δ^{34}S isotope values of dissolved sulfate (SO_4^{2-}) as a tracer for battery acid (H_2SO_4) contamination in groundwater

Thomas Pichler

Abstract The application of sulfur isotope (δ^{34}S) values of sulfate in groundwater provided the information necessary to evaluate the source, transport and fate of battery acid and associated contaminants at the Gulf Coast Recycling (GCR) facility. The chemical and isotopic composition of groundwater beneath the (GCR) property, a battery recycling facility in east Tampa, Florida, varies more than expected for an area of comparable size. Sulfate (SO_4^{2-}) values, for example, range from 1.2 to 11,500 mg/L and oxygen and hydrogen isotopes do not attenuate towards the weighted annual mean. Those samples that are high in sulfate generally have a low pH, which immediately indicates battery acid (H_2SO_4) contamination as a potential source for the sulfate. The low pH and high reactivity of the sulfuric acid groundwater cause the formation of hydrogeological microenvironments due to preferential dissolution of carbonate minerals, which in turn causes enhanced recharge and groundwater flow in certain areas; thus, the extreme scatter in the data set. Because of the difficult hydrogeology it is not straightforward to delineate the point-sources of contamination and up to five potential scenarios have to be evaluated: (1) seawater intrusion, (2) upwelling of high-sulfate groundwater, (3) local dissolution of gypsum, (4) an up-gradient contaminant source to the northeast of the GCR property and (5) battery acid contamination.

Keywords Tracers · Isotope · Sulfur · Groundwater contamination · δ^{34}S · Florida · USA

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Introduction

Ground and surface water contamination with sulfuric acid (H_2SO_4) and lead (Pb), as a result of battery manufacturing or recycling, is a common problem (Palacios and others 2002). This type of contamination is generally characterized by increased sulfate and heavy metal concentrations in combination with low pH values (Charlet and others 2001). Surprisingly little scientific study has been carried out to assess and address the ramifications of this type of contamination, despite a global increase in battery recycling (Tsoulfas and others 2002; Roberts 2003). This is surprising when considering that from a remediation perspective, acid contamination is extremely difficult to assess. Enhanced water-rock interaction and particularly dissolution of aquifer matrix caused by low pH values has the potential to dramatically change local hydrogeological conditions. In addition, heavy metals released due to water-rock interaction will make it increasingly difficult to distinguish between primary and secondary sources of contaminants (Adar and Natic 2003).

The purpose of this paper is to evaluate the use of δ^{34}S isotopes of SO_4^{2-} in conjunction with basic water quality data as a possible tool to assess and investigate sulfuric acid contamination in groundwater.

Site and problem description

This study was a component of a larger corrective measures study (CMS) that was required by the U.S. Environmental Protection Agency (EPA) as part of a site remediation program at the Gulf Coast Recycling (GCR) facility. The site is in an industrial area in southeast Tampa, approximately 3 km northeast of Hillsborough Bay (Fig. 1). Battery recycling has been ongoing for more than 20 years.

A multilayered groundwater flow system exists beneath the GCR property, which is characteristic for the eastern Tampa Bay area (Basso 2002). The shallowest aquifer is the unconfined Surfical Aquifer, which overlies the confined Upper Floridan Aquifer. The Hawthorn Group, a 5 to 7 m thick, clay-rich layer of low permeability, separates the two aquifers. The Surfical Aquifer is composed of fine-grained Holocene to Pleistocene sands that originated as terrace
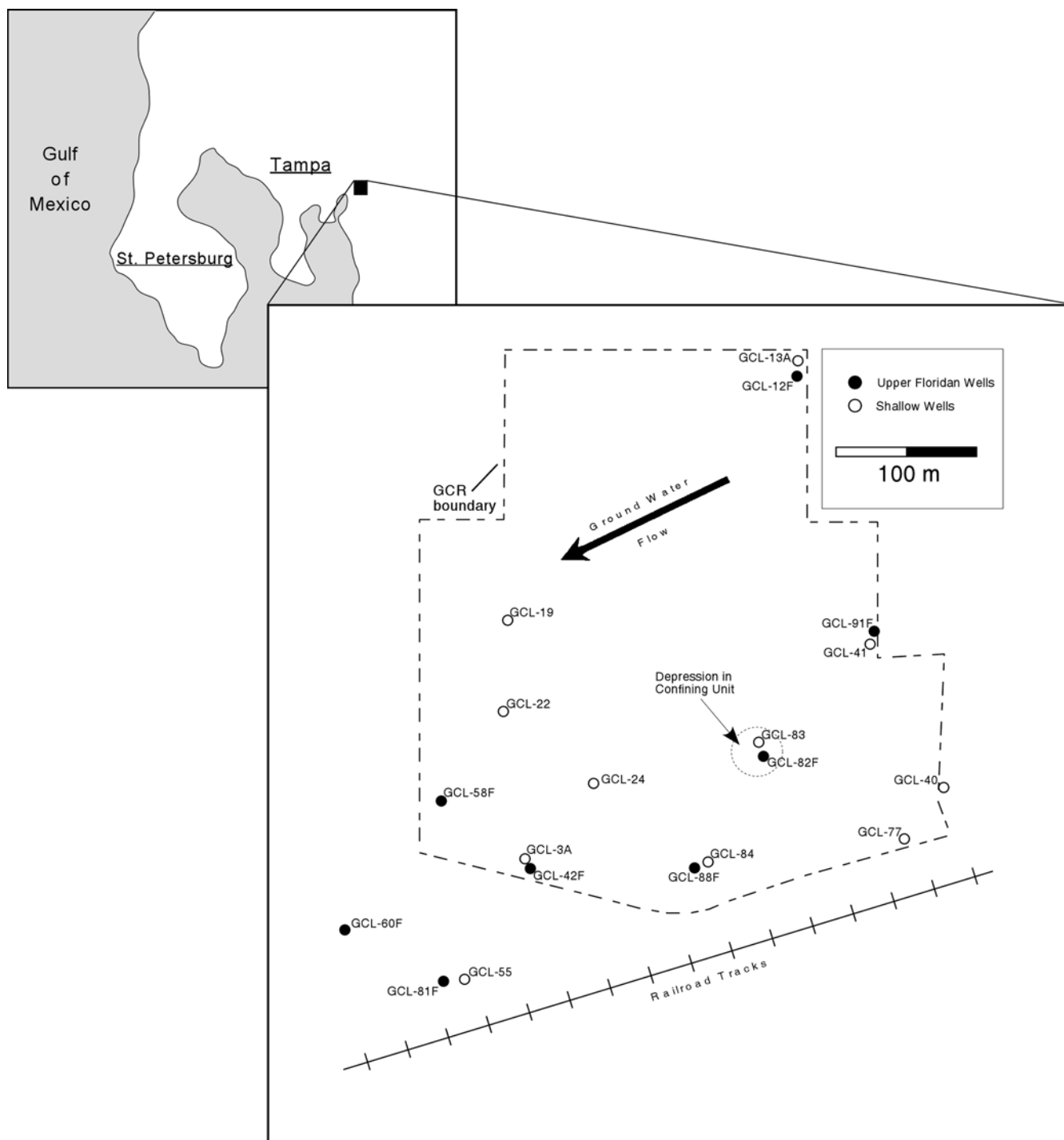
Fig. 1
Map of the Gulf Coast recycling facility in east Tampa

