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INFLUENCE OF AFFORESTATION ON SOIL: THE CASE OF MINERAL WEATHERING

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Abstract

Although concerns have been raised that increased nutrient demand by fast growing tree species could deplete soil nutrient pools, recent research suggests that some species are able to obtain nutrients via soil mineral weathering. Hybrid poplars, which are fast growing and nutrient demanding species, are increasingly used in intensive silvicultural settings. Understanding whether hybrid poplars have an effect on long term nutrient availability and can promote soil mineral weathering is therefore important. We investigated the levels of base cations (i.e. K, Ca, Mg, and Na) of surface soils (0-20 cm) in 13 hybrid poplar plantations in Quebec, and compared the results with those of adjacent abandoned agricultural fields. To evaluate whether exchangeable base cation pools and non-exchangeable pools (i.e. those in the crystal lattice of minerals) were being depleted, we used a sequential leach with diluted salt ($BaCl_2$ for exchangeable) and weak acid solutions (HCl and HNO_3 for non-exchangeable). Levels of exchangeable and non-exchangeable cations were not statistically different between land use types. Exploratory analyses, however, revealed trends toward a greater depletion of Ca, Mg and Na in non-exchangeable forms following afforestation. The depletion of these non-exchangeable base cations due to afforestation occurred at sites where greater levels where initially present in soil. The results suggest increased soil mineral weathering due to greater amounts of minerals susceptible to dissolution and, in part, high clay content. Based on Ca, Mg and K concentrations of the different leaches and their molar ratios Ca/ΣAl+Fe, Mg/ΣAl+Fe and K/ΣAl+Fe), we propose a lesser role of soil mineral weathering on Ca cycling than Mg and K, which could lead to faster depletion of exchangeable Ca pools of the surface soil due to fast growth and high Ca demand by the poplars.

Keywords: Base cations, Intensive silviculture, *Populus*, Sequential leach, Long-term soil fertility, Tree nutrition.

1. Introduction

Throughout the world, the increasing demand for wood products and the growing pressures to set aside forested areas for conservation purposes are generating an increasing interest in fast-growing tree species. By 2050, FAO (2001) predicts that plantations will cover 5 to 10% of the world's forested land area and that close to 50% of commercially harvested wood will come from these plantations. For example, poplars (*Populus spp*.) have the ability to propagate from cuttings and can be used to create hybrids possessing very high growth rates (Reimenschneider et al., 2001; Stanturf et al., 2001). Poplar plantations therefore have the potential to quickly produce large amounts of fiber to be used in valuable wood products such as pulp, lumber, panels, and engineered wood products (Heilman, 1999; Zhang et al., 2003). However, concerns about the effects of such intensive plantations on long term nutrient availability and site productivity have been raised (Vanguelova and Pitman, 2009) and fertilization may be required to avoid nutrient depletion (Fox, 2000; Jokela et al., 2010).

The magnitude of the reduction in soil nutrient availability is likely influenced by the species involved and their growth rate. A study by Paré et al. (2002) on nutrient contents in stem wood of common North American temperate tree species suggests that Ca, Mg and K (hereafter referred to as base nutrients) immobilization rates in the stem in mesic sites follow the pattern *Picea mariana/Pinus banksiana* < *Abies balsamea* < *Betula* *papyrifera* < *Populus tremuloides*. This was demonstrated on a site index basis (15, 18, 21 and 24 m) at 50 years. In Minnesota, Alban (1982) showed a decrease in mineral soil Ca pools following rapid immobilization by trees in 40-year-old stands. In this case, mineral soil Ca pools followed the pattern *Populus tremuloides* < *Picea glauca* < *Pinus resinosa/Pinus banksiana*. Alban (1982) explained that Ca uptake by the roots and immobilization in the stem occurred at a greater rate with *Populus tremuloides* (and *Picea glauca*) because of faster growth and greater Ca requirements compared to the two *Pinus* species. This apparently led to the impoverishment of mineral exchangeable Ca pools, a phenomenon also observed by Ruark and Bockheim (1988) in Wisconsin with *Populus tremuloides*.

The negative correlation between soil nutrient availability and increased growth (and nutrient uptake) in intensive silviculture is not, however, consistent with all scientific literature. For example, intensive silviculture (Eriksson and Rosen, 1994) or aggrading natural stands (Paré and Bergeron, 1996) did not always result in impoverished mineral soil nutrient pools. The lack of effects of fast tree growth on mineral soil pools may be due to a high buffer capacity of the soil (e.g. high clay with high cation exchange capacity). However, if soils are poorly buffered (e.g. loamy sand with low cation exchange capacity), this lack of effect could also be due to the functional traits of the tree species. For example, *Picea abies* uses long-term strategies to maintain the soil exchangeable base nutrient pools intact such as the : (i) filtering of aerosols due to a canopy with a large surface area; (ii) increase of nutrient fluxes by increasing soil mineral weathering (Binkley and Giardina, 1998; Augusto et al., 2002); and (iii) possible reduction of nutrient leaching by using more water in fast growing sites (Bélanger et al., 2004).

