time lag between contaminant loading at the water table and the arrival of affected water at a PSW is an important factor to consider for explaining or anticipating the water quality at a PSW.

Emphasizing the seasonal collection (wet and dry conditions) of both microbiological data along with major ions, nutrients, boron, and bromide in areas near septic tank and other waste disposal sites would be helpful in future studies to determine what combination of tracers are most useful in identifying health concerns associated with degraded groundwater quality. More information is needed on the temporal variability of chloride and bromide in groundwater systems and how the concentrations of these and other chemical constituents relate to the transient nature of contamination from enteroviruses and fecal coliforms. Additional studies need to consider incorporating critical information about the location of wells relative to the nearest septic tank(s) and position in the groundwater flow system, seasonal water-table fluctuations, septic tank density, and septic-tank age and maintenance. As the density and areal extent of septic systems increase in residential areas, less dilution from mixing with ambient groundwater would occur. Less natural recharge may occur in these areas due to increased impervious surfaces, and effluent from septic systems may represent points of focused recharge of contaminants to groundwater systems.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhydrol.2010.11.017.

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