and undifferentiated deposits (Scott 1988). In the vicinity of the GCR property the thickness of the surficial sediments and confining unit are approximately 4 and 7 m, respectively. Groundwater flow in both aquifers is approximately to the southwest in the general direction of Old Hillsborough Bay (Fig. 1) (Basso 2002; Foster 2002). The depth to the water table (DTW) in the Surficial Aquifer is approximately 2 m and in the Upper Floridan Aquifer approximately 4 m (Foster 2002).

The contamination problem has been known for an extended period of time as a result of ongoing monitoring of the Surficial and Upper Floridan Aquifers. There are currently more than 80 wells on or near the GCR property. Historically, groundwater shows varying degrees of contamination throughout the area with values of SO_4^{2-} ranging from 1.2 to 12,000 mg/L, Pb^{2+} ranging from <0.005 to 2 mg/L and pH ranging from 1.9 to 7.5. Contamination in both aquifers is generally highest near the center of the GCR property and therefore, construction of a slurry wall is considered as an option for pollutant containment. The slurry wall would extend downward

from the surface through the Surfical Aquifer into the Hawthorn Group and follow the GCR property boundary. This would prevent the contaminated groundwater in the Surfical Aquifer from reaching Old Hillsborough Bay. However, high SO_4^{2-} values in several Upper Floridan wells are problematic, because the slurry wall approach will only work if the confining unit is ubiquitously impermeable below the GCR property.

During the installation of additional monitoring wells in the beginning phase of the CMS, a depression in the confining unit in the area around wells GCL-83 and GCL-82F was found (Fig. 1). Here, the top of the confining unit is found approximately 7.5 m below the surface, compared to typically 4 m. Groundwater at this location had a low pH (1.5) and a high SO_4^{2-} (11,500 mg/L) concentration. Battery acid (H_2SO_4), due to its higher specific gravity than water, could have migrated to this depression and "pooled" on top of the confining unit. Subsequent reaction with battery acid has the potential to break down clay minerals (Smek and Novak 1993) and compromise the impermeability of the confining layer thus creating a possible leak for contaminated groundwater to move into the Upper Floridan Aquifer.

From a remediation perspective it is extremely important to assess this possible leak and determine if there are additional ones below the GCR property.

Field methods

To assess the integrity of the Hawthorn Group below the GCR property a detailed geochemical survey was initiated. The following wells were chosen for sampling: GCL-3A, GCL-12F, GCL-13A, GCL-19, GCL-22, GCL-24, GCL-40, GCL-41, GCL-42F, GCL-55, GCL-58F, GCL-60F, GCL-77, GCL-81F, GCL-82F, GCL-83, GCL-84, GCL-88F and GCL-91F (Fig. 1). Well GCL-12F was drilled and developed exclusively for this study to serve as a reference for "undisturbed" groundwater. With respect to the direction of groundwater flow in the area, this well is upgradient to the other wells studied (Fig. 1). Those wells ending with "F" are screened in the Upper Floridan Aquifer, whereas all others are screened in the Surfical Aquifer. Wells were chosen to (1) represent the variety of geochemical environments at the GCR site (based on previous data), (2) provide sampling locations up- and down-gradient with respect to the GCR site and (3) to allow direct spatial comparison between Surfical and Upper Floridan waters (i.e., to assess leakage from the Surfical into the Upper Floridan Aquifer). The following are well pairs with sampling intervals in the Surfical and Upper Floridan Aquifer that are directly adjacent to each other: 55&81F, 3A&42F, 84&88F, 83&82F, 41&91F and 13A&12F. Groundwater samples were collected with a peristaltic pump connected to a 0.45 μm-filtration system. Temperature, pH and total dissolved solids (TDS) were constantly monitored during pumping and a sample was collected after the reading stabilized. Alkalinity was measured immediately after

sampling by titration with 1.6 N H_2SO_4 to an end point between pH 4.5 and 5.1, depending on the amount of alkalinity present (Hach Company 1997). All samples were tested for the presence of sulfide (H_2S, HS^- and S^{2-}) using a Hach field kit. Samples for laboratory chemical and isotopic analyses were stored in high-density polyethylene bottles and aliquots for cation analyses were acidified with ultra pure HNO_3.

Laboratory methods

The anions F^-, Cl^-, NO_3^-, Br^-, NO_2^-, PO_4^{2-} and SO_4^{2-} were determined on a Dionex DX500 liquid chromatograph following the EPA 300 method. Bicarbonate concentrations were calculated from alkalinity titration values. $H_4SiO_4^0$, Na^+, Mg^{2+}, K^- and Ca^{2+} were determined by inductively coupled plasma – emission spectroscopy (ICP-OES) following the EPA 200 method. Both ion chromatography and ICP-OES analyses were performed at the University of South Florida Center for Water Analysis. Oxygen and hydrogen isotope ratios were determined at the G.G. Hatch Isotope Laboratory, University of Ottawa. Oxygen was analyzed following CO_2 equilibration at 25 °C on a triple collector VG SIRA 12 mass spectrometer. The CO_2-water fractionation factor used is 1.0412 (Friedman and O'Neil 1977). The routine precision (2σ) on the analyses is 0.10‰. Hydrogen isotopes were determined on H_2 generated by zinc reduction in an automated double collector VG 602D mass spectrometer. The routine precision (2σ) for these analyses is 1.5‰.

