



An assessment of the Ca weathering sources to surface waters on the Precambrian Shield in central Ontario

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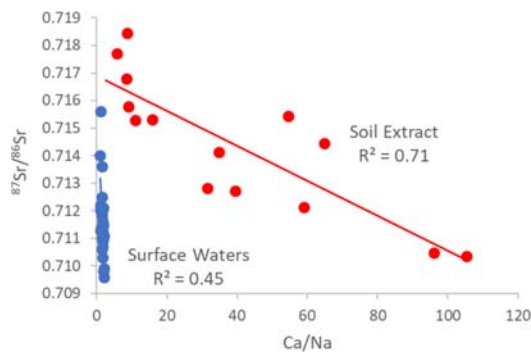


HIGHLIGHTS

- Relationships between Ca and Ca/Sr in surface waters indicate regional influence of non-silicate minerals
- Weak acid extracts from soils indicate the presence of non-silicate minerals with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
- Range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in low Ca surface waters and weak acid extracts from soil is similar
- Isotopic and elemental data indicate important Ca contributions from deeper soil or bedrock

GRAPHICAL ABSTRACT

Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Na ratios in surface waters and weak acid extracts from soils in central Ontario.



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ABSTRACT

There is increasing concern over the negative ecological impacts caused by falling calcium (Ca) concentrations in lakes, particularly in central Ontario, Canada. Forecasting regional changes in lake Ca concentrations relies on accurate estimates of mineral weathering rates that are not widely available. In this study, bulk atmospheric deposition, surface water and soil chemistry along with $^{87}\text{Sr}/^{86}\text{Sr}$ isotope measurements were used to provide regional insight into weathering controls on Ca concentrations in lakes. Regionally, Ca concentrations in 90% of 129 lakes sampled in central Ontario were $<0.1 \text{ mmol L}^{-1}$ and the Ca/Sr ratio in lakes increased and the K/Sr ratio decreased with increasing Sr concentration, which is indicative of greater Ca sources from calcite or apatite in the higher Ca lakes. Significant relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Ca/Sr ratios in dilute acid (0.1 M HCl) soil extracts are also indicative of the presence of trace amounts of calcite or apatite in surficial soils. Within the low ($<0.7 \text{ mmol L}^{-1}$) Ca lakes, defined in this study that are considered most at risk from falling Ca concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios fell within the range observed in weak acid soil extracts and were also significantly related to Ca/Na and K/Sr ratios in surface waters. There were large inconsistencies however, between Ca/Na ratios and Ca/Sr in surface waters and soil acid extracts that suggest differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in surface waters of the low Ca lakes do not simply reflect differences in Ca derived from non-silicate minerals in surficial soils and that Ca sources from deeper soil or bedrock are also important contributors to surface water Ca in these low Ca lakes.

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1. Introduction

Calcium (Ca) concentrations in surface waters throughout much of Europe and eastern North America are declining and this decrease is

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primarily attributed to decreasing acid leaching as sulfate (SO_4) and more recently nitrate (NO_3) deposition has been reduced (Keller et al., 2001; Reid and Watmough, 2016; Watmough et al., 2003, 2005). Declining concentrations of Ca in acid-sensitive lakes have delayed their chemical recovery from acidification, although most biogeochemical modeling studies suggest that Ca (and other base cations) are returning to their pre-industrial state and this is viewed as a positive recovery process (Clair et al., 2011; Tominaga et al., 2010). However, recent paleolimnological studies have suggested that lake Ca concentrations are currently lower than existed in pre-industrial times and this is resulting in a suite of adverse ecological impacts, including “aquatic osteoporosis” and the “jellification of lakes” as Ca-rich taxa such as *Daphnia* and crayfish are lost and Ca-poor taxa such as *Holopedium glacialis* dominate (Edwards et al., 2015; Hadley et al., 2015; Jeziorski et al., 2008, 2012, 2014). Given these concerns and inconsistencies between approaches, it is necessary to better understand the long-term weathering Ca sources to regional surface waters, especially in lakes with low Ca concentration and are most at risk from falling Ca levels (Ashforth and Yan, 2008; Tan and Wang, 2010).

In undisturbed environments, Ca in surface waters is derived from atmospheric deposition, which is relatively easy to quantify, and mineral weathering, which is associated with much greater uncertainty (Klaminder et al., 2012). Isotopes of strontium (Sr) have been used for several decades to differentiate Ca sources in biota, soils and surface waters as well as to characterize mineral contributions to Ca weathering (Bélanger et al., 2012; Blum et al., 2002; Miller et al., 1993). The Sr isotopic technique takes advantage of the fact that Sr is geochemically similar to Ca and substitutes for Ca in mineral lattices. Strontium 86 is non-radiogenic and ^{87}Sr is produced by decay of ^{87}Rb (half-life = 4.8×10^{10} years); Rb is geochemically similar to K and substitutes for K in the mineral lattice (Clow et al., 1997). Therefore, in K-bearing minerals such as K-feldspar and biotite the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase over time, leading to progressively increasing isotopic separation between individual bedrock minerals. One of the main challenges of Sr isotope tracer studies is defining the isotope composition of the weathering-derived Sr. Whole rock or soil dissolution does not give a fair representation of the weathering ratio because of different weathering rates and stabilities of minerals in the weathering environment. A range of leachate and extraction techniques, usually employing organic acids, have been used to determine the weathering component of Sr in soils (Åberg et al., 1989; Blum et al., 2002; Bélanger et al., 2012; Wickman and Jacks, 1992). The basic premise in using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in weathering studies is that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in natural water is a reflection of the contributions made by various minerals as they dissolve.

