Mobile sediment in an urbanizing karst aquifer: implications for contaminant transport

B.J. Mahler · L. Lynch · P.C. Bennett

Abstract Here we investigate geochemical characteristics of sediment in different compartments of a karst aquifer and demonstrate that mobile sediments in a karst aquifer can exhibit a wide range of properties affecting their contaminant transport potential. Sediment samples were collected from surface streams, sinkholes, caves, wells, and springs of a karst aquifer (the Barton Springs portion of the Edwards (Balcones Fault Zone) Aquifer, Central Texas) and their mineralogy, grain-size distribution, organic carbon content, and specific surface area analyzed. Statistical analysis of the sediments separated the sampling sites into three distinct groups: (1) streambeds, sinkholes, and small springs; (2) wells; and (3) caves. Sediments from the primary discharge spring were a mix of these three groups. High organic carbon content and high specific surface area gives some sediments an increased potential to transport contaminants; the volume of these sediments is likely to increase with continued urbanization of the watershed.

Key words Karst · Sediment · Contaminant transport

Introduction

Mobile particulates play a fundamental role in determining water quality; sediment is itself a contaminant, and also profoundly affects the transport and fate of other contaminants. The impact of mobile sediment on contaminant transport in surface water systems is well documented, but its importance in groundwater systems is less recognized. In porous-media aquifers the solid phase is regarded as immobile; sorption and partitioning to immobile solid phase surfaces retard contaminant transport. In the last decade, however, researchers have begun to include a mobile, colloidal solid phase in contaminant transport models (e.g. McCarthy and Zachara 1989; Saiers and Hornberger 1994). In karst aquifers, particulate transport is not limited to the colloidal-size fraction: large pore diameters and rapid flow velocities result in turbulent flow and the transport of particles in a wide range of sizes (White and White 1968; Gale 1984; Thrailkill 1989). Mobile sediment in karst has the potential to act as a vector for contaminant transport (Ford and Williams 1989), particularly for poorly soluble compounds such as metals, hydrocarbons, and pesticides (McCarty and others 1981; Schwarzenbach and others 1993). This study investigates the geochemical characteristics of sediments in a karst aquifer and evaluates their potential importance in contaminant fate and transport.

Karst aquifers constitute an important part of the world's potable water, supplying drinking water to an estimated 25% of the global population (Ford and Williams 1989). These highly productive aquifers are more susceptible to pollution than those in any other type of geologic media because of their: (1) thin soils, which act as poor filtering agents and allow rapid infiltration; (2) lack of granular texture, which inhibits mechanical filtration as a self-purification mechanism; and (3) short residence times, which reduce the time available for biological purification processes (White 1988). The highly localized, heterogeneous, and anisotropic permeability of karst combined with turbulent flow make karst systems notoriously difficult to model (Yevjevich 1981).

Researchers have long been intrigued by the presence of mobile sediments in karst aquifers (e.g. Bretz 1942). White and White (1968) postulate that gravel and sand are transported through cave systems as bedload while clay is transported as suspended load. White (1988) suggests that rapid facies changes in cave sediments are evidence of stream flow "subject to large annual fluctuations," and states that "transport in caves is highly episodic ... little is known of the actual transport rates [of sediments] or how the loads are distributed among flood pulses of various magnitudes." Thrailkill (1989) suggests that shallow conduit-flow carbonate aquifers may both

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transport and store surface sediments, and that these sediments may play a role in the fate of contaminants. Despite this interest in mobile sediments in carbonate aquifers, only a few researchers have characterized actual sediment material. These investigations have included quantification of particle size distribution in spring discharge (Atteia and Kozel 1997), age-dating of underground river sediments using radionuclides (Murray and others 1993), evaluation of sediment grain size to determine hydraulic conditions in groundwater conduits (Gale 1984), and use of infrared spectroscopy to determine sediment source (White 1977).

Mobile sediments in karst aquifers are of concern for several reasons: their deposition within the aquifer may decrease aquifer permeability, fill in wells, and cause pumps to fail; their deposition at spring mouths may destroy species habitat; their presence impairs the esthetic appearance of spring water; and they may act as vectors for nutrient or contaminant transport. Sediments in karst originate both at the surface (allochthonous) and within the aquifer (autochthonous). Allochthonous sediments filter in through openings at the surface, wash in through sinking streams, and in some cases are even pushed into the system during backflooding (White and White 1968; Ford and Williams 1989). Autochthonous sediments, in contrast, are derived from weathering within the subsurface as the conduit network is enlarged by dissolution.

Sediments have the potential to transport contaminants into and through the aquifer. Many contaminants sorb onto solid surfaces in concentrations orders of magnitude greater than that of their equilibrium concentration in the aqueous phase. The degree to which this occurs for an individual contaminant is a function of the organic carbon content, specific surface area, and mineralogy of the sediment. Contaminants sorb to mineral particles largely through one of two mechanisms: partitioning into organic matter coating the particle, and direct sorption to the mineral surface. Both neutral and ionizable organic chemicals can partition into organic matter and adsorb to polar mineral surfaces (Schwarzenbach and others 1993). Metallic ions are adsorbed into clay layers and onto oxide and carbonate surfaces by ion exchange (McCarthy and Zachara 1989).

This paper describes geochemical characteristics of surface and subsurface sediments collected from a karst aquifer, including mineralogy, organic carbon content, specific surface area, and size distribution, and discusses their potential role in determining the contaminant transport potential of mobile sediments in the aquifer. The karst aquifer investigated is the Barton Springs segment of the Balcones Fault Zone Edwards Aquifer (referred to here as the Barton Springs Aquifer) in central Texas (Fig. 1), one of the most rapidly urbanizing regions in the United States. Increased amounts of sediment in wells and springs in the Barton Springs Aquifer have been documented over the last decade, and elevated levels of arsenic, lead, and aluminum are associated with sediments in a number of well samples (Hauwert and Vickers 1994). In particular, the following questions are addressed: What is (are) the origin(s) of sediment in this aquifer? What is the nature of mobile sediments in a karst aquifer? Is there a potential for sediment in karst to transport/store contaminants?

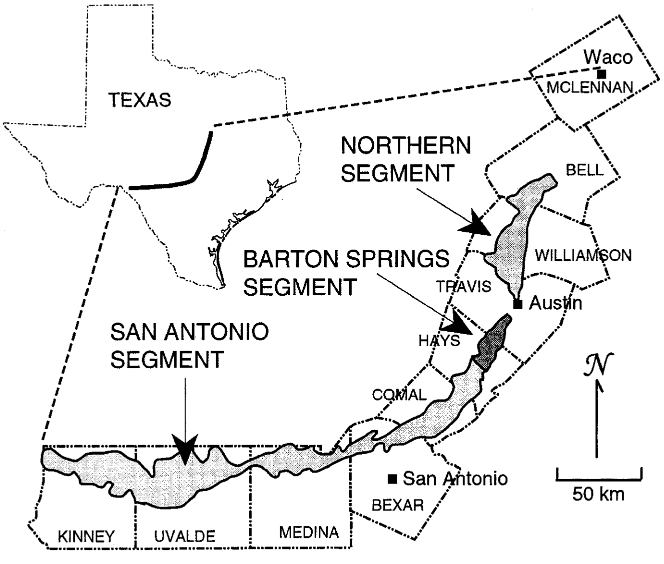


Fig. 1
Location of the three segments of the Edwards (Balcones Fault Zone) Aquifer in Central Texas. The Barton Springs segment, the smallest of the three, is hydrogeologically separated from the San Antonio segment by a groundwater divide and from the northern segment by the Colorado River

Hydrogeologic framework

The depositional and structural history of the Central Texas area has shaped the unusual hydrogeologic regime of the Barton Springs Aquifer. The Barton Springs Aquifer extends across 391 km^2 southwest of Austin, Texas, and is composed of eastward-dipping lower Cretaceous limestone and dolomites (Slade and others 1986). It is characterized by both lateral and vertical secondary porosity, which developed at different periods in the aquifer's history. Surface water flow is generally from west to east, but the predominant direction of groundwater flow is NNE; about 90% of flow discharging from this karst groundwater system emerges from Barton Springs, located at the northernmost part of the aquifer (Fig. 2).

