

Isotopic Characterization of Sulfate in a Shallow Aquifer Impacted by Agricultural Fertilizer

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Abstract

The stable isotope ratios of groundwater sulfate ($^{34}\text{S}/^{32}\text{S}$, $^{18}\text{O}/^{16}\text{O}$) are often used as tracers to help determine the origin of groundwater or groundwater contaminants. In agricultural watersheds, little is known about how the increased use of sulfur as a soil amendment to optimize crop production is affecting the isotopic composition of groundwater sulfate, especially in shallow aquifers. We investigated the isotopic composition of synthetic agricultural fertilizers and groundwater sulfate in an area of intensive agricultural activity, in Ontario, Canada. Groundwater samples from an unconfined surficial sand aquifer (Lake Algonquin Sand Aquifer) were analyzed from multi-level monitoring wells, riverbank seeps, and private domestic wells. Fertilizers used in the area were analyzed for sulfur/sulfate content and stable isotopic composition ($\delta^{18}\text{O}$ and/or $\delta^{34}\text{S}$). Fertilizers were isotopically distinct from geological sources of groundwater sulfate in the watershed and groundwater sulfate exhibited a wide range of $\delta^{34}\text{S}$ (−6.9 to +20.0‰) and $\delta^{18}\text{O}$ (−5.0 to +13.7‰) values. Quantitative apportionment of sulfate sources based on stable isotope data alone was not possible, largely because two of the potential fertilizer sulfate sources had an isotopic composition on the mixing line between two natural geological sources of sulfate in the aquifer. This study demonstrates that, when sulfate isotope analysis is being used as a tracer or co-tracer of the origin of groundwater or of contaminants in groundwater, sulfate derived from synthetic fertilizer needs to be considered as a potential source, especially when other parameters such as nitrate independently indicate fertilizer impacts to groundwater quality.

Introduction

Groundwater quality, whether it be in urban or rural areas, as it relates to potable water supplies or ecological impacts, is an issue of concern in Canada (e.g., CCA 2009; Grannemann and Van Stempvoort 2016). In agricultural watersheds, much of the focus with respect to

groundwater contamination has historically been on nitrate (NO_3^-) due to its prevalence and its potential human and ecological health impacts. In contrast, sulfate (SO_4^{2-}) in shallow groundwater is not generally considered a chemical of environmental concern, partly due to the fact that geological sources of sulfate can naturally produce high concentrations of sulfate in groundwater. In fact, sulfate is the second most common anion in freshwater, second only to bicarbonate. Like nitrate, sulfate is very soluble and mobile in water. The drinking water limit for sulfate in Canada is an aesthetic limit of 500 mg/L (Health Canada 1994), which is a high concentration for a dissolved constituent in freshwater. Furthermore, there is no sulfate water quality guideline set for the protection of aquatic life in Canada.

While sulfate in groundwater may largely be from natural, geological sources, especially at greater depths, shallow groundwater quality is more susceptible to surface derived inputs. In agricultural areas, synthetic and organic fertilizers are potential sources of sulfate that can enter the groundwater system. Sulfate can be a counter-anion in fertilizers or present as a slow release coating (e.g., sulfur [S]-coated urea) and thereby added to crops as a consequence of delivering the other target nutrients and not necessarily intended as a nutrient addition itself. Historically, sulfur deficiency in soils was not a big concern since sufficient amounts of elemental sulfur

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existed in most mineral and organic soils and atmospheric deposition of sulfur was higher before the implementation of controls on sulfur dioxide emissions. However, in more recent years, soil sulfur deficiency has been noted in some agricultural areas with the heavy production of sulfur absorbing crops (canola, barley, etc.) and therefore fertilizers containing sulfur are increasingly being used by the agricultural sector to augment soil sulfur content (e.g., Alberta Government 2013; Ontario Ministry of Agriculture, Food, and Rural Affairs 2017; Government of Saskatchewan 2019).

Insights from Sulfate Stable Isotope Ratios

Understanding the origin of contaminants in aquatic systems is a critical step toward the development of protection and mitigation strategies. Given the importance of sulfate as a link between groundwater nitrate and the release of sediment-bound P (e.g., Smolders et al. 2010), understanding the sources and cycling of groundwater sulfate in agricultural landscapes is important, especially in areas where groundwater could be contributing to stream or near-shore eutrophication problems. Furthermore, given that sulfate concentration and isotopic composition are used as tracers to assess anthropogenic and natural impacts on water quality, and to determine the origin of groundwater and groundwater contaminants (e.g., Kaown et al. 2009; Hosono et al. 2011; Jakóbczyk-Karpierz et al. 2017), the potential impact of fertilizer sulfate needs to be considered. Sulfate isotope analysis can also provide information on the biogeochemical processes that affect groundwater sulfate concentrations, such as sulfate reduction and mineral sulfide oxidation.

Dual isotope analysis ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$) of groundwater sulfate has been used to investigate anthropogenic impacts on sulfate sources and sulfur cycling in forested watersheds (e.g., Mitchell et al. 1998; Mayer et al. 2010), wetlands (e.g., Novák et al. 2005; Schiff et al. 2005), urban groundwater (e.g., Houhou et al. 2010; Hosono et al. 2011), agricultural areas (e.g., Vitòria et al. 2008; Kaown et al. 2009; Urresti-Estala et al. 2015), and other systems. With respect to agricultural fertilizers as a sulfate source to groundwater, Vitòria et al. (2004) provide the most comprehensive look at the isotopic composition of fertilizer constituents, including sulfate, analyzing 27 commercial fertilizers used in Spain. The study concluded that coupled $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analysis of groundwater sulfate can be used to distinguish fertilizer-derived sulfate from several natural sources, with the caveat that there may be some overlap with other anthropogenic sources.

Sulfate isotopes have been used as co-tracer along with other geochemical and stable isotope tracers (e.g., $\delta^2\text{H}\text{-H}_2\text{O}$, $\delta^{18}\text{O}\text{-H}_2\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$) to determine contaminant sources and to trace the geological origin of groundwater in southern Ontario and the Great Lakes Region (Weaver et al. 1995; McIntosh and Walter 2006; Freckelton 2013; Skuce et al. 2015; Smal 2016; Matheson et al. 2018). Given that these studies deal with bedrock aquifers under varying depths of surficial deposits, only geological sources of sulfate were considered. A study of

groundwater discharge to the Grand River between Cambridge and Brantford, Ontario, did consider atmospheric deposition and fertilizers as potential sources of sulfate (Westberg 2012); however, the isotopic compositions of local sulfate sources were not measured directly, instead relying on published literature values.

The objective of this study was to determine the isotopic composition of synthetic fertilizers and groundwater sulfate in a shallow, unconfined aquifer and investigate the potential of using sulfate isotopes as tracers of the origin of sulfate and/or groundwater in watersheds impacted by intensive agriculture.

Study Site

This study was conducted in the southern Nottawasaga River Watershed, located near Alliston, Ontario, Canada (Figure 1). Land use in the area is dominated by agriculture, including the cultivation of corn, potatoes, and sod (Van Stempvoort et al. 2016; Figure S1) that are grown on sandy loam to loamy sand soils (Hoffman et al. 1962). The area has a temperate climate and receives approximately 834 mm of precipitation annually, 152 mm as snow (Government of Canada 2019; Alliston Nelson station, 1981–2010 period). The coldest (January) and warmest (July) months have mean daily temperatures of -6.5 and 21.0°C , respectively (Government of Canada 2019).