The sulfate $\delta^{34}S$ was determined on $BaSO_4$ at the University of Calgary (Mayer and others 1995). $BaSO_4$ was precipitated with $BaCl_2$ and collected on a 0.45 μm filter. The pH was lowered to approximately 4 to 5 to prevent precipitation of $BaCO_3$. The precision for $\delta^{34}S$ is better than 0.25‰ (B. Mayer, pers. comm.).

Results

Field measurements and isotopic and chemical data are summarized in Tables 1 and 2. Sulfide was not detected in any of the samples. Alkalinity, as determined in the field, is presented as $CaCO_3$ in mg/L; these values were also used for the determination of the bicarbonate (HCO_3^-) concentration. Samples GCL-19, 22, 24 and 83 do not possess any alkalinity, which is due to their low pH, i.e., all carbonate is present as carbonic acid. Field measurements of TDS are not reported, because the sole purpose of this type of measurement was to determine if the wells were purged sufficiently prior to sampling. Charge balance values were better than 3%, with the exception of sample GCL-12F (5%). Values for isotopes are presented in the delta notation ($\delta^{18}O$, δD and $\delta^{34}S$), which is relative to the international standards VSMOW (Vienna Standard Mean Ocean Water) for oxygen and hydrogen and CDT (Canyon Diabolo Troilite) for sulfur.

Table 1
Temperature, pH, alkalinity, chemical and isotopic composition of groundwater samples collected from single wells on or near the Gulf Coast Recycling property. Chemical data are reported in mg/L and alkalinity as the CaCO$_3$ equivalent in mg/L. Isotope values are in per mil (‰)

Sample ID	GCL-19	GCL-22	GCL-24	GCL-40	GCL-58F	GCL-60F	GCL-77
Temperature (°C)	25	25	24.7	23.9	25.5	24.6	25.3
pH	4.6	2.6	2.7	5.8	6.5	6.5	6.1
Alkalinity	na	na	na	82	338	202	216
F$^-$	0.5	1.0	1.8	<0.1	0.9	0.1	<0.1
Cl$^-$	68	170	319	76	140	64	17
NO$_2^-$	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Br$^-$	<0.5	<0.5	9.4	<0.5	<0.5	0.5	<0.5
NO$_3^-$	<0.5	<0.5	<0.5	18.0	<0.5	<0.5	<0.5
HCO$_3^-$	na	na	na	100	412	246	263
HPO$_4^-$	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO$_4^{2-}$	1209	5533	6522	248	1725	479	89
Na$^+$	472	2120	2920	92.2	444	36.4	49.2
Mg$^+$	7.0	11.6	13.5	8.7	63.5	12.6	12.6
K$^+$	10.9	33.1	88.5	4.49	12.7	0.926	4.05
Ca^{2+}	173	438	239	111	608	292	98.6
Si0	35.6	57.3	62.6	3.12	19.4	10.4	5.43
δ^{18}O (VSMOW)	−2.1	−1.9	−1.4	−2.4	−2.3	−2.9	−2.6
δ D (VSMOW)	−4.0	−4.5	−2.6	−4.1	−1.2	−8.4	−12.0
δ^{34}S (CDT)	13.8	10.1	n.d.	8.6	4.7	6.6	11.3

Both, the isotopic and chemical data scatter much more than expected for the size of the study area (Tables 1 and 2). TDS values that were calculated from chemical analyses range from 104 to 18,700 mg/L and the water characteristics as explored in a Piper diagram (Fig. 2) do not separate into Surfical Aquifer and Upper Floridan Aquifer as expected for shallow and deeper ground water in central Florida (Sacks 1996).

The sulfate values in the Upper Floridan wells GCL-42F, GCL-88F and GCL-81F are substantially higher than those in the corresponding Surfical wells (Table 2). This is surprising because background sulfate values in the Upper Floridan aquifer are generally much lower (Sacks and others 1995). The on-site up-gradient Upper Floridan co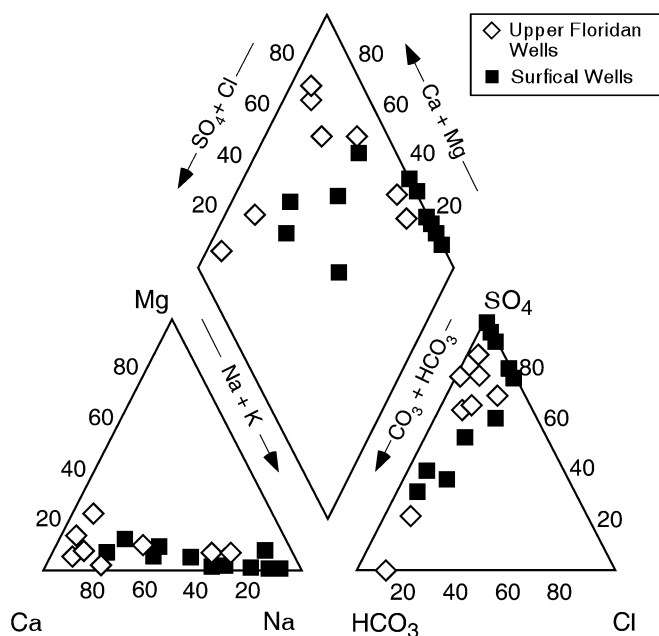ntrol sample GCL-12F, for example, contains only 1.2 mg/L of SO$_4^{2-}$. The Surfical Aquifer wells along the east side of the GCR property, GCL-13A, 40, 41 and 77 show SO$_4^{2-}$ concentrations ranging from 89 to 248 mg/L. These wells are up-gradient with respect to the direction of groundwater flow and thus the elevated sulfate concentration could either be natural or related to industrial emissions to the east of GCR.

