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

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ABSTRACT

Geologic and geochemical variations across a 4200 $km^2$ 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.


## 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:* PCO2, 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 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:

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O \quad (1)$$

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$^2$ 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