The study area is underlain by the Lake Algonquin Sand Aquifer (LASA), a large unconfined aquifer that is part of the Alliston Sand Plain (Sibul and Choo-Ying 1971). The LASA consists of medium to fine grained sands that were deposited by glacial Lake Algonquin and are underlain by a unit of till (Sibul and Choo-Ying 1971). The LASA supplies potable water for rural residents in the southern Nottawasaga River Watershed and, along with the Nottawasaga River and its tributaries, is also used for the irrigation of crops. High groundwater nitrate concentrations have been documented in the LASA and attributed to heavy fertilizer application associated with agriculture, specifically potato production in the watershed (Hill 1982). Hill (1982) found that 42% of 164 groundwater samples collected from domestic wells and riverbank seeps had nitrate concentrations over the Canadian drinking water quality guideline (10 mg N/L; Health Canada 2013), with concentrations reaching 95 mg N/L. Similarly, when groundwater in the area was resampled three decades later, Senger (2016) found that 36% of wells and 37% of seeps were above the drinking water guideline, with nitrate concentrations ranging from <0.02 to 73 mg N/L.

Potential Sources of Sulfate in the Lake Algonquin Sand Aquifer

In order to utilize sulfate stable isotope ratios as a geochemical tool, both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of potential sulfate sources must be known or determined. In the southern Nottawasaga River Watershed, the main potential sources of sulfate to the LASA consist of both natural (atmospheric deposition, dissolution of sulfate

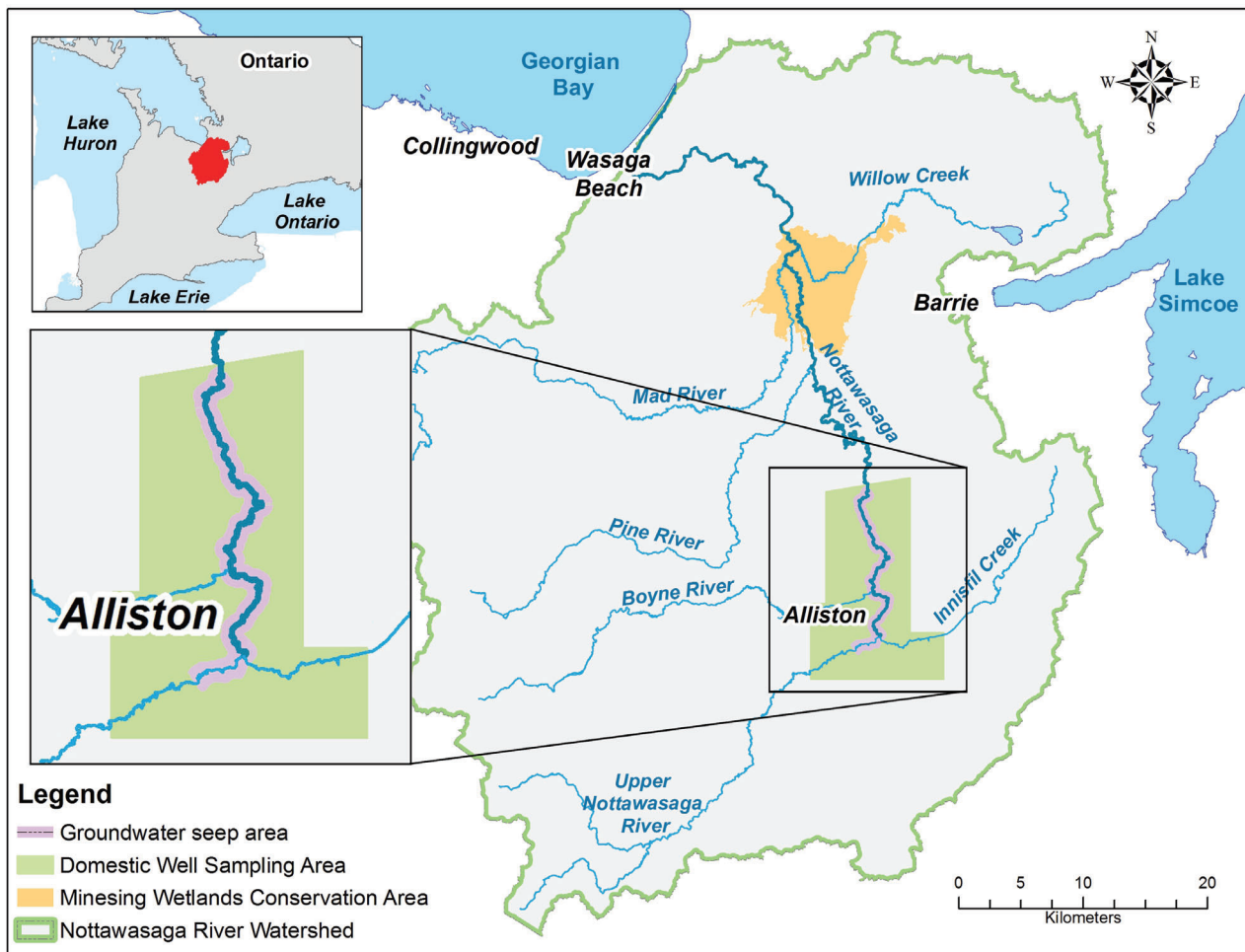


Figure 1. Map of study area. The green shaded area encompasses the area where domestic wells were sampled. The multi-level wells are located in the southern part of the green shaded area, near the confluence of Innisfil Creek and the Upper Nottawasaga River. Groundwater seep samples were collected along the highlighted (purple) portion of the Nottawasaga River. The upper inset map shows the location of Nottawasaga River Watershed within southern Ontario, Canada.

minerals, oxidation of sulfide minerals) and anthropogenic (agricultural fertilizers, domestic wastewater) sources. Some studies have also considered the soil as a potential source of sulfate to groundwater (e.g., Vitòria et al. 2004; Kaown et al. 2009; Hosono et al. 2011); however, we consider soil sulfate to be a mixture of the other sources listed above and therefore do not treat it as a distinct source in this study.

Atmospheric Deposition

Atmospheric deposition of sulfate, whether as wet (rain, snow) or dry deposition (particulate, gaseous), is a potential source of sulfate to groundwater. In areas near marine environments, sea spray can also be an important source of sulfate deposition. However, this is not the case for the Nottawasaga River Watershed as it is approximately 1200 km from the nearest ocean.

Precipitation chemistry data obtained from the Canadian Air and Precipitation Monitoring Network (Environment and Climate Change Canada 2018) station located in Egbert, Ontario (approximately 17 km northeast of Alliston, Ontario) was used to determine a

volume-weighted concentration of sulfate in precipitation of 0.88 mg/L for the 2010 to 2013 period. Even if an evapoconcentration factor of three is assumed for recharging precipitation, the concentration of atmospheric sulfate in groundwater could only be around 2.6 mg/L. Given that sulfate concentrations in the LASA are significantly higher than what is possible from atmospheric deposition, precipitation must not be a major source of sulfate to groundwater in the Nottawasaga River Watershed.

