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Estimating base cation weathering rates in Canadian forest soils using a simple texture-based model

Ina S. Koseva · Shaun A. Watmough · Julian Aherne

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Abstract Mineral weathering is the primary source of long-term buffering capacity in soils and is important for forest nutrient sustainability. Regional assessments of weathering rates in Canada and the U.S. have employed an empirical clay-based Soil Texture Approximation (STA) owing to limited data availability, although the STA is rarely calibrated before application to a study area. Soil weathering rates estimated with the STA at 75 sites in Canadian forests (6–367 eq ha^{-1} $year^{-1}$) were on average seven times lower than estimates obtained using the PROFILE model and when mineralogy was not available, the Analysis to Mineralogy model and parameter estimation (143–2,119 eq ha^{-1} $year^{-1}$). Comparison with a catchment mass balance at a subset of sites in Ontario ($n = 19$) demonstrated the reliability of PROFILE weathering estimates. A revised (generalized) STA model for total base cation weathering was developed at the 75 study sites to incorporate soil silt content (%) and loss-on-ignition (LOI, %) ($BC_w = (1.73 + 0.03 \cdot silt - 0.06 \cdot LOI) \cdot 1{,}000 \cdot depth$). The model performance ($R^2_{adj} = 73\%$) and relative bias (−1%) suggested that the revised STA may have broad application to forest soils in Canada but may not necessarily be suited to all soil texture classes.

I. S. Koseva (✉) · S. A. Watmough · J. Aherne
Environmental and Resource Studies, Trent University, 1600 West Bank Drive, Peterborough, ON K9J 7B8, Canada
e-mail: inakoseva@trentu.ca

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Introduction

Mineral base cation weathering is the primary source of long-term buffering capacity in soils (Schnoor and Stumm 1985; Clayton 1988) and is important for soil fertility and long-term sustainable forest management (Akselsson et al. 2006). Weathering provides the largest sink of protons in soils (Schnoor and Stumm 1985) and can buffer soils from acidification under conditions of high acid deposition or intensive harvesting (Clayton 1988). Furthermore, weathering rates are central to critical load assessments, yet they are the main source of uncertainty (Skeffington 2006; Li and McNulty 2007) as mineral weathering is difficult to measure (Kolka et al. 1996; Ouimet and Duchesne 2005).

Many methods have been used to estimate mineral weathering rates and although no method is considered superior (Kolka et al. 1996; Watmough and Dillon 2003a, b; Langan et al. 2004; Ouimet and Duchesne 2005; Whitfield et al. 2006), the PROFILE model (Sverdrup and Warfvinge 1988a, b; Warfvinge and Sverdrup 1992) is probably the most widely used approach throughout Europe (Sverdrup and Warfvinge 1993; Sverdrup and de Vries 1994; Sverdrup and Warfvinge 1995) and North America (Foster et al. 2001; Watmough and Dillon 2003a, b, c; Watmough and Dillon 2004; Whitfield et al. 2006; Whitfield et al. 2009;

Mongeon et al. 2010). However, the availability of quantitative mineralogical data limits the regional application of PROFILE. Accordingly, simple empirical approaches are used to estimate weathering rates, such as the clay-based Soil Texture Approximation (STA) models used in Europe (Umweltbundesamt 2004) and North America (Ouimet et al. 2006; McNulty et al. 2007; Nasr et al. 2010). The uncertainty associated with these pedotransfer functions has not been investigated and the models are rarely re-calibrated or revised prior to application in national or regional assessments (Jeffries and Ouimet 2005; McNulty et al. 2007; Nasr et al. 2010). Mongeon et al. (2010) and Whitfield et al. (2010) proposed similar empirical pedotransfer functions suitable to forest soils in British Columbia and Alberta, respectively, that were developed from weathering rates estimated using PROFILE. PROFILE is a process-oriented model based on mineralogy—the primary determinant of mineral weathering—as such PROFILE is associated with lower uncertainty and is widely used when compared with other weathering determination methods (Jönsson et al. 1995; Hodson and Langan 1999). Other studies have compared the performance of the European and North American STA models with PROFILE estimates, though no new generalized approach was recommended (Hodson and Langan 1999; Whitfield et al. 2006).

The objective of the present study was to evaluate and revise the North American STA model for use in Canadian forests. The performance of this STA model was compared with PROFILE weathering estimates for soils at 75 sites in Canada. Given the limited availability of quantitative mineralogy, a method for mineralogical determination from total oxide content was developed using parameter estimation (Doherty 2004) and a mineralogical model (Analysis to Mineralogy; Posch and Kurz 2007). The relative ability of the STA and PROFILE models to provide reasonable weathering rates was evaluated using base cation Mass Balances at a subset of sites in Ontario ($n = 19$). Finally, the STA was revised based on the relationship between soil properties and PROFILE weathering estimates.

