Filling the gap in Ca input-output budgets in base-poor forest ecosystems: The contribution of non-crystalline phases evidenced by stable isotopic dilution

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Abstract

In terrestrial ecosystems, plant-available pools of magnesium and calcium are assumed to be stored in the soil as exchangeable cations adsorbed on the surface of mineral and/or organic particles. The pools of exchangeable magnesium and calcium are measured by ion-exchange soil extractions. These pools are sustained in the long term by the weathering of primary minerals in the soil and atmospheric inputs. This conceptual model is the base of input-output budgets from which soil acidification and the sustainability of soil chemical fertility is inferred. However, this model has been questioned by data from long-term forest ecosystem monitoring sites, particularly for calcium. Quantifying the contribution of atmospheric inputs, ion exchange and weathering of both primary, secondary and non-crystalline phases to tree nutrition in the short term is challenging.

In this study, we developed and applied a novel isotopic dilution technique using the stable isotopes of magnesium and calcium to study the contribution of the different soil phases to soil solution chemistry in a very acidic soil. The labile pools of Mg and Ca in the soil (pools in equilibrium with the soil solution) were isotopically labeled by spraying a solution enriched in ^{26}Mg and ^{44}Ca on the soil. Labeled soil columns were then percolated with a dilute acid solution during a 3-month period and the isotopic dilution of the tracers was monitored in the leaching solution, in the exchangeable (2 sequential 1 mol L^{-1} ammonium acetate extractions) and non-crystalline (2 sequential soil digestions: oxalic acid followed by nitric acid) phases.

Significant amounts of Mg and Ca isotope tracer were recovered in the non-crystalline soil phases. These phases represented from 5% to 25% and from 24% to 50%, respectively, of the Mg and Ca labile pools during the experiment. Our results show that non-crystalline phases act as both a source and a sink of calcium and magnesium in the soil, and contribute directly to soil solution chemistry on very short-term time scales. These phases are very abundant in acid soils and, in the present study, represent a substantial calcium pool (equivalent in size to the Ca exchangeable pool). The gradual isotopic dilution of Mg and Ca isotope ratios in the leaching solution during the experiment evidenced an input flux of Mg and Ca originating from a pool other than the labile pool. While the Mg input flux originated primarily from the weathering of primary minerals and secondarily from the non-crystalline phases, the Ca input flux originated primarily from the non-crystalline phases. Our results also show that the net calcium release flux from these phases may represent a significant source of calcium in forest

ecosystems and actively contribute to compensating the depletion of Ca exchangeable pools in the soil. Non-crystalline phases therefore should be taken into account when computing input-output nutrient budgets and soil acid neutralizing capacity.

1. INTRODUCTION

Magnesium and calcium play an essential role both in soil fertility (as major nutrients for plants and by improving the physical and biological properties of soils) and the acid neutralizing capacity of the soil. In the soil, plant-available pools of Mg and Ca are assumed to be stored on the cationic exchange capacity of the soil and are conventionally measured by ion-exchange soil extractions (NH_4Cl, NH_4oAc, $BaCl_2$, cobaltihexamine, etc.). In the long-term, Mg and Ca exchangeable pools are sustained by the weathering of primary minerals in the soil as well as atmospheric and possible anthropogenic inputs (Likens et al., 1977). Acid inputs to the soil either from atmospheric origin or related to net cation uptake by plants contribute to the depletion of Mg and Ca from exchangeable pools. This conceptual model is the base of input-output budgets (Bormann and Likens, 1967; Ranger and Turpault, 1999) from which soil acidification and the sustainability of soil chemical fertility is inferred in forest ecosystem studies. Although the acidity of atmospheric deposition has strongly decreased in the past decades (Waldner et al., 2014), natural recovery of ecosystems from soil acidification has not systematically been observed (van der Heijden et al., 2011; Jonard et al., 2012; Lawrence et al., 2015). Unlike sulphur, nitrogen deposition has not decreased in most cases (Vuorenmaa, 2004; Waldner et al., 2014) and deposition rates of Mg and Ca have decreased in many ecosystems (Hedin and Likens, 1996). In addition, forest policies encourage shorter silvicultural rotations and increased biomass harvest in forests (e.g. whole tree harvesting) in order to meet the increasing demand for bio-energy produced from wood products (Ericsson, 2004; COM, 2006; Puech, 2009). Such practices may in the long-term reduce the pools of plant-available nutrients in the soil (Feller, 2005; Kreutzweiser et al., 2008; Thiffault et al., 2011), delay the recovery of soils from past acidification or cause further soil acidification (biological acidification) (Löfgren et al., 2017). The long-term sustainability of forest soil fertility and soil acidification recovery is a major concern for future forest productivity and surface water quality.

