



# Impact of anthropogenic geochemical change and aquifer geology on groundwater phosphorus concentrations



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## ABSTRACT

Geologic and geochemical variations across a 4200 km<sup>2</sup> area of south-central Wisconsin (USA) were used to examine their relationship to phosphorus concentrations in groundwater from more than four hundred private water supply wells. Surficial geology in the study area ranged from Cambrian sandstones to Ordovician dolomites. Groundwater phosphorus concentrations were higher in aquifers of older Cambrian age compared to the concentrations in aquifers of younger Cambrian and Ordovician age. Because iron concentrations were relatively low in these waters and agricultural land use was similar in all geologic regions, we propose that the differences in bedrock phosphorus and anthropogenic geochemical impacts explain the differences in phosphorus concentrations between aquifers. Within the older Cambrian aquifers, groundwater phosphorus concentrations were elevated in groundwater with higher nitrate-nitrogen concentrations. This finding is consistent with the presence of phosphorus within sediment in these strata and geologic conditions that weakly buffered pH reduction from anthropogenic acidification. In contrast, groundwater phosphorus concentrations in younger Cambrian and Ordovician aquifers were not elevated in samples with higher nitrate. Anthropogenic acidification in these carbonate-rich aquifers was neutralized through increased carbonate weathering, which led to higher groundwater calcium and alkalinity and would limit the dissolution of phosphate-rich minerals, such as apatite, where present. Low iron concentrations observed in most samples suggest that the phosphorus release in the Cambrian strata occurs beyond the zone of secondary mineral retention in the soil. These results have important implications for the eutrophication of inland surface waters in areas with bedrock phosphorus and anthropogenic acidity that is not neutralized before it contacts phosphatic rock.

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## 1. Introduction

Groundwater phosphorus from leaching of soil or bedrock phosphorus could be an important control over the biological productivity of groundwater-fed lakes and streams. Higher phosphorus concentrations lead to increased aquatic biological productivity as measured by a variety of metrics (Dodds, 2006; Robertson et al., 2006). Most efforts to control the transfer of phosphorus from land to water focus on phosphorus from surficial soil that is transported in surface runoff. This is an important but

episodic source of phosphorus that may respond over the short-term to land management strategies (for example, tillage changes or riparian buffer strips). In contrast, discharge of groundwater phosphorus to surface water systems is a baseline phosphorus transfer reflecting effects at a decadal time scale and cannot be managed over the short-term. The link between land management and increased groundwater phosphorus transfer is more equivocal than the association between land management and surficial phosphorus transfer (Sims et al., 1998; Holman et al., 2008; Browne et al., 2008). The potential importance of groundwater contributions to the trophic condition of surface waters necessitates a better understanding of the relationship between groundwater phosphorus, land management strategies, and geologic conditions.

Previous research suggests two explanations for higher groundwater phosphorus concentrations: 1) movement of surficial phosphorus through the soil profile; and, 2) weathering of phosphorus-rich minerals within the soil and underlying geologic

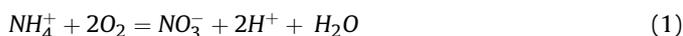
Abbreviations: PCO<sub>2</sub>, partial pressure of carbon dioxide (expressed as percentage of atmospheric pressure); PHREEQC, computer program for speciation calculations (Parkhurst and Appelo, 1999).

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strata. The movement of surficial phosphorus through the soil profile is often strongly controlled by reactions with secondary minerals of iron and aluminum. The high affinity of these minerals for phosphorus leads to low phosphorus concentrations in soil percolate and low export from the soil profile (Walker and Syers, 1976; Smeck, 1985). Phosphorus retained in the profile is subject to biological uptake and cycling to the surface in vegetation (Syers et al., 2008; Crews and Brookes, 2014). Elevated groundwater phosphorus has been observed where secondary mineral retention of phosphorus is weak. For example, higher phosphorus leaching rates or higher phosphorus concentrations in groundwater are found in very young soils where secondary minerals are less abundant (Boyle et al., 2013) or where secondary minerals are reductively dissolved (Domagalski and Johnson, 2011). Similar conditions are reported where high phosphorus application rates have saturated the capacity of the secondary minerals (McDowell et al., 2002), or where tile drainage shortens phosphorus migration paths through secondary mineral zones (Sims et al., 1998). Most of these studies have shown higher groundwater phosphorus concentrations over relatively short travel distances, and the extent to which this leads to watershed-scale increases in phosphorus transfer is not known. Groundwater phosphorus concentrations may also reflect the abundance and weathering rate of phosphorus-rich minerals in the soil and bedrock (Meybeck, 1982; Mulholland, 1992). Porder et al. (2007) suggest that phosphorus in the soil profile transitions from phosphorus retained by secondary minerals in the upper profile to phosphorus that occurs in primary minerals at depth. That is similar to the transition from primary mineral phosphorus to secondary mineral phosphorus that occurs in the profile over time (Walker and Syers, 1976; Smeck, 1985). The rate and location of phosphorus mineral weathering in the soil profile and its proximity to the zone of retention and biotic cycling could control the rate of phosphorus leaching and groundwater phosphorus concentrations. Rock weathering reactions can extend more than several meters into the soil profile (Jin et al., 2008; White, 2014) and beyond where biological uptake most effectively cycles phosphorus back to the surface. This suggests that spatial variations in weathering rates, retention mechanisms, the timing and rate of water movement, and differences in rock phosphorus can combine and affect groundwater phosphorus concentrations.