Oxygen and hydrogen isotope values plot close to the local meteoric water line (Fig. 3), but scatter significantly more than expected when considering the relatively size of the sampling area. The δ^{18}O in Surfical Aquifer wells at GCR, for example, varies by more than 3‰, while comparable samples from central Florida vary by 1‰ (e.g., Sacks 1996). Similar to δ^{18}O and δD, δ^{34}S values also scatter more than expected. However, there is a clear trend for

Table 2
Temperature, pH, alkalinity, chemical and isotopic composition for well pairs with sampling points above and below the confining layer. Chemical data are in mg/L and alkalinity as the CaCO$_3$ equivalent. Isotope values are in per mil (‰)

Sample ID	GCL-13A	GCL-12F	GCL-3A	GCL-42F	GCL-41	GCL-91F	GCL-55	GCL-81F	GCL-83	GCL-82F	GCL-84	GCL-88F
T (°C)	22.7	24.7	27.8	25.4	22.6	23.5	25	24.5	25.8	25.4	26.5	25.1
pH	6.3	7.2	5.0	6.5	6.2	6.8	5.9	6.6	1.8	5.7	4.9	5.9
Alkalinity	208	166	32	534	108	244	160	232	na	890	12	766
F$^-$	0.1	0.1	0.3	0.9	<0.1	0.2	0.2	0.1	144.8	0.4	1.0	2.7
Cl$^-$	43	13	244	270	34	21	14	52	103	49	293	955
NO$_2^-$	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Br$^-$	<0.5	<0.5	2.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	15.2	9.6
NO$_3^-$	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
HCO$_3^-$	254	202	39	651	132	297	195	283	na	1085	15	934
HPO$_4^-$	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	365.0	<0.5	<0.5	<0.5
SO$_4^{2-}$	128	1.2	1331	4903	144	64	97	443	11497	2766	1443	4375
Na$^+$	118	5.28	507	1800	58.9	22.3	22	84.6	1300	140	838	2110
Mg$^+$	5.3	6.8	11.3	106	5.8	7.9	3.6	5.2	220	212	5.8	90
K$^+$	1.51	1.1	30.4	2.85	0.87	1.4	48.4	0.934	105	1.9	19.9	34.3
Ca^{2+}	75	62	239	773	67	136	63	260	417	1050	102	644
SiO	3.1	15	22.7	23	2.69	17.3	1	6.1	57.3	17.5	7.18	7.3
δ^{18}O (VSMOW)	−2.7	−3.2	−2.3	−2.3	−2.8	−2.9	−3.3	−2.6	−1.7	−2.0	−0.1	−1.1
$\delta\Delta$ (VSMOW)	−4.3	−6.9	−8.5	−0.8	−9.2	−9.3	−16.9	−8.0	19.8	34.7	1.8	8.7
δ34S (CDT)	10.7	n.d.	15.7	5.0	8.5	19.6	23.6	6.8	5.5	4.8	8.0	5.4

Fig. 2
Chemical composition of water collected from Surfical and Upper Floridan aquifer wells at the Gulf Coast Recycling facility

Surfical aquifer wells, (c) the Surfical aquifer wells without GCL-83 and (d) the Floridan wells (Table 3). The Surfical aquifer wells were correlated without GCL-83 to alleviate the outlier effect (caused by the extremely high SO_4^{2-} value), which can produce a higher degree of correlation than actually warranted by the data (Swan and Sandilands 1995). Correlation coefficients (r^2) above 0.8 were only rarely observed, indicating a significant chemical hetero-geneity beneath the GCR facility.

Discussion

General hydrogeological considerations

The extreme scatter of the chemical and isotopic data that were collected (Figs. 2 and 3) is a clear indication of the complex nature of subsurface conditions below the GCR property. Because of the low pH and high reactivity of the groundwater, hydrogeological microenvironments are likely created by preferential dissolution and therefore, cause enhanced recharge and groundwater flow in certain areas. The large spread in $\delta^{18}O$ is a good indication of this phenomenon. Under "normal" hydrogeological conditions in fine-grained sediments, a much larger attenuation towards the weighed annual mean of local precipitation is expected (Darling and Bath 1988; Rank and others 1992). Nevertheless, the wells that were sampled for this study can be divided into 3 groups, based on their geographic location and chemical and isotopic composition. Groundwater flow above and below the confining unit is approximately towards Hillsborough Bay (west-southwest) (Basso 2002) and thus one group of samples are those "up-gradient" from well GCL-82. They are characterized by low TDS and do not show signs of contamination by battery acid, such as low pH and high sulfate. This group consists of wells GCL-12F, 13, 91F, 41, 40 and 77. Group 2 are the wells GCl-19 and 22, which are inside an area where old battery casings were buried. These wells show all the

