Factors Affecting Public-Supply Well Vulnerability in Two Karst Aquifers

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Abstract

Karst aquifers occur in a range of climatic and geologic settings. Nonetheless, they are commonly characterized by their vulnerability to water-quality impairment. Two karst aquifers, the Edwards aquifer in south-central Texas and the Upper Floridan aquifer in western Florida, were investigated to assess factors that control the movement of contaminants to public-supply wells (PSWs). The geochemistry of samples from a selected PSW or wellfield in each aquifer was compared with that from nearby monitoring wells and regional PSWs. Geochemistry results were integrated with age tracers, flow modeling, and depth-dependent data to refine aquifer conceptual models and to identify factors that affect contaminant movement to PSWs. The oxic Edwards aquifer is vertically well mixed at the selected PSW/wellfield, although regionally the aquifer is geochemically variable downdip. The mostly anoxic Upper Floridan aquifer is affected by denitrification and also is geochemically variable with depth. In spite of considerable differences in geology and hydrogeology, the two aquifers are similarly vulnerable to anthropogenic contamination. Vulnerability in studied PSWs in both aquifers is strongly influenced by rapid karst flowpaths and the dominance of young (<10 years) groundwater. Vulnerability was demonstrated by the frequent detection of similar constituents of concern in both aquifers (nitrate, atrazine, deethylatrazine, tetrachloroethene, and chloroform). Specific consideration of water-quality protection efforts, well construction and placement, and aquifer response times to land-use changes and contaminant loading are discussed, with implications for karst groundwater management.

Introduction

The vulnerability of drinking water from public-supply wells (PSWs) to contamination has raised numerous health concerns. Anthropogenic contaminants, such as solvents, other volatile organic compounds (VOCs), disinfection byproducts, and pesticides, have been detected in low concentrations in water from PSWs across the United States (Gilliom et al. 2006; Zogorski et al. 2006; Hopple et al. 2009). Contamination from nutrients such as nitrate is also widespread (Nolan et al. 1998). Such contamination has important consequences for water supply and management. In response to these concerns, the U.S. Geological Survey National Water Quality Assessment (NAWQA) program began a series of studies in 2001 to assess the vulnerability of PSWs to contamination. Studies of the transport of anthropogenic and naturally occurring contaminants to PSWs (TANC) have evaluated a range of hydrogeologic settings (Eberts et al. 2013) and included two regionally important karst aquifers: The Edwards aquifer (EA) in south-central Texas and the Upper Floridan aquifer (UFA) in western Florida. Drawing from information collected in the TANC studies, we examine the common and contrasting characteristics of these two karst aquifers to investigate factors that affect PSW and aquifer vulnerability to contamination.

Karst aquifers supply about 40% of the Nation’s public drinking water (Karst Waters Institute 2012). In karst aquifers most groundwater storage occurs within a low hydraulic-conductivity aquifer matrix, but transport occurs primarily within conduits; conduit flow often dominates groundwater flow, and provides little opportunity for filtration, sorption, or degradation of contaminants (White 1988). Karst aquifers are recognized for their vulnerability to contamination, but their complexities make characterization of vulnerability difficult (Goldscheider 2005; Ford and Williams 2007; Fournier et al. 2007). Although karst
aquifers occur in a wide variety of settings with varying characteristics, they are generally subject to rapid changes in flow and discharge, a high degree of surface-water/groundwater interaction, and extreme vulnerability to water-quality impairment (Lindsey et al. 2009). The EA and UFA provide drinking water to millions of people, and contaminants such as nutrients and organic compounds have been documented in both aquifers (Fahlquist and Ardis 2004; Katz 2004; Berndt and Crandall 2009; Musgrove et al. 2010). TANC studies of these aquifers applied numerous geochemical and hydrologic tools to assess factors controlling the transport of contaminants to a selected PSW. The two karst aquifers are notably different with respect to their hydrogeologic setting, climate, land use, and recharge and discharge characteristics. Their comparison provides an improved understanding of common factors that affect the vulnerability of PSWs to contaminants in karst aquifers, with implications for karst groundwater management.

**Hydrogeologic Settings and Characteristics of the Study Sites**

The EA, near San Antonio, Texas, and the UFA in west-central Florida near Tampa (Figure 1) are productive water resources. The study areas are rapidly growing—population increased >20% in Bexar County, Texas and Hillsborough County, Florida between 2000 and 2010 (U.S. Census Bureau 2010)—with increasing demands on water resources. Characteristics of the study areas are detailed in Table S1 and summarized below.