Anthropogenic acidity that increases rock weathering could increase the weathering rates of primary phosphorus minerals and ultimately increase groundwater phosphorus concentrations. A role for anthropogenic acidification on phosphorus concentrations in groundwater was suggested by Browne et al. (2008) who found increased groundwater phosphorus concentrations accompanied higher nitrate concentrations from agricultural fertilizers and increased calcium concentrations from rock weathering. Anthropogenic changes to groundwater geochemistry can arise from nitrification of land-applied ammonia in fertilizers, manures and wastewater which increases nitrate concentration and acidity (Eckhardt and Stackelberg, 1995; Hamilton and Helsel, 1995). The nitrification of ammonia can be written as:



Accelerated mineral weathering from nitrification can increase concentrations of calcium and magnesium in groundwater (Semhi et al., 2000; Aquilina et al., 2012). This acidity can also increase phosphorus retention in the secondary mineral zone through dissolution of aluminum and then precipitation of phosphorus-containing solid phases (Zanini et al., 1998). Because most instances of elevated groundwater phosphorus have been in shallow aquifers, short travel distances, or where secondary iron minerals

may be saturated with phosphorus or reductively dissolving, the significance of accelerated mineral weathering deeper in the profile or underlying bedrock to the concentration of phosphorus in groundwater is not known.

This study examines subsurface controls over groundwater phosphorus concentrations by evaluating the relationship between groundwater phosphorus, geologic setting, and anthropogenic changes to groundwater geochemistry. We hypothesized that aquifers could differ in their groundwater phosphorus concentrations because of mineralogic differences in aquifer solids, and that groundwater nitrate concentrations could be used to infer the degree of anthropogenic acidification from nitrogen addition. We explored these relationships with the results from sampling a large number of private drinking water wells across a gradient of surficial geology from Cambrian sandstones to Ordovician dolomites. Groundwater phosphorus concentrations were compared to the surficial geology at the well location and the groundwater nitrate concentration.

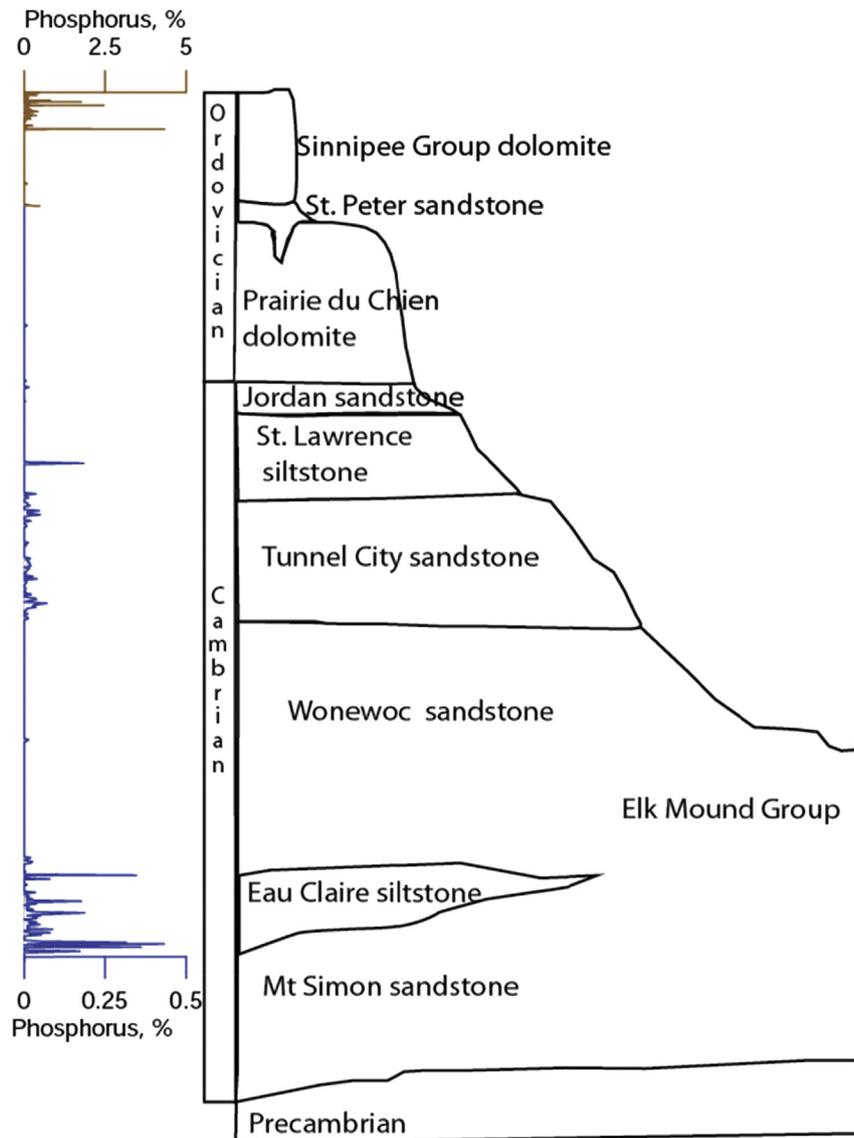
## 2. Experimental methods

### 2.1. Study area

This study area encompasses two adjacent counties within the Driftless Area of southwestern Wisconsin. The Driftless area remained un-glaciated during the Pleistocene Epoch, resulting in relatively high relief and elevation compared to surrounding glaciated regions of the Upper Midwest (Mickelson et al., 1982). The study area encompassed 4200 km<sup>2</sup> and varies from 220 to 524 m above mean sea level. The Driftless area is characterized by a mature, dendritic drainage system and is highly dissected by streams. Broad upland areas with shallow depth to bedrock lie between river valleys containing alluvial deposits. The uplands are capped by the youngest geologic formations and older bedrock is exposed along valley walls. Low-lying river valleys typically contain tens of meters of alluvial deposits overlying bedrock. Land use in the study area is a mixture of agriculture, forested and urban.

Fig. 1 illustrates the geologic setting, which includes Precambrian basement rock overlain by layered carbonate and siliciclastic strata of Cambrian and Ordovician age. In the northern portion of the study area, dolomitic formations of the Prairie du Chien Group are present in upland areas and older, Cambrian strata (Tunnel City Group and Wonewoc Formation) constitute the uppermost bedrock at lower elevations. To the south, the surficial geology in upland areas is dominated by the dolomitic Sinnipee Group. The St. Peter sandstone, Prairie du Chien dolomite and uppermost Cambrian Formations (Jordan and St Lawrence) are exposed at lower elevations.