Materials and methods

Study area

The study sites ($n = 75$) are located in a broad range of eco-zones, including temperate, boreal, coastal and alpine forests in the Carolinian, Boreal, Pacific and Atlantic Maritime ecozones in Canada (Fig. 1; Table 1). Soils are generally podzol or brunisol

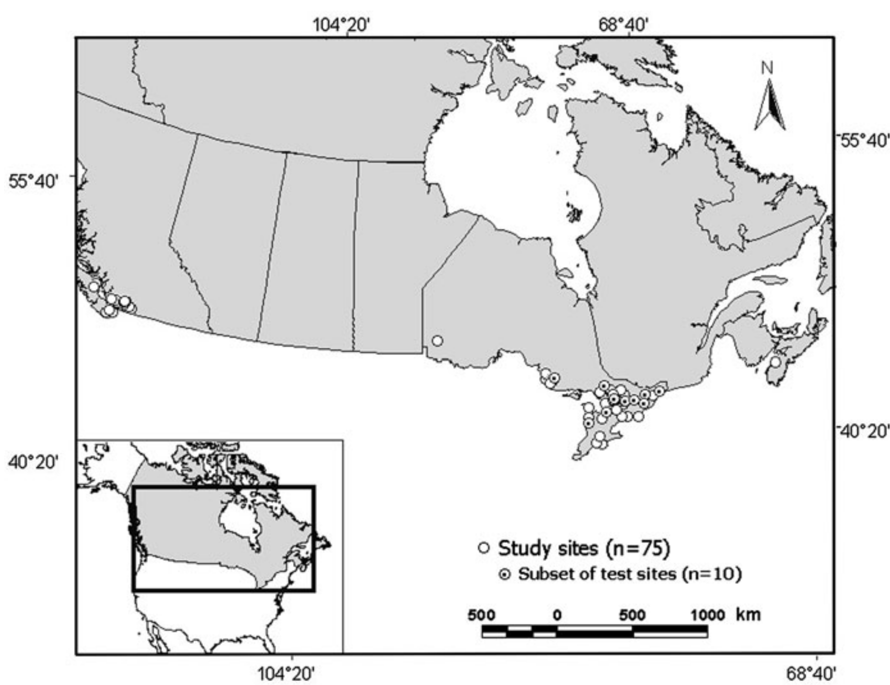

Fig. 1 Location of the 75 study sites in Canada: Nova Scotia, Ontario and British Columbia. Detailed mineralogy and total oxide content were available at 10 test sites in Ontario indicated as *concentric circles*. Sites located in close geographical proximity are indicated as *overlapping circles*

Table 1 Physiography of the study area and physical characteristics of forest soils at 75 study sites in Canada: Nova Scotia (NS), Ontario (ON) and British Columbia (BC)

	Western Canada			Eastern Canada		
Province	Southwestern BC	Southwestern NS	North western ON	Central ON	South-central ON	Southern ON
Region	Georgia Basin	Appalachian Range	Precambrian Shield	Algoma, Precambrian Shield	Muskoka -Haliburton, Precambrian Shield	Great Lakes-St Lawrence Lowlands
No. sites	19	1	1	9	29	16
Climate[a–e]	Humid continental, montane, sub-alpine	Humid continental	Continental	North temperate	North temperate	North temperate
Temperature (°C)	7.4 (4.2–9.8)	6.0	2.2	3.2 (2.7–3.9)	4.8 (3.4–6.3)	6.6 (5.9–7.9)
Vegetation[a–e]	Coastal, montane, sub-alpine mixed coniferous	Mixed coniferous, mixed deciduous	Boreal, mixed coniferous	Mixed coniferous	Mixed hardwood, mixed coniferous	Mixed hardwood
Geology[b–h]	Volcanic, sedimentary, granodiorite, diorite, quartzite	Greywacke, gneiss, granitoid, quartzite	Greywacke, tonalite, diorite, granitoid	Granodiorite, ortho gneiss, tonalite, granite, quartzite	Volcanic, sedimentary, granodiorite, diorite, quartzite	Limestone, dolostone, sandstone, marble
Soil type[a–e]	Podzols	Poorly developed podzols	Humic regosols, sombric brunisols	Homo-ferric, ferro-humic podzols	Grey-brown podzols, brunisols	Grey-brown luvisols, grey-brown podzols, brunisols
Depth[i] (m)	0.2 (0.01)	0.5 (0.1)	0.4	0.2 (0.02)	0.4 (0.02)	0.3 (0.02)
LOI (%)	13.5 (1.2)	6.8	2.7	10.9 (0.6)	8.5 (0.5)	5.6 (0.9)
Sand (%)	65.2 (2.1)	50.0	81.0	53.7 (1.5)	63.3 (1.8)	60.5 (4.9)
Silt (%)	24.8 (1.6)	35.0	15.0	39.2 (1.4)	27.6 (2.0)	28.9 (5.2)
Clay (%)	4.3 (0.6)	15.0	4.0	4.9 (0.2)	4.0 (0.3)	4.7 (0.7)

Average and range are shown for temperature; average and standard error are shown for soil properties

[a] Mongeon et al. (2010), [b] Whitfield et al. (2006), [c] Warkentin (1968), [d] Chapman and Putnam (1984), [e] Lamontagne and Schiff (1999), [f] Wheeler et al. (1997), [g] Massey et al. (2005), [h] Ontario Geological Survey (2006), [i] Soil depth of tree rooting

(Canadian System of Soil Classification 1998) and overlay a range of bedrock types, including carbonate and sedimentary rocks, granodiorite, and gneiss (Table 1; Warkentin 1968; Bird 1972; Clayton and Marshall 1972; Chapman and Putnam 1984; Whitfield et al. 2006; Mongeon et al. 2010).