**Edwards Aquifer**

The EA (Figure 1a) lies within a narrow band along the Balcones fault zone. Late Cenozoic faulting of the predominantly flat-lying Cretaceous-aged carbonates formed a series of normal en echelon down-toward-the-coast faults. The faulting resulted in a series of blocks of EA rocks that are partially to completely offset and divide the confined and unconfined parts of the aquifer (Maclay and Small 1983). The aquifer ranges in thickness from 107 to 152 m and is characterized by relatively high transmissivities (Maclay 1995; Lindgren 2006). As a result of faulting, stratigraphic aquifer units are located progressively deeper in the downdip subsurface with PSW depths exceeding 610 m (2000 ft) below land surface downdip. The climate is humid subtropical. Mean annual rainfall is 82 cm, although rainfall is highly variable annually and the region is prone to drought. Discharge occurs naturally at large springs and by well withdrawals (Hamilton et al. 2009). Average annual recharge of 690 Mm³ (Hamilton et al. 2009) predominantly occurs (60 to 80%) via losing
streams as they flow across the unconfined (recharge) zone (Klem et al. 1979; Maclay and Land 1988; Thorkildsen and McElhaney 1992). Most remaining recharge occurs as direct infiltration on the recharge zone (Sharp and Banner 1997). Previous studies indicate that groundwater flow is focused in highly permeable units and is affected by faulting (Abbott 1975; Woodruff and Abbott 1979; Maclay and Small 1986; Maclay and Land 1988). Water levels and spring discharge can change rapidly in response to rainfall and corresponding recharge. Characteristics of the EA that influence water quality have been previously described by Bush et al. (2000), Fahlquist and Ardis (2004), and Musgrove et al. (2010), among others.

**Upper Floridan Aquifer**

The northern Tampa Bay area includes three principal hydrogeologic units: with increasing stratigraphic depth these are the surficial aquifer system (SAS), the intermediate confining unit (ICU), and the UFA. The SAS is contiguous with land surface in the study area and consists of unconsolidated to poorly indurated clastic deposits (Southeastern Geological Society 1986). The SAS is recharged by rainfall, in some areas relatively rapidly because of high permeability and a shallow (3 to 15 m below land surface) water table. The ICU, which confines the UFA and controls downward SAS leakage, has varying amounts of sand, clay, and chert. The UFA is unconfined where the aquifer crops out near the surface or where confining units are absent; the UFA is classified as semiconfined where confining units are <30-m thick and (or) breached, and is confined where confining units are ≥30 m (Miller 1986). The extent, thickness, and permeability of the ICU are variable; breaches form locally when the underlying limestone dissolves and overlying clay layers collapse. These breaches are preferential flowpaths to the UFA. Groundwater generally moves laterally within the SAS and downward to the UFA through breaches in the ICU. The Oligocene- to Eocene-aged carbonate UFA is 200 to 400 m thick (Miller 1986) with many solution-enlarged fractures yielding large supplies of water to wells. Karst features (springs, conduits, and sinkholes) are common, and may provide direct pathways from the land surface to the UFA (Miller 1986). The climate is humid subtropical. Mean annual rainfall is 118 cm and the region is subject to tropical storms and hurricanes. About 85% of the average annual rainfall is directly from precipitation, with about 15% from losing streams (Crandall 2007). Flow in the UFA is transmitted vertically and laterally through karst conduits and enlarged fracture planes; discharge occurs to wells, springs, rivers, and the Gulf of Mexico (Crandall 2007). Horizontal hydraulic conductivity of the UFA has a large range (0.2 to 2000 m/d) (Bush and Johnston 1988; Knochenmus and Robinson 1996), with larger variability where karst features create secondary porosity (Langevin 1998). Characteristics of the UFA that influence water quality have been previously described by Sprinkle (1989), Katz (1992), and Swancar and Hutchinson (1995), among others.

**Methods**

TANC studies were conducted at two scales: regional (Figure 1a and 1c) and local (Figure 1b and 1d). Regional-scale groundwater flow models have been previously developed for both aquifers (Crandall 2007; Lindgren et al. 2009). The regional scale provides insight into movement of water and solutes along groundwater flowpaths to PSWs. A single PSW in each aquifer, representative of construction and operational practices regionally, was selected for detailed study. Local-scale groundwater flow models, nested within the regional-scale models, were developed for each TANC study area (Crandall et al. 2009; Lindgren et al. 2011). Local-scale areas were based on the modeled area contributing recharge to the selected PSWs, and as a result, were different in size (Figure 1b and 1d). Contributing recharge areas for the selected PSWs were delineated using particle-tracking software as described by Crandall et al. (2009) and Lindgren et al. (2011). Potential sources of contaminants in both study areas are predominantly urban and industrial. Spearman’s rho, a nonparametric rank-based statistical test (Helsel and Hirsch 2002), is used to determine correlations between geochemical variables. Statistical results with \( p < 0.05 \) were considered statistically significant; only correlations with \( p < 0.05 \) are reported.