Water wells were grouped by the surficial geology at each well location. Within the Driftless Area, surface geology is a reasonable approximation of the aquifer geology because the closely spaced network of incised streams results in local flow systems, with recharge occurring on ridge tops and hillslopes. Although the regional water table is typically at depths ranging from 35 to over 100 m, groundwater flow to these wells most likely originates within the local ridge and valley sequence. To the south within the study area, the uppermost portion of the Sinnipee Group constitutes an aquitard. Wells completed in these areas typically draw water from the underlying St. Peter sandstone, which is thought to be recharged by infiltration through the base of the Sinnipee and along hillslopes where the upper Sinnipee Group is eroded (Carter et al., 2011). Four hydrogeologic groupings were developed based on regional geologic and hydrogeologic interpretations (Batten and Attig, 2010; Clayton and Attig, 1990; Gotkowitz et al., 2005). These include the Sinnipee Group dolomites, the St. Peter sandstone



**Fig. 1.** Generalized surficial geologic stratigraphy in the study area (right) (Batten and Attig, 2010; Clayton and Attig, 1990; Gotkowitz et al., 2005) shown with the x-ray fluorescence (XRF) measurement of phosphorus content on the left (upper scale for Sinnipee Group and St. Peter Formations; lower scale for Prairie du Chien through Eau Claire Formations).

through the St. Lawrence Formation, the Tunnel City Group, and the Elk Mound Group. These were further generalized by combining the Sinnipee and St. Peter-St. Lawrence Formations (referred to as upper Cambrian/Ordovician wells) and the Tunnel City and Elk Mound Groups (referred to as the lower Cambrian wells). Wells completed where the surficial geology included alluvial aquifers, typically in valley bottoms, were not included in this study because groundwater recharge to those wells may not flow through the bedrock aquifer system. Water samples were collected from private wells from 2002 through 2015. The samples were collected as part of drinking water education programs through the University of Wisconsin-Extension. Well owners were provided with two sample bottles and were directed to collect one sample from a household fixture in the acidified bottle. This was analyzed for major cations and phosphorus. They were directed to collect the other sample near the entry point to the household water system. This sample was not acidified and was analyzed for total alkalinity, chloride and nitrate/nitrite nitrogen (combined). All samples were analyzed at the Water and Environmental Analysis Laboratory at the University of Wisconsin-Stevens Point. The alkalinity was measured by

titration, pH was measured in the laboratory, chloride by ion chromatography, and the sum of nitrate and nitrite (reported here as nitrate) using flow injection analysis. The calcium, magnesium, sodium, potassium, iron, sulfur and phosphorus were measured by ICP-OES on the acidified sample. Samples with evidence of home water softening were not included by excluding samples with total hardness less than  $0.1 \text{ meq L}^{-1}$  ( $5 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$ ). In addition, only samples with a calculated charge balance within twenty percent and detectable alkalinity (greater than  $0.1 \text{ meq L}^{-1}$ ) were used. A total of 461 water samples met these criteria.

## 2.2. Geochemical modeling

The PHREEQC model (Parkhurst and Appelo, 1999) was used to understand the equilibrium relationships expected for alkalinity, calcium and magnesium with a carbonate solid, varying  $\text{PCO}_2$  to simulate soil conditions, and acid additions to simulate nitrification. Acidity was modeled at a 2:1 M ratio of acid to nitrate-N as expected for nitrification of ammonium shown in Equation (1) (Bohlke, 2002). Model systems were simulated with PHREEQC for

both open and closed conditions. The open system mimicked respiration and diffusion acting to keep  $\text{PCO}_2$  levels constant. The closed model system assumed an initial equilibration with a carbonate solid at a fixed  $\text{PCO}_2$  was followed by closed system acid addition in the presence of the solid. This allowed the final  $\text{PCO}_2$  to vary. All equilibrium calculations assumed  $10^\circ\text{C}$  and used PHREEQC 3.1.4 with the PHREEQC.dat database.

### 2.3. Statistics

Comparisons of groundwater chemistry were made between groups of samples using the Mann-Whitney nonparametric rank sum test after grouping based on the concentrations of other analytes. Samples with concentrations of nitrate or phosphorus below their method detection limits were included at that concentration. The nitrate detection limit was  $0.1\text{ mg N L}^{-1}$  and the phosphorus detection limits ranged from  $0.005$  to  $0.012\text{ mg P L}^{-1}$  during the study. All statistical comparisons were made using R (i386 3.0.2).

### 2.4. Analysis of rock core

A handheld Thermo Fisher Niton XL3t GOLDD + hand-held x-ray fluorescence (XRF) analyzer was used to identify phosphorus-enriched intervals in the bedrock formations of interest. Core from the study area, held in the Wisconsin Geological and Natural History Survey (WGNHS) core repository, was analyzed for major and trace elemental concentrations. Clean rock surface analyses were completed in “Test All Geo” mode and utilized the 8 mm aperture opening with a 50 kV beam at a 75 s read time (filter intervals: Main Range 15 s, Minor Range 15 s, High Range 15 s, and Light Range 30 s). Analyses were spaced from 6 to 30 cm intervals along the core, with closer spacing through lithologically complex sections. Five U.S. Geological Survey standards for shale, carbonate, and quartz sandstone were used to track XRF performance.

## 3. Results and discussion

### 3.1. Background geochemistry

Phosphorus-enriched intervals were identified within three formations in the study area. As shown in Fig. 1, XRF analysis revealed elevated phosphorus in the uppermost portion of the Sinnipee Group at about an order of magnitude greater than those identified within the Tunnel City Formation, and the Eau Claire Formation of the Elk Mound Group. Isolated measurements of enriched phosphorus were present in several other formations, but do not indicate significant enrichment in these strata. Those results are consistent with earlier reports of phosphorus in Sinnipee Group rocks and the association between phosphatic solids and Cambrian glauconites and shales (Heyl et al., 1951; Cook and Shergold, 1984).