Geological Sources of Sulfate in Groundwater

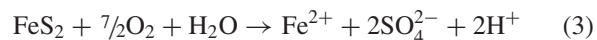
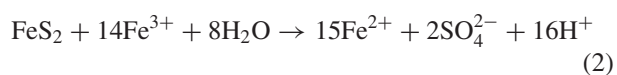
Sulfide Mineral Oxidation: The oxidation of naturally occurring sulfide minerals can be an important source of sulfate to groundwater. The specific sulfide minerals present in an area is largely controlled by local geology, with the most commonly occurring form being pyrite (iron sulfide).

Sulfate produced from the oxidation of sulfide minerals under aerobic or anaerobic conditions will have $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values controlled by the isotopic composition of the original sulfide, available O_2 and H_2O , and fractionation effects. Due to the lack of significant

sulfur isotopic fractionation during sulfide oxidation, the $\delta^{34}\text{S}$ value of sulfate produced will have essentially the same $\delta^{34}\text{S}$ value as the parent sulfide mineral (Taylor et al. 1984). Since $\delta^{34}\text{S}$ values of sulfide minerals were not determined for the LASA, for calculation purposes it was assumed that the $\delta^{34}\text{S}$ value of mineral sulfides would be similar to that of the shallow sand aquifer at Long Point, Ontario ($-4\% \pm 3\%$; Aravena and Robertson 1998).

During oxidation of sulfur, a percentage of the oxygen comes from available oxygen gas (O_2) in the system and the rest is derived from available water. The $\delta^{18}\text{O}$ value of the resulting sulfate can be calculated from Equation 1, which is derived from Reactions 2 and 3 (van Everdingen and Krouse 1985),

$$\delta^{18}\text{O}_s = Y(\delta^{18}\text{O}_w + \varepsilon_w) + (1 - Y) \\ (0.875[\delta^{18}\text{O}_a + \varepsilon_a] + 0.125[\delta^{18}\text{O}_w + \varepsilon_w]) \quad (1)$$



where Y (0 to 1) represents the fraction of sulfate produced by Reaction 2, ε_w and ε_a are enrichment factors representing kinetic isotope effects during the incorporation of O_w (O from water) and O_a (O from O_2) into sulfate. Values for ε_w and ε_a of $+4.1\%$ and -11.2% , respectively (van Everdingen and Krouse 1985), were used, as well as a value of $+23.5\%$ for atmospheric O_2 ($\delta^{18}\text{O}_a$; Kroopnick and Craig 1972). The average $\delta^{18}\text{O}$ - H_2O value for groundwater samples collected in the southern Nottawasaga River Watershed ($-11.4\% \pm 0.7\%$, $n = 164$) was used as the $\delta^{18}\text{O}$ - H_2O value. Using Equation 1 and the parameter values listed above, a range of -7.3% to $+9.9\%$ was calculated for $\delta^{18}\text{O}$ values for sulfate derived from sulfur oxidation at this site. It is expected that, in the saturated zone where oxygen availability is lower or absent, the amount of sulfate produced from Reaction 3 would be minimal and therefore the dominant or sole source of oxygen would be from water via Reaction 2, resulting in $\delta^{18}\text{O}$ - SO_4^{2-} values at the lower end of the calculated range.

In addition to sulfate produced by sulfur oxidation under aerobic conditions, denitrification under anaerobic conditions can produce sulfate using nitrate as the oxidizing agent instead of oxygen. When denitrification proceeds with sulfur as the electron donor, groundwater concentrations of ferrous iron (Fe^{2+}) and sulfate increase in conjunction with decreasing nitrate concentrations (e.g., Aravena and Robertson 1998). Additionally, denitrifiers preferentially reduce nitrate containing the lighter isotopes (^{14}N and ^{16}O), thereby decreasing nitrate concentrations while simultaneously increasing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the residual nitrate (e.g., Kendall 1998). Sulfate produced by denitrification is expected to have $\delta^{34}\text{S}$ values similar to the sulfide source. The $\delta^{18}\text{O}$ value of nitrate may also influence $\delta^{18}\text{O}$ - SO_4^{2-} values when sulfate is produced in

conjunction with denitrification, although the details of this mechanism are not currently known.

Dissolution of Sulfate Minerals

Sulfate in groundwater can be derived from the weathering of sulfate-containing minerals (e.g., gypsum, anhydrite, barite) in the aquifer bedrock or unconsolidated materials. Based on the bedrock and surficial geology of the area (Sibul and Choo-Ying 1971), potential geological sources of sulfate include late Ordovician to middle Silurian marine evaporites. Compared to other natural sulfate sources in the watershed, marine evaporite sulfate is enriched in ^{34}S and ^{18}O , with $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values expected in the range of $+25$ to $+32\%$ and $+12$ to $+18\%$, respectively (Claypool et al. 1980). Another potential geological source in the aquifer is sulfate derived from the Queenston Formation, which outcrops in the Nottawasaga River Watershed to the west of the study area (R. Mulligan, personal communication, 2019). The Queenston Formation is a shallow coastal deposit from the upper Ordovician consisting primarily of red silty shales, with gypsum locally present (Broglie et al. 1998). The red shales are terrestrial to marginal marine in origin (Armstrong and Carter 2010) and therefore may contain gypsum with an isotopic composition that is not typical of marine sulfate from the late Ordovician (Matheson et al. 2018). The isotopic signature of groundwater sulfate from the Queenston Formation has not been well characterized, however three such samples had $\delta^{34}\text{S}$ - SO_4^{2-} values averaging $+15.6 \pm 2.6\%$ (Matheson et al. 2018). The corresponding oxygen isotope composition has not been reported but, since they are a mix of terrestrial and marine sources, $\delta^{18}\text{O}$ - SO_4^{2-} values are expected to be lower than for purely marine sulfate of the same age.

Agricultural Fertilizers

Some fertilizers, such as potassium magnesium sulfate ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$, or $\text{K} \cdot \text{Mg} \cdot \text{SO}_4$) and ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$), contain sulfur in sulfate form and therefore sulfate leaches to the groundwater system by dissolution of the fertilizer and downward percolation following irrigation or rainfall. Other fertilizers, such as sulfur-coated urea and elemental sulfur, have sulfur in a reduced or organic form that must be oxidized to sulfate before it can readily enter the groundwater system. The isotopic composition of fertilizers can vary widely (e.g., Vitória et al. 2004) and therefore the isotopic composition of potential sulfate sources must be evaluated locally to determine if sulfate isotopes can be used to quantify the impact of fertilizers on groundwater sulfate concentrations.

Sanitary Wastewater

Spiegelstra et al. (2017) demonstrated that groundwater from some domestic wells and groundwater seeps in the southern Nottawasaga River Watershed contains artificial sweeteners, indicating the presence of septic system effluent. Domestic wastewater can be another source of sulfate to the environment (e.g., Otero et al. 2008; Houhou

et al. 2010). The current study is focused on sulfate from agricultural fertilizers in groundwater and therefore samples with 5% or more of the water being derived from septic system effluent, as calculated by Spoelstra et al. (2017) using acesulfame concentrations, were not included in the current study. This screening resulted in the elimination of three seep and two domestic well samples from subsequent analysis.