**Results**

TANC study results are described in detail by Jagucki et al. (2011), Lindgren et al. (2011), and Musgrove et al. (2011) for the EA, and by Katz et al. (2007),
## Table 1

Sampling Networks and Summary of Geochemistry for the Edwards and Upper Floridan Aquifer Studies.

| Well Category | Number of Wells | Well Type | Year(s) Sampled | Well Depth Range (m) (Median) | Age (Years) | Dissolved Oxygen (mg/L) | Specific Conductance (µS/cm) | Mg/Ca (Molar) | Nitrate (mg/L) | Atrazine (µg/L) | Deethylatrazine (DEA) (µg/L) | PCE (µg/L) | Chloroform (µg/L) | Trichloroethene (µg/L) | Carbon Disulfide (µg/L) |
|---------------|----------------|-----------|----------------|-------------------------------|-------------|------------------------|-----------------------------|---------------|----------------|----------------|----------------------------|------------|----------------|--------------------------|--------------------------|
| **Edwards Aquifer** | | | | | | | | | | | | | | | | |
| Regional Edwards aquifer PSWs (33 confined, 5 unconfined) (regional study and model area) | 39 | PSW | 2004–2005 | 65.5–716 (232) | 51.6 | 5.1; (1.5–9.4) | 556; (479–740) | 0.32; (0.09–0.46) | 1.9; (0.73–3.1); 100% | 0.005; (0.007–0.014); 60% | 0.008; (0.006–0.013); 74% | 0.008; (0.03–0.036); 22% | 0.020; (0.038–0.023); 9% | 0.038; 0% |
| Selected PSWs (well or wellfield) (TANC local-scale study and model area) | 5 | PSW | 2007 | 242–251 (248) | 17.4; (3.4–18.4) | 4.3; (4.3–5.3) | 589; (587–592) | 0.24; (0.26–0.30) | 2.2; (2.0–2.3); 100% | 0.015; (0.009–0.017); 100% | 0.015; (0.010–0.015); 100% | 0.176; (0.115–0.223); 100% | all <0.02; 0% | (0.06–0.074); 20% |
| Monitoring wells (TANC local-scale study and model area) | 5 | Monitoring | 2007–2008 | 65.5–200 (222) | 27.5; (1.3–41) | 4.6; (3.7–4.7) | 592; (587–611) | 0.29; (0.25–0.30) | 1.9; (1.7–2.7); 100% | 0.009; (0.008–0.014); 80% | 0.013; (0.009–0.021); 80% | 0.174; (0.007–0.066); 80% | 0.013; 0% | (0.06–0.075); 50% |
| **Upper Floridan Aquifer** | | | | | | | | | | | | | | | | |
| Surficial aquifer system (TANC local-scale study and model area) | 12 | Monitoring | 2003–2006, 2010 | 6.1–19.5 (9.8) | 3.5; (1–15) | 3.1; (0.3–8.0) | 475; (65–791) | 0.04 (0.13–17); 100% | 1.6; (0.04–6.1); 100% | 0.007; (0.007–0.118); 31% | 0.016; (0.014–0.053); 31% | 0.07; (0.03–0.26); 31% | 0.02; (0.07–1.2); 9.7% | 0.04–0.12; 22.5% |
| Intermediate confining unit (TANC local-scale study and model area) | 4 | Monitoring | 2003–2005 | 12.2–32.0 (16.2) | 14; (13–14) | 2.7; (0.3–7.5) | 288; (299–456) | 0.15; (0.13–0.16) | 2.2; (0.3–3.5); 100% | 0.007; (0.007–0.002); 100% | <0.03; (0.003–0.010); 100% | 0.02; (0.007–0.027); 100% | <0.03; (0.007–0.027); 100% | 0.004; (0.004–0.075); 50% |
| Regional Upper Floridan aquifer PSWs (regional study and model area) | 30 | PSW | 2002 | 27.4–256 (172) | 0.61; (0.17–4.7) | 401; (224–1017) | 0.12; (0.04–0.35) | <0.06; (0.006); 100% | <0.007; (0.006–0.036); 64% | 0.006; (0.006–0.048); 19% | 0.048; (0.034–0.096); 19% | 0.038; (0.031–0.073); 12% | 0.006; (0.004–0.073); 12% |
| Selected PSW TT4 (TANC local-scale study and model area) | 1 | PSW | 2003–2006, 2010 | 53 | 8; (5–10) | 0.4; (0.2–1.0) | 607; (584–643) | 0.16; (0.14–0.16) | 0.9; (0.6–1.4); 100% | 0.007; (0.007–0.014); 100% | E0.008; (0.03–0.12); 100% | <0.03; (0.03–0.037); 44% | 0.17; (0.04–0.037); 100% | <0.03; (0.04–0.037); 100% |
| Additional PSW TT9 (TANC local-scale study and model area) | 1 | PSW | 2010 | 51.8 | 1.5; (1–2.9) | 1.0; (0.8–1.2) | 610; (627–593) | 0.13; (0.13–0.14) | 2.8; (2.5–3.1); 100% | all E0.007; (0.001–0.015); 100% | E0.012; (0.19–0.22); 100% | 0.20; (0.49–0.85); 100% | E0.04; (0.03–0.04); 100% | <0.04; 0% |
| Upper Floridan aquifer monitoring wells (TANC local-scale study and model area) | 13 | Monitoring | 2003–2006, 2010 | 19.5–91.4 (51.8) | 26; (12–36) | 0.3; (0.1–2.3) | 578; (219–1070) | 0.18; (0.08–0.21) | <0.06; (0.004–2.8); 100% | <0.007; (0.007–0.016); 23% | <0.014; (<0.03–0.04); 25% | 0.059; (<0.03–0.087); 75% | 0.042; (<0.04–0.077); 57% |