Background groundwater geochemistry was evaluated using samples with concentrations of both nitrate nitrogen and chloride below their overall median values of  $2.7$  and  $9.4\text{ mg/l}$ , respectively. In this group of 181 samples, we expected to exclude the groundwater most strongly influenced by agricultural fertilizers, on-site waste systems or road deicing chemicals. Fig. 2 shows the relationship between calcium, magnesium and alkalinity in these samples was generally consistent with dolomite dissolution with nearly a 1:1 relationship between calcium and magnesium and between the sum of calcium and magnesium with alkalinity (Williams et al., 2007). At the pH of this groundwater (median 7.8), most of the total alkalinity is likely bicarbonate. Similar to groundwater geochemistry in Michigan described by Williams et al., the calcium concentrations were often higher on a molar basis than magnesium, likely reflecting some calcite with the

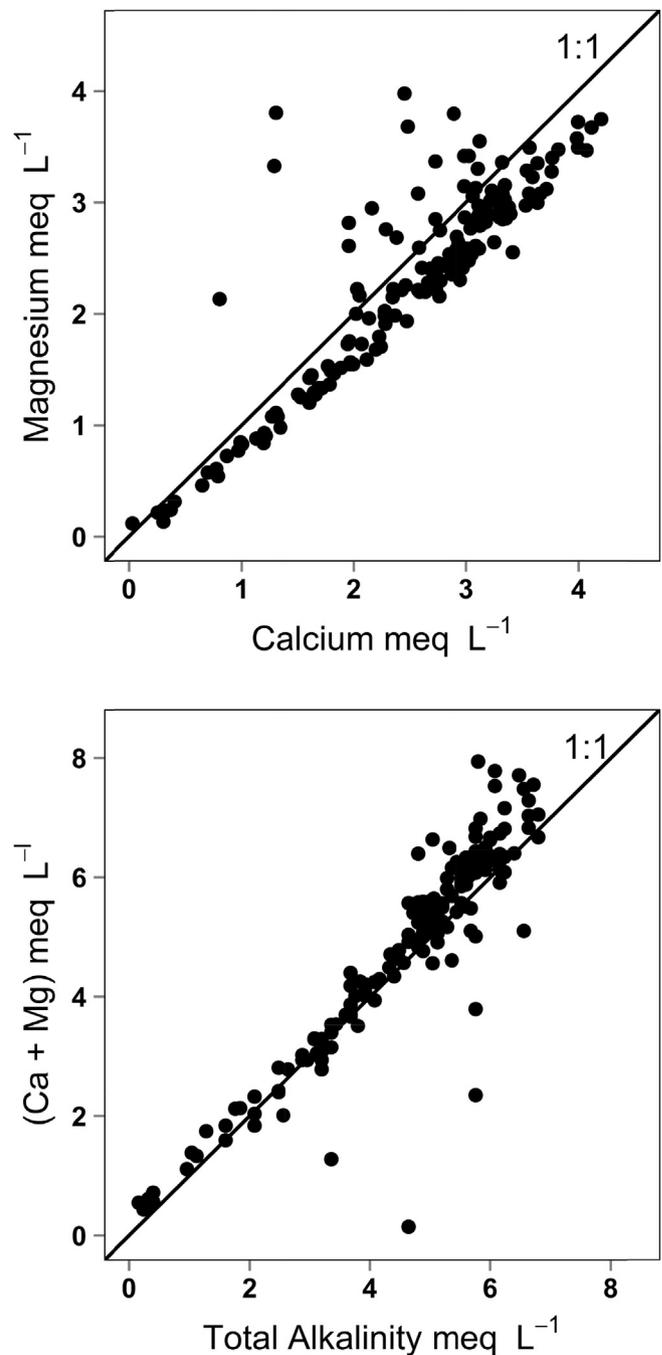
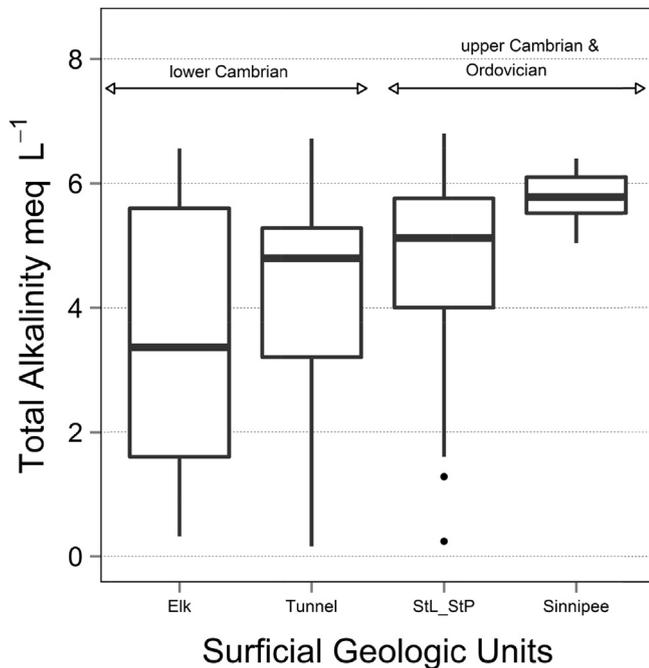


Fig. 2. Calcium, magnesium and alkalinity in the groundwater with nitrate and chloride below their overall median concentrations.

dolomite. The groundwater alkalinity in the study area is shown in Fig. 3 by surficial geology at the well location. The lowest alkalinity samples were found in the lower Cambrian and higher alkalinity were found in the upper Cambrian/Ordovician surficial geology. These differences in alkalinity are consistent with the differences in the carbonate content of the bedrock. As shown in Fig. 1, lower Cambrian rocks in this region are the Elk Mound group quartz sands, sandstone with some dolomite. Residential wells are primarily completed in the sandstone of the uppermost Wonewoc Formation and the glauconitic sandstone of the overlying Tunnel City (Gotkowitz et al., 2005). The upper Cambrian through Ordovician groups includes sandstones of the Jordan and St. Peter



**Fig. 3.** Total alkalinity in those samples that have both nitrate and chloride below the overall median concentrations shown by surficial geology at the well.

formations and the dolomites of the Prairie du Chien and Sinnipee Group (Fig. 1). The higher alkalinity in the groundwater from the upper Cambrian through Ordovician coincides with an increasing occurrence of dolomitic formations.