Methods

Groundwater Sampling

Groundwater was collected from multi-level monitoring wells, groundwater seeps (springs) discharging along the banks of the southern Nottawasaga River, and private domestic wells (Figure 1). The multi-level wells were originally installed in 1982/1983 on two fields as part of a groundwater nitrate study (Starr et al. 1987). Multi-level wells MC-2 and MC-4 were sampled in August and December 2010, April 2011, and June 2012; wells W-4 and W-5 were sampled in September 2010, April 2011, and June 2012. Each multi-level well contained up to eleven 1 cm internal diameter polyethylene tubes surrounding a central PVC pipe. Each sample tube terminated at a different depth with a 20 cm slotted interval wrapped in a Nytex screen. Wells were purged and sampled using a peristaltic pump (Masterflex E/S Portable Sampler). A YSI 600QS Multiparameter Sonde and flow-through cell were used to monitor and record the temperature, dissolved oxygen (DO), pH, and conductivity of the groundwater. Once parameters stabilized, samples were collected for chemical and stable isotope analyses.

Using a small boat or canoe, groundwater seep samples were collected along the banks of the southern Nottawasaga River (Figure 1) on three occasions, September 2010 ($n = 66$), May 2011 ($n = 25$), and June 2013 ($n = 56$). Due to the diffuse nature of groundwater discharge at most of the seeps, field parameters (e.g., pH, temperature, conductivity, DO) were not measured. Samples were collected and stored in coolers with ice until they could be filtered, partitioned, and preserved later each day.

Groundwater from 59 rural domestic wells was collected in June/July 2011. In most cases, well water was collected from outside taps that bypassed water treatment systems (e.g., water softeners). Field parameters were monitored and recorded with a YSI 600QS Multiparameter Sonde, and once values stabilized, samples were collected and preserved for analysis of chemical and isotopic parameters. Further details on the sampling and analysis of the groundwater from domestic wells is provided by Senger (2016) and Spoelstra et al. (2017).

Laboratory Protocols

Major Anions

Samples for major anions, including nitrate and sulfate, were filtered in the field to $0.45 \mu\text{m}$ and then stored cold until analysis at the Canada Centre for Inland

Waters, Burlington, Ontario. Anion concentrations were determined using a Dionex 2500 ion chromatograph and values calibrated using commercially available multi-ion standards that were run with each batch of samples. The detection limits for nitrate and sulfate were 0.016 mg N/L and 0.05 mg/L , respectively.

Sulfate Isotope Ratios

For the analysis of sulfate stable isotope ratios, a barium sulfate precipitate method was used (Yeung et al. 2013). Isotope ratios of the dried barium sulfate were determined at the Environmental Isotope Lab, University of Waterloo. For $\delta^{18}\text{O-SO}_4^{2-}$ analysis, barium sulfate was combusted using a HEKAtech HT Oxygen Analyzer coupled to a Eurovector EA, which was connected to a GVI Isoprime IRMS. Sulfur isotope ratios were determined using a Costech Elemental Analyzer coupled to a GVI Isochrom IRMS. Results are reported in delta notation relative to Vienna Standard Mean Ocean Water (VSMOW) and Vienna Canyon Diablo Troilite (VCDT) for $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$, respectively. The analytical precision (2σ) was 0.3‰ for both stable isotope ratios.

Insufficient volumes and/or low sulfate concentrations prevented some samples from being run for sulfate isotope ratios. Furthermore, domestic well samples were not run for sulfate isotopes. Of the 147 seep and 107 multi-level well samples used in this study, sulfate isotope ratios were determined for 83 and 58 samples, respectively (Tables S1–S3).

Nitrate Isotope Ratios

Nitrate nitrogen isotope ratios ($^{15}\text{N}/^{14}\text{N}$) were determined using the bacterial denitrification method (e.g., Sigman et al. 2001; Casciotti et al. 2002) at the Stable Isotope Facility at the University of California—Davis. The isotope ratios of the resulting nitrous oxide were measured on a ThermoFinnigan GasBench and PreCon trace gas concentration system interfaced with a ThermoScientific Delta V Plus IRMS. The precision of the method (1σ) was 0.4‰ for $\delta^{15}\text{N}$ (relative to N_2 air).

Fertilizer Analysis

Samples of 10 agricultural fertilizers commonly used in the southern Nottawasaga River Watershed were obtained from Alliance Agri-Turf, a supplier of agricultural products in the area. Sulfate content of the fertilizers was determined by grinding the samples to a fine powder, dissolving in distilled water, and analyzing for major anions as described above. For fertilizers that contained sulfate, $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$ values were determined from dissolved samples using the same process as outlined above and by Yeung et al. (2013). The sulfur content of fertilizers was measured on powdered samples using a Costech Elemental Analyzer coupled to a GVI Isochrom IRMS at the Environmental Isotope Lab, University of Waterloo. For non-sulfate sulfur-containing fertilizers (sulfur-coated urea, elemental sulfur), $\delta^{34}\text{S}$ values were determined at the same time.

Table 1
Sulfur and Sulfate Contents and Stable Isotope Values for Agricultural Fertilizers Used in the Southern Nottawasaga River Watershed

Fertilizer Type	%S	$\delta^{34}\text{S}$	%SO ₄ ²⁻	$\delta^{34}\text{S-SO}_4^{2-}$	$\delta^{18}\text{O-SO}_4^{2-}$
	Non-SO ₄ ²⁻	‰ Rel. VCDT		‰ Rel. VCDT	‰ Rel. VSMOW
Ammonium nitrate	0%		0%		
Ammonium sulfate	0%		74%	-1.2	+16.2
Elemental sulfur	80%	+23.7	0%		
Potassium-magnesium sulfate	0%		64%	+9.2	+6.6
Mono-ammonium phosphate	0%			+7.8	+18.0
Potash	0%		0%		
Red potash	0%		0%		
NPK (17-17-17)	0%		4%	+5.0	+13.7
Urea	0%		0%		
Sulfur-coated urea	18%	+3.6	0%		

Table 2
Summary of Published Dual Sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) Isotope Ratios for Agricultural Fertilizers

Fertilizer Type	n	$\delta^{34}\text{S-SO}_4^{2-}$	$\delta^{18}\text{O-SO}_4^{2-}$	Country	Reference
		‰ Rel. VCDT	‰ Rel. VSMOW		
Superphosphate	5	mean = +17.2	mean = +12.7	New Zealand	Robinson and Bottrell 1997
(NH ₄) ₂ SO ₄	2	-1 to +0.9	+9.5 to +10.0	Spain	Vitòria et al. 2004
NH ₄ NO ₃	2	+0.7 to +8.7	+13.4 to +15.0	Spain	Vitòria et al. 2004
NH ₄ NO ₃ SO ₄	1	+8.1	+11.9	Spain	Vitòria et al. 2004
K ₂ SO ₄	1	+7.1	+13.5	Spain	Vitòria et al. 2004
NPK	12	-6.5 to +11.5	+7.7 to +14.6	Spain	Vitòria et al. 2004
Mg(NO ₃) ₂	1	+11.7	+16.5	Spain	Vitòria et al. 2004
MgSO ₄	1	+21.4	+11.2	Spain	Vitòria et al. 2004
FeSO ₄	1	-1.8	+15.1	Spain	Vitòria et al. 2004
CuSO ₄	1	+6.1	+8.9	Spain	Vitòria et al. 2004
Unspecified	2	-4.4 to -6.1	+14.6 to +15.9	Korea	Kaown et al. 2009
(NH ₄) ₂ SO ₄	1	+0.8	+10.1	Philippines	Hosono et al. 2010
NPK	2	-0.2 to +0.1	+9.9 to +10.4	Philippines	Hosono et al. 2010
(NH ₄) ₂ SO ₄	4	-2.1 to +4.8	+10.1 to +16.8	USA	Szynkiewicz et al. 2015
Sulfuric acid	3	+1.4 to +1.6	+9.1 to +9.6	USA	Szynkiewicz et al. 2015
Gypsum	1	+9.3	+17.1	USA	Szynkiewicz et al. 2015
Unspecified	4	+0.1 to +13.6	+8.3 to +16.9	USA	Szynkiewicz et al. 2015
Unspecified	2	+12.5 to +16.7	+28.6 to +37.2	China	Liu et al. 2017
(NH ₄) ₂ SO ₄	4	-2.1 to +8.6	+0.1 to +15.3	Canada	Dubinsky et al. 2020