Notes: Organic contaminants detailed are those most frequently detected in each aquifer.
which have been widely detected in both aquifers. We focus herein on nitrate and organic contaminants, of concern for the EA (Musgrove et al. 2010). As a result, natural contaminants such as uranium and radon are not by arsenic (Katz et al. 2007), although arsenic and other high as 5.3 mg/L. The UFA is vulnerable to contamination samples had measurable nitrate, with concentrations as likely occurs in parts of the aquifer, although some Anoxic conditions in the UFA indicate that denitrification to 36 years. Ages for samples from the selected PSWs/wellfield than in the regional PSWs. The most frequently detected organic contaminants in the UFA were the same as for the EA and additionally included the solvents tetrachloroethene (TCE) and carbon disulfide. Relatively high median concentrations of TCE and carbon disulfide were associated with anoxic water samples from the UFA. In general, more organic contaminants were detected in the SAS than in the underlying ICU and UFA, and detection frequencies were generally higher in the SAS and ICU than in the regional UFA (Table 1). Nitrate concentrations (as N) for the EA ranged from 0.73 to 3.1, with a median concentration for the regional PSWs of 1.9 mg/L. The EA is oxic, with a median dissolved oxygen concentration for the regional PSWs of 5.1 mg/L. Nitrate concentrations (as N) in the UFA study ranged higher, with the highest value measured for the SAS (6.1 mg/L). Median nitrate concentrations for the mostly oxic SAS and ICU were similar (1.6 and 2.2 mg/L, respectively); higher nitrate concentrations in the SAS and ICU likely result from past agricultural practices (Katz et al. 2007). Nitrate concentrations from the UFA were generally low (median <0.06 mg/L). Anoxic conditions in the UFA indicate that denitrification likely occurs in parts of the aquifer, although some samples had measurable nitrate, with concentrations as high as 5.3 mg/L. The UFA is vulnerable to contamination by arsenic (Katz et al. 2007), although arsenic and other natural contaminants such as uranium and radon are not of concern for the EA (Musgrove et al. 2010). As a result, we focus herein on nitrate and organic contaminants, which have been widely detected in both aquifers.

Groundwater ages provide insight into timescales and trends of contamination, recharge rates, and resource characterization, which in turn is useful for understanding aquifer and PSW vulnerability. A common aquifer conceptual model is that groundwater age generally increases with depth; younger, recent recharge occurs in shallow parts of an aquifer, while older recharge is found deeper in an aquifer, associated with longer travel times. This has been demonstrated in selected aquifers where groundwater ages have been applied to assess recharge rates (McMahon et al. 2011). Nonetheless, the interpretation of groundwater ages is generally not straightforward in complex hydrogeological systems and is subject to a variety of uncertainties (Phillips and Castro 2004; Bethke and Johnson 2008). This is particularly the case for karst aquifers, where groundwater samples may comprise a mixture; components of a complex flow system that combines flow from conduit, fracture, and matrix porosity, each with different ages (Long and Putnam 2006).
Although a piston-flow model for age interpretation might not be valid for karst aquifers because of such mixing, these ages provide a basis for comparison. For the EA, the approximately 40-year range in age-tracer results from the wellfield PSW and MWs showed no consistent variability with well depth (Figure 2a). This is in contrast with samples from the UFA, where groundwater age increased with depth in the aquifer (Figure 2d).