those samples high in SO_4^{2-}, to have $\delta^{34}S$ values around 5 to 6‰ (Fig. 4). With the exception of GCL-83 those samples are from below the confining unit. The determination of $\delta^{34}S$ in the control sample GCL-12F was not possible, due to the extremely low SO_4^{2-} concentration in this sample. Sample GCL-91F, which is also up-gradient from the GCR property has the second lowest SO_4^{2-} con-centration (64 mg/L) and a $\delta^{34}S$ of 19.6‰. These values are close to those expected for uncontaminated Floridan groundwater (Sacks and others 1995; Sacks 1996; Sacks and Tihansky 1996).
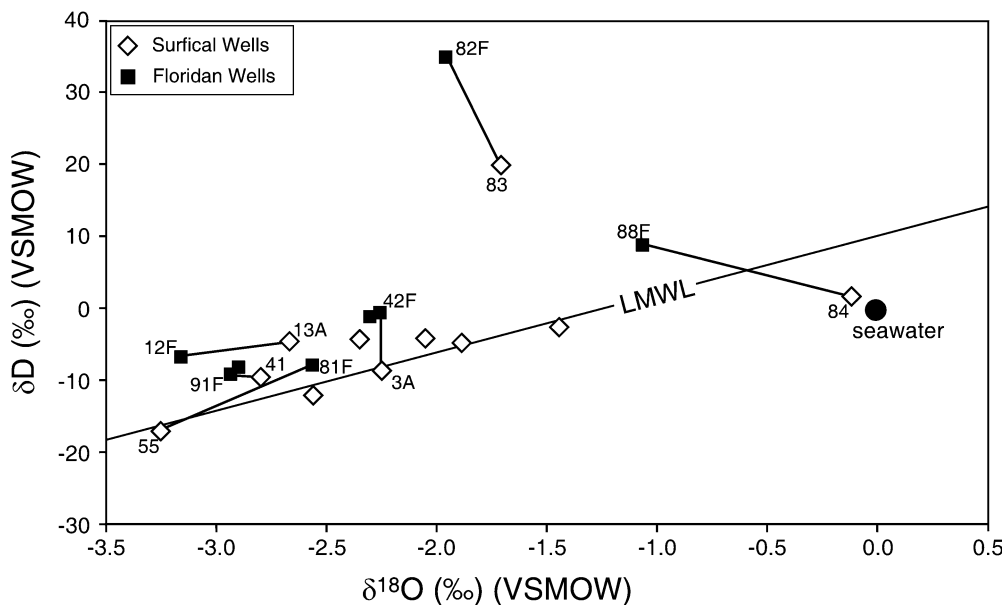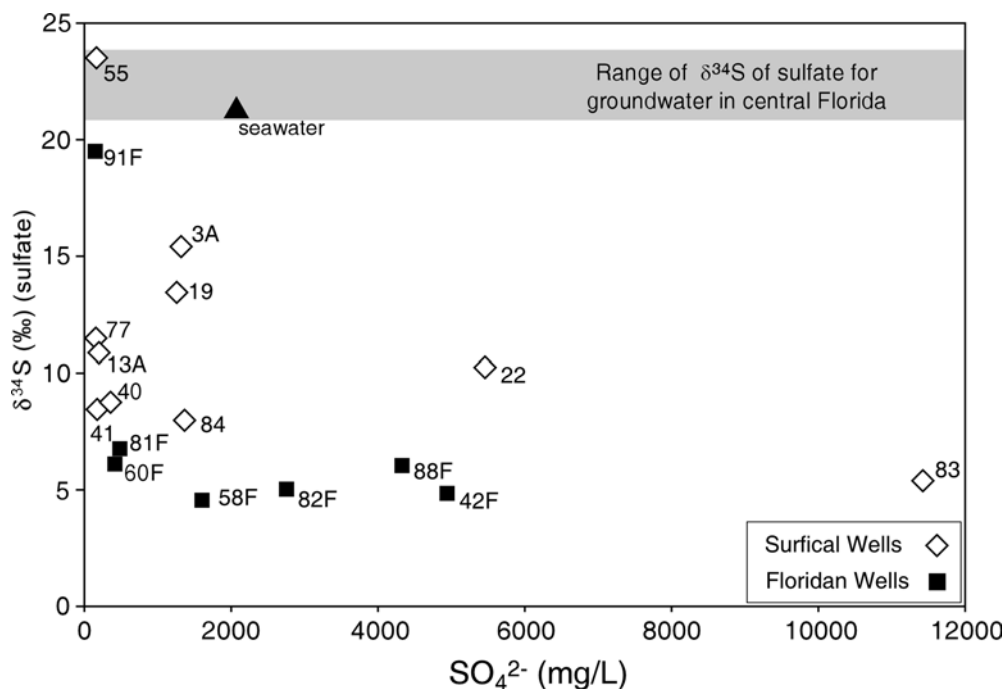
Simple linear regression analyses of key parameter pairs were carried out for (a) samples from all wells, (b) the

Fig. 3
The isotopic composition of GCR groundwater samples compared to seawater and the Local Mete-oric Water Line (LMWL) for the Tampa area from Netratanawong and Sackett (1995)

Fig. 4
$\delta^{34}S$ in sulfate vs. concentration of SO_4^{2-} in water collected from Surfical and Upper Floridan aquifer wells. The grey area is the $\delta^{34}S$ range for uncontaminated groundwater in central Florida from Sacks and others (1995). The $\delta^{34}S$ value for modern seawater is from Rees and others (1978)

signs of battery acid contamination, including high sulfate. Group 3 are those Floridan and Surfical wells that are "downstream" from well GCL-83. These wells are all characterized by varying degrees of contamination and the fact that their sulfate concentrations, except for GCL-24, are higher in the Floridan than in the Surfical Aquifer.

Sulfate source to the Surfical Aquifer

The elevated sulfate concentration in groundwater in the Surfical Aquifer at the Gulf Coast Recycling (GCR) facility is without doubt caused by the escape of sulfuric acid (H_2SO_4) from various point-sources as part of the recycling process. The high values in GCL-19 and 22 reflect their location on the GCR property, which is in an area where spent battery casings are buried. GCL-24, which shows the highest sulfate values in the Surfical Aquifer is directly beside an acid storage tank that, at the time of sampling, showed signs of leaking. The only other potential sources of sulfate could be: (a) an up-gradient contaminant source or (b) the dissolution of gypsum from the aquifer matrix. The hypothesis of a potential up-gradient source is easily dismissed, because all samples that were taken along the up-gradient side of the GCR property had much lower sulfate values than those in the center (Table 1). If gypsum ($CaSO_4 * 2H_2O$) is a major source of sulfate, then the Ca^{2+}/SO_4^{2-} ratio (in mg/L) in the corresponding groundwater is approximately 0.4 and the $\delta^{34}S$ of SO_4^{2-} should be very close to that of the gypsum (e.g., Mayer and others 1995). Only GCL-55 satisfies these requirements (Fig. 5), thus the dissolution of gypsum in an unlikely source for the elevated sulfate in the Surfical Aquifer.

Sulfate source to the Floridan Aquifer

The possible sources of sulfate to the Upper Floridan aquifer are slightly more difficult to assess than those of the Surfical aquifer. Five potential sources have to be

evaluated: (1) seawater intrusion, (2) upwelling of high-sulfate groundwater, (3) local dissolution of gypsum, (4) an up-gradient contaminant source to the northeast of the GCR property and (5) battery acid contamination. In the coastal areas of southwest Florida, uncontaminated groundwater in the Upper Floridan aquifer can have sulfate concentrations as high as 2,500 mg/L (Sacks and Tihansky 1996). These elevated values are caused by either seawater intrusion or by upwelling of deeper groundwater. Seawater incursion is relatively easy to detect because high-sulfate waters should also be high in chloride (Stuyfzand 1999); the corresponding chloride/sulfate ratios (in mg/L) being approximately 7.8. The chloride/sulfate ratios for the GCR wells are much lower than that, ranging from 0.01 to 0.33, thus seawater intrusion can be ruled out as a source of sulfate. The upwelling of a groundwater rich in sulfate is slightly more difficult to evaluate. Although the calcium/sulfate ratio can be a good indicator of gypsum dissolution, its application in an upwelling scenario is hampered, because, unlike chloride, calcium does not behave conservatively along a flowpath. The precipitation or dissolution of calcite, for example, has an immediate affect. Sacks and others (1995), who studied the sources of sulfate in the Upper Floridan aquifer were able to identify gypsum dissolution, based on $\delta^{34}S$ values and chloride/sulfate ratio in the corresponding groundwater. A range of $\delta^{34}S$ from approximately 20 to 25‰, combined with a low chloride/sulfate ratio indicates gypsum dissolution. With the exception of sample GCL-91F, the control sample, none of the Upper Floridan wells at the GCR property had a $\delta^{34}S$ above 6.8‰ (Figs. 4 and Fig. 6, Tables 1 and 2), although chloride/sulfate ratios are low. Thus, without the distinctive $\delta^{34}S$ signature, upwelling of a high-sulfate groundwater could be a possible interpretation of the high sulfate values seen in the Upper Floridan groundwater below the GCR property.