Both in Europe and North America, some tree species were shown to favor soil mineral weathering, thus increasing the availability of some nutrients for tree growth. In France, Augusto et al. (1998; 2000) showed that *Picea abies*, *Pinus sylvestris*, *Quercus petraea*, *Quercus rubor*, *Fagus sylvatica* were capable of lowering soil pH and in turn, of dissolving test-minerals inserted in the soil. Results suggested that hardwood species were not as effective as conifers to lower soil pH and to dissolve the test-minerals. Similarly, Leyval and Berthelin (1991) showed enhanced weathering of phlogopite (mica) by *Pinus sylvestris* in test lysimeters. In North America, Quideau and Bockheim (1997) observed greater Ca losses under *Pinus resinosa* than under prairie vegetation following afforestation of prairie with pine. The Ca losses were attributed to increased soil mineral weathering due to afforestation. In sand-box experiments, Bormann et al. (1998) and Quideau et al. (1996) showed that two other North American *Pinus* species were also effective in releasing non-exchangeable base cations by promoting weathering reactions, whereas *Quercus berberidifolia* was slightly less effective.

The ability of tree species to increase nutrient fluxes by increasing soil weathering is likely an important mechanism by which trees may compensate rapid growth and nutrient uptake and, as such, avoid soil nutrient depletion, at least in the short-term (Bormann et al., 1998). The literature suggests that this process is more efficient under conifers (notably *Picea abies*) than deciduous tree species (Augusto et al., 2002; Bormann et al., 1998; Leyval and Berthelin, 1991), probably because the large amounts of low molecular-weight acid exudates that conifer roots produce act as effective chelating agents that enhance base cation release from the crystal lattice of soil minerals (Raulund-Rasmussen et al., 1998; Strobel et al., 1999). As a whole, however, studies on the effects of deciduous tree species on soil mineral weathering are lacking. For example, Dijkstra et al. (2003) studied the effects of different North American temperate deciduous species (along with *Tsuga canadensis*) in Connecticut, USA, but they found that the low weathering rates were more controlled by parent material than by tree species (despite differences in mycorrhizae, i.e. ecto vs. endo). The effects of different land uses and associated vegetation covers (e.g. forest, pasture or agriculture) on soil mineral weathering are also poorly elucidated (Kelly et al., 1998).

If the ability of tree species to increase nutrient fluxes by increasing soil weathering has often been overlooked for most species, even less is known about the potential of trees to induce soil mineral weathering across a range of soil productivity. Contradictory results have been reported in the literature. On the one hand, Finzi et al. (1998) found that the levels of exchangeable nutrients are positively correlated to the levels of total soil nutrients and thus suggested that more intense soil mineral weathering had to occur where soil productivity levels were at their highest. On the other hand, Wallander and Nylund (1992) and Wallander and Thelin (2009) observed that soil nutrient deficiency induced ectomycorrhizal growth in forest trees. Because mycorrhizae are well known to favor soil mineral weathering (Hoffland et al., 2004), the observations by Wallander and coworkers suggest that soil mineral weathering by trees (and associated ectomycorrhizae) is more intense where nutrient availability is low.

Soil weathering by trees has traditionally been considered to be a very slow process and unlikely to change over short periods of time (i.e. a few decades) (Mareschal et al., 2012). However, if some tree species augment soil mineral weathering relative to other species (e.g. relative to herbs, grasses and agricultural crop species in an afforestation context), they could lead to increased CO_2 sequestration, not just due to a change in C sequestration rates in biomass, but also because of the increased release and leaching of Ca (and Mg) and HCO_3^- from the soil system, which will eventually precipitate in oceans as carbonate minerals (Berner, 1997; Gaillardet et al., 1999). In this paper, we sought to assess the effects of afforestation (i.e. fast growing hybrid poplar plantations) on the soil base cation status (Ca, Mg, K, Na) by using a sequential leaching method that separates exchangeable cations from those in the crystal lattice of minerals. Contrary to most studies which focused on microscale experiments to explore the specifics of soil mineral dissolution by trees, this study uses a macroscale approach to show how different land use types (i.e. tree plantation vs. abandoned agricultural fields), soil properties and time influence mineral weathering. This approach allowed testing the following hypotheses: (i) hybrid poplars increase soil mineral weathering relative to plants that occupy nearby abandoned agricultural fields; (ii) soil mineral weathering induced by hybrid poplars is increased in base poor soils.