In carbonate groundwater systems, geochemical tracers of mineral-solution reactions such as Mg/Ca ratios can be indicative of groundwater residence time, with higher relative Mg/Ca ratios associated with more geochemically evolved, longer residence time groundwater (Plummer 1977; Fairchild et al. 2000). This has been previously demonstrated for the EA (Musgrove and Banner 2004; Musgrove et al. 2010). Age-tracer results for the EA, however, do not correlate with Mg/Ca ratios (Figure 2b) or with several other geochemical indicators of groundwater residence time or of relatively recent anthropogenic effects on water quality (Musgrove et al. 2011). These results indicate that hydrogeologic conceptual models used in age interpretations might not adequately account...
for mixing in the EA. As a result, other geochemical indicators of residence time, specifically Mg/Ca ratios, are considered herein for the EA in lieu of groundwater age results in discussing relations between groundwater residence time, travel times, and geochemistry. Samples from the EA PSW/wellfield and MWs showed little variability in Mg/Ca ratios with well depth (Figure 2c). The utility of Mg/Ca ratios, however, is demonstrated at the scale of the regional aquifer, where PSWs from a larger range of well depths, and correspondingly, aquifer depths, showed increasing Mg/Ca ratios with well depth (Figure 2c). This relation is indicative of longer groundwater residence times associated with samples from the deeper wells. The wellfield PSW samples are approximately midrange with respect to both well depth and Mg/Ca ratios (Figure 2c).

In contrast to the EA, well depth for the UFA PSW and MWs varied with both groundwater age and Mg/Ca ratios (Figure 2d and 2f). Older groundwater was associated with deeper wells (Figure 2d), as commonly observed in groundwater systems (McMahon et al. 2011). These trends are consistent with longer residence time and more geochemically evolved groundwater at deeper depths in the UFA. A relation between well depth and Mg/Ca ratios, however, is not observed for the regional UFA PSWs (Figure 2f). This apparent contradiction likely reflects differences in well construction. The UFA MWs were completed at specific depths with relatively small open intervals (3 m) that allow geochemical differences with depth in the aquifer to be observed. The PSWs were generally constructed with relatively large open intervals (median 120 m) that allow for mixing in the wellbore of waters from a range of depths with a range of ages and chemical compositions.

Anthropogenic Contaminants as Indicators of Vulnerability

Contaminants of concern in both aquifers for the long-term sustainability of the groundwater resources include nitrate and organic contaminants (Table 1). Anthropogenic activities at the land surface in both areas provide numerous potential sources of contamination associated with urbanization. For the EA, oilfield-related sources of contamination are present in the southern part of the study area overlying the confined aquifer. Agricultural sources of contamination are small in both study areas (Table S1). Although agriculture is 12% of the land use in the EA study area (Table S1), it mostly overlies the confined aquifer; agriculture is <0.1% of the land use in the recharge zone for the PSW (Musgrove et al. 2011). Although the EA study area is dominantly rangeland and forest and less urbanized than the UFA study area (Table S1), the urban San Antonio area has been previously documented as a source of contaminants to the aquifer; shallow unconfined MWs in urban San Antonio have statistically higher median concentrations and higher detection frequencies of atrazine, DEA, and PCE than the regional aquifer (Musgrove et al. 2010). The common detection of atrazine, DEA, PCE, and chloroform is not unique to either the EA or the UFA. Lindsey et al. (2009) report similar findings for other carbonate aquifers. Atrazine is one of the most widely used herbicides in the U.S. for agriculture and urban applications, and is, correspondingly, frequently detected in surface water and groundwater (Gilliom et al. 2006). Chloroform, a common byproduct of drinking-water treatment, is the most frequently detected VOC in groundwater in the United States (Zogorski et al. 2006). The frequent detection of chloroform in a variety of well-types and land-use settings has been partly attributed to recycling of chlorinated waters (Zogorski et al. 2006). PCE is the second most frequently detected VOC in groundwater in the United States (Zogorski et al. 2006).