Data collection

Soil samples were collected at study sites in British Columbia, Ontario and Nova Scotia during 2001–2006, where the majority of sites are considered acid sensitive due to the slow-weathering bedrock (Warkentin 1968; Bird 1972; Clayton and Marshall 1972; Chapman and Putnam 1984; Whitfield et al. 2006; Mongeon et al. 2010). Depth and rock content measurements were recorded for each soil horizon at 1–5 soil pits per site. Composite soil samples were collected by horizon for each pit and dried (ambient air or 70°C) prior to analysis. Organic matter content was determined by loss on ignition (*LOI*, 8 h, 400°C) for individual horizon samples. Weighted averages (Helliwell et al. 1998) for the tree rooting zone in the soil were used to estimate soil bulk density (ρ_b) from a relationship between soil organic matter content and soil mass (Eq. 1; de Vos et al. 2005).

$$\rho_b = 1.775 - 0.173 \cdot \left(LOI^{1/2}\right) \tag{1}$$

The superior performance of this method in comparison with other pedotransfer functions has been established for over 1,500 soils in Europe (de Vos et al. 2005), and this method has since been used in studies in North America (Whitfield et al. 2009; Whitfield et al. 2010). Loss-on-ignition values were also used to calculate organic carbon content using the van Bemmelen factor (1.724), which is widely used in Canadian forest databases (Kalra and Maynard 1991).

Bulked horizon samples for each site were also analyzed for soil texture (sand, silt and clay content), mineral composition and total oxide content. Particle size distribution at all sites was determined on a per weight basis using a Partica LA-950 Laser Diffraction Particle Size Analyzer (Horiba Ltd.). The proportions of sand, silt and clay (f_{Sand}, f_{Silt}, f_{Clay}) particle size fractions were further used to calculate soil surface area (*SA*) based on the relationship between total surface area, mineral cleavage and soil particle size distribution that was developed by Sverdrup et al. (1990) for Swedish podzols and re-calibrated to Brunauer–Emmett–Teller (BET) measurements of surface area (via physical gas adsorption) for a range of soil types and texture classes, including humo-ferric podzols (Hodson et al. 1998).

$$SA = \left(0.006 \cdot f_{Sand} + 0.024 \cdot f_{Silt} + 0.047 \cdot f_{Clay}\right) \cdot 1000 \cdot \rho_b \tag{2}$$

Particle size distribution and organic carbon content were also used to estimate soil moisture content following Rawls et al. (2003). This relationship of soil water retention with soil texture and organic content as related to soil density and pore space was calibrated to 12,000 soils and 5 soil classes in the U.S., including podzols (Rawls et al. 2003).

Soil mineralogical composition was measured at 10 sites in Ontario (Fig. 1) via the Rietveld method and X-ray diffraction using a Siemens (Bruker) D5000 Bragg–Brentano Diffractometer. Soil total oxide content was measured at 55 sites in Ontario via X-ray fluorescence using a Phillips PW31400 Wavelength Dispersive XRF Spectrometer. Soil pH was measured at all sites in a 1:4 soil to liquid slurry using a glass electrode Oakton pH/MVC meter. Base saturation at the sites was calculated as the percentage of exchangeable base cations (1 M NH_4Cl extract) relative to the soil cation exchange capacity estimated from extractable NH_4^+ (2.0 M NaCl extract).

The average annual precipitation and air temperature for each site used as input to the PROFILE model were obtained from a global scale database interpolated to a 35 × 35 km grid for the period 1961–1990 (New et al. 1999). The mean annual runoff was calculated from modeled precipitation and soil evapotranspiration (M. Posch personal communication). Wet and dry deposition values for S, N, base cations and chloride were obtained from Environment Canada deposition fields for forest land cover in Ontario and Nova Scotia during 1994–2002 (M. Shaw personal communication). Sulfur and N deposition values based on emission inventories for 2002 for sites in the Georgia Basin, BC were obtained from the AURAMS (A Unified Regional Air-quality Modeling System) deposition fields mapped to a 42 × 42 km grid for generalized land cover (Moran et al. 2008).

Weathering rate estimation

Weathering rates at the 75 study sites were estimated using the STA and PROFILE models. A multi-step approach was used to obtain mineralogical input to PROFILE for sites with unknown quantitative mineralogy, including (1) evaluation of the Analysis to Mineralogy model and determination of a regional mineral list and stoichiometry for Ontario and (2) application of the Analysis to Mineralogy model to estimate quantitative mineralogy from total oxide content (Table 2). Base cation weathering rates for all sites were estimated using the STA and PROFILE models, and they were evaluated for comparability (3). An independent assessment of PROFILE was performed using a catchment mass balance at 19 sites in Ontario (4). Finally, the STA method was revised using the relationship between PROFILE weathering estimates, soil texture and organic matter content (5).

PROFILE

Mineral weathering rates of base cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) for forest soils at the 75 study sites were estimated using PROFILE (Version 5.1), a widely used soil chemical model that includes a weathering sub-model for the release of base cations via mineral breakdown (Sverdrup and Warfvinge 1988a, b; Warfvinge and Sverdrup 1992). The combination of minerals of different weathering classes and reactive surface area are considered the primary determinants of soil weathering (Brahy et al. 2000; Malmström et al. 2000). Previous investigations of the sources of uncertainty and sensitivity in PROFILE have identified key soil parameters in the model, including moisture content, mineral surface area (Hodson and Langan 1999) and calcite content (I. Koseva unpublished data).

Weathering rates for soils at the 75 study sites were estimated using site-specific weighted averages of soil physicochemical properties and site-specific precipitation, runoff, temperature and deposition chemistry. PROFILE inputs for soil carbon dioxide partial pressure (15 × atm, Bouten et al. 1984) and dissolved organic carbon (7 mg L^{-1}, Findeis et al. 1993) were assumed according to published measurements for soils in Canada and for similar soil types in Europe. Gibbsite dissolution constants (8.5) were set based on recommended values in the Mapping Manual (Umweltbundesamt 2004) and calculations for soils in British Columbia (Mongeon et al. 2010). Nitrogen dynamics, uptake by vegetation and canopy exchange were not included in the model simulations for the purpose of simplicity. Soil mineralogy inputs at the study sites were available from measurements at 34 sites (Ontario: 14, British Columbia: 19, Nova Scotia: 1) and mineralogy that was modeled at 41 sites in Ontario.