The Barton Springs Aquifer is bounded to the north by the Colorado River, to the west by the fault-controlled interruption of the Edwards limestone, to the south by a groundwater divide, and to the east by the "bad-water line", beyond which the water contains more than 1000 mg/l of dissolved solids (Slade and others 1986).

Three formations comprise the Barton Springs Aquifer: the Kainer, the Person, and the Georgetown (Maclay and Small 1984). The Kainer and Person Formations, roughly 150 and 50–60 m thick, respectively, comprise the Ed-

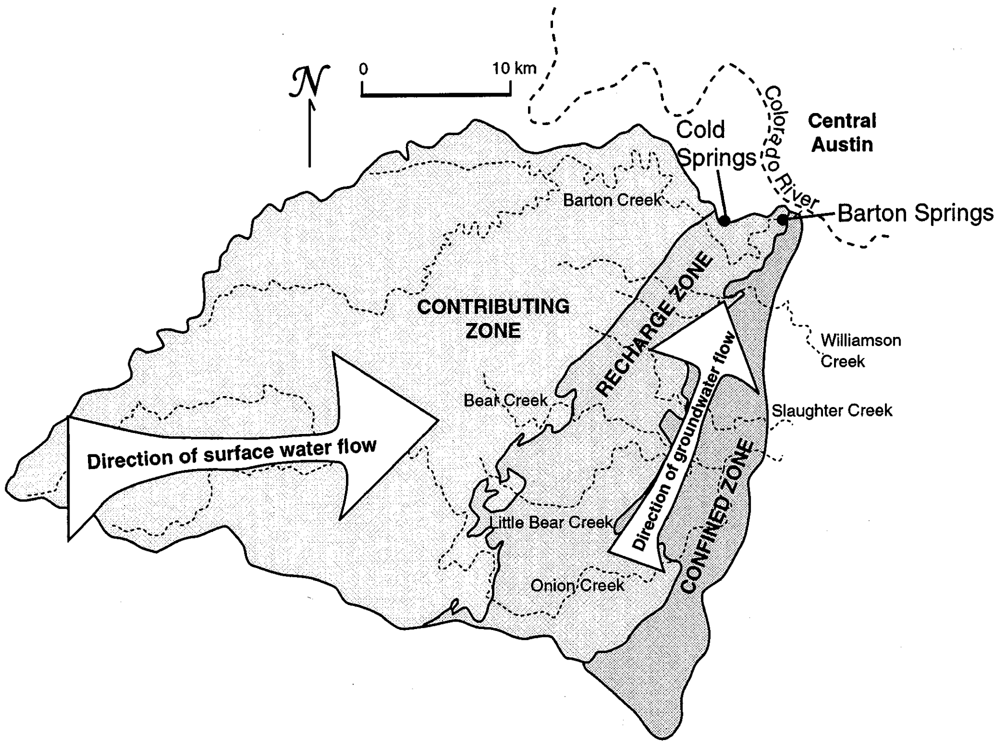


Fig. 2
Map showing the Barton Springs watershed (contributing and recharge zones) and aquifer (recharge and confined zones). Surface water flows across the contributing zone to the east, groundwater flows through the recharge and confined zones of the aquifer to the NNE

wards Group, and are divided by the Regional Dense Member, a laterally extensive bed which acts as a vertical flow barrier. The Person is unconformably overlain by the Georgetown Formation, approximately 25–30 m thick. Three horizontal cavernous zones contain virtually all of the recognized caves in the area (Hauwert and Vickers 1994). These are (1) an upper cavernous zone, 3-m thick, in the Marine Member; (2) a central cavernous zone, 15-m thick, in the units overlying and underlying the Regional Dense Member; and (3) a lower cavernous zone, 6-m thick, near the base of the Dolomitic Member.

The carbonates of the Edwards Group in this area accumulated as lagoonal and rudist reef deposits in the shallow inland sea which covered most of Texas in the Cretaceous Period. Karstification of these rocks during brief periods of subaerial exposure at that time created lateral porosity in the aquifer, primarily along bedding planes (Maclay and Small 1984). Vertical porosity was created during the Oligocene - Miocene epochs, when vertical displacement along NNE-trending high-angle normal faults (the Balcones fault zone) allowed the infiltration of meteoric water (Slade and others 1986). During the Cenozoic Era the inland sea withdrew gradually to its present shoreline at the Gulf of Mexico.

The Edwards Group conformably overlies the Glen Rose limestone, and is unconformably overlain by the Georgetown limestone, which is in turn overlain by the relatively impermeable Del Rio Clay. Displacement along the Balcones fault zone and subsequent erosion resulted in the juxtaposition of the outcrop of the older Glen Rose Formation with that of the younger Edwards (Fig. 3). This juxtaposition forms the western boundary of the Barton Springs Aquifer, with the downwarping of the shelf toward the Gulf of Mexico resulting in the younging of exposed sediments to the east.

The Barton Springs Aquifer and its watershed are divided into three areas: the contributing zone, the recharge zone, and the artesian zone (Fig. 2). The contributing zone and the recharge zone comprise the aquifer watershed. The 684 km^2 contributing zone is that area of outcropping Glen Rose Formation that does not overlie the aquifer but a portion of whose surface runoff becomes aquifer recharge. The 233 km^2 recharge zone is defined by the outcrop of the hydraulically-connected Edwards and Georgetown limestones. The artesian zone (or confined zone) is the eastern part of the aquifer, covering 158 km^2, where the Edwards and Georgetown limestones are confined by the relatively impermeable Del Rio clay. Seasonal fluctuations in the water table cause a narrow strip of the artesian zone adjacent to the recharge zone to be under water-table conditions at some times (Fig. 3).

Surface water flows east across the contributing zone via one of six main creeks (Barton, Williamson, Slaughter, Little Bear, Bear, and Onion). As these creeks cross onto the recharge zone, surface water infiltrates through sinkholes and fractures in the creekbeds, providing approximately 85% of the total aquifer recharge (Slade and others, 1986). The direction of groundwater flow, in contrast to that of surface flow, is NNE, following the trend of the Balcones fault zone; about 90% of aquifer flow discharges at Barton Springs, while the remaining 10% discharges at Cold Springs or small, intermittent springs (Fig. 2).

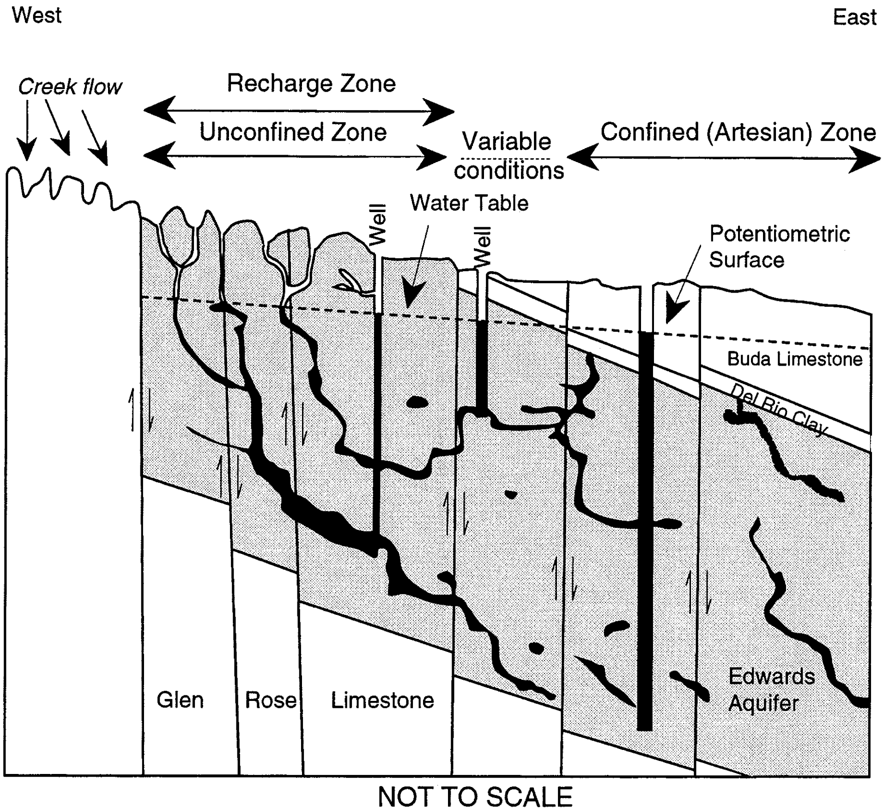


Fig. 3
Conceptual cross-section of the Barton Springs Aquifer (adapted from Slade and others 1986)