For both aquifers, concentrations of commonly detected contaminants and the number of organic contaminants detected generally decreased with depth (Figure 3; nitrate, atrazine, and chloroform, which are shown, are representative of other frequently detected contaminants). For the UFA, nitrate concentrations were generally higher in samples from the SAS and ICU MWs, which were mostly oxic, than from the UFA MWs (Figure 3e, Table 1). Controls on nitrate variability with depth are likely different for the two aquifers. For regional EA PSWs, nitrate concentrations decreased with well depth (Figure 3a). A previous study noted higher concentrations in shallow groundwater in urban San Antonio, consistent with greater amounts of anthropogenically derived nitrate (Musgrove et al. 2010). The UFA is largely anoxic with low dissolved oxygen concentrations and denitrification likely occurs, which could result in low nitrate concentrations with depth (Katz et al. 2007). Detectable concentrations of nitrate of as much as 2.8 mg/L, however, were measured in some samples collected from UFA MWs (Figure 3e). PSW TT4 and TT9 both had higher nitrate concentrations (medians of 0.9 and 2.8 mg/L, respectively) than the UFA MWs and the regional UFA PSWs whose median values were both below detection (<0.06 mg/L) (Table 1).

In addition to decreasing concentrations of organic contaminants with well depth (Figure 3b, 3c, 3f, and 3g), the total number of organic contaminants detected (ranging from 0 to 10 in both aquifers), which is broadly indicative of the influence of anthropogenic contamination, decreased with well depth for both aquifers (Figure 3d and 3h). For the EA, the pattern of decreasing concentrations of organic contaminants with well depth was often bimodal, with consistently higher median concentrations and detection frequencies for wells that were less than about 300 m deep (Musgrove et al. 2011). Deeper wells are likely to intercept longer regional flowpaths with higher fractions of older water that has been less affected by anthropogenic contamination. This hypothesis is consistent with the observed decrease in Mg/Ca ratios with depth (Figure 2c) for EA regional PSWs, and with statistically significant relations between Mg/Ca ratios with nitrate concentration (Spearman’s rho = −0.42) and with the number of organic compounds detected (Spearman’s rho = −0.64). For the UFA, the
Figure 3. Edwards and Upper Floridan aquifer study results, respectively, for well depth vs. nitrate (a, e) concentration, atrazine concentration (b, f), chloroform concentration (c, g), and the number of organic compounds detected (d, h). Note scale differences between aquifers.
SAS had higher concentrations of nitrate than the UFA (Figure 3e, Table 1), attributed to oxic conditions and, based on nitrogen isotope data, likely from a fertilizer source (Katz et al. 2007). The SAS also tended to have higher concentrations and (or) more frequent detections of organic contaminants than samples from the UFA MWs and from the selected PSW (Figure 3f through 3h, Table 1) (Katz et al. 2007). These results are consistent with young groundwater that is influenced by contaminant loading from urban land uses occurring in the SAS.

Results for the EA indicate that the selected PSW/wellfield is representative of the regional aquifer with respect to general geochemistry (Musgrove et al. 2011). Nitrate concentrations were similar in the regional PSWs, the selected PSW/wellfield, and the MWs (Figure 3a, Table 1). Median concentrations and detection frequencies for atrazine, DEA, and chloroform were higher in the PSW/wellfield samples relative to the regional PSWs, but were generally within a similar range of values. These results might partly reflect the influence of urban sources of contamination to the selected PSW/wellfield relative to the rural location of many of the regional PSWs. PCE concentrations for the selected PSW/wellfield and nearby MWs were notably higher than those for the regional PSWs (Table 1), indicating that one or more local urban source(s) of PCE is likely contributing to the selected PSW/wellfield.

Results for the UFA indicate that the selected PSW (TT4) and PSW (TT9) nearby are not generally representative of the regional aquifer; TT4 and TT9 had higher concentrations and (or) higher detection frequencies of nitrate and most organic contaminants than the regional UFA PSWs (Table 1; Figure 3e through 3g). The geochemistry of TT4 samples is similar to that of samples from the SAS, and as a result, Katz et al. (2007) proposed that TT4 receives a mixture of water from both the SAS and the UFA, with the SAS contributing contamination to the PSW. This is consistent with the presence of stratigraphic breaches in the ICU that provide preferential flowpaths to the underlying UFA (Katz et al. 2007). Young oxic water from the SAS appears to be diverted directly into a conduit where it is captured by the PSW and mixes with water from the UFA. Mass-balance mixing models indicate that 50 to 70% of water from TT4 is contributed from the SAS, and 30 to 50% is from the UFA (Katz et al. 2007). Potential contaminant attenuation processes, such as denitrification, may not progress as far in those parts of the aquifer with large solutional openings and (or) conduit systems as in other parts of the anoxic UFA. TT4 is not the only UFA PSW with relatively high concentrations of nitrate (Figure 3e) or organic contaminants (Figure 3f and 3g), or a relatively high number of organic compounds detected (Figure 3h). These results suggest that other PSWs in the UFA might also be affected by mixing with water from the SAS.