Analysis to Mineralogy and parameter estimation

The Analysis to Mineralogy model (Posch and Kurz 2007) was used to develop a regional method for mineralogical determination for forest soils in Ontario where no knowledge of mineral abundance was available. The Analysis to Mineralogy model operates via a matrix of mathematical functions that calculate relative mineral abundance as the centroid of the solution matrix according to the element oxide content of minerals and the total oxide content of soils at the study sites. The model is best suited for complex matrices that contain a greater number of minerals than the number of element oxides used in the analysis (Posch and Kurz 2007). The positive solution of the model matrix depends on the list of element oxides and minerals and on the mineral stoichiometry that are used. Phyllosilicate minerals that allow for element substitution between the silicate layers can have different stoichiometry, depending on what element substitution prevails (e.g. Iron actinolite: $Ca_2Fe(II)_5$

Table 2 Multi-step approach to estimating weathering rates for forest soils in Nova Scotia (NS), Ontario (ON) and British Columbia (BC)

Progress	Sites	Region
1. Evaluate Analysis to Mineralogy model	10	ON
2. Obtain mineralogy using Analysis to Mineralogy model	51	ON
3. Compare Soil Texture Approximation and PROFILE models	75	BC, NS, ON
4. Compare PROFILE weathering rates with mass balance	19	ON
5. Revise Soil Texture Approximation model	75	BC, NS, ON

$Si_8O_{22}(OH)_2$; magnesium actinolite: $Ca_2Mg_5Si_8O_{22}(OH)_2$; iron-magnesium actinolite: $Ca_2Fe(II)_2Mg_3Si_8O_{22}(OH)_2$). In order to determine the stoichiometry for minerals with such endmembers, the Analysis to Mineralogy model was automated with the use of a parameter estimation software (Version 5; Doherty 2004) that repeated the solution matrix using different mineral stoichiometries while comparing the modeled mineral content with observations. The parameter estimation software optimized the mineral stoichiometry against observations based on a sensitivity analysis with a Jacobian matrix (Doherty 2004). Ranking of the optimized stoichiometry is based on sum of squares of residuals, Akaike's Information Criterion, Bayesian Information Criterion and eigen values (Doherty 2004).

Optimization of mineral stoichiometry in the Analysis to Mineralogy model using parameter estimation was carried out at the 10 test sites in south central Ontario where both mineralogy and total oxide content measurements were available. Mineralogical composition at these sites identified a maximum of 15 minerals grouped into 11 mineral classes based on weathering potential (Hodson et al. 1997; Chou et al. 1989; Morse and Arvidson 2002; Essington 2003; Umweltbundesamt 2004). The regional list contained a fixed number of minerals with the exception of the fast weathering calcite mineral, which was assigned only to soils that react vigorously upon exposure to an acidic solution (Denholm and Schut 1993) or soils with pH (H_2O) above 6.0, soil base saturation above 60%, (Hornung et al. 1995) or with underlying calcareous rocks (Umweltbundesamt 2004). The accuracy of the Analysis to Mineralogy model was evaluated based on the deviation of modeled mineralogy from observed mineralogy at the 10 test sites in Ontario and based on the deviation of PROFILE weathering rates estimated using modeled mineralogy from PROFILE weathering estimates obtained using observed mineralogy. The optimized regional mineral list and mineral stoichiometry were further used to estimate soil mineralogical content at the 41 sites in Ontario with no available mineralogy.

Soil Texture Approximation

The STA method used in this study is an empirical pedotransfer function that was first developed for European soils (de Vries 1991; de Vries et al. 1993) and later adapted to soils in Canada and the U.S. (Watmough et al. 2004; Ouimet 2005). The method estimates total base cation weathering rates (BC_w, sum of Ca^{2+}, Mg^{2+}, Na^+ and K^+), based on the relationship between established weathering classes (Sverdrup and Warfvinge 1988a, b) and clay content of soils for different acidity classes—acidic, intermediate and basic (Eqs. 3–5; Nasr et al. 2010). In this study, the acidity class of soils at the study sites was determined from surficial geology and mineralogy (Umweltbundesamt 2004), complemented with soil pH (H_2O) and base saturation measurements (Hornung et al. 1995) where available (Ontario: 51 sites; British Columbia: 19 sites). The flux of weathered base cations (BC_w, units: eq ha^{-1} $year^{-1}$) was estimated from soil clay content (*clay, %*), corrected for the kinetic effect of ambient temperature (T, °K) on mineral weathering (Sverdrup 1990) and further adjusted for soil depth (units: m; Watmough et al. 2004; Ouimet 2005; Nasr et al. 2010).