Methodology

Sample Collection

Sediment samples were collected from creeks, sinkholes, caves, wells, and springs, as well as from source rocks from the aquifer and confining unit. Sampling methods varied depending on the site. Creek, sinkhole, and cave samples were scooped with an aluminum-foil-wrapped spoon into cleaned and baked glass jars, Whirl-Pac bags, or ziploc bags. Well samples were either collected as solid samples with a gravity corer, or as suspended sediment in water in 20-l polyethylene containers. The suspended samples were either pumped directly from the well, or recovered from the bottom of collection tanks using a peristaltic pump. The sediment fraction was separated in the laboratory using a flow-through centrifuge. Spring samples, with the exception of those collected at the main orifice of Barton Springs, were collected where they settled just after emerging from the spring mouth.

A composite sediment sample was collected from Barton Springs on three cotton string bundles placed inside a kick-net, which was secured in the main spring orifice for 24 h following rainfall, then removed and rinsed out into a container. The sample was then passed through a 63-μm sieve to remove cotton fibers and the <63 μm fraction checked under a binocular microscope to ensure that no fibers were present. Other samples were collected in 20-l polyethylene containers (two per sample) over the course of the storm response and the particulate fraction concentrated by in-line centrifugation. Mineralogic results for these samples were weight-averaged to produce a composite mineralogy for the storm.

Analyses

Aquifer sediment samples were analyzed for total organic carbon content, specific surface area, grain-size distribution, and whole rock mineralogy. All analyses were performed at the University of Texas at Austin Department of Geological Sciences.

Total organic carbon content (TOC) of the sediments was determined by dissolution of the carbonate minerals with nitric acid and analysis of both non-purgeable organic carbon (NPOC) and soil organic carbon (SOC). Carbon analyses were performed on a Dohrmann DC-180 carbon analyzer. The NPOC in the acid leachate was analyzed by UV-promoted wet-oxidation and infrared detection of the evolved CO_2. The SOC in the acid-leached sediment was determined by high-temperature oxidation to CO_2 followed by infrared detection. TOC was computed as the sum of NPOC and SOC.

Specific surface area (SSA) was determined by multipoint nitrogen BET using a static-volumetric sorptometer (Quantachrome Autosorb 1).

Whole-rock mineralogy was analyzed by powder X-ray diffraction with a Siemens D-500 diffractometer, using a 0.020 2θ-step and a 2-s time count. The data were interpreted as described in Lynch (1997).

Grain-size distributions of sediments were determined by ro-tap sieving of the >63 μm fraction and by the pipette method for the ≤ 63 μm fraction (Folk 1980). Cumulative percent weight was plotted versus grain size (phi scale) using a probability ordinate, and 16, 50, and 84 percentiles were graphically determined. The Graphic Mean (M_z) was computed to determine overall size, where $M_z = (\phi 16 + \phi\ 50 + \phi\ 84)/3$. The Graphic Standard Deviation (σ_G), a measure of the sorting of sediments, was computed as $\sigma_G = (\phi\ 84 - \phi\ 16)/2$. The Graphic Skewness ($Sk_G$), a measure of the skewness as represented by the displacement of the median from the average of the ϕ 16 and ϕ 84 points, was computed as $Sk_G = (\phi\ 16 + \phi\ 84 + 2{*}f\ 50)/(\phi\ 84 - \phi\ 16)$.

Selected samples were analyzed for total petroleum hydrocarbon concentration (TPH) by thermal desorption gas chromatography. Sediment samples were air-dried and loaded into pre-baked glass tubes packed with silanized glass wool on both ends, and desorbed at 250 °C. Separation was performed on a 30 m SPB-1 Macrobore capillary column (0.5 mm) using hydrogen as the carrier gas. Temperature was programmed from 40 °C to 260 °C at 6 °C/m, with detection by a flame ionization detector using a diesel fuel reference standard. (This method is different than USEPA Method 418.1 and the results are not comparable.)

Differences and similarities between aquifer sediment sample characteristics were analyzed statistically. Samples were divided into groups based on their origin: sinkhole, streambed, confined well, unconfined well, cave, spring, or source rock. Tested variables, as detailed above, included mineralogy (dolomite, calcite, quartz, and clay content), organic carbon content, specific surface area, and grain-size distribution (Graphic Mean, Graphic Standard Deviation, and Graphic Skewness). For each variable, the Kruskal-Wallis non-parametric test was used to test the hypothesis that samples from different types of sites came from the same population; this was used in lieu of means testing with a standard t-test because the between-groups variances for some parameters were significantly different. The hypothesis that the sample groups came from the same population was rejected for $p < \alpha = 0.05$. Correlation coefficients between all variables were computed, both for each sample group and for all samples combined. Linear discriminant analysis was used to determine if samples could be classified into one of several mutually exclusive groups based on linear combinations of predictor variables. Variables were entered into the analysis phase in the order which maximized the Mahalanobis' distance between the two closest groups. The test of significance of separation between groups assumes equality of variances, but is not seriously affected by limited departures from this (Davis 1973).

Results

Mineralogic analyses of the sediments show that they contain dolomite, calcite, quartz, and clay as their principal constituents. A few samples contain minor amounts of plagioclase and potassium feldspar (2% or less), and three samples contain more than 5% of either. Figure 4 shows the composition of sediment samples, grouped by sample type, plotted on ternary diagrams. In Fig. 4a, clay and quartz are grouped together on a single apex, and calcite and dolomite are each assigned their own apex; in Fig. 4b, clay and quartz are each assigned an apex, and calcite and dolomite are grouped together on the third. Separating calcite and dolomite proves more useful in visually differentiating between groups of samples than

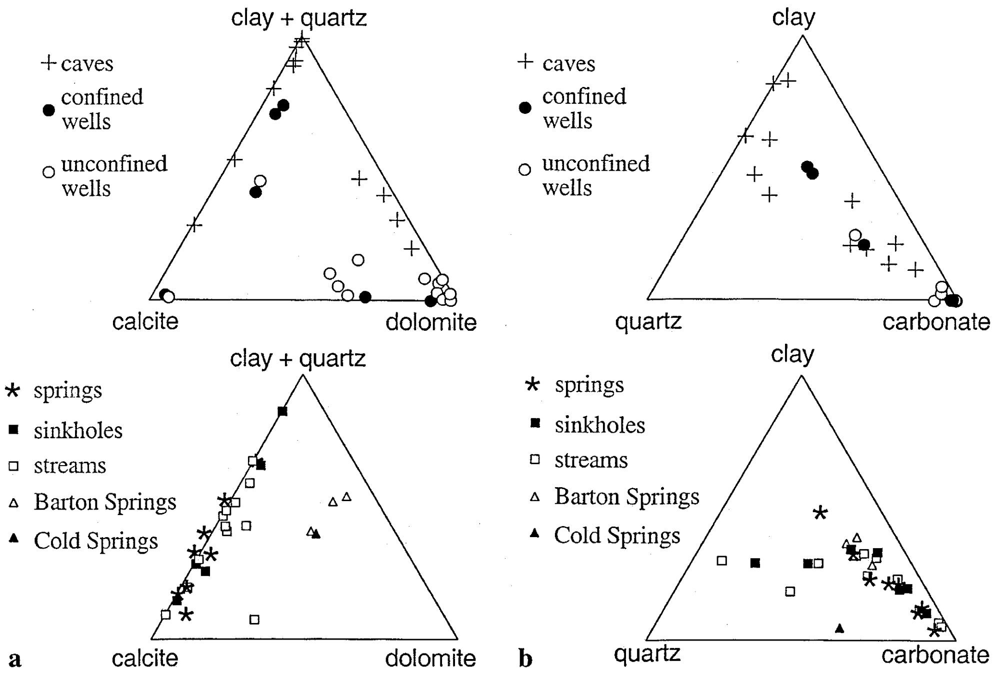


Fig. 4
Whole rock mineralogy of aquifer sediments. **a** ternary diagram vertices are clay + quartz, calcite, and dolomite; **b** ternary diagram vertices are clay, quartz, and carbonate (calcite + dolomite)