### 3.2. Anthropogenic nitrogen and major ion chemistry

The relationship between major ions and nitrate-nitrogen was evaluated by comparing major ion chemistry within three nitrate concentration groups: less than 1 mg L<sup>-1</sup> N, between 1 and 5 mg L<sup>-1</sup> N and greater than 5 mg L<sup>-1</sup> N. Median concentrations

within each nitrate group and rank sum comparisons using the Mann-Whitney test are summarized in Table 1, which shows that several major ions are elevated in higher nitrate samples. The calcium, magnesium and alkalinity concentrations increased with increasing nitrate concentrations in the high nitrate group in the upper Cambrian/Ordovician surficial geology consistent with the increased weathering of carbonate minerals expected following nitrification (Browne et al., 2008; Gandois et al., 2011). The increased concentrations of chloride and sodium with increasing nitrate concentrations in both surficial geology groups was consistent with the application of potassium chloride fertilizers and deicing salts, and mineral weathering (McGinley, 2008; Jin et al., 2008). Potassium increases in samples with elevated nitrate concentrations was also consistent with the addition of potassium fertilizer. Wastewater disposal, manure application and enhanced mineral weathering may also have contributed to increased potassium levels.

We used geochemical modeling with PHREEQC to understand the relationships between calcium and alkalinity from dolomite weathering with the acidity generated during nitrification. The PHREEQC results in Fig. 4 show the expected calcium and alkalinity concentrations as nitrate increases in the presence of dolomite. Groundwater chemistry from wells with surficial upper Cambrian/Ordovician geology was generally consistent with the presence of dolomite and carbon dioxide content (PCO<sub>2</sub>) near 1%–2%. This PCO<sub>2</sub> is similar to that expected in the soil profile during the year with changes in temperature and with variations in respiration in cultivated and uncultivated recharge areas (Jones and Mulholland, 1998; Karberg et al., 2005). In contrast, groundwater from the lower Cambrian formations exhibits a lower and wider range of calcium and alkalinity concentrations. Because the partial pressure of carbon dioxide during weathering is likely similar in the two geologic regions, this difference suggests incomplete equilibration with carbonates in groundwater in the lower Cambrian. This finding is not surprising because wells completed in this lower carbonate strata are open (that is, uncased) across multiple geologic strata, allowing mixing of waters that have evolved with and without equilibration with carbonates. The geochemical model results in Fig. 4 show at nitrate concentrations less than 5 mg L<sup>-1</sup> N, only a small increase in groundwater calcium or change in alkalinity is

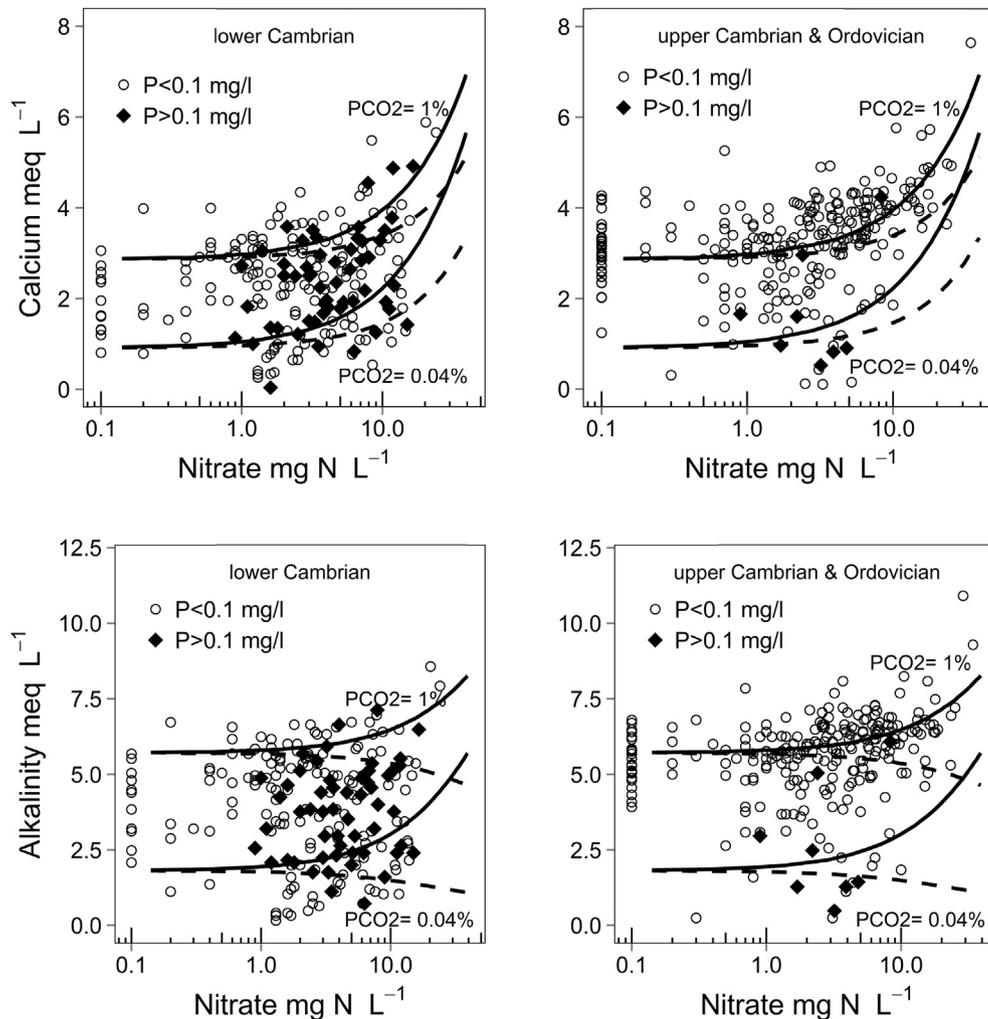
**Table 1**  
Medians and comparison of groundwater composition within nitrate concentration ranges.