Results and Discussion

Isotopic Composition of Fertilizer-Derived Sulfate

Of the 10 types of local fertilizers analyzed, ammonium nitrate, potash, red potash, and urea did not contain sulfur or sulfate (Table 1). Not surprisingly, ammonium sulfate and potassium-magnesium sulfate fertilizers were composed of a significant fraction of sulfate, 74% and 64%, respectively, with mono-ammonium phosphate and NPK fertilizers also containing sulfate but at much lower levels (5% and 4%, respectively). Two fertilizers contained sulfur in a nonsulfate form; elemental sulfur (80% S) and sulfur-coated urea (18% S).

While the sulfur isotope composition of fertilizers has been widely reported in the literature, the concomitant

analysis of both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of synthetic fertilizers is only reported in a limited number of studies (Table 2). The wide ranging stable isotope composition of sulfate in fertilizers has been attributed to variations in the materials and methods used to manufacture fertilizers (Vitòria et al. 2004). The isotopic signature of sulfate in NPK fertilizer from the Nottawasaga River Watershed fits within the large $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ ranges measured by Vitòria et al. (2004) but is higher than those from Hosono et al. (2010) (Tables 1 and 2). Comparing ammonium sulfate fertilizers, the $\delta^{34}\text{S}$ values measured in this study were similar to the other studies and $\delta^{18}\text{O}$ values were high relative to the Spanish and Philippine studies but within the upper ranges of the United States and other Canadian studies. In contrast to Vitòria et al. (2004),

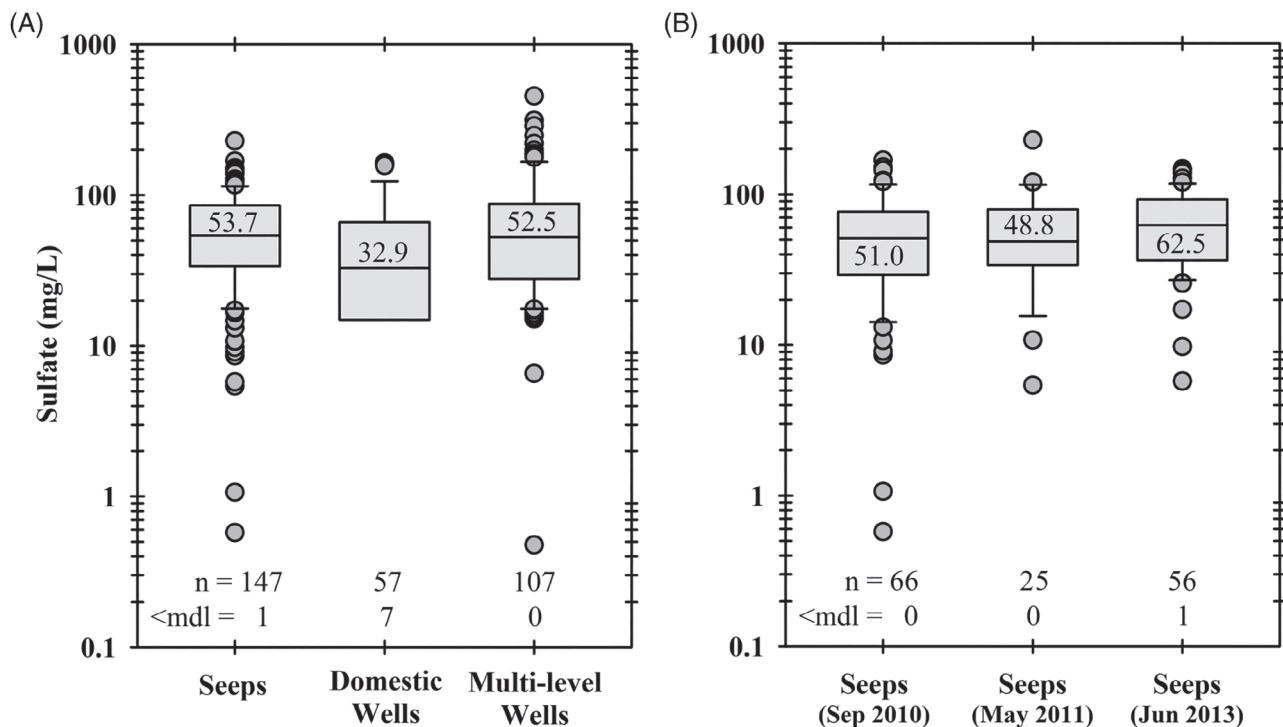


Figure 2. Summary of groundwater sulfate concentrations measured in the Nottawasaga River Watershed. The box ends correspond to the 25th and 75th percentile of the data and the whiskers represent the 10th and 90th percentiles. The line within the box is the median. The number of samples analyzed (*n*) for each set is indicated, as well as the number of samples with SO_4^{2-} concentrations less than the method detection limit (mdl) of 0.05 mg/L. Although zero values are not shown, they are figured into the box plot statistics.

our ammonium nitrate fertilizer did not contain detectable levels of sulfate.

For sulfur fertilizers, only $\delta^{34}\text{S}$ values can be measured directly (Table 1), whereas the $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values for sulfate produced from the oxidation of these compounds were calculated using Equation 1. The sulfate produced from the oxidation of fertilizer sulfur can have a range of $\delta^{18}\text{O}$ values depending on fractionation effects occurring during oxidation and the $\delta^{18}\text{O}$ values of available oxygen sources. Therefore the same range of $\delta^{18}\text{O}$ values (-7.3 to $+9.9\%$) calculated for mineral sulfide oxidation are also expected for sulfate produced by fertilizer sulfur oxidation at this site.

Sulfate Concentrations in Groundwater

Sulfate concentrations in groundwater ranged from nondetectable (<0.05 mg/L) to a maximum value of 454 mg/L, with median values of 53.7, 32.9, and 56.1 mg/L for the groundwater seeps, domestic wells, and multi-level wells, respectively (Figure 2A). No groundwater samples exceeded the drinking water aesthetic guideline of 500 mg/L for sulfate. With the exception of a few low values (<2 mg/L), the bulk of the samples from the three different groundwater types had similar overall ranges (Figure 2A).

The 57 groundwater samples from domestic wells had sulfate concentrations ranging from below the detection limit (<0.05 mg/L, $n = 7$) to 164 mg/L, with a median

value of 32.9 mg/L. Samples with no detectable sulfate also had no nitrate and DO values of 0.5 mg/L or less, indicating redox conditions favorable for denitrification and possibly sulfate reduction.