Conceptual Models of Aquifers and Groundwater Flow

Generalized conceptual models for the EA and the UFA (Figure 4) show hydrologic features such as aquifer recharge, discharge, and groundwater flow. Although the hydrologic settings of the two aquifers are different in many aspects (Table S1), both aquifers are affected by rapid flow processes that affect the transport of recent recharge and contaminants. Although the EA is partially confined (Figures 1a and 4a), because recharge dominantly occurs via losing streams in the unconfined zone, overlying confining units do not effectively limit contamination entering the aquifer. The UFA is also partially confined (Figures 1c and 4b), but the overlying SAS is highly permeable, and sinkholes and preferential flowpaths allow for rapid downward movement of water and associated contaminants. High pumping stresses on TT4, or other PSWs similarly affected by mixing with water from the SAS, would likely enhance the downward movement of water to the UFA (Katz et al. 2007). The movement of contaminants induced by the pumping of PSWs might lead to increased vulnerability for some PSWs relative to the rest of the aquifer.

Figure 4. Schematic diagrams of conceptual models for the Edwards (a) and Upper Floridan (b) aquifers. Modified from Musgrove et al. (2011) and Katz et al. (2007), respectively.
Susceptibility is confirmed based on frequent detections to existing contamination sources (Figure 5). This indicates that both aquifers are particularly susceptible to contamination and the dominance of young groundwater that contributes to the selected PSWs more susceptible to contamination and the dominance of young groundwater is within this range. Young groundwater is inherently younger ages, whereas only 4% of the EA PSW water has a larger component of slightly older water than the UFA PSW, with 31% of the water from 10 to 30 years of age, whereas only 4% of the EA PSW water is less than 10 years of age and 52% is less than 10 years of age. The UFA PSW has a larger component of slightly older water than the EA PSW, with 31% of the PSW water from 10 to 30 years in age, whereas only 4% of the EA PSW water is within this range. Young groundwater is inherently more susceptible to contamination and the dominance of young groundwater that contributes to the selected PSWs indicates that both aquifers are particularly susceptible to existing contamination sources (Figure 5). This susceptibility is confirmed based on frequent detections of nitrate and organic contaminants (Table 1; Figure 3).

Simulated age distributions (Figure 5) provide insight into the timescales for changes in water quality at a PSW in response to changes in land-use and associated contaminant loadings. The distribution of particle-tracking results was used to simulate response at the PSWs in both aquifers to hypothetical contaminant loadings. Simulations were done with consideration of contaminant degradation and natural attenuation processes, such as denitrification, which occurs in the UFA. The large proportion of young water produced at the studied PSWs in both aquifers indicates short response times for water quality to be affected by contaminant loading. For the EA, concentrations of a hypothetical contaminant, such as nitrate, at the PSW would begin to respond to contaminant loading within a year; contaminant concentration at the PSW would respond equally quickly when contaminant loading ceased, although it would take decades to reach near-background concentrations (Musgrove et al. 2011). Similarly, for the UFA, the response time reflects the large proportion of young water produced by the PSW (Figure 5). For nitrate, the modeled response indicates a 1- to 10-year lag time between peak loading and peak concentration at the PSW (Crandall et al. 2009). For simulated conditions of current nitrate loading from fertilizer application and land use, and accounting for denitrification rates, nitrate concentrations in the UFA PSW will likely remain in the 1 to 3 mg/L range for several decades (McMahon et al. 2008; Crandall et al. 2009).

Temporal variability is another factor indicative of vulnerability for the two aquifers and associated PSWs. Karst aquifers are characterized by rapid response to changes in environmental, climatic, and hydrologic conditions (Desmarais and Rojstaczer 2002; Winston and Criss 2004). Temporal variability in climatic and hydrologic conditions for the EA and UFA is apparent in records for rainfall, aquifer recharge, and spring flow. Changes in hydrologic conditions can influence factors such as water levels, aquifer recharge, and groundwater travel times. Processes such as water-rock interaction, dilution and mixing of recharge, and the chemistry of recharge can also be affected by changes in hydrologic conditions. Changes in hydrologic conditions have previously been demonstrated to be a factor affecting groundwater chemistry in the EA, and concentrations of specific contaminants of concern such as nitrate and atrazine vary temporally in response to hydrologic conditions (Mahler and Massei 2007; Musgrove et al. 2010; Wong et al. 2012). Groundwater chemistry for the PSW and selected MWs in the EA varied in response to a rainfall and recharge event (Musgrove et al. 2011). Temporal variability in groundwater chemistry for the UFA was substantial in the SAS, but not for the PSWs (TT4 and TT9) and UFA MWs (Katz et al. 2007). Temporal variability in water quality for wells tapping other parts of the UFA, however, is largely unstudied. Additional studies of temporal variability in water chemistry and its relation to changes in hydrologic conditions for both aquifers would provide insight into transport processes and the effects of urbanization, as well as providing a foundation to assess long-term changes in water quality.