separating clay and quartz. Some of the groups have a unique mineralogic signature, and others are fairly similar. Confined and unconfined wells had similar mineralogy, although many more of the unconfined wells contained more than 90% dolomite; two of the confined well samples contained 70% clay and quartz, whereas only one of the unconfined well samples contained more than 25% clay and quartz. Spring, sinkhole, and stream sediments were all similar mineralogically, containing a mix of calcite, clay, and quartz, but almost no dolomite. Cave samples fell into two categories: those that contained no dolomite, and those that contained no calcite. Samples from Barton Springs and Cold Springs contained proportions of all three constituents. Two things, overall, are distinctive about the mineralogy of the sediments: (1) in the ternary diagram that separates calcite and dolomite (Fig. 4a), samples, with the exception of those from Barton and Cold Springs, group along the sides of the ternary diagrams (that is, most samples are lacking in one of the three constituents: calcite, dolomite, or clay and quartz); (2) in the ternary diagram that separates clay and quartz (Fig. 4b), the points group on a line which extends from 100% carbonate to a 60:40 mix of clay and quartz (i.e., as the carbonate content decreases, both quartz and clay content increase in a fairly fixed ratio). Eight different samples of the Edwards Group were analyzed: rocks from the Grainstone, Basal Nodular, Leached Collapsed, upper Dolomitic, and rhythmic beds of the Dolomitic Members; marls from the Leached Collapsed and Regional Dense Members; and pulverulite from the Kirschberg Member. A sample of Del Rio Clay was also analyzed. The mineralogy of these samples is shown in Fig. 5. With one exception, the rocks from the Edwards Group are primarily calcite with a small amount of clay; the exception is the sample from the Kirschberg Member, which is composed entirely of dolomite. The Del Rio Clay contains a mix of clay, calcite, and quartz.

The total organic carbon content and specific surface area for the sediment samples are shown in Fig. 6. Organic carbon content and surface area varied greatly between the sediments, but samples from similar source types tend to group together. In general, samples from wells in the unconfined zone had both the lowest organic carbon content and specific surface area. Cave sediments also had a low organic carbon content but comprised those samples with the highest specific surface area. Sinkhole and stream sediment samples had the highest organic carbon content, ranging from 0.5 to 4% by weight. Spring samples (excluding Barton Springs) were intermediate for both organic carbon content and surface area. Concentrations of total petroleum hydrocarbons (TPH) are shown in Table 1. The highest TPH concentrations were found in cave and surface sediments; sediments from wells and springs had relatively low TPH.

The results of statistical comparison of sediment groups from different types of sample sites by the Kruskal-Wallis test are shown in Fig. 7. The proportion of all four mineralogic constituents (calcite, dolomite, clay, and quartz) are statistically different for samples from unconfined

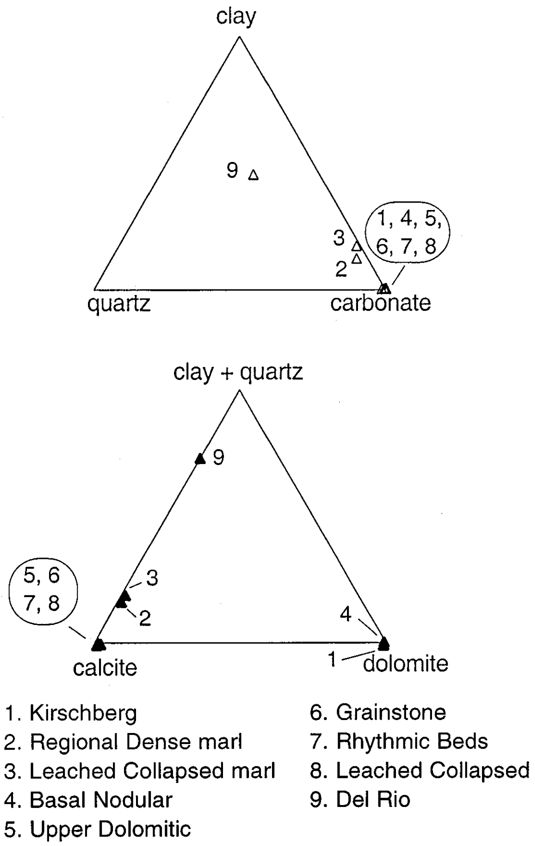


Fig. 5
Ternary diagrams of Edwards rock and Del Rio Clay whole rock mineralogy

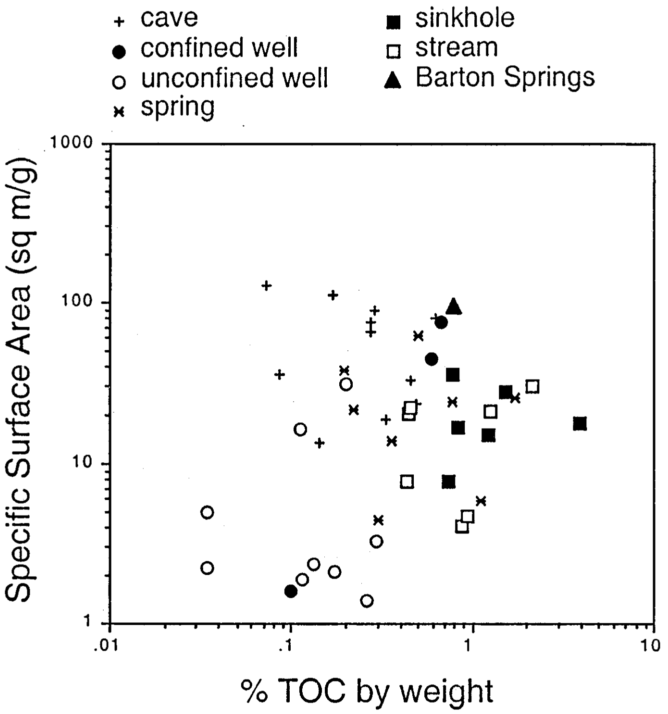


Fig. 6
Comparison of organic carbon content (TOC) and specific surface area for aquifer sediments

Table 1
Total petroleum hydrocarbon (TPH) concentrations of selected samples as determined by thermal desorption gas chromatography

Total petroleum hydrocarbons	
Site type	TPH (mg/kg)
Formation rock	0.1
Spring	1.4
Spring	10.9
Spring	10.0
Well	12.6
Well	12.0
Sinkhole	25.7
Sinkhole	29.5
Stream	31.3
Cave	25.9
Cave	47.4
Cave	61.7
Cave	75.7

Table 2
Results of discriminant function analyses of aquifer samples. Standardized canonical discriminant function coefficients for each of the variables, and eigenvalues and percent variance explained by each function are shown here. Over 90% of the variance between sample groups is explained by the first two functions. F statistics and significances (F statistic above significance in each case) between pairs of groups after five variables were entered into the discriminant function analysis are also given. The hypothesis that samples from two different groups come from the same population is rejected for significance value $p < \alpha = 0.05$

Standardized canonical discriminant function coefficients

	FUNC 1	FUNC 2	FUNC 3	FUNC 4	FUNC 5
QUARTZ	0.70	0.48	−0.08	−0.05	−1.07
DOLO	1.12	−0.18	−0.26	0.71	0.09
CLAY	−1.35	0.71	−1.53	0.39	0.84
SURFACE	1.80	−0.15	1.63	0.12	0.17
TOC	−0.52	−0.22	0.50	0.81	0.06