Table 3
Correlation matrix for linear regression analyses of selected parameters for (a) all Wells, (b) all Surficial Wells, (c) Surficial Wells excluding GCL-83 and (d) all Floridan Wells. Correlation coefficients are reported as r^2; coefficients above 0.8 are in bold

(a)	pH	Cl	SO_4	Na	Mg	K	Ca	Si	$\delta^{18}O$	δD	$\delta^{34}\Sigma(SO_4)$
pH		0.02	0.63	0.64	0.09	0.68	0.01	0.72	0.27	0.10	0.02
Cl	0.02		0.13	0.20	0.03	0.08	0.13	0.01	0.41	0.06	0.12
SO_4	0.63	0.13		**0.95**	0.45	0.64	0.21	0.63	0.24	0.32	0.21
Na	0.64	0.20	**0.95**		0.29	0.71	0.10	0.60	0.28	0.19	0.16
Mg	0.09	0.03	0.45	0.29		0.12	0.60	0.09	0.07	**0.81**	0.31
K	0.68	0.08	0.64	0.71	0.12		0.00	0.49	0.15	0.06	0.00
Ca	0.01	0.13	0.21	0.10	0.60	0.00		0.05	0.08	0.56	0.36
Si	0.72	0.01	0.63	0.60	0.09	0.49	0.05		0.10	0.08	0.03
$\delta^{18}O$	0.27	0.41	0.24	0.28	0.07	0.15	0.08	0.10		0.24	0.23
δD	0.10	0.06	0.32	0.19	**0.81**	0.06	0.56	0.08	0.24		0.38
$\delta^{34}S(SO_4)$	0.02	0.12	0.21	0.16	0.31	0.00	0.36	0.03	0.23	0.38	

(b)	pH	Cl	SO_4	Na	Mg	K	Ca	Si	$\delta^{18}O$	δD	$\delta^{34}S(SO_4)$
pH		0.15	**0.88**	0.80	0.52	0.60	**0.90**	**0.91**	0.20	0.56	0.13
Cl	0.15		0.04	0.28	0.00	0.02	0.13	0.08	0.65	0.09	0.05
SO_4	**0.88**	0.04		0.56	**0.81**	0.75	0.76	0.72	0.11	0.71	0.20
Na	0.80	0.28	0.56		0.16	0.26	**0.81**	0.75	0.27	0.28	0.12
Mg	0.52	0.00	**0.81**	0.16		0.75	0.38	0.36	0.04	0.73	0.18
K	0.60	0.02	0.75	0.26	0.75		0.45	0.41	0.03	0.42	0.00
Ca	**0.90**	0.13	0.76	**0.81**	0.38	0.45		**0.92**	0.08	0.36	0.10
Si	**0.91**	0.08	0.72	0.75	0.36	0.41	**0.92**		0.09	0.38	0.08
$\delta^{18}O$	0.20	0.65	0.11	0.27	0.04	0.03	0.08	0.09		0.33	0.27
δD	0.56	0.09	0.71	0.28	0.73	0.42	0.36	0.38	0.33		0.49
$\delta^{34}S(SO_4)$	0.13	0.05	0.20	0.12	0.18	0.00	0.10	0.08	0.27	0.49	

(c)	pH	Cl	SO_4	Na	Mg	K	Ca	Si	$\delta^{18}O$	δD	$\delta^{34}\Sigma(SO_4)$
pH		0.30	**0.93**	**0.92**	0.17	0.21	**0.86**	**0.88**	0.21	0.15	0.01
Cl	0.30		0.24	0.33	0.05	0.10	0.20	0.12	0.67	0.37	0.06
SO_4	**0.93**	0.24		**0.98**	0.19	0.17	**0.90**	**0.81**	0.14	0.12	0.03
Na	**0.92**	0.33	**0.98**		0.15	0.16	**0.82**	0.74	0.24	0.19	0.05
Mg	0.17	0.05	0.19	0.15		0.00	0.37	0.23	0.01	0.00	0.07
K	0.21	0.10	0.17	0.16	0.00		0.16	0.10	0.00	0.12	0.53
Ca	**0.86**	0.20	**0.90**	**0.82**	0.37	0.16		**0.88**	0.05	0.05	0.01
Si	**0.88**	0.12	**0.81**	0.74	0.23	0.10	**0.88**		0.06	0.08	0.00
$\delta^{18}O$	0.21	0.67	0.14	0.24	0.01	0.00	0.05	0.06		0.66	0.25
δD	0.15	0.37	0.12	0.19	0.00	0.12	0.05	0.08	0.66		0.53
$\delta^{34}S(SO_4)$	0.01	0.06	0.03	0.05	0.07	0.53	0.01	0.00	0.25	0.53	

(d)	pH	Cl	SO_4	Na	Mg	K	Ca	Si	$\delta^{18}O$	δD	$\delta^{34}S(SO_4)$
pH		0.18	0.29	0.08	0.72	0.19	0.66	0.01	0.59	**0.86**	0.40
Cl	0.18		0.46	0.74	0.03	**0.88**	0.06	0.11	0.75	0.03	0.14
SO_4	0.29	0.46		**0.80**	0.42	0.27	0.57	0.09	0.60	0.22	0.45
Na	0.08	0.74	**0.80**		0.08	0.50	0.16	0.00	0.56	0.01	0.22
Mg	0.72	0.03	0.42	0.08		0.02	**0.93**	0.16	0.33	**0.90**	0.38
K	0.19	**0.88**	0.27	0.50	0.02		0.05	0.11	0.72	0.03	0.13
Ca	0.66	0.06	0.57	0.16	**0.93**	0.05		0.18	0.40	0.75	0.59
Si	0.01	0.11	0.09	0.00	0.16	0.11	0.18		0.03	0.03	0.04
$\delta^{18}O$	0.59	0.75	0.60	0.56	0.33	0.72	0.40	0.03		0.34	0.31
δD	**0.86**	0.03	0.22	0.01	**0.90**	0.03	0.75	0.03	0.34		0.26
$\delta^{34}S(SO_4)$	0.40	0.14	0.45	0.22	0.38	0.13	0.59	0.04	0.31	0.26	

