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Evaluation of three methods for estimating the weathering rates of base cations in forested catchments

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ABSTRACT

This paper investigates three techniques that are commonly used to generate estimates of base cation (BC) weathering rates, i.e. the profile mass balance (PEDON), the watershed input-output budget (WATERSHED) and the PROFILE model (MODEL). These methods were compared for their relative performance in estimating BC weathering rates for 21 watersheds located in southern Quebec that vary with respect to hydro-climatic conditions, soil properties and forest cover. Average total BC weathering rates for the 21 watersheds were 0.41 ± 0.09 (±SE), 1.20 ± 0.17 and 1.71 ± 0.22 $kmol_c\ ha^{-1}\ yr^{-1}$ for PEDON, WATERSHED and MODEL, respectively. Passing and Bablok regression analysis demonstrated good agreement between WATERSHED and MODEL {regression formula: WATERSHED = −0.08 + 0.74 MODEL, with 95% CI for intercept [−1.13; 0.25] and for slope [0.40; 1.43]}, while poorer agreements were observed between these two methods and PEDON. Contrary to the WATERSHED and the MODEL methods, BC weathering rates obtained with PEDON were not significantly associated with the spatial variation of the soil calcite content and of the size of the soil exchangeable BC pools. We hypothesized that in the calcite-containing watersheds, the performance of PEDON was negatively impacted by environmental conditions that favored the partial dissolution and leaching of the calcite contained in the initial parent material, including in the material situated at the base of the profile (C horizon).

1. Introduction

Soil mineral weathering is a key component of biogeochemical cycles in terrestrial ecosystems (Sverdrup and Warfvinge, 1988; Riebe et al., 2004; Whitfield et al., 2010). It involves major changes in the mineral assemblage, chemical composition and physical properties of soils (Murakami et al., 2003; Whitfield et al., 2006), and therefore contributes chiefly to soil development. Mineral alteration, notably silicate weathering, is recognized as an important long-term control on atmospheric CO_2 (Berner and Lasaga, 1989). It also plays a central role on plant nutrition by releasing nutrients, like base cations (BC = Ca, Mg, K, Na), from minerals into an available form that can be taken up by plants. The weathering process further contributes to the neutralization of acidic compounds in soils (Bain et al., 1993; Mortatti and Probst, 2003; Whitfield et al., 2010). Therefore, quantifying long-term mineral weathering rates is crucial to improve our understanding of the biogeochemical cycling of elements in terrestrial ecosystems, to evaluate the relative sensitivity of ecosystems to environmental stresses and to further develop sustainable forest management strategies.

The evaluation of BC weathering rates requires reliable quantitative methods of analysis. However, there is no recognized standard procedure for quantifying the rate at which minerals release BC under field conditions. Estimates of BC weathering rates have been obtained from a number of methodological approaches such as laboratory dissolution experiments (Chou and Wollast, 1984; Oelkers et al., 1994; Huertas et al., 1999; Amram and Ganor, 2005), test-mineral techniques (Ranger et al., 1990), strontium isotope ratio methods (Åberg et al., 1989; Shand et al., 2007), geochemical modeling using PROFILE (Sverdrup and Warfvinge, 1993; Whitfield et al., 2006, 2010; Sverdrup, 2009; Houle et al., 2012; Whitfield and Reid, 2013) or MAGIC (Cosby et al., 2001; Whitfield et al., 2006), watershed input-output budgets (Clayton, 1979; Velbel, 1985; White and Blum, 1995; Velbel and Price, 2007) and soil profile mass balance calculations (Brimhall et al., 1991a; White et al., 1998; Egli and Fitze, 2000; Anderson et al., 2002). The empirical clay-based Soil Texture Approximation was also used to assess weathering rates in Canada and the United States (Koseva et al., 2010). Each estimation method is based on specific assumptions, and their performance therefore largely depends on how far the data and field conditions can meet these requirements.

It is generally accepted that several environmental factors act simultaneously to influence the rates at which BC are released through the

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weathering of minerals. The main factors include variables related to soil properties, biotic activity and climatic conditions (Sverdrup and Warfvinge, 1988; Courchesne et al., 2002; Wilson, 2004; Gordon, 2005; Egli et al., 2006; Ouimet, 2008; Augustin et al., 2015a,b). However, no single estimation method integrates all these factors specifically. Comparing the performance of the methods under different site conditions is thus needed to better understand the functioning of the methods and to identify possible bias that can be induced by some field conditions. Among the methods cited above, the watershed input-output budget, the soil profile mass balance and the geochemical model PROFILE are recurring in the scientific literature, and have been used, alone or in combination, at diverse geographic locations. The first approach takes into account pedogenic processes occurring at the scale of the catchment, whereas the other two methods are based on soil data collected from the rhizosphere, at the scale of the soil profile. Moreover, modeling with PROFILE and the watershed budget method are considered to reflect contemporary weathering fluxes, whereas soil mass balances yield historic weathering rates covering the total duration of soil genesis.