Eigenvalues and percent variance explained by each function

FCN	EIGENVALUE	VARIANCE	CUM PCT VARIANCE
1*	3.99	73.84	73.84
2*	0.96	17.83	91.66
3*	0.29	5.31	96.98
4*	0.16	2.95	99.93
5*	0.00	0.07	100.00

Discriminant F ratios

GROUP	Springs	Unconfined wells	Sinkholes	Streams	Caves
Unconfined wells	8.69 0.00				
Sinkholes	1.92 0.12	12.65 0.00			
Streams	0.66 0.65	11.01 0.00	0.64 0.67		
Caves	9.31 0.00	5.96 0.00	13.90 0.00	13.12 0.00	
Confined wells	7.00 0.00	2.00 0.10	10.07 0.00	9.30 0.00	4.27 0.00

wells relative to springs, sinkholes, and streams. Proportions of three out of four constituents are different for samples from caves versus source rocks, and from unconfined wells versus caves. Regarding organic carbon content and specific surface area, samples from caves and unconfined wells again differed the most from the other groups. Confined wells, possibly in part because of the relatively small number of samples, were not statistically distinguishable from any of the other groups in specific surface area, and were distinguishable only from sinkholes in organic carbon content. Sample grain-size distributions varied widely from one sample group to the next. From the Kruskal-Wallis test, the hypothesis that the samples came from the same population, based on median grain size, was rejected for caves relative to unconfined wells, sinkholes, and streams. Parameters for grain sorting and skewness did not differentiate between any of the groups.

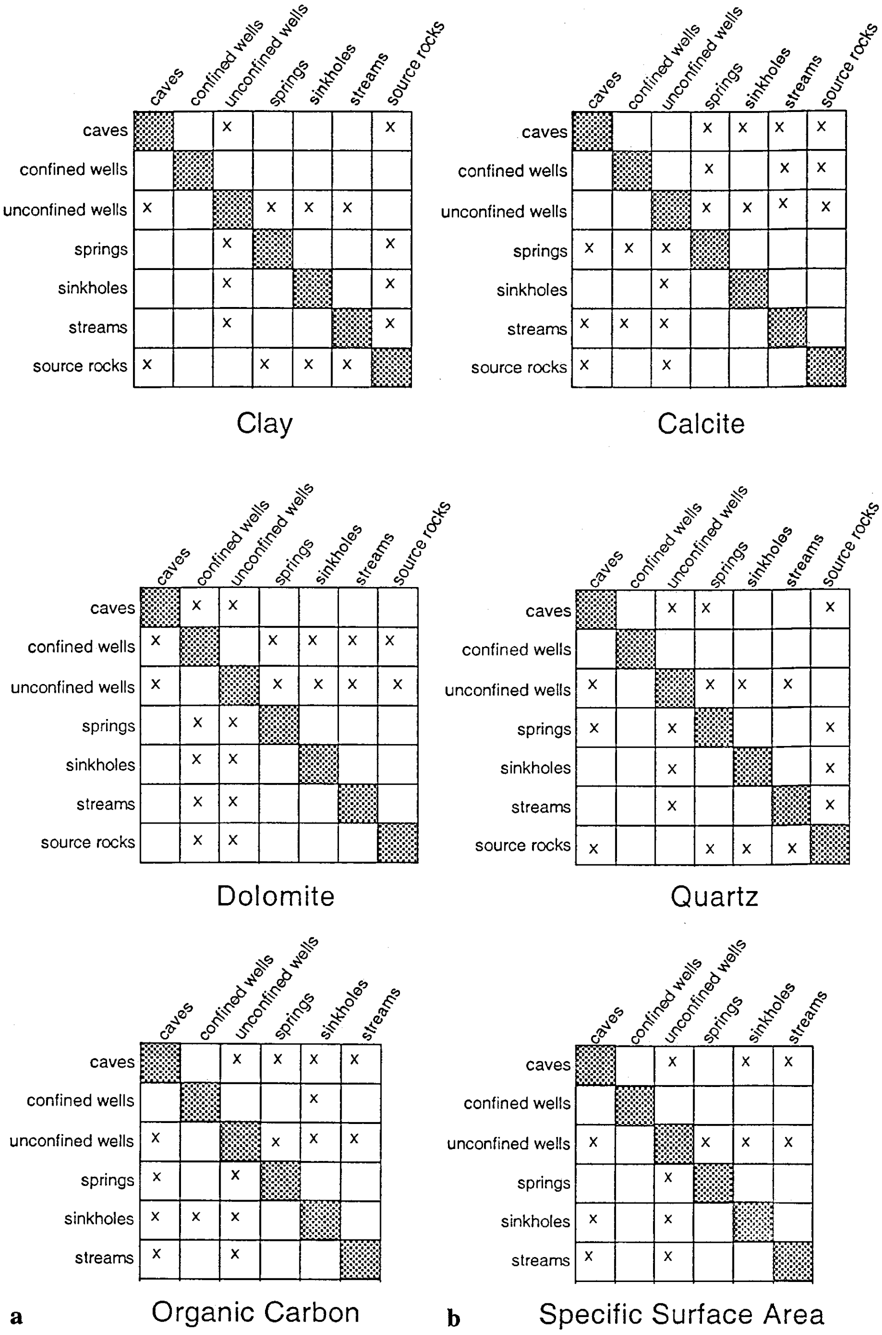
A number of the parameters were significantly correlated, based on an alpha of 0.01. When all samples are grouped, a positive correlation exists between clay and quartz content ($r = 0.64$), and clay content and specific surface area ($r = 0.88$). Grainsize and sorting were negatively correlated ($r = -0.90$), as were specific surface area and dolomite content ($r = -0.46$).

Discriminant analysis was performed on all groups (springs, unconfined wells, confined wells, streams, sinkholes, and caves) using variables for calcite, dolomite, clay, and quartz content, specific surface area, and organic carbon content. Standardized canonical discriminant function coefficients, cumulative variance explained by the functions, pairwise F ratios (or Mahalanobis distances–a measure of the separation between two multivariate means), and significance between pairs of groups are given in Table 2. At a significance level of 0.01, samples from springs, streams, and sinkholes could not statistically be distinguished between, nor could wells from the unconfined zone be distinguished from those in the confined zone.

Discussion

Allochthonous versus autochthonous sediments

Autochthonous sediments, defined as those originating within a karst aquifer, generally consist of clay and quartz, resulting from the chemical weathering of limes-



Clay

	caves	confined wells	unconfined wells	springs	sinkholes	streams	source rocks
caves	▨		x				x
confined wells		▨					
unconfined wells	x		▨	x	x	x	
springs			x	▨			x
sinkholes			x		▨		x
streams			x			▨	x
source rocks	x			x	x	x	▨

Calcite

	caves	confined wells	unconfined wells	springs	sinkholes	streams	source rocks
caves	▨			x	x	x	x
confined wells		▨		x		x	x
unconfined wells			▨	x	x	x	x
springs	x	x	x	▨			
sinkholes			x		▨		
streams	x	x	x			▨	
source rocks	x		x				▨

Dolomite

	caves	confined wells	unconfined wells	springs	sinkholes	streams	source rocks
caves	▨	x	x				
confined wells	x	▨		x	x	x	x
unconfined wells	x		▨	x	x	x	x
springs		x	x	▨			
sinkholes		x	x		▨		
streams		x	x			▨	
source rocks		x	x				▨

Quartz

	caves	confined wells	unconfined wells	springs	sinkholes	streams	source rocks
caves	▨		x	x			x
confined wells		▨					
unconfined wells	x		▨	x	x	x	
springs	x		x	▨			x
sinkholes			x		▨		x
streams			x			▨	x
source rocks	x			x	x	x	▨

a Organic Carbon

	caves	confined wells	unconfined wells	springs	sinkholes	streams
caves	▨		x	x	x	x
confined wells		▨			x	
unconfined wells	x		▨	x	x	x
springs	x		x	▨		
sinkholes	x	x	x		▨	
streams	x		x			▨

b Specific Surface Area

	caves	confined wells	unconfined wells	springs	sinkholes	streams
caves	▨		x		x	x
confined wells		▨				
unconfined wells	x		▨	x	x	x
springs			x	▨		
sinkholes	x		x		▨	
streams	x		x			▨

Fig. 7
Results of Kruskal-Wallis test for difference in populations for (**a**) whole rock mineralogy, and (**b**) organic carbon content and specific surface area. The null hypothesis is that sample groups come from the same populations. Pairs of sample groups for which the hypothesis is rejected ($p < \alpha = 0.05$) are marked with an *x*

tone (White and White 1968). Allochthonous sediments are those that enter the karst aquifer from the surface. White and White (1968) report that “the karst drainage net must often carry a large load [of sediment] brought in by sinking streams.” Indeed, the recharging of sediment-laden water into the Barton Springs Aquifer is visible as turbid stormflow in creeks is sucked into vortices of whirlpools overlying sinkholes.