Strontium in itself is of little biological interest, but has been used as a tracer for Ca in ecological studies. Bélanger et al. (2012) outlined three conditions for the $^{87}\text{Sr}/^{86}\text{Sr}$ technique to be used to successfully assess the relative contribution of various potential Ca sources present in soil, surface waters or plants. The $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in end members must be sufficiently different; the variability in the end-member $^{87}\text{Sr}/^{86}\text{Sr}$ ratios must be small and the mixing of Sr and Ca in the soil-plant system must be conservative (Bélanger et al., 2012). In practice, these conditions are rarely met as there is more than one end member because Ca is derived from multiple minerals present in soil and bedrock with potentially varying $^{87}\text{Sr}/^{86}\text{Sr}$ signatures (Bélanger et al., 2012; Milkova, 2012) and Ca/Sr ratios can be strongly affected by biotic processes (Bullen and Bailey, 2005; Drouet and Herbauts, 2008; Watmough, 2014). Nevertheless, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been used in association with Ca/Sr ratios to characterize the relative contributions of various minerals and atmospheric deposition to Ca levels in surface waters and biota (Bélanger et al., 2012; Blum et al., 2002). Further, a number of studies have indicated that calcite and apatite, which are present only in trace amounts in soil may contribute greatly to Ca levels found in plants and streams (Bélanger et al., 2012; Blum et al., 2002; Clow et al., 1997).

South-central Ontario, Canada is characterized by shallow (often <1 m deep) soils derived from granitic glacial till overlying the Precambrian

(Canadian) Shield (Jeffries and Snyder, 1983). Several studies have suggested that many lakes in the region are undergoing pronounced ecological changes (extirpation of Ca-rich species) caused by falling Ca concentrations (Edwards et al., 2015; Hadley et al., 2015; Jeziorski et al., 2008, 2012, 2014). Soils in the region are dominated by silicate minerals with low mineral weathering rates and atmospheric Ca deposition to lakes is also low (Watmough and Aherne, 2008; Watmough and Dillon, 2003, 2004). The mean lake Ca concentration in 104 lakes sampled periodically in the region decreased by 30% since the 1980s (Reid and Watmough, 2016) and Ca levels in many lakes in the region are currently below a critical range of $1.5\text{--}2\text{ mg L}^{-1}$ ($0.037\text{--}0.05\text{ mmol L}^{-1}$), which is necessary to sustain Ca-demanding keystone aquatic biota (Ashforth and Yan, 2008; Tan and Wang, 2010). Past studies in this region have traditionally assumed that Ca weathering is dominated by silicate minerals such as plagioclase or hornblende due to their dominance in soils and the observation that Ca-rich minerals such as calcite or apatite are often absent or present only in trace amounts (Kirkwood and Nesbitt, 1991; Koseva et al., 2010; Watmough and Aherne, 2008). However, a recent study by Baker et al. (2015) identified trace amounts of dilute HCl phosphorous (P) in soils, even at sites with very low Ca levels, suggesting that trace amounts of apatite may occur especially in deeper (B-horizon) soil horizons.

In this study, surface water, atmospheric deposition and soil chemistry along with $^{87}\text{Sr}/^{86}\text{Sr}$ measurements are used to assess whether variability in observed Ca concentrations among lakes with low Ca concentrations (and hence of ecological concern) can be attributed to differences in mineral weathering sources, even over a very narrow range in Ca concentration.

2. Materials and methods

2.1. Study area

The chemistry of surface waters in south-central Ontario is determined in general terms by geographic location relative to the boundary of the Precambrian Shield. All lakes in this study are situated on the Precambrian Shield; a region of predominately silicate bedrock (Jeffries and Snyder, 1983). There are several localized exceptions, but the bedrock and surficial geology of the region results in lakes and streams that contain soft waters with low Ca concentrations (Watmough et al., 2003). The surficial geology of the area ranges from exposed bedrock, to shallow till (<1 m), rock ridges to minor till plains of 1–10 m depth (Jeffries and Snyder, 1983). Soils are generally thin (<1 m) acidic podzols and brunisols (Soil Classification Working Group, 1998) derived from non-carbonate tills or directly overlying granitic gneiss Precambrian Shield bedrock. The climate of the study area is north temperate, with long-term annual average precipitation ranging between ~800–1100 mm, with one quarter to one third falling as snow. The mean monthly temperature ranges between $-5\text{ }^\circ\text{C}$ and $-10\text{ }^\circ\text{C}$ in the coldest winter months and between 22 and $25\text{ }^\circ\text{C}$ in the summer (Ontario Ministry of the Environment and Climate Change; OMOECC, unpublished data). The study area lies within the Great Lakes St. Lawrence region of Ontario and is dominated by mixed hardwood forests. Stands are typically mixed age and sugar maple (*Acer saccharum*) forest stands dominate much of the landscape, especially in the eastern section although white pine (*Pinus strobus*) is dominant in some areas. Small wetlands dominated by white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) are common throughout the entire region.

2.2. Surface water and bulk precipitation chemistry

Surface water chemistry data from 129 lakes were collected through a regional lake sampling program conducted in 2013 and 2014 by the District of Muskoka (Table 1). A composite water sample from each lake was taken to the Secchi depth measurement. When a lake was sampled in both years the average chemistry was used (Fig. 1). Chemical

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