Acidic substrate

$$BC_w = \left(56.7 \cdot clay - 0.32 \cdot clay^2\right) \cdot depth \cdot e^{\left(\frac{3600}{281} - \frac{3600}{T}\right)} \quad (3)$$

Intermediate substrate

$$BC_w = (500 + 53.67 \cdot clay - 0.18 \cdot clay^2) \cdot depth \cdot e^{\left(\frac{3600}{281} - \frac{3600}{T}\right)} \quad (4)$$

Basic substrate

$$BC_w = (500 + 59.2 \cdot clay) \cdot depth \cdot e^{\left(\frac{3600}{281} - \frac{3600}{T}\right)} \quad (5)$$

Mass balance

While PROFILE is widely used, there is no 'correct' method for estimating base cation weathering rates. Therefore, as an additional independent measure of the total base cation weathering, a catchment mass balance (Clayton 1979) at 19 sites in Ontario was used for the assessment of the PROFILE model. The mass balance operates on the principle of equilibrium between cation pools in catchments such as vegetation, forest floor and soil pools, whereby the difference between the base cation export and base cation inputs from deposition (BC_{dep}) into the catchment may be attributed to input from base cation release during mineral weathering (Eq. 6). The base cation flux from 19 forested catchments was estimated using an 8- to 10-year average of measured base cation concentration in lake water (BC_{lake}) and the 1961–1990 catchment runoff (Q; M. Posch personal communication). The input of base cations from deposition at each catchment was estimated as the average deposition during 1994–2002 (M. Shaw personal communication).

$$BC_w = BC_{lake} \cdot Q - BC_{dep} \qquad (6)$$

Estimates of the base cation weathering flux obtained using the mass balance are generally expected to be higher than PROFILE estimates, as the mass balance represents a catchment scale weathering flux, while weathering in PROFILE is limited to the soil pedon.

Revised Soil Texture Approximation

A revised Soil Texture Approximation method was developed at the 75 study sites, in order to provide a simple but robust method for weathering rate determination for Canadian forest soils. A backward step-wise multiple regression using soil physicochemical properties and depth-normalized PROFILE estimates of weathering rates as model parameters was utilized to calibrate the STA for the study area. Model suitability was evaluated based on the squared sum of residuals ($R_{residual}$), model fit (R^2) and number of significant model parameters. The model goodness-of-fit was further evaluated using the Nash–Sutcliffe statistic—the equivalent of variance explained (R^2) in linear regressions—and by estimating the relative model bias (McCuen et al. 2006).

Results

Mineralogy estimation

Mineralogy obtained using the Analysis to Mineralogy model showed general agreement with observed data; although statistically significant, differences between modeled and observed mineralogy were generally <10% (Fig. 2). The maximum absolute differences for fast-weathering minerals such as calcite and anorthite were <0.5 and 8%, respectively; whereas the maximum deviation of modeled data for slow-weathering and inert minerals reached 12% (Fig. 2). However, PROFILE weathering estimates obtained using modeled mineralogy did not deviate from rates obtained using mineralogical measurements (Kendall: $\tau = 0.69$, $P < 0.05$; Fig. 3, Table 3).

Soil Texture Approximation

Mineral weathering rates calculated with the STA method at 75 sites in Canada (6–367 eq ha^{-1} year^{-1}) were up to 38 times lower (seven times on average) than rates estimated with PROFILE (143–2,119 eq ha^{-1} year^{-1}; Wilcox $Z = 7.52$, $P < 0.0001$).

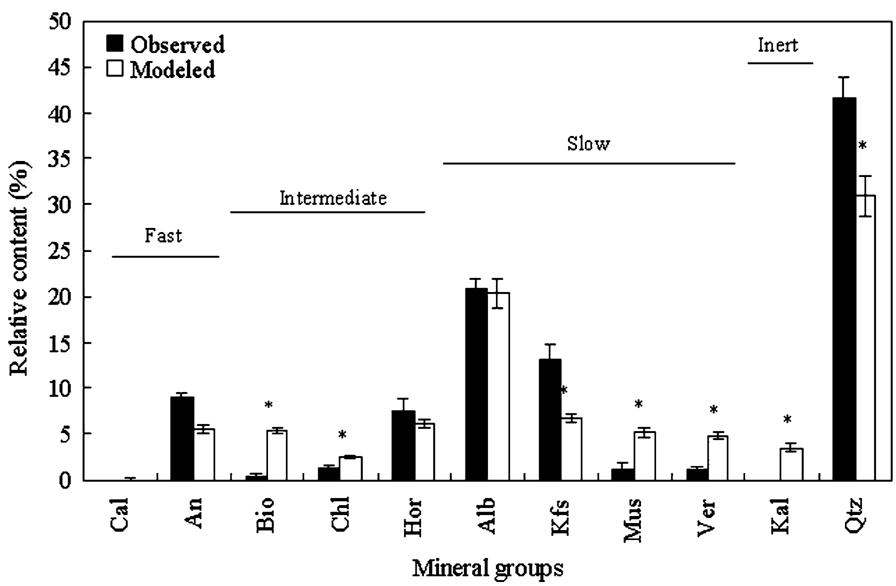

Fig. 2 Comparison of observed mineral composition at 10 test sites in Ontario with mineral composition estimated using the Analysis to Mineralogy model. Significant differences between mineral content within each mineral class are indicated by an *asterisk*. Mineral weathering classes: *Cal* calcite, *An* anorthite, *Bio* biotite, *Chl* iron chloride, *Hor* hornblende, *Alb* albite, *Kfs* potassium feldspar, *Mus* muscovite, *Ver* magnesium vermiculite, *Kal* kaolinite, *Qtz* quartz