The distribution of sulfate concentrations in river-bank seeps was similar for the three sampling periods (Figure 2B), with at least 50% of samples in each period falling between 30 and 90 mg/L. Median sulfate concentrations for the September 2010, May 2011, and Jun 2013 sampling periods were 51.0, 48.8, and 62.5 mg/L, respectively (Figure 2B).

Sulfate concentrations in the MC wells were generally higher (mean \pm SD = 124 ± 83 mg/L) than those from the W-series wells (36 ± 21 mg/L) (Figures 3, S2, and S3). The sites are approximately 2 km apart and therefore differences in groundwater chemistry are largely the result of differences in land use in the recharge areas rather than differences in aquifer geology. Groundwater flow is largely horizontal in the LASA and therefore increasing depth below the water table generally corresponds to increasing groundwater age. Furthermore, the water at depth entered the ground at a greater distance upgradient of the well compared to the shallower groundwater. As such, only the shallowest depths of the multi-level wells are likely influenced by land-use activities in the fields directly adjacent to the wells. The relationships between groundwater depth, age, and recharge area distance are well illustrated in figure 5 of Zebarth et al. (2015).

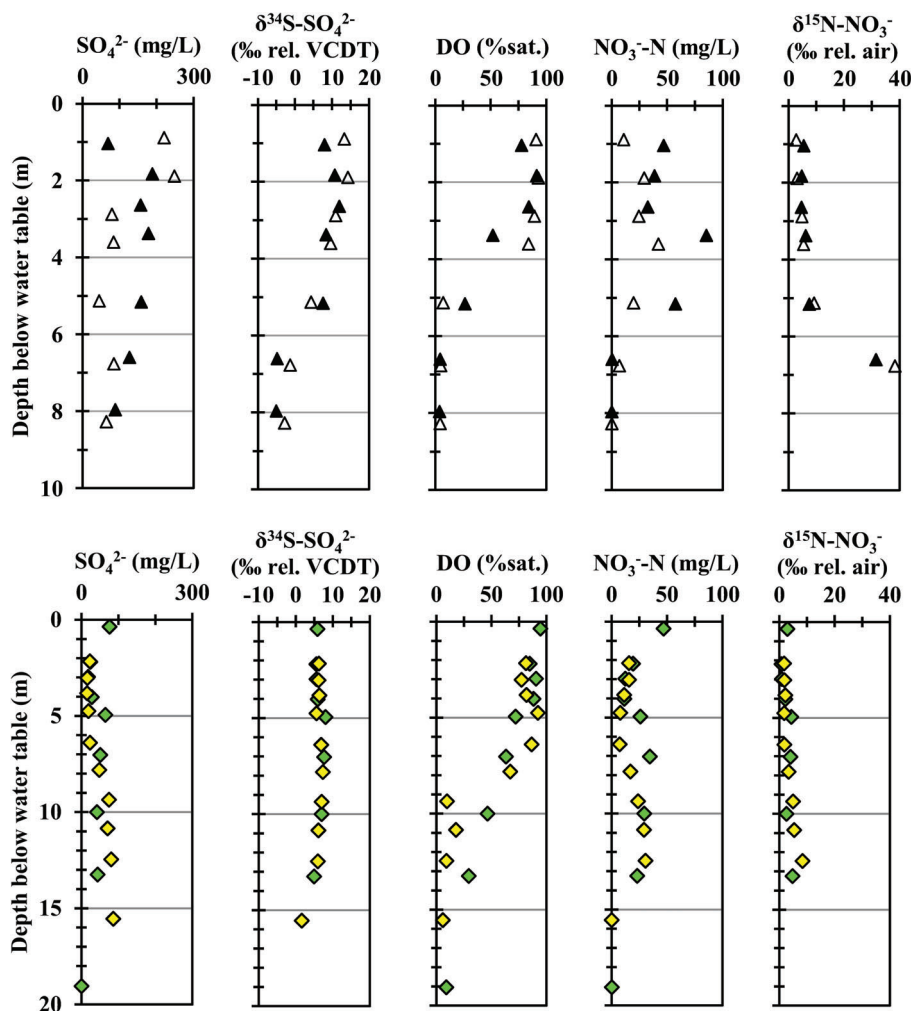


Figure 3. Depth profiles for sulfate concentration and $\delta^{34}\text{S}$, nitrate concentration and $\delta^{15}\text{N}$, and dissolved oxygen (DO) for multi-level wells MC-2 (black triangles), MC-4 (white triangles), W-4 (green diamonds), and W-5 (yellow diamonds) in June 2012. DO is expressed as percent saturation.

Groundwater Nitrate–Sulfate Relationship

In areas where fertilizer is used, a relationship between groundwater nitrate and sulfate concentrations would be expected if a sufficiently large fraction of the groundwater sulfate was derived from fertilizers. In contrast, if sulfate in groundwater is predominantly from geological sources, then elevated sulfate may be observed without a relationship to nitrate concentrations. Groundwater samples exhibited a general trend of increasing sulfate concentrations with increasing nitrate, more significant for the seeps ($r^2 = 0.50$) compared to the domestic wells ($r^2 = 0.25$) (Figure 4). For the multi-level wells, a general trend of increasing sulfate with increasing nitrate was also observed for W-4 ($r^2 = 0.71$), W-5 ($r^2 = 0.25$), and MC-2 ($r^2 = 0.38$), but not MC-4 ($r^2 = <0.01$) (Figure 4). When all the groundwater data is considered together, the regression has an r^2 value of 0.22 (Figure S4). If all the sulfur and nitrogen in the sulfur-coated urea and NPK fertilizers were converted to sulfate and nitrate in the soil, the sulfate: nitrate-N ratios would be 0.85 and 0.24, respectively. However, with the high crop demand for nitrogen compared to sulfur, the sulfate:

nitrate-N ratios of fertilizer residues leaching to groundwater would be somewhat greater. In fact, most of the groundwater samples had sulfate: nitrate-N ratios greater than 1:1 (Figure 4).

Some groundwater samples, including seeps, domestic wells, and MC-4 in particular, had very elevated sulfate: nitrate-N ratios and appear to have a significant additional source of sulfate that is not associated with nitrate. These no-N sources of sulfate could include fertilizers such as MAP and K-Mg-SO₄, as well as geological sulfate contributed through irrigation with deeper groundwater. Additional insights into the identity of the no-N sulfate source are presented later in the manuscript.