Conclusions and Implications

Spatial and vertical variability in groundwater geochemistry in the two aquifers provided insight into factors affecting the vulnerability of these aquifiers and the studied PSWs to contamination. Knowledge of well-construction and geochemical evolution processes were integral in developing refined conceptual models for the two aquifers. PSWs are commonly constructed across large (greater than 30 m) open intervals to improve well yields; this construction, along with large withdrawals of groundwater during pumping, can contribute to rapid movement of contaminants (Zinn and Konikow 2007). In the EA, depth-dependent sampling at the PSW and MWs indicated
that the aquifer is vertically well mixed. Geochemical variability with depth for the regional aquifer indicated that deeper wells likely intercept longer regional flowpaths with higher fractions of older, more geochemically evolved groundwater that is less affected by anthropogenic contaminants. In the EA, PSWs are typically constructed with open intervals through most or all of the aquifer’s hydrostratigraphic units. As a result, geochemical differences with depth for the regional aquifer do not reflect different hydrostratigraphic units, but rather reflect the depth of the aquifer in the subsurface as a result of faulting, with deeper wells typically located down dip where the same aquifer units are deeper in the subsurface. Because of this combination of vertical homogenization in the aquifer and aquifer structure and faulting, factors affecting the distribution of contaminants is evident in spite of the typical large open-interval construction used for EA PSWs.

PSWs in the UFA are also typically constructed with large open intervals, which allows for mixing of waters from a range of depths with a range of ages and compositions; this mixing obscures vertical differences in groundwater chemistry. As a result, understanding factors affecting the distribution of contaminants is better facilitated by data collected from the UFA MWs, with small open intervals that document vertical differences.

Though different in many aspects of their hydrologic setting and characteristics, commonalities between the EA and UFA yield similar results for PSW vulnerability. Vulnerability is strongly influenced by rapid flowpaths and the dominance of young groundwater. Contaminants of concern, including nitrate, atrazine, DEA, PCE, and chloroform, which are frequently detected in both aquifers, likely reflect common effects of urbanization. Similar results for these two contrasting karst aquifers are indicative of some generalities with respect to aquifer vulnerability for a wide range of karst environments. Geochemistry, flow modeling, and other interpretive tools can be integrated to assess vulnerability in karst groundwater systems. This knowledge contributes to effective policies for aquifer protection. Conceptual models and vulnerability assessments for the EA and UFA indicate specific considerations for management decisions:

- **Water-quality protection efforts.** For the EA, managing urbanization, industrial processes, and land use in the recharge zone in particular but also in the contributing zone can aid in the protection of groundwater quality. Because streams are the dominant recharge source, protection of stream-water quality is important for the protection of groundwater quality. For the UFA, the similarity of PSW geochemistry to the SAS could be used as criteria to define PSW vulnerability. For PSWs that intersect solution features and are influenced by mixing with the SAS, secondary protection areas and land-use planning would facilitate groundwater protection.
- **Well construction and placement.** For the EA, vertical mixing within the aquifer indicates that the construction practice of large open intervals does not contribute to water-quality degradation. Deeper downgradient wells likely intersect flowpaths with older groundwater that is less affected by anthropogenic contaminants. For the UFA, PSW vulnerability is likely variable, depending in part on connection with the SAS. For some PSWs that are influenced by water from the SAS, deepening the well and the interval from which production occurs, or targeting different aquifer levels, might yield water from the UFA that is not mixed with as large a proportion of SAS water.

**Aquifer response times.** Contaminant concentrations in the PSWs respond rapidly to changes in land use and contaminant loading based on groundwater flow modeling (Crandall et al. 2009; Musgrove et al. 2011). Contaminant degradation by natural attenuation processes, such as denitrification, is unlikely to occur in the oxic EA. In contrast, denitrification likely occurs in the largely anoxic UFA. The large proportion of young water produced at the studied PSWs indicates short response times before water quality is affected by contaminant loading.

**Supporting Information**

Additional Supporting Information may be found in the online version of this article:

**Table S1.** Hydrologic Setting and Characteristics of the Edwards and Upper Floridan Aquifers

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