Several authors conducted comparative analyses across estimation methods (Kolka et al., 1996; Starr et al., 1998; Hodson and Langan, 1999; Ouimet and Duchesne, 2005; Whitfield et al., 2006; Houle et al., 2012). Such comparison is of interest because, for example, critical loads estimates (Hodson and Langan, 1999; Mongeon et al., 2010; Futter et al., 2012) are often based on weathering rates obtained from methods that differ across studies. On the one hand, some studies have shown that, for a given watershed, little overall difference was found between the weathering rate estimates when different methods were used (Starr et al., 1998; Houle et al., 2012). For example, Starr et al. (1998) calculated weathering rates for four soil profiles using three different methods (soil profile mass balance, Ca + Mg / temperature sum regression, and the PROFILE model). They observed that the weathering rates calculated by the three methods were similar, although the soil profile mass balance method gave the highest values and PROFILE the lowest. On the other hand, many studies found significant differences in weathering rates calculated using different methods simultaneously (Langan et al., 1995, 1996, 2001; Hodson and Langan, 1999; Watmough and Dillon, 2003). Langan et al. (1995) observed that BC weathering rates obtained with the soil profile mass balance method were significantly lower than those simulated with PROFILE in Scottish soils. With a few exceptions, these studies were performed for a limited number of sites and their results were often not analyzed statistically. Houle et al. (2012) evaluated base cation weathering rates in 21 watersheds located on the Canadian Shield that were part of the Québec lakes network, using both the watershed input-output budget and the geochemical model PROFILE. They found that Ca and Mg weathering rates simulated with the PROFILE model were significantly correlated with rates estimated using the watershed budget method. The BC weathering rates reported by Augustin et al. (2015a, 2015b) for southern Quebec using the soil profile mass balance method were, however, generally lower than those obtained by Houle et al. (2012) for the same 21 catchments with the watershed input-output model and PROFILE model. Preliminary investigations (Houle, unpublished data) into the factors explaining these differences suggested that the lower estimates yielded by the soil profile mass balance method were not systematic across sites and tended to be associated with catchments containing soil calcite and having the largest soil exchangeable BC reservoirs among the studied watersheds.

Overall, the above considerations suggest that our understanding of the relative performance of these commonly used methods for estimating BC weathering rates is still incomplete. In this context, the primary objective of this analysis was to compare the soil profile mass balance method with both the watershed input-output budget calculation and the geochemical model PROFILE. In this endeavour, we seek: 1) to establish the concordance/discordance between the methods for estimating the sum of Ca, Mg, Na and K weathering rates (or total BC weathering rates), and 2) to explain their relative performance under a spectrum of environmental conditions.

2. Material and methods

2.1. Site description

The study area encompasses twenty-one (21) forested catchments of the Québec lakes network (Houle et al., 2004). Briefly, the watersheds cover a wide range of geological, pedological and hydro-bioclimatic conditions (Lachance et al., 1985; Augustin et al., 2015a). They are located on the Canadian Shield, within an ~90,000 km^2 area in southern Québec that is parallel to the St. Lawrence River and bordered by the Ottawa and Saguenay rivers (Fig. 1). According to Lachance et al. (1985), there are two main types of geological substrates in the area: igneous (granite, syenite, anorthosite) and metamorphic (gneiss, granitic gneiss, paragneiss, marble) rocks. In the southwestern part of the study area, nearly half of the studied watersheds are located in an area where carbonates are present in the soil parent material (Augustin et al., 2015a, 2015b). Most soils have been classified as orthic and gleyed humo-ferric or ferro-humic podzols (Soil Classification Working Group, 1998). They are medium to coarse textured, shallow and acidic. The vegetation is mostly mixed forests dominated by deciduous species such as sugar maple (*Acer saccharum* Marsh.) in the southwest, and by coniferous species, predominantly balsam fir (*Abies balsamea* L.) or black spruce (*Picea mariana* Mill.) in the northeast. In the region, total annual precipitation averages 1162 mm, of which about a third falls as snow. The mean annual air temperature was 2.0 °C over the last three decades. The characteristics of the studied catchments are described in detail elsewhere (Houle et al., 2004, 2006, 2012; Augustin et al., 2015a,b).

2.2. Data sources and estimation methods

The total BC weathering fluxes reported in this study for each of the 21 catchments have been calculated from weathering rate data obtained for individual base cations (Ca, Mg, Na and K) using three different estimation methods. The BC weathering rates simulated with the geochemical model PROFILE (Sverdrup and Warfvinge, 1993) as well as those obtained using the watershed input-output budgets (Clayton, 1979; Velbel, 1985; Velbel and Price, 2007) were published in Houle et al. (2012) for the 21 catchments. The soil surface area and mineralogical composition data, used as key inputs to PROFILE, were acquired as described in Houle et al. (2012) and Augustin et al. (2015a). Briefly, soil mineral surface area was obtained from soil bulk density and soil particle size distribution according to the texture based - Eq. 25 from Sverdrup and Warfvinge (1995). The mineralogical composition of the soil samples was quantitatively estimated from the bulk chemistry, using the stoichiometric model UPPSALA (Sverdrup, 1990; Sandén and Warfinge, 1992; Houle et al., 2012; Augustin et al., 2015a, 2015b). The BC weathering rates estimated with the soil profile mass balance method (Anderson et al., 2002; Brimhall et al., 1991a; Egli and Fitze, 2000) were presented in Augustin et al. (2015a). Detailed information on sample collection and handling can be found in Houle et al. (2012) and in Augustin et al. (2015a). For the soil rooting zone, the amounts of NH_4Cl-exchangeable Ca, Mg and K were also determined as described in Houle et al. (2012). The three methods for estimating mineral weathering rates investigated in this study have been described in details and their respective advantages and limitations discussed in several publications (Bain et al., 1993; Hodson et al., 1997, 1998; Hodson and Langan, 1999; Holmquist et al., 2003; Futter et al., 2012; Houle et al., 2012). Here, we summarize the main characteristics and special features of the three methods.

2.2.1. Geochemical model PROFILE (MODEL)

The geochemical model PROFILE was developed by Sverdrup and Warfvinge (1988, 1993) for estimating current mineral weathering