The presence of organic carbon is unambiguously allochthonous. Organic carbon originates outside of the aquifer; it is produced as plant matter decays, and is incorporated into the soil profile. It is also a product of domestic waste, and can enter the aquifer through leaking sewer lines or poorly functioning septic systems. It may leach into interstitial soil water or be leached out by rain water as dissolved organic carbon, which then may sorb to mineral particles, especially clays, and iron and aluminum oxides (Thurman 1985). Most organic carbon will enter sorbed to allochthonous sediments, although it is possible that some dissolved organic carbon enters the aquifer with recharge and then sorbs to autochthonous sediments. Unconfined well and cave sediments contained the smallest proportion of organic carbon (Fig. 6), significantly different from the amount contained in surface sediments (Fig. 7). Surface sediment samples from streams and sinkholes contained the most organic carbon, which is not surprising as they are, by definition, allochthonous. Organic carbon in small springs was intermediate, suggesting an allochthonous component. Interestingly, two of the three confined wells from which a large enough sample was collected to make possible an organic carbon analysis contained almost as much organic carbon as the surface samples; these two wells were those with a large clay content, suggesting that the clay that they transport may have an allochthonous origin. Cave sediments present an interesting case, in that cave sediments in general are agreed to contain a mix of autochthonous sediment (remnants of chemical weathering) and allochthonous sediment that has been washing into the system since the onset of karstification (White and White 1968). The low organic carbon content of some of the Barton Springs Aquifer cave sediments suggests that the sediment they contain, while possibly allochthonous, is not recently deposited - that it is paleo-fill. Three of the eleven cave samples, however, contained more than 0.4% organic carbon by weight, indicating that parts of the cave system are indeed receiving contemporary allochthonous input. Russell (1996) notes that at Blowing Sink Cave (in the Barton Springs Aquifer), fine black clay and organic debris from the surface is transported into the aquifer by floodwater.

The presence of feldspars in a carbonate aquifer is also indicative of allochthonous sediment. The three samples containing a significant amount of feldspar are all from surface sites: two sinkholes and a streambed, containing 9%, 33%, and 13% total feldspar, respectively. The sinkholes both drain residential developments and the streambed drains a water quality pond behind a large commercial development. Possible origins of the feldspar minerals include landscaping fill and sandbed filters. Nine other samples contained trace (1–3%) amounts of total feldspar: one sinkhole, one streambed, one confined well, and six cave samples. This suggests that some caves are receiving contemporary allochthonous input. In contrast, none of the source rocks analyzed contained any feldspar.

The presence of calcite in sediment may also be an indication of allochthonous input. The amount of calcite present in cave and well sediments was significantly lower than those found in the surface samples, possibly because of weathering processes. During chemical weathering, the dominant weathering process in the subsurface, calcite is dissolved and removed in solution while detrital quartz and clay are transported as particulates. At the surface, where mechanical weathering also contributes to mineral breakdown, calcite particles may be more prevalent.

Many of the sediment samples contained a fine, well-sorted dolomite sand. Although abundance of dolomite sand in many of the well samples suggests an autochthonous origin, its presence in two of the surface samples indicates at least a limited allochthonous source as well. The sand is made up of single and intergrown dolomite crystals, ranging in size from 10 to 60 μm in diameter. Many of the crystals are of either the limpid euhedral or the hollow box form described by Folk and Siedlecka (1974) and Folk and Land (1975). Folk and Siedlecka (1974) suggest that this crystal form is one indicator of a schizo-haline diagenetic environment (i.e., one which alternates between hyper-saline and freshwater conditions), which provided both the high Mg/Ca ratio and slow crystallization kinetics necessary for precise Ca-Mg ordering. The limpid dolomite crystals thus formed, because of their well-ordered crystalline structure, are more resistant to dissolution than both ordinary dolomite and calcite (Folk and Land 1975). The dolomite sediments we collected are morphologically similar to dolomite found in portions of the Kirschberg Member of the Edwards; these units conform to the description of “massive dolomite” given by Fisher and Rodda (1969): fine- to coarse-grain size (10–150 μm), loosely-knit fabric of euhedral crystals, moderate to high porosity, well developed rhombs, and thickness of individual dolomite units greater than 0.6 m. The Kirschberg and Grainstone Members, both of which contain recessive, pulverulitic sections characterized by cavernous porosity (Small and others 1996), crop out sporadically across the aquifer in a swath from the middle of the southern end of the recharge zone to a narrow strip at the northwest corner of the recharge zone, and are exposed along kilometer-long stretches or more of streambed, particularly along Onion Creek, Little Bear Creek, and Barton Creek. To the east of the outcrop, as a result of the high-angle normal faulting in the area (fault blocks downthrown to the southeast), the Kirschberg and Grainstone members are overlain by younger units.

Sediment samples from wells in the recharge zone (unconfined well samples) are composed almost exclusively of this dolomite sand; eight of eleven samples contained 90% or more dolomite. Hauwert and Vickers (1994) noted high rates of sedimentation in many of these wells, on the scale of meters per year, although the sediment composition was not described. Several of these wells are located along a known trough in the potentiometric surface, thought to signify a fault-controlled flow conduit (Hauwert 1995). This suggests that groundwater flow through conduits is of a velocity sufficient to mechanically erode and entrain dolomite crystals from the Kirschberg Member. In contrast, wells in the confined zone contain relatively small amounts (4–14%) of dolomite, with two exceptions. These exceptions, containing 70 and 91% dolomite, are located on Bear Creek, in a region where fluctuations of the water table can cause the wells to be under water table (unconfined) conditions when the aquifer level is low (Fig. 3; N. Hauwert, personal communication). This suggests that flow velocity in many portions of the confined aquifer is not sufficient to transport the dolomite particles, and there is thus a greater potential for sediment transport in the unconfined portion of the aquifer than in the confined portion. This type of behavior was observed also by Veni (1988) who, in a survey of over 200 Texas caves, noted that in unconfined aquifers, sediment load did not exceed stream competence, whereas in confined aquifers, sediment load commonly exceeded stream competence.

The carbonate mineralogy of the cave sediments seems to reflect the mineralogy of the aquifer members in which they formed. Cave mineralogy falls into two distinct categories: those sediments that contain no dolomite, and those that contain no calcite (Fig. 4a). The four cave samples containing dolomite sand are all from the same cave system, Whirlpool Cave, which is in the Kirschberg and Grainstone Members; flow through the conduits forming the cave entrained and transported the dolomite sand.

The prevalence of dolomite sand in subsurface samples, compared to surface samples, suggests that its predominant source is autochthonous: in the subsurface, chemically-resistant dolomite rhombs are freed by the chemical dissolution of the surrounding calcite matrix; the rhombs are subsequently entrained and transported away, creating the cavernous porosity found in the Kirschberg and Grainstone Members. The presence, however, of more than 5% dolomite sand in two of the surface samples indicates that an allochthonous source must be considered. Although 15 of the 17 samples of surface water (streams and sinkholes) contained less than 5% dolomite, one sinkhole sample contained 9% dolomite and one stream sample contained 30% dolomite. The sinkhole is located in the northwest part of the aquifer in an area where the Kirschberg dolomite is patchily exposed. The stream sample was collected from Onion Creek where it formed a distinctive creamy white layer at the bottom of a shallow pool, approximately 2-km downstream of a long stretch of creek flowing across the Kirschberg. Therefore, although it is likely that the origin of much of the dolomite sand is autochthonous, caused by the internal erosion of the Kirschberg and Grainstone Members, the possibility of an allochthonous component cannot be discarded.