The local dissolution of gypsum present in the Upper Floridan aquifer matrix immediately below the GCR property can be ruled out based on the same argument that was used for the Surficial aquifer. If gypsum ($CaSO_4 \cdot 2H_2O$) is a major source of sulfate, then the Ca^{2+}/SO_4^{2-} ratio (in mg/L) in the corresponding groundwater is approximately 0.4 and the $\delta^{34}S$ of SO_4^{2-} should be very close to that of the gypsum (Mayer and others 1995), which is not seen in any of the Upper Floridan samples (Fig. 5). An up-gradient sulfate source is also extremely unlikely, because the on-site control well GCL-12F and well GCL-91F, which is exactly up-gradient (Fig. 6), do not show any of the chemical characteristics that would indicate an up-gradient contaminant source, such as low pH and high sulfate.

With four of the possible five sources ruled out, the only remaining likelihood for the observed high sulfate and low pH in Upper Floridan groundwater is the leakage of battery acid. Conceptually, however, this scenario has been difficult to understand, because sulfate values are higher in several of the Upper Floridan wells than in the corresponding Surficial wells (Table 2, Fig. 6). Extensive
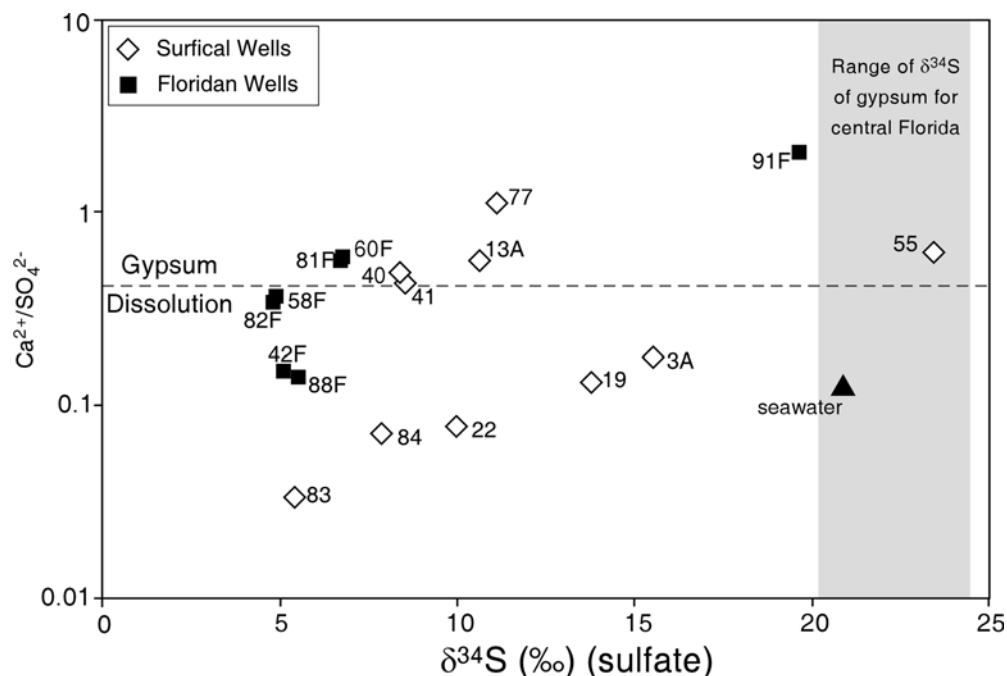
coring and study of the confining unit below the GCR property by ground penetrating radar did not indicate a compromise of its hydraulic impermeability, except for the depression around the well pair GCL-83 and GCL-82F, where extreme alteration and thinning of the confining layer occurred (Foster 2002; Foster and Pichler 2002). The measured hydraulic conductivity of core material was $4*10^{-5}$ cm/s (corresponding to clayey sand), which is much higher than the $5*10^{-7}$ cm/s (corresponding to a clay) obtained for the confining unit outside the depression (Foster 2002). Due to the much higher permeability of the confining unit at this location, sulfate (and potentially other contaminants) can move from the Surficial Aquifer into the Upper Floridan Aquifer. The downward flow into the Upper Floridan Aquifer is also facilitated by the difference in hydraulic head between the Surficial (DTW ~2 m) and Upper Floridan Aquifer (DTW ~4 m) at the GCR site.

Prior to a restructuring of the GCR facility, the area around well GCL-83 was the site where battery casings were cracked open upon arrival at the plant (Larry Maron, pers. comm.). Battery acid and water were collected in an open pond at approximately the same location as the depression. Due to its greater density than water, the battery acid migrated downwards into and through the surficial aquifer, pooling on top of the confining unit. As a result the original mineralogical compositions of the Surficial Aquifer and the confining unit were altered and increased permeability allowed acid-contaminated water to breach the confining unit into the Upper Floridan. This is mainly manifested in the high sulfate values in samples from the Floridan wells GCL-82F, 88F, 42F, 81F and 60F, but even more so by the conspicuously similar $\delta^{34}S$ of this set of samples. Values for pH are also relatively low, but not nearly as low as those in well GCL-83. Reaction with selected minerals in the subsurface such as apatite and calcite, which are common in Surficial Aquifer, confining unit and Upper floridan

Aquifer in central Florida and below the GCR property (Scott 1988), likely caused this increase in pH. This pond was later drained, filled in and is now covered by a concrete surface. These conditions clearly decrease recharge into the aquifer and diminish the input of new acid at this location. As a result: (1) the body of extremely contaminated groundwater in the area of well GCL-83 is moving downward at a much slower rate than when the pond was present and (2) the high sulfate values in the Upper Floridan are likely a relict from times when the pond was present and are currently dissipating and traveling southwest with the groundwater. The attenuation along the flow path towards more "normal" conditions is clearly seen in the increase in pH and $\delta^{34}S$ and decrease in sulfate along the flowpath from GCL-83 to GCL-60F (Fig. 6).