Analyte	Surficial geology group <sup>a</sup>	Nitrate-N <= 1 (mg L <sup>-1</sup> )		1 < Nitrate-N <= 5 (mg L <sup>-1</sup> )		Nitrate-N > 5 (mg L <sup>-1</sup> )	
		Median		Median	p <sup>b</sup>	Median	p <sup>b</sup>
Chloride (mg L <sup>-1</sup> )	Lower-C	2.2		9.2	<0.001	19.4	<0.001
	Upper-C/O	2.5		7.8	<0.001	20.5	<0.001
Sulfate (mg L <sup>-1</sup> )	Lower-C	13.4		11.9	0.987	13.9	0.065
	Upper-C/O	17.7		15.8	0.402	25.2	<0.001
Alkalinity (meq L <sup>-1</sup> )	Lower-C	4.80		3.84	0.135	4.32	0.372
	Upper-C/O	5.52		5.68	0.681	6.40	<0.001
Sodium (mg L <sup>-1</sup> )	Lower-C	2.5		3.9	<0.001	7.2	<0.001
	Upper-C/O	2.4		3.8	<0.001	6.8	<0.001
Potassium (mg L <sup>-1</sup> )	Lower-C	0.7		0.9	<0.001	1.4	<0.001
	Upper-C/O	0.8		0.9	0.808	1.1	0.003
Calcium (mg L <sup>-1</sup> )	Lower-C	48.5		45.8	0.752	52.9	0.090
	Upper-C/O	60.0		63.2	0.553	80.1	<0.001
Magnesium (mg L <sup>-1</sup> )	Lower-C	27.7		23.4	0.074	28.3	0.557
	Upper-C/O	34.8		35.9	0.968	46.1	<0.001
pH	Lower-C	7.90		7.82	0.066	7.63	<0.001
	Upper-C/O	7.86		7.82	0.826	7.83	0.215
Phosphorus (mg L <sup>-1</sup> )	Lower-C	0.016		0.060	<0.001	0.067	<0.001
	Upper-C/O	0.012 <sup>c</sup>		0.016	0.698	0.012 <sup>c</sup>	0.566

<sup>a</sup> Lower-C: lower Cambrian; Upper-C/O: upper Cambrian/Ordovician.

<sup>b</sup> p value for Mann-Whitney comparison with low nitrate-N concentration group. Values shown in bold for p < 0.025.

<sup>c</sup> Median concentration at the method detection limit (i.e., the concentration is below the detection limit in at least half of the samples).



**Fig. 4.** Comparison of groundwater calcium (upper) and alkalinity (lower) at different nitrate-N concentrations in the lower Cambrian (left) and the upper Cambrian and Ordovician surficial geology (right). PHREEQC simulation results shown as solid lines for closed system and dashed lines for open system in equilibrium with dolomite at the PCO<sub>2</sub> indicated. The symbols show the phosphorus concentration range for each sample.

expected, and that could be obscured by carbon dioxide variations and mixing from different flow paths. At nitrate concentrations greater than 5 mg L<sup>-1</sup> N in the presence of dolomite, there is a larger increase in calcium and an increase in alkalinity concentrations when the weathering is predominately closed-system. That explains why the results in Table 1 show increased calcium and alkalinity concentrations with increased nitrate only in the highest nitrate concentration group and then only in the higher carbonate rock content upper Cambrian/Ordovician aquifers.

### 3.3. Phosphorus variations with anthropogenic nitrogen concentrations

Groundwater phosphorus concentrations in the study area ranged from undetected (<0.005 mg L<sup>-1</sup>) to 2.4 mg L<sup>-1</sup>. The mean phosphorus concentration in the groundwater overall was 0.053 mg L<sup>-1</sup> and the median concentration was 0.020 mg L<sup>-1</sup>. Groundwater phosphorus concentrations differed with the surficial geology at the location of the well, as shown in Fig. 5. Median phosphorus concentrations were higher (0.059 mg L<sup>-1</sup>) in the lower Cambrian group compared to the upper Cambrian/Ordovician group (0.012 mg L<sup>-1</sup>) with a significant difference in phosphorus concentration between the two groups ( $p < 0.001$  (Mann-

Whitney test)). We explored differences in the surficial phosphorus movement by examining the land use and evidence of secondary mineral iron chemistry in the two geologic regions. The two surficial geology groups have similar fractions of agricultural land in a 500 m buffer around each well, with median percentages of 42% and 44% in the lower Cambrian and upper Cambrian/Ordovician, respectively. Iron concentrations were also similar, with a median iron concentration of 0.007 mg L<sup>-1</sup> in both groups of wells. Ninety percent of the samples had an iron less than 0.07 mg L<sup>-1</sup> in the lower Cambrian and less than 0.10 mg L<sup>-1</sup> in the upper Cambrian/Ordovician. Fig. 6 shows illustrates that phosphorus concentrations are consistent across the three classes of iron concentrations within each geologic group, supporting the conclusion that differences in phosphorus concentrations between geologic settings cannot be attributed to dissolution of iron oxides under reducing conditions (Vadas and Sims, 1998; Domagalski and Johnson, 2011). The relatively low iron concentrations and absence of a relationship between iron and phosphorus concentrations suggests rock weathering rather than dissolution of secondary minerals is the source of groundwater phosphorus.