Quartz and clay, the minerals remaining after dissolution of limestone, were found in both surface and subsurface samples. Because chemical weathering occurs both at the surface and in the subsurface, quartz and clay can be expected to be found in both autochthonous and allochthonous sediments. In general, sediments collected from streambeds and sinkholes contained a lower proportion of clay minerals than subsurface samples. This, however, may reflect hydrology rather than source: the small size and platey shape of clay particles will cause them to stay in suspension as other minerals settle out, and clay suspended in surface water is thus likely either to enter the aquifer with recharge or to be carried out to the Colorado River. By the time that stormflow in the creeks has slowed to a velocity allowing clay deposition, the sediment load it carries is minimal.

Aquifer compartments

Statistical analysis suggests that sediment in different parts of the aquifer originates from different sources. Comparing sample types based on individual characteristics (Fig. 7) and grouped characteristics (discriminant analysis), the sediments fall into three discrete groups: (1) springs, streams, and sinkholes; (2) caves; and (3) wells.

The characteristics of sediments collected from small springs are evidence of the transport of allochthonous sediments through the aquifer. The small springs, each of which drains a shallow, localized system (Slade and others 1986), have mineralogies consisting of clay, quartz, and calcite, indistinguishable from the mineralogies of stream and sinkhole sediments and dissimilar to those found in both caves and wells (Fig. 7). In addition, the spring sediments have an organic carbon content similar to that of surface sediments. This suggests the existence of a shallow, perched conduit system that directly transports stormwater recharge from the surface to local springs.

Caves can be part of either the paleo- or current-conduit system of the aquifer. However, by virtue of their accessibility, the caves sampled for this study are either no longer water-bearing or only ephemerally water-bearing. Sediments found in caves may have washed in any time from millions of years ago to during the most recent rain, or may consist of the detritus remaining after chemical removal of calcite. The presence of organic carbon and feldspar, two indicators of allochthonous input, in some cave samples suggests that at least some caves in the Barton Springs Aquifer are currently acting to transport sediments from the surface into the aquifer.

If allochthonous sediments are moving through the aquifer, why are they not present in the sediments from wells in the unconfined zone? These samples contain predominantly dolomite. Quartz, clay, and organic carbon, all present in allochthonous sediment, occur only in extremely low concentrations in most of these samples. There are at least two explanations. One is that two different types of flow systems are present in the aquifer: a shallow, perched conduit system that directly transports stormwater recharge from the surface to springs, as suggested above, and a more extensive, deep phreatic conduit system that is fed by diffuse flow and is accessed by wells in the unconfined zone. As the shallow conduit system responds to a storm, it transports surface sediments entering it with recharging surface water; in contrast, surface particulates are not transported through the deeper, diffuse system, but once the diffuse flow feeds into a conduit network, a flow velocity sufficient to erode autochthonous sediments is attained.

A second explanation is that allochthonous sediments are moving through the conduits intersected by the unconfined wells, but that clay does not collect in the wells. As high velocity storm flow slows, the large particles are deposited, while fine-grained clay remains in suspension; organic carbon content, well correlated with clay content, would also be expected to be low. This explanation does not, however, explain the absence of quartz or calcite, which are also expected to settle, in these samples.

Sediment samples from wells in the confined zone, interestingly, have a more allochthonous signature. Two of the three samples analyzed for organic carbon contained a higher TOC than any of the samples from the unconfined zone; two of the six samples analyzed for mineralogy contained a larger percentage of clay and quartz than unconfined zone wells and four samples contained less than 15% dolomite. The mineralogy of these sediments could be affected by detrital clay and quartz transported down from the overlying Del Rio Clay. This ongoing process may be increasing: the owner of one of the confined wells reports to have seen an increase in the suspended sediment coming from his 20-year-old well over the past 3–5 years; he has had to install both a holding tank and filters between the well and his house so that his clothes, according to him, “will come out of the washing machine cleaner than when they went in” (R Bettis, personal communication). The cause of the increase is not immediately apparent.

Barton Springs sediments

More than 90% of the discharge from the Barton Springs Aquifer exits at Barton Springs. The Barton Springs watershed, unlike those of the small, localized springs discussed above, is extremely large, on the scale of hundreds of square kilometers. Integrating as it does flow from all parts of the aquifer, it is not surprising that sediments discharging from Barton Springs appear to represent a mix of the three sediment compartments. This mix is reflected in the mineralogy of sediment samples issuing from Barton Springs in response to storms (Fig. 4a): sediments from different aquifer compartments group along the axes of the ternary diagram, whereas the Barton Springs samples plot toward the middle. The mineralogy of Barton Springs sediments thus suggests a mix of both allochthonous and autochthonous sediments. Interestingly, the mineralogy of a sample collected at Cold Springs has a mineralogy virtually identical to the composite sample collected at Barton Springs. Groundwater discharge from Cold Springs is about 0.08 m^3/sec (in contrast to average flow at Barton Springs of 1.4 m^3/s). Although the area contributing flow to Cold Springs was thought to be hydrologically independent from that contributing to Barton Springs (Slade and others 1986), recent dye trace studies have shown a connection between Barton Creek and Cold Springs under some flow conditions (N Hauwert and others, unpub. data). This suggests that Barton Springs and the smaller Cold Springs have a similar recharge source, and that their mineralogy reflects an integration of allochthonous and autochthonous sediments.

Visual inspection of Barton Springs sediments indicated some allochthonous contribution. Sediments issuing from the spring after a storm contained fibers in a variety of colors. Similarity in organic carbon content of the composite sample and surface samples is additional evidence of the transport of allochthonous material through the aquifer.

Implications for contaminant transport

Contamination of the Barton Springs Aquifer is not hypothetical; although in general water quality is considered good, contamination from both point and non-point sources is a concern (Hauwert and Vickers 1994). Catastrophic events in the area have occurred: oil pipelines crossing the aquifer have ruptured, and spills reported to the Texas Water Commission from 1986 to 1992 included gasoline and diesel fuels, pesticides, ammonia, sodium hydroxide, hydrochloric acid, trichloroethane, and perchloroethene (US Fish and Wildlife Service 1994). Several contaminants have recently been detected in the aquifer, including petroleum hydrocarbons, pesticides, arsenic, and lead in wells and springs (Hauwert and Vickers 1994), low levels of tetrachlorethylene in Barton Springs (R.M. Slade Jr., unpub. data), and high levels of polycyclic aromatic hydrocarbons (PAHs) in sediments in Barton Creek and Barton Springs pool (City of Austin, unpub. data). Some samples of aquifer sediments analyzed in this study for total petroleum hydrocarbons (TPH) show that man’s activities are beginning to affect aquifer sediments (Table 1). What role do mobile sediments in the subsurface play in the transport of these contaminants?

All but four sediment samples analyzed in this study have an organic carbon content (f_{oc}) greater than 0.1%, the threshold value at which partitioning of neutral organic compounds into organic carbon dominates sorption. Thus the sorption of hydrophobic organic contaminants (HOCs) is likely to be far more significant in the Barton Springs Aquifer than adsorption of neutral organics to polar mineral surfaces. Surface samples have the highest organic carbon content, and thus have a high potential to bring HOCs into the aquifer via recharging waters. Contaminants of concern in this category include petroleum hydrocarbons, PAHs, and perchloroethene. That these contaminants have the potential to travel through the aquifer and emerge from springs in the sorbed state is evidenced by moderately high spring f_{oc} values, which range from 0.22 to 1.1%. Interestingly, Allen-King and others (1996) found that at low concentrations, organic-carbon correlation equations significantly underpredicted sorption of perchloroethene, and that the importance of sediment-mediated transport of perchloroethene (and other chlorinated solvents) may thus be even greater than predicted.