Sulfate Reduction

Under anaerobic conditions, sulfate reduction, if occurring, decreases sulfate concentrations and concomitantly increases the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the residual sulfate (e.g., Antler et al. 2013). Sulfate reduction comes after denitrification in the redox sequence and therefore significant sulfate reduction is not expected until available nitrate has been denitrified (e.g., McMahon and

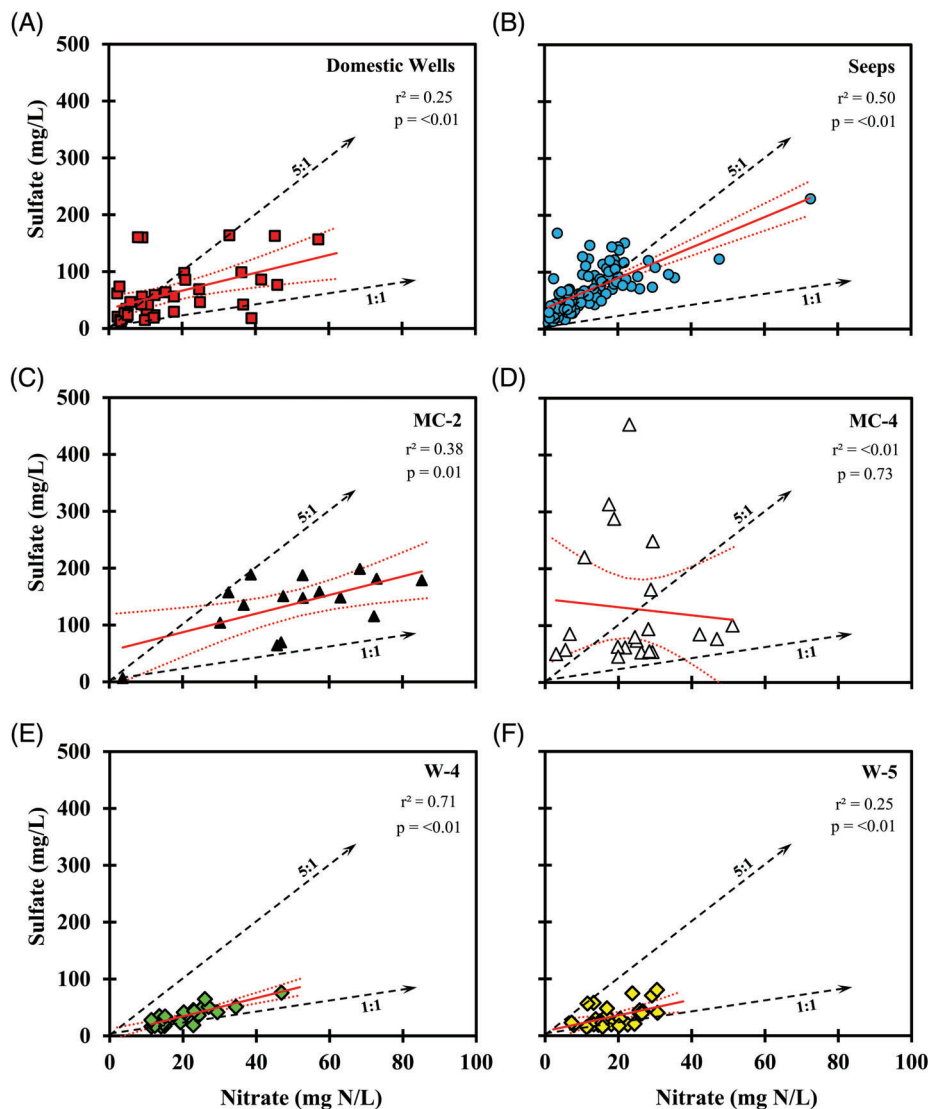


Figure 4. Relationship between sulfate and nitrate concentrations in groundwater samples with nitrate concentrations >1 mg N/L. Dashed lines indicate sulfate: nitrate-N ratios of 1:1 and 5:1. The solid and dashed red lines correspond to the linear regression and 95% confidence interval of the regression for each plot, respectively. The r^2 and p -values of the regressions are also indicated.

Chapelle 2008). Even though DO and nitrate concentrations decline at depth, the deep groundwater sulfate does not become isotopically enriched (Figures 3, S2, and S3), suggesting that sulfate reduction is not occurring to a significant degree. In fact, $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values generally decrease under the anaerobic conditions at depth in the multi-level wells, as do $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values (Table S3). In contrast, the effects of denitrification were observed in both the nitrate concentrations at depth and increasing $\delta^{15}\text{N}$ -nitrate values (Figure 3, S2, and S3).

Isotopic Composition of Groundwater Sulfate in the Lake Algonquin Sand Aquifer

The expected isotopic composition of potential sources of sulfate in the LASA exhibited a large range and good separation relative to analytical error ($\pm 0.3\text{‰}$) for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Figure 5). Fertilizers used in the Nottawasaga River Watershed had distinct sulfate isotopic

compositions relative to one another and to the natural geological sulfate sources in the area. Groundwater samples also exhibited a large range of $\delta^{34}\text{S}\text{-SO}_4^{2-}$ (-6.9 to $+20.0\text{‰}$) and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ (-5.0 to $+13.7\text{‰}$) values. To avoid the complicating effects of sulfate reduction on the interpretation of sulfate sources, only samples with nitrate greater than 1 mg N/L (seeps: $n = 75$; multi-level wells: $n = 48$) are plotted in Figures 5 and 6. Another consequence of this data filtering mechanism is that it also selects for samples that are most likely impacted to some degree by anthropogenic nitrogen inputs. When only considering samples with nitrate greater 1 mg N/L, the range of $\delta^{34}\text{S}$ values was slightly narrower (-2.2 to $+18.4\text{‰}$) and the $\delta^{18}\text{O}\text{-SO}_4^{2-}$ range remained unchanged, with the bulk of samples having a sulfate isotope composition consistent with sulfate derived from a mix of sulfur-coated urea, NPK, $\text{K}\cdot\text{Mg}\cdot\text{SO}_4$, mineral sulfide, and gypsum (Figure 5). Several samples with low $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values

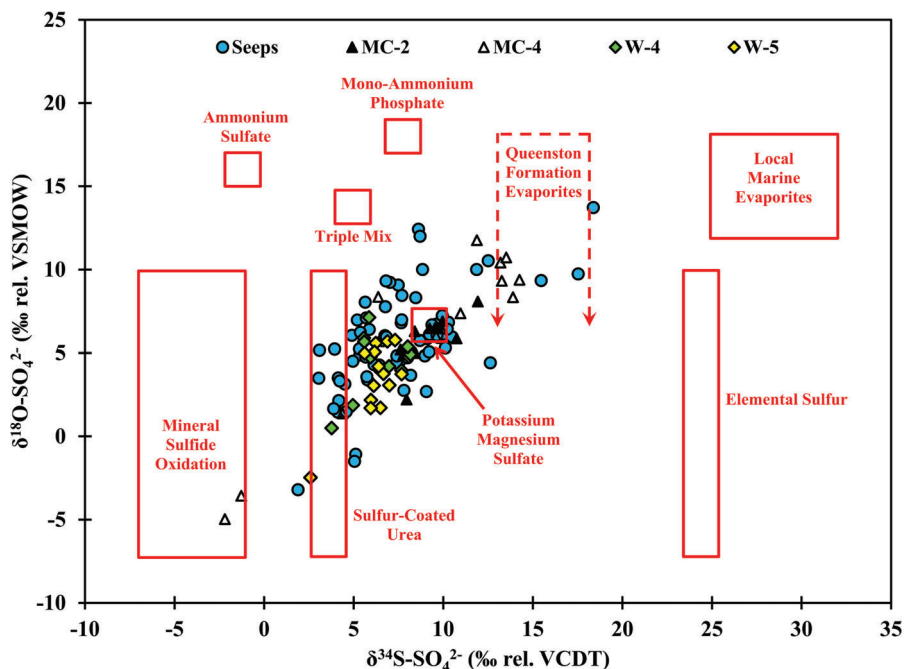


Figure 5. Sulfate dual isotope plot for groundwater samples from the Nottawasaga River Watershed. To eliminate the complicating effect of sulfate reduction on source identification, only samples with nitrate >1 mgN/L are shown (seeps: $n = 75$; multi-level wells: $n = 48$). Measured or calculated ranges for potential sources of groundwater sulfate in the watershed are shown. The $\delta^{18}\text{O-SO}_4^{2-}$ range for Queenston formation evaporites is unknown but expected to be equal to or somewhat less than local marine evaporites (see Introduction section).