To explore the relationship between anthropogenic nitrogen and groundwater phosphorus, we examined phosphorus concentrations at three classes of nitrate concentrations in samples from

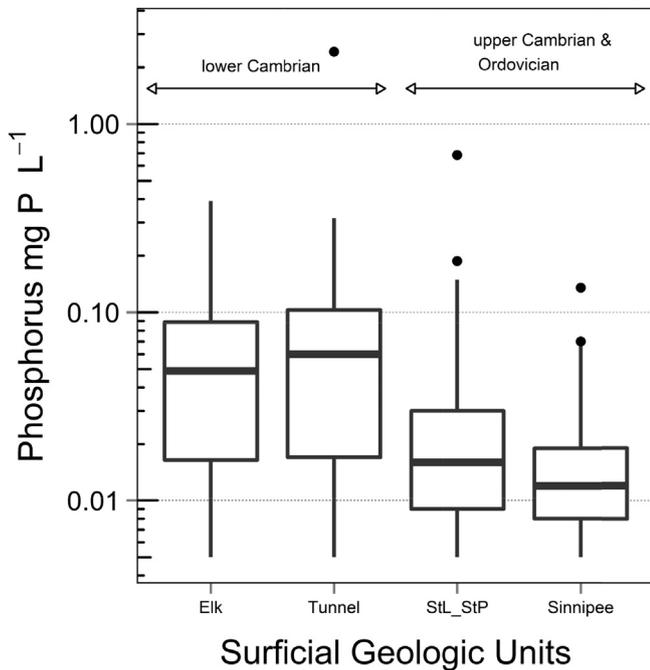


Fig. 5. Phosphorus concentration distribution in the groundwater shown by surficial geology at the well.

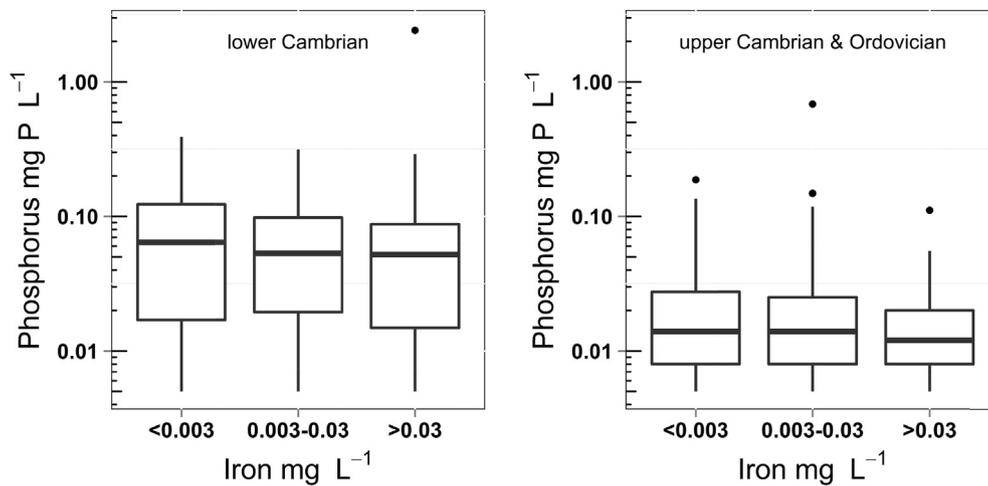


Fig. 6. Groundwater phosphorus concentrations in different iron concentration ranges for the two surficial geological groups.

the lower Cambrian and upper Cambrian/Ordovician surficial geology groups. Fig. 7 and Table 1 show little variation in phosphorus concentrations in samples from the upper Cambrian/Ordovician strata. This is consistent with abiotic retention of surficial phosphorus by secondary minerals and biotic cycling in the soil profile (Walker and Syers, 1976; Smeck, 1985). The soils in this area have moderately acid subsoils and carbonate bedrock that can neutralize the acidity generated during nitrification (USDA, 1962). The result is increased calcium, magnesium and alkalinity concentrations with increasing nitrate and a neutralization of pH. This would limit the dissolution of authigenic phosphorus solid phases such as apatite. As illustrated in Fig. 7, this contrasts sharply with samples from the lower Cambrian aquifers. The lower Cambrian aquifers show a weaker relationship between carbonate rock weathering products and nitrate concentration (Fig. 4), and the groundwater phosphorus concentrations increase with elevated nitrate concentrations. Soils

above the lower Cambrian bedrock can be less than 2 m thick and formed in loess or sandstone residuum (USDA, 1980). The groundwater geochemistry is consistent with the weaker neutralization of anthropogenic acidity and lower concentrations of calcium resulting from an incomplete equilibration with carbonates. These conditions would accelerate the weathering of authigenic phosphorus solid phases such as apatite at depth, beyond the zone of secondary mineral formation, and lead to higher groundwater phosphorus concentrations.

The contrast in groundwater phosphorus concentrations between the two geologic groups is consistent with bedrock weathering as an important contributor to groundwater phosphorus in the lower Cambrian surficial geology. The lower Cambrian aquifers are those with elevated phosphorus in several strata. Such phosphorus-containing solids have been observed elsewhere in Cambrian sediment (Cook and Shergold, 1984; Creveling et al., 2014). Fig. 4 showed that samples from the lower Cambrian aquifers with high (>0.1 mg L<sup>-1</sup>) phosphorus concentrations spanned a range of calcium and alkalinity concentrations. The increased phosphorus does not appear to simply reflect an increased weathering of carbonate materials. This differs from Mulholland (1992) who found a correlation between calcium and phosphorus from springs in a dolomitic aquifer and suggested the dolomite weathering was controlling phosphorus inputs to the stream, and Browne et al. (2008) who also found increased groundwater phosphorus coincided with increased calcium concentrations. In

our study area, the higher phosphorus concentrations in groundwater from the lower Cambrian aquifers could result when water subject to anthropogenic acidification but weak carbonate neutralization recharges aquifers with phosphorus-containing solid phases. This acidity would increase the dissolution of primary phosphorus minerals such as apatite (Guidry and Mackenzie, 2003; Alt et al., 2013), while the lower calcium concentrations allow higher equilibrium phosphorus concentrations. Fig. 8 and Table 1 show the only decrease in pH with nitrate concentration was found at high nitrate concentrations in the lower Cambrian surficial geology ( $p < 0.025$ ). This lower pH could increase the retention of phosphorus by secondary minerals in the soil profile (Traina et al., 1986; Zanini et al., 1998), but in our samples, the lower pH is associated with higher groundwater phosphorus concentrations. This provides further evidence that low pH buffering in the lower Cambrian strata supports dissolution deeper in the soil