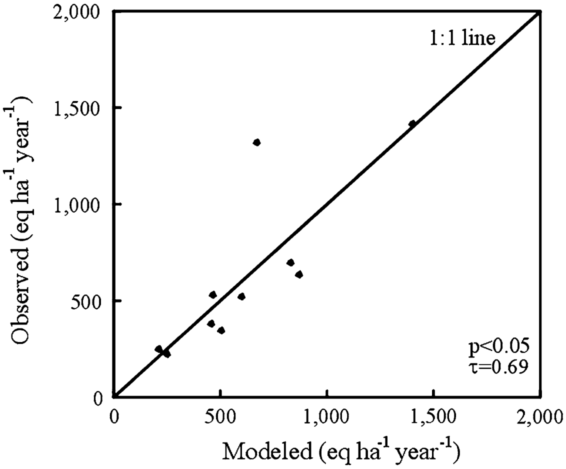

Fig. 3 Site-specific comparison of total soil base cation weathering rates for soils at 10 test sites in Ontario. Weathering rates were estimated with PROFILE using observed and modeled mineralogy

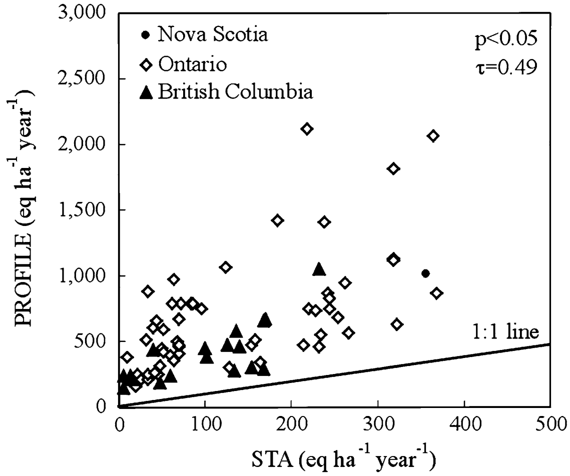

Fig. 4 Comparison between weathering rates for soils at 75 sites in Canada estimated using PROFILE and the Soil Texture Approximation (STA) model for North America

Table 3 Individual and total base cation weathering rates estimated with PROFILE using observed and modeled mineralogy at 10 test sites in Ontario

Base cations	Weathering rate (eq ha^{-1} year^{-1})			
	Observed		Modeled	
	Average	SE	Average	SE
Ca^{2}	231	48	178	43
Mg^{2+}	160	38	213	34
K^{+}	60	13	70	12
Na^{+}	177	36	168	35
Total base cations	628	132	629	110

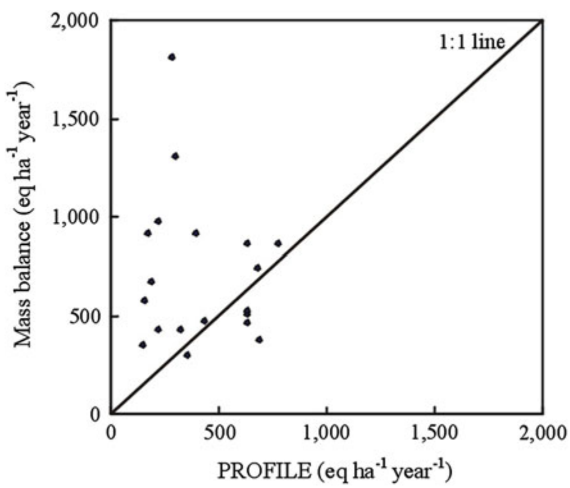

Fig. 5 Comparison of base cation weathering rates estimated using PROFILE and catchment mass balance at 19 sites in Ontario

Despite deviations from the 1:1 line (Fig. 4), weathering estimates obtained using the STA method were significantly correlated with PROFILE weathering estimates (Kendall: $\tau = 0.49$, $P < 0.05$).

Mass balance

Comparison between the catchment mass balance and PROFILE at 19 sites in Ontario showed that PROFILE (210–790 eq ha^{-1} year^{-1}) weathering estimates for the soil pedon were mostly within the range obtained from the catchment mass balance (294–1,806 eq ha^{-1} year^{-1}; Fig. 5). Further, PROFILE estimates of weathering were generally lower than the catchment estimates, as expected, although five sites had slightly higher weathering rates according to PROFILE.

Revised Soil Texture Approximation

Soil silt content was the strongest single predictor of depth-normalized weathering rates obtained using PROFILE ($F_{1,73} = 30.03$, $SS_{\text{residual}} = 23.79$, $P < 0.0001$, $R^2_{\text{adj}} = 0.28$). Soil silt content was also

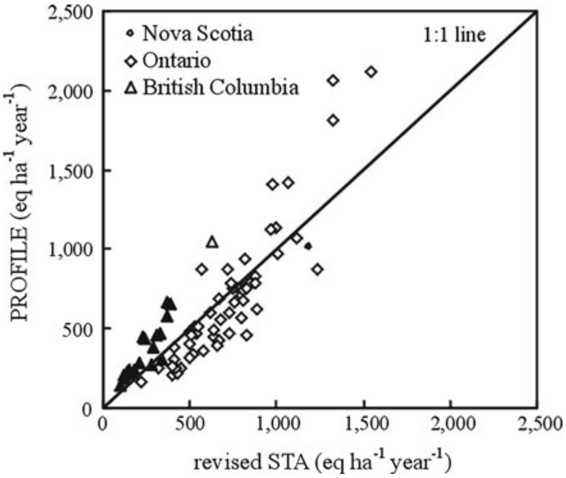

Fig. 6 Comparison of base cation weathering rates estimated using the revised Soil Texture Approximation (STA) model against PROFILE weathering estimates for the soil rooting depth in Canadian forests ($n = 75$)

positively correlated with clay content ($R^2_{adj} = 0.28$). The best model ranked in the backward stepwise regression analysis included soil silt content and LOI as predictors of weathering rates for depth-normalized weathering rates (Eq. 7; $R^2_{adj} = 0.42$, $F_{1,73} = 27.87$, $SS_{residual} = 18.92$, $P < 0.0001$). The model goodness-of-fit was high (Fig. 6; $R^2_{adj} = 0.73$, relative bias = −1%, RMSE = 208) despite the relatively low parameter fit in the model. The breakdown of weathering rates per region also suggested a negative bias for soils in British Columbia and a small positive bias for soils in Ontario forests. Overall, this model was developed for upland mineral soils with temperatures, silt content and loss on ignition within the range of values measured at the 75 study sites (silt: 2–68%; LOI: 3–23%; temperature: 2–10°C).