The mass balance model has however been repeatedly questioned by data from long-term forest ecosystem monitoring sites (Paré and Thiffault, 2016; Löfgren et al., 2017). Divergent results of Mg and Ca depletion between empirical studies and theoretical models have been reported in numerous studies (Johnson et al., 1982; Johnson and Todd, 1998; Hazlett et al., 2011; van der Heijden et al., 2011). In a recent study of the impact of whole-tree harvesting on soil fertility in Sweden, Zetterberg et al. (2016) showed that, compared to the long-term empirical data, mass balances and dynamics models tend to exaggerate

exchangeable Ca depletion. Other studies have reported discrepancies between tree nutrition indicators and exchangeable pools of Mg and Ca in the soil (Lucash et al., 2012; van der Heijden et al., 2013b). The divergent results between the different approaches show the limits of (i) conventional methods to studying soil fertility and (ii) our knowledge of how trees cope with very low nutrient resources, and suggest that sources are not currently accounted for.

Ca nutrition in forests has been shown to rely mainly on atmospheric inputs (Kennedy et al., 2002; Drouet et al., 2015; van der Heijden et al., 2015) in particular in low-fertility ecosystems (Hynicka et al., 2016). As atmospheric inputs of Mg and Ca decrease and biological acidification processes intensifies, mineral weathering will become increasingly essential to tree nutrition and to mitigate soil acidification. Yet estimating mineral weathering inputs is challenging. Although most primary mineral dissolution rates have been experimentally measured, scaling rates to the soil environment is complicated, and requires in depth exploration of soil mineral phases, and process-oriented modeling. On one hand, many indirect field estimation methods (e.g. mass balance, zircon depletion, climate correlation, geochemical models) have been developed but important variations between methods have been reported (Klaminder et al., 2011). On the other hand, soil column leaching experiments in the laboratory (Kolka et al., 1996; van der Salm et al., 1998; Taylor et al., 2000) do not enable to isolate the mineral weathering flux from Mg and Ca desorption fluxes from the exchangeable pools. Though isotope ratios are a promising tool to trace these different sources (Blum et al., 2002; Ryu et al., 2011), natural variations of Mg, Ca and Sr isotope ratios are often too small to be able to accurately measure the mineral weathering flux (Holmden and Bélanger, 2010; Bolou-Bi et al., 2012). Isotopic labeling techniques on the other hand enable to overcome the small natural isotope variations and measure very small fluxes. For example, Gruber et al. (2013) measured the Si flux released during the experimental dissolution of albite from the isotopic dilution of the ^{29}Si labeled reactor inflow solution. However, to our knowledge, no study has attempted to measure the mineral weathering flux of Mg and Ca in the soil by isotopic dilution of Mg and Ca stable isotopes.

In a previous study of the forest at the Breuil-Chenue experimental site in the Morvan Mountains (Burgundy, France) we showed that, although soil base saturation and exchangeable Mg (33 kg ha^{-1}) and Ca (61 kg ha^{-1}) pools are very low in the rooting zone (0–70 cm) (van der Heijden et al., 2013b), it supports the growth of a 40-yr-old productive European beech (*Fagus sylvatica*) plantation. In the soil of this stand, Mg exchangeable pools have decreased between the 1970s and today while Ca