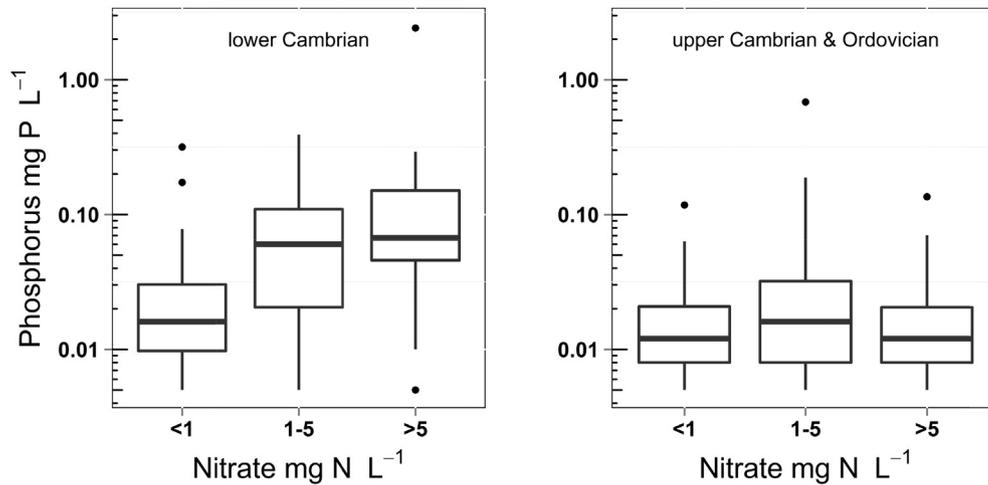


Fig. 7. Groundwater phosphorus concentrations in different nitrate concentration ranges for the two surficial geologic groups.

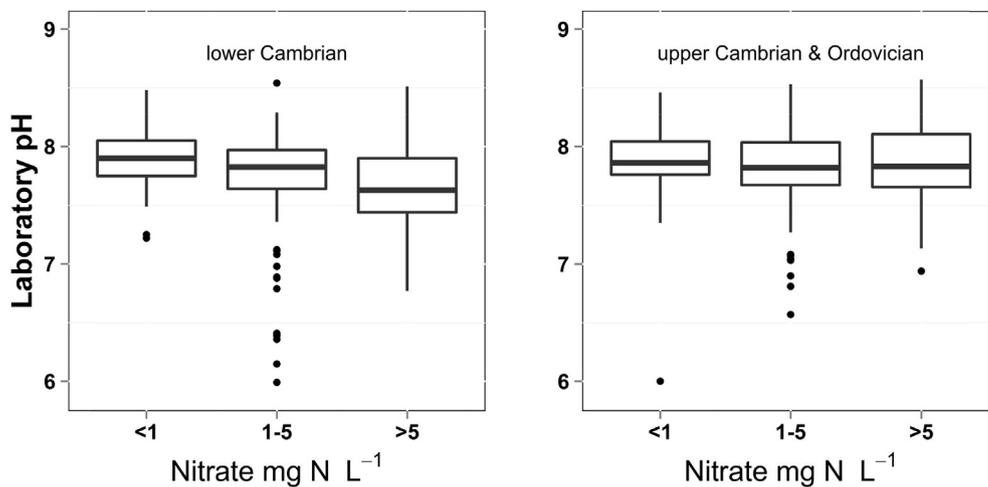


Fig. 8. Groundwater pH in different nitrate concentration ranges for the two surficial geologic groups.

profile or in the bedrock, where phosphorus retention by secondary minerals is unlikely.

#### 4. Conclusions and implications

The results of this study demonstrate that geologic setting and anthropogenic change to groundwater geochemistry combine to influence groundwater phosphorus concentrations. Although groundwater throughout the geologic regions had some elevated nitrate concentrations, only groundwater from the lower Cambrian showed an association between higher phosphorus and elevated nitrate. In the more carbonate-rich upper Cambrian/Ordovician groundwater, increased nitrate concentrations were accompanied by increases in calcium, magnesium and alkalinity, as expected from accelerated weathering of carbonate minerals, but there was no associated increase in the groundwater phosphorus concentrations. In contrast, groundwater sampled from the lower Cambrian bedrock displayed a weaker relationship between nitrate and calcium, magnesium and alkalinity but a marked increase in groundwater phosphorus with elevated nitrate. These results are consistent with anthropogenic acidity leading to phosphorus mineral weathering beyond zones where secondary minerals would retain phosphorus. This suggests that differences in

groundwater phosphorus concentrations at the watershed-scale reflect contrasts in the spatial distribution of bedrock phosphorus and rock weathering that control major ion chemistry.

These results have important implications for the transfer of terrestrial phosphorus to surface waters. In our study area, we found groundwater phosphorus concentrations could be increased by a factor of five at a nitrate concentration of  $10 \text{ mg N L}^{-1}$ . Because phosphorus-containing mineral phases have relatively wide occurrence within Cambrian bedrock, groundwater phosphorus may be an increasingly important component of phosphorus transfer from terrestrial to aquatic systems as anthropogenic geochemical change impacts a larger proportion of groundwater aquifers. Increased transport of phosphorus at a watershed scale would pose an important challenge to surface water management at decadal time scales as these changes propagate through aquifers, and downstream water resource systems are affected by changes in groundwater chemistry.

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