$$BC_w = (1.73 + 0.03 \cdot silt - 0.06 \cdot LOI) \cdot 1,000 \cdot depth \quad (7)$$

Discussion

Mineralogy estimation

Reliable estimates of weathering require knowledge of mineralogy, as base cation weathering involves the release of base cations from mineral breakdown. Mineral-based methods are the preferred approach to weathering estimation (Ouimet and Duchesne 2005; Whitfield et al. 2006) but these methods are often limited in their regional application by the availability of mineralogical data. Although the use of total oxide measurements in correlation analysis (e.g. UPPSALA) is associated with a high degree of accuracy and representation of the geology of the study area (Hodson and Langan 1999; Ouimet and Duchesne 2005), most methods are data-intensive (e.g. SEDNORM; Rosen and Abbyasov 2003), poorly calibrated with normative mineralogy (e.g. MINLITH model) or not calibrated at all (Akselsson et al. 2006). The Analysis to Mineralogy model and parameter estimation software provide a reasonable compromise, where mineralogical determination can be based on inexpensive mineralogical measurements such as mineral optical count or on a previously optimized mineral list and molecular formulas, as used in this study. The successful use of the Analysis to Mineralogy model at 10 study sites in Ontario to estimate mineralogical content and the successful application to weathering determination with PROFILE demonstrated the potential use of this method for regional weathering estimation.

Mineralogy obtained using the Analysis to Mineralogy model and parameter estimation provided a good approximation of mineralogy quantified by X-ray diffraction at the 10 test sites in Ontario. The introduction of all detected minerals in the regional mineral list in the Analysis to Mineralogy model provided (1) a better representation of the varied geology of south-central Ontario that includes small deposits of minerals with high weathering rates (e.g. calcite); and (2) a constraint to prevent the over-representation of individual minerals that were detected at few sites.

Arguably, the use of soil pH and base saturation in addition to surficial geology in the multi-criterion assignment of calcareous classes might provide a better representation of the weathering capacity of forest soils. Phillips (2010) argued that soil weathering depends mostly on mineralogy of the surficial soil horizons, rather than on surficial bedrock. Furthermore, the use of geological maps, which often have a coarse resolution of 1:250,000 (Massey et al. 2005) to 1:500,000,000 (Wheeler et al. 1997), might not detect small deposits of fast-weathering minerals in crystalline rocks or secondary minerals in modified rocks, thus underestimating base cation weathering in soils

(Hosein et al. 2004). Even small under- or over-estimation of calcite and dolomite content in modeled mineralogy will greatly influence the weathering rate (Hosein et al. 2004; White et al. 2005). Weathering rates in this study were generally comparable when using modeled or observed mineralogy although there were small but significant differences between modeled and observed content of phyllosilicate minerals (Table 3; Fig. 3).

Evaluation of the Soil Texture Approximation

Comparison between the STA and PROFILE weathering estimates and assessment of PROFILE against mass balance for catchment soils suggested that while PROFILE produces reasonable weathering estimates for soils at the study sites, the North American clay-based pedotransfer function is not suited to the study sites and requires revision prior to regional application. PROFILE weathering estimates were similar, but generally lower than mass balance estimates as expected from soil pedon estimation. However, PROFILE estimates were higher than the mass balance at five sites in Ontario (Fig. 5). This was most likely due to (1) lack of spatial scaling of both estimates and (2) unaccounted sinks of weathered base cations that were not reflected in the mass balance estimate, including uptake by vegetation and burial in lake sediments. The STA used in this study appears to follow a trend in regional dependency on soil texture. Weathering rates obtained using the STA at the 75 study sites greatly underestimated PROFILE values and were lower than the range of weathering rates reported for other weathering approaches (230–8,600 eq ha^{-1} $year^{-1}$; Arp et al. 1996; Watmough and Dillon 2003a, b, c). In contrast, previous applications of this STA model in regions with acidic, and sandy soils have produced weathering rates comparable with PROFILE estimates (e.g. Nova Scotia: Whitfield et al. 2006; Alberta: Whitfield et al. 2010) or only 1.6-fold discrepancy with PROFILE in other regions in Eastern North America (E. Miller personal communication).

The low weathering rates estimated using the STA at the study sites might be attributed to the need to employ measures of soil texture other than clay that will represent the range of texture classes and mineralogy in the study area. Despite the use of soil acidity classes that distinguish the high weathering potential associated with calcareous soils from the low weathering potential of acidic soils, differences between weathering rates estimated using the STA and PROFILE estimates for the study sites were more pronounced for calcareous soils where carbonate minerals dominated the weathering process (White et al. 1999). Accordingly, Mongeon et al. (2010) showed that a revised STA model incorporating calcite content provided a better relationship between soil texture and weathering rates at sites in the Georgia Basin, BC. Weathering rate estimates obtained for soils at the study sites using the clay-based North American STA resulted in lower weathering rates even for acidic soils, where mineral weathering was dominated primarily by the production of vermiculite from micas and phyllosilicates in the clay size fraction (Brahy et al. 2000; Bain 2007). This suggested that the STA may be suitable mainly to soils with a small suite of minerals dominated by quartz and to soils with sand-dominated texture. Accordingly, the use of this STA model in the 2004 Canadian Acid Rain Assessment (Ouimet et al. 2006) may have introduced bias to the critical loads for forest soils in Ontario.