A simple example illustrates the importance of sediments in concentrating contaminants in a karst system. Assume an input into the karst system of water with a TSS of 500 mg/l or 5×10^{-4} kg/L and contaminated with pyrene, a PAH commonly found in roadway runoff. The surface sediment distribution coefficient for pyrene, $K_{d,pyr}$, defined as the ratio of the concentration of pyrene on the solid divided by the dissolved concentration, is given by

$$K_{d,pyr} = 2 f_{oc} K_{om,pyr} \tag{1}$$

where f_{oc} is the fraction of organic carbon contained by the sediments and $K_{om,pyr}$ is the organic matter distribution coefficient of pyrene. Given the average TOC of surface sediments found in this study ($f_{oc} = 0.014$), and a $K_{om,pyr}$ for pyrene of log 4.5, for this example $K_{d,pyr}$ is about 885 L/kg. The fraction of pyrene in the dissolved phase at equilibrium, $f_{w,pyr}$, is

$$f_{w,pyr} = \frac{1}{1 + (TSS\,K_d)} \tag{2}$$

or for this example about 0.7. If the sediment-laden water discharges from the aquifer and the sediment settles at the mouth of a spring, creating a layer of sediment with a porosity of 80%, it will occupy a space about 0.01% of the original volume, but will contain 30% of the original mass of contaminant.

Conversely, consider a situation in which pyrene-contaminated roadway runoff containing no suspended sediments enters the aquifer and comes to rest within a cave system. The fraction of pyrene in the dissolved phase at equilibrium once the water has infiltrated into the cave sediments is

$$f_{w,pyr} = \frac{1}{1 + \left(\rho_s \frac{1-n}{n}\right) K_d} \qquad (3)$$

where n is sediment porosity and ρ_s is sediment density. Given an average f_{oc} of 0.003, the pyrene distribution coefficient for cave clays is about 190. Assuming a density of 2.5 g/cm^3 and a porosity of 0.4, the fraction of pyrene remaining in the dissolved phase will be 0.0014. Thus more than 99.8% of the pyrene will sorb to the cave clays.

Even in the absence of organic carbon karst sediments can concentrate contaminants. In the samples collected, specific surface area (SSA) was highly correlated with clay content, as expected. The SSA of a sorbent is strongly related to the extent of contaminant adsorption possible; both HOCs and organic bases (for example, atrazine and paraquat) can bond directly to a mineral surface in an amount proportional to the available SSA (Schwarzenbach and others 1993). The highest SSA was found in cave sediments, followed by sediments from confined wells. While these clays remain in place, they act to retard the transport of the contaminant; once mobilized, they will transport the contaminant through the aquifer.

Lead and arsenic are other contaminants of concern in the Barton Springs Aquifer; Hauwert and Vickers (1994) found that concentrations of total lead significantly exceeded those of dissolved lead in most of the wells, demonstrating the importance of sorption in the transport of this metal. In the groundwater environment, the distribution coefficient of lead between minerals and groundwater ranges from about 30 to over 200, with sorption increasing as quartz $<$ calcite $<$ kaolinite (Freedman and others 1994). Minerals in all compartments of the aquifer thus have the potential to concentrate and transport lead, from the dolomite crystals in the unconfined wells to the clays and quartz in the surface and spring sediments.

Sorption of arsenic, in contrast, is correlated to Fe- and Al-oxide content. Oxide content was not analyzed in this study, but the distinctive red color of many of the cave clays was determined to be due to goethite ($FeO \cdot OH$). Arsenic thus might be expected to sorb to cave clays, but in most environments to be fairly mobile.

The Austin, Texas area is representative of many regions in the country where suburban development is encroaching onto sensitive watersheds; increasing the amount of impervious cover across the watershed (for example, rooftops, roadways, parking lots) will result in a corresponding increase in the sediment load entering the Barton Springs Aquifer. Increases in impervious cover alter surface hydrology, resulting in a decrease in infiltration and an increase in the volume and velocity of runoff entering surface streams during rain events (Arnold and Gibbons 1996). The net result is to decrease baseflow, increase stormflow, and increase creek turbidity for a given rainfall intensity. Because most of the recharge entering the Barton Springs Aquifer infiltrates through fissures in major creekbeds, an increase in turbidity of surface streams will correspond to an increase in the load of surface sediment in aquifer recharge. This study shows that at least some portion of these allochthonous sediments move through the aquifer to emerge at springs.

The presence of highly erodable dolomite lenses within the aquifer suggests that changes in surface hydrology caused by increased impervious cover may also affect erosional processes in the subsurface. Of the rainfall falling directly on the recharge zone itself (as opposed to that falling on the contributing zone), approximately 60% enters the aquifer through direct recharge features such as sinkholes. With urbanization, small sinkholes and other recharge features are filled in or paved over. As a result, for a given rainfall intensity, (1) those features still exposed receive more runoff than previously; and (2) head in the creeks will be higher, resulting in more recharge. Each of these factors increases the velocity of conduit flow. In the areas where the conduits pass through the dolomite lenses, increased flow velocity will result in increased subsurface erosion. Enlargement of conduit diameters will have two positive feedback effects: it will allow increased penetration of fresh water for additional calcite matrix dissolution, and will allow earlier onset of turbulence and accompanying entrainment of more sediment. Additionally, higher velocity groundwater will better entrain clays, which, due to their cohesiveness, require a higher velocity than larger, more spherical particles to bring into suspension.

The evidence for transport of allochthonous sediment through karst aquifers indicates that a mobile solid phase should be included in models of contaminant transport in karst. The parameters necessary to describe this aspect of contaminant transport include sediment density, sediment grain-size range, and characteristics determining the contaminant distribution coefficient, i.e., organic carbon content, specific surface area, and mineralogy (Wu and Gschwend 1988). The results of this study illustrate that in a karst aquifer, these parameters are not uniform throughout the aquifer. The four major mineralogies present in the sediment have different densities, different size distributions, and different potentials for contaminant sorption. Furthermore, aquifer compartments contain sediments having a different potential for contaminant transport and different hydrodynamic responses. For example, surface sediments enter the aquifer already in suspension, acting as a source of contaminants, while autochthonous sediments act as a sink for contaminants until those sediments are mobilized, at which point they become a source.

Conclusion

The Barton Springs Aquifer contains different sediment compartments, each with a distinct mineralogy and organic carbon content. Sediment samples from streams, sinkholes, and small springs, characterized by quartz, calcite, clay, and a fairly high organic carbon content, were statistically indistinguishable. Samples from wells in the confined and unconfined zones of the aquifer mostly contained a fine dolomite silt and had a low organic carbon content, although samples from a few wells in the confined zone contained a high percentage of clay and a high organic carbon content. Cave samples contained a high proportion of clay and quartz and either calcite or dolomite but not both; organic carbon content was medium to low.

Aquifer sediments have both allochthonous and autochthonous sources. Indicators of allochthonous source include feldspar, organic carbon, and possibly calcite, as typified by sediments from surface streams and sinkholes. None of the sediment characteristics analyzed can be said to be unambiguously autochthonous. Sediment issuing from small, localized springs has an allochthonous signature. Sediments in caves consist of both detrital remnants of internal erosion (clay and quartz) and allochthonous sediment washed in from the surface, as evidenced by organic carbon and sporadic occurrence of feldspar. The dolomite silt found in many of the wells likely has an autochthonous origin, although the possibility of an allochthonous source cannot be discarded.

Sediments issuing from Barton Springs, the main outlet for the aquifer, have a signature indicating a mix of sediments from all compartments, with both allochthonous and autochthonous contributions. The presence of organic matter and colored fibers suggests allochthonous input; mineralogic content of up to 30% dolomite silt suggests some autochthonous contribution.

The transport of allochthonous sediment through the aquifer combined with a moderately high organic carbon and clay content point to a high potential for contaminant transport via a mobile solid phase in karst aquifers. An increase in the amount of sediment entering the aquifer, as well as new sources of contamination, can be expected as urbanization over the aquifer continues. Models of contaminant transport therefore should include a mobile solid phase; this study demonstrates that mobile sediments in a karst aquifer can exhibit a wide range of properties, including mineralogy, organic carbon content, specific surface area, and source, that affect their contaminant transport potential.

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