2. Material and Methods

2.1 Site selection and location

Plantations were selected in order to cover the largest possible range in terms of age, soil texture and climatic conditions. Plantations were either commercial plantations established by private producers or forest companies or experimental plantations established by the Quebec Ministry of Natural Resources for clonal testing (Boutin et al., 2006). Plantations were established with various hybrids of *P. maximowiczii* crossed with *P. deltoides*, *P. nigra*, and *P. balsamea*. Prior to plantation, each agricultural field had been abandoned. A total of thirteen plantations aged from 1 to 22 years with different growth rates were selected for the study (Table 1, Fig. 1). Most soils are Podzols or Gleysols (Soil Classification Working Group 1998), have clay, loam or silt textures and are well drained with the exception of the Gleysols (Table 1). The age sequence was used to infer the prolonged effects of poplar growth and nutrient sequestration on soil nutrient availability.

2.2 Soil sampling and analysis

Three 400 m^2 circular plots were established in each of the thirteen plantations: two were located within the plantation, and one was established in an adjacent non-planted abandoned agricultural field to serve as a control. Within the plantations, plots were located approximately 50 m apart, in areas showing the least variability in tree size. This procedure was chosen to avoid areas with high tree mortality which could have masked afforestation effects on soil weathering. The location of the control plot was carefully selected for the best representativity of conditions prior to poplar planting at each site. Specifically, the control plot was installed in the nearest abandoned agricultural field, approximately 30 m from the plantation, where soil texture assessed in the field was thought to be similar to the plantation. Soil texture assessed in the laboratory (see below for details) later confirmed that it was similar between treatments (c.v. <50%).

Within each plot, soils were sampled at four locations at a distance of 2 m from the center of the plot and aligned along north-south and east-west axes. Mineral soil samples were collected at 0-20 cm depth [corresponding to the Ap horizon or plowed layer, Soil Classification Working Group (1998)] using a steel cylinder (diameter 4.8 cm; length 25 cm). Samples were then taken to the soil laboratory where they were kept at 4°C. Prior to analysis, soil samples were oven dried at 70°C for 72 h and sieved through a 2-mm mesh to remove any coarse fragments. For each plot, soil samples were analyzed individually.

In order to determine the concentration of exchangeable (i.e. adsorbed on exchange surfaces) and non-exchangeable (i.e. contained in the crystal lattice of minerals) base cations (i.e. Ca, Mg, K, and Na) and acid cations (i.e. Al, Fe) in the mineral soil, we combined the sequential leaching procedure developed by Nezat et al. (2007) to selectively dissolve minerals from soils, notably apatite, with a simple weak HCl leach to dissolve calcite (Drouet et al., 2005) and possibly apatite (Bélanger et al. 2012). Nezat et al. (2007) separated individual silicate minerals from granitic material, assessed the chemistry of each mineral, and sequentially leached synthetic mineral mixtures to link mineral dissolution to each leach. Apatite, including free apatite and armoured apatite found along grain boundaries or mineral fractures, was almost entirely dissolved with 1 N HNO_3 at 20°C for 20 h at a soil:solution ratio of 10. Weaker leaches such as 0.1 HNO_3 failed to dissolve apatite and are therefore only appropriate for soils containing calcite or other readily dissolved minerals. The method was validated using soils from the Hubbard Brook Experimental Forest where the mineralogy is well known and other soils from northeastern U.S.A. (Nezat et al., 2008). Their work along with subsequent field studies (Bélanger and Holmden, 2010; Holmden and Bélanger, 2010) helped determine that other minerals are being leached in each sequential steps. The latter studies specifically showed that small amounts of hornblende, biotite (or chlorite or vermiculite) and epidote are also attacked with a 1 N HNO_3 leach.

In our study, exchangeable cations were initially extracted from a 3-g sample for 2 h using 30 mL of unbuffered 0.1 M $BaCl_2$ (Hendershot et al., 2007). Then, cations from highly soluble minerals such as free calcite were retrieved using 30 mL of 0.1 N HCl for 2 h. Finally, cations from more refractory minerals such as apatite, hornblende, biotite and epidote were retrieved using 30 mL of 1 N HNO_3 for 2 h. Plagioclase feldspars, K-feldspars, muscovite, quartz and other refractory minerals are only marginally attacked by these leaches (Nezat et al. 2007). All leaches were done on an end-over-end shaker at room temperature (20-21°C). Cations were determined by atomic absorption (Ca, Mg, Al, Fe) and emission (K, Na) (Varian AA240FS Sequential Atomic Spectrometer). The method is used to provide operationally-defined mineral groupings of weathering susceptibilities. In reality, acid leaches cannot be used to abruptly divide mineral groups as easily because a relative continuum of mineral susceptibilities to weathering exists. This continuum reflects the chemical structure as well as the "historical" exposure of the surface to weathering agents and in turn, the weakening of the crystal lattice of the mineral prior to the