Revised Soil Texture Approximation

Despite differences between model estimates, PROFILE and STA weathering estimates were positively correlated. Strong correlation between PROFILE weathering estimates and soil texture and organic content was expected as mineral weathering depends on the mineral surface area, soil age and pedogenesis, which are correlated with soil particle size distribution and soil organic matter (Phillips 2010; R. Ouimet personal communication). The latter can be used as a proxy for soil mass or depth as it is often correlated with soil bulk density (this study: $R^2 = 0.83$; Mongeon et al. 2010: $R^2 = 0.88$). While other STA models (de Vries et al. 1993; Ouimet 2005; Whitfield et al. 2010) reinforce the importance of soil clay content as an indicator of soil weathering rates, silt content of soils appears to capture the range of soil texture classes in this study.

Rather than an indicator of weathering potential, clay content is likely an indicator of the current weathering class of soils or the product of past weathering processes that result in high levels of micas and phyllosilicate minerals remaining in the clay fraction (Brahy et al. 2000; Bain 2007). Clay content may not be the strongest predictor of soil weathering rates, as the age of the soil, mineralogical composition and mineral cleavage influence different soil size fractions (Phillips 2010). Fine sandy loam (or coarser) soils have been shown to have non-reactive secondary (clay) mineral phases as a result of the complete exhaustion of reactive mineral phases, such as calcite and biotite (NEG ECP 2001). To that effect, weathering estimates should be corrected for the influence of clay minerals on measurements of soil surface area in soils dominated by till from granitic or metamorphic rocks (White et al. 1996). Conversely, the consideration of mineral phases in addition to soil texture in clay-rich or calcareous soils is more likely to result in higher estimates of reactive surface area (NEG ECP 2001). Only 50% of the clay size fraction in these soils is considered reactive, whereas 100% of clay particles in non-calcareous sedimentary soils (e.g. Alberta, Whitfield et al. 2010) are reactive (White et al. 1996).

Soil silt content is potentially a better predictor of soil weathering rates across a range of soil types, as it was detected in soils at all study sites and was positively correlated with clay content. The clay content of soils is more likely to have a large margin of error owing to the small fraction of clay size particles. In addition, acidic soils are often dominated by slow weathering, secondary silicate minerals that are found in the clay size fraction, while soils in British Columbia (Mongeon et al. 2010) and Ontario contained a range of carbonates and secondary minerals that are not confined to the clay size fraction. In this study, soils at the sites ranged from acidic to calcareous and had a wide range of silt and organic matter content (2–68 and 3–23%, respectively).

Overall, weathering rates estimated at the majority of sites, particularly in Ontario, were greater than 600 eq ha^{-1} $year^{-1}$, and 8% of sites had estimated rates between 1,000 and 1,800 eq ha^{-1} $year^{-1}$. Weathering rates estimated at the study sites were higher than previous estimates for Nova Scotia (30–130 eq ha^{-1} $year^{-1}$; Whitfield et al. 2006), Quebec (190–1,310 eq ha^{-1} $year^{-1}$; Courchesne et al. 2001; Ouimet and Duchesne 2005) and Alberta (STA: 0–720 eq ha^{-1} $year^{-1}$, PROFILE: 16–740 eq ha^{-1} $year^{-1}$; Whitfield et al. 2010) although these studies encompassed a range of soil acidity classes.

Further research and model improvement

Calibration of the STA model to upland forest soils in distinct regions of Canada limited the method application to a specific range of silt and organic matter (LOI) content, which may differ drastically even within the study region due to the heterogeneity of the landscapes. The shift in STA formulation to incorporate a measure of soil texture with a wide range of values across different texture classes and an indicator of soil mass and depth provide a better representation of the different soil types, which was also suggested by the pedotransfer functions developed for soils in British Columbia (Mongeon et al. 2010) and for soils in Alberta (Whitfield et al. 2010). The applicability of the model proposed in this study can be expanded to a broad regional scale by (1) standardization to soil organic matter content, moisture, bulk density and temperature, and (2) evaluation for soils outside the study area.

Conclusions

The application of STA models in national acid deposition assessments without model re-calibration or revision might introduce a bias to weathering rates in mineral soils. However, the application of detailed models (e.g. PROFILE) or development of a regional STA to these models presents the challenge of obtaining mineralogical data, which is generally not available in regional datasets. To overcome these limitations, the Analysis to Mineralogy model and parameter estimation were used at 10 sites in Ontario and were shown to provide a reasonable approximation of mineralogical data, which could then be used for sites that only have oxide data available. Weathering estimates obtained with PROFILE at 75 sites in Ontario were up to 38 (seven on average) times greater than weathering rates obtained using the North American STA model. Model comparison at the 75 study sites and catchment mass balance at a subset of 19 sites confirmed that PROFILE provides reasonable estimates of weathering rates and that the clay-based model underestimates the weathering flux in soils throughout the study area. A revised STA model was developed for soils at 75 sites in Canadian forests from the relationship between soil silt and organic matter content with base cation weathering rates. This model may be more widely applicable in Canada, but may not necessarily be suited to all regions.

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