While there are no published data for the isotopic composition of sulfuric acid used in batteries, it is unlikely that uniformly its $\delta^{34}S$ value is approximately 5 to 6‰. The approximate isotopic composition of sulfuric acid, however, can be inferred by considering how it is produced. In the United States approximately 85% of sulfuric acid are produced domestically, of which 89% come from a process that involves elemental sulfur and the remaining 13% are a byproduct of base-metal mining (e.g., Cu, Zn, etc.) (Ober 2003). The worldwide isotopic composition of elemental sulfur and base-metal sulfides is more or less always between −1 and 6‰ (Hoefs 1997). Thus the range of $\delta^{34}S$ in sulfuric acid should be in the same range. The $\delta^{34}S$ for those Surficial wells that are also high in sulfate ranges from 5 to 15.7‰. Thus, the $\delta^{34}S$ in well GCL-83 should represent an average for sulfuric acid that has migrated into the depression and homogenized. Microbial activity, in particular sulfate reduction by *Desulfovibrio desulfuricans*, has the potential to dramatically alter the isotopic composition of sulfate (Harrison and Thode 1958). At the GCR site, however, the absence of sulfide rules out any significant microbial activity.
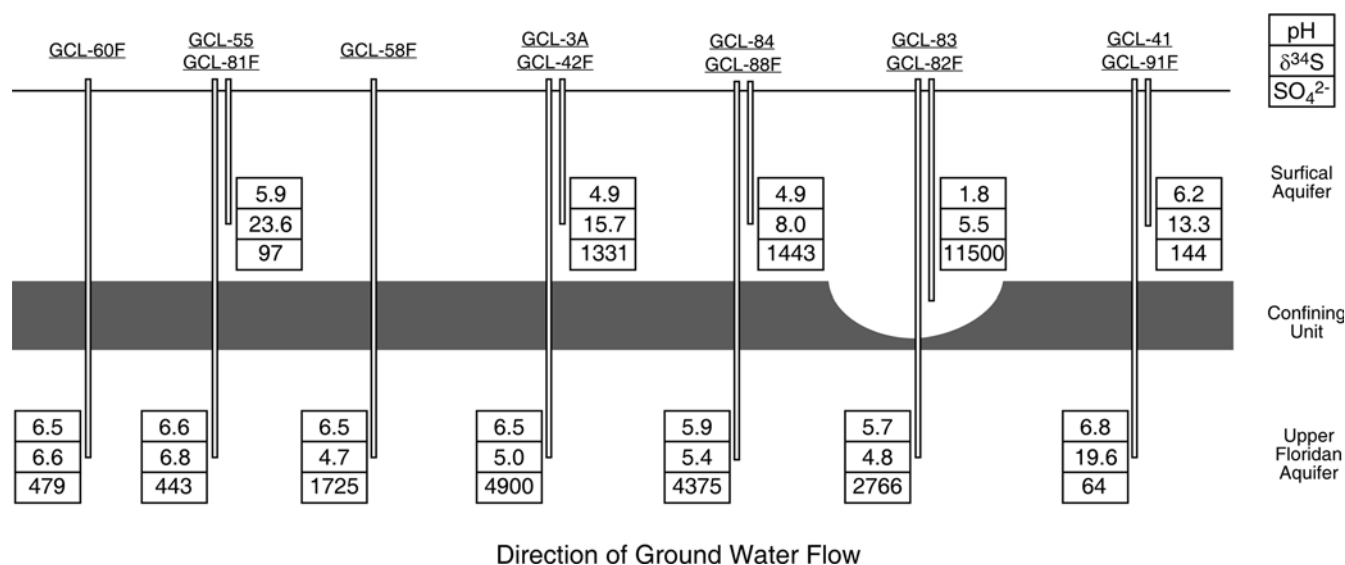
Fig. 6

Wells: GCL-60F | GCL-55 / GCL-81F | GCL-58F | GCL-3A / GCL-42F | GCL-84 / GCL-88F | GCL-83 / GCL-82F | GCL-41 / GCL-91F

Legend box: pH / $\delta^{34}S$ / SO_4^{2-}

Surficial Aquifer

Well	pH	$\delta^{34}S$	SO_4^{2-}
GCL-55 / GCL-81F	5.9	23.6	97
GCL-3A / GCL-42F	4.9	15.7	1331
GCL-84 / GCL-88F	4.9	8.0	1443
GCL-83 / GCL-82F	1.8	5.5	11500
GCL-41 / GCL-91F	6.2	13.3	144

Confining Unit

Upper Floridan Aquifer

Well	pH	$\delta^{34}S$	SO_4^{2-}
GCL-60F	6.5	6.6	479
GCL-55 / GCL-81F	6.6	6.8	443
GCL-58F	6.5	4.7	1725
GCL-3A / GCL-42F	6.5	5.0	4900
GCL-84 / GCL-88F	5.9	5.4	4375
GCL-83 / GCL-82F	5.7	4.8	2766
GCL-41 / GCL-91F	6.8	19.6	64

Direction of Ground Water Flow

Fig. 6
Schematic NE-SW trending cross-section of the subsurface beneath the GCR property. The rectangular boxes contain the pH, $\delta^{34}S$ and sulfate values for groundwater from the adjacent wells

Summary and conclusions

Prior to the application of $\delta^{34}S$ of sulfate as a tracer it was not possible to determine the exact source of the high sulfate values in the Upper Floridan Aquifer below the Gulf Coast Recycling facility in east Tampa, Florida. Extremely complex local hydrogeological conditions, as seen in the large scatter in the chemical and isotopic data, prevented the use of basic chemical tracers. The complex hydrogeology is caused in part by the contaminant itself. Because of the low pH and high reactivity of sulfuric acid contaminated groundwater, hydrogeological microenvironments are likely created by preferential dissolution. In particular, the large spread in $\delta^{18}O$ is a good indication of this phenomenon. Under "normal" hydrogeological conditions in fine-grained sediments, a much larger attenuation towards the weighed annual mean of local precipitation is expected.

The results of this study clearly reveal the usefulness of $\delta^{34}S$ as a tracer for sulfate contamination in complex hydrogeological environments.

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