indicate sulfate primarily derived from mineral sulfide oxidation, while others with $\delta^{34}\text{S}$ values greater than about +12‰ suggest groundwater sulfate predominantly from marine evaporites and/or possibly from the Queenston formation ($\delta^{34}\text{S} = +15.6 \pm 2.6\text{‰}$, $\delta^{18}\text{O} = \text{unknown}$; see Introduction section). No groundwater samples had sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values near the isotopic compositions of the ammonium sulfate or elemental sulfur fertilizers, indicating that these fertilizers were not major sources of sulfate to groundwater in the LASA. Isotope data from seepage samples taken along the banks of the Nottawasaga River are closely aligned to those of the groundwater samples from the multi-level wells, indicating that sources of groundwater sulfate are similar across the southern Nottawasaga River Watershed.

The isotopic composition of groundwater sulfate in the LASA generally plots along a mixing line expected for sulfate coming from sulfide mineral oxidation and evaporite sulfate sources, a pattern that has been observed in other studies that have analyzed dual sulfate isotopes in groundwater (e.g., Westberg 2012; Freckleton 2013; Jakóbczyk-Karpierz et al. 2017). The trend of a concomitant increase in $\delta^{34}\text{S}$ and $\delta^{18}\text{O-SO}_4^{2-}$ values is not due to sulfate reduction. All samples in Figure 5 have nitrate concentrations greater than 1 mgN/L and the three seep samples with the highest $\delta^{34}\text{S}$ values have nitrate concentrations of 4.6, 10.4, and 10.8 mgN/L, and therefore redox conditions favorable for sulfate reduction are unlikely. Furthermore, there is no trend of increasing $\delta^{34}\text{S}$ values with decreasing sulfate concentrations, as would be expected for sulfate reduction (Figure 6). In

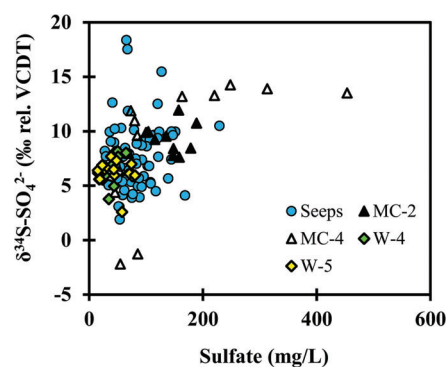


Figure 6. Sulfur isotope ratios in relation to groundwater sulfate concentrations for samples with nitrate concentrations >1 mgN/L.

the LASA, some samples with $\delta^{18}\text{O-SO}_4^{2-}$ values that trend above the geological source mixing line possibly indicate a contribution of sulfate from fertilizers with elevated $\delta^{18}\text{O-SO}_4^{2-}$ values (ammonium sulfate, NPK, mono-ammonium phosphate). Both the sulfur-coated urea and K·Mg·SO₄ fertilizers plot along the geological sources mixing line and therefore the contribution of sulfate from these fertilizers cannot be distinguished using the sulfate isotope data alone.

Groundwater from the MC-4 multi-level stands out for several reasons. The low $\delta^{34}\text{S}$ values at depth (Figure 3) indicate sulfate solely from the oxidation of mineral sulfides. In contrast, the high concentrations at shallower depths (Figures 3, S2, and S3) and their

accompanying high $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Figure 5) indicate a significant contribution of sulfate from evaporites. Furthermore, the shallower groundwater at MC-4 also has distinctly high sulfate/nitrate-N ratios (Figure 4). This area is irrigated with groundwater and, if taken from the deeper part of the aquifer, would contain geological sulfate but little to no nitrate. Throughout the LASA, many fields are irrigated with either surface water from the Nottawasaga River (approximately 25 mg/L sulfate, see Table S4) or one of its tributaries, or with groundwater. While this contribution is obvious for the MC-4 multi-level well, which plots relatively close to the isotopic signature expected geological sulfate sources, irrigation with groundwater would also contribute geological sulfate to the shallow aquifer elsewhere in the southern Nottawasaga River Watershed wherever groundwater is used for crop irrigation.

Although potential sulfate sources in the Nottawasaga River Watershed were isotopically distinct, quantitative determinations of the contributions from the various fertilizer and natural sources of groundwater sulfate could not be made based on sulfate isotope data alone. Additional information and analyses would be needed to determine how much sulfate is being added to groundwater from the various sources. For example, some studies have used strontium isotope analysis ($^{87}\text{Sr}/^{86}\text{Sr}$) in conjunction with sulfate isotope to examine the impact of fertilizers on surface and ground waters (Vitòria et al. 2004; Hosono et al. 2007, 2011). Furthermore, information on the quantities of the various fertilizers used in the area, both currently and historically, could help constrain source calculations in future studies.

Conclusions

We demonstrate that agricultural fertilizers can impact the concentration and isotopic composition of groundwater sulfate. In groundwater systems that are known to be impacted by fertilizers (e.g., nitrate contamination), or those deemed vulnerable to surface-derived contamination (e.g., unconfined shallow aquifers), the potential influence of fertilizer sulfate sources, both on groundwater sulfate concentration and isotopic composition, should be considered when using sulfate isotope analysis as a tracer of groundwater origin or contaminant source tracking.

Fertilizers that represent potential sources of sulfate to groundwater were isotopically distinct from one another and from natural geological sources and therefore dual sulfate isotope analysis is potentially useful for examining the impact of agriculture on groundwater sulfate. The overlapping $\delta^{34}\text{S}$ ranges of possible sulfate sources in groundwater demonstrates the futility of solely using $\delta^{34}\text{S}$ values to identify sulfate sources. Even with the addition of $\delta^{18}\text{O}$ analyses, quantification of source contributions may not be possible unless used in conjunction with other chemical and isotope tools. Furthermore, the isotopic enrichment effects of sulfate reduction, which would bias the calculations toward the evaporite sulfate endmembers, needs to be ruled out or accounted for when interpreting

groundwater sulfate isotope ratios. Groundwater samples potentially impacted by sulfate from wastewater (e.g., septic systems) were factored out in the current study by eliminating samples that contained artificial sweeteners. Sulfate from wastewater would otherwise need to be considered as another potential source in areas where septic systems are present and in peri-urban areas where leaky sewer systems may impact the shallow groundwater.

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Authors' Note

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally *not* peer reviewed.

Figure S1. Map showing 2011 land use in the southern Nottawasaga River Watershed.

Figure S2. Depth profiles for select groundwater chemistry and stable isotopes—Aug/Sep 2010.

Figure S3. Depth profiles for select groundwater chemistry and stable isotopes—Apr 2011.

Figure S4. Relationship between sulfate and nitrate concentrations in groundwater samples.

Table S1. Chemistry and stable isotope data for groundwater collected from riverbank seeps

Table S2. Chemistry and stable isotope data for groundwater collected from domestic wells

Table S3. Chemistry and stable isotope data for groundwater collected from multi-level wells

Table S4. Sulfate concentrations in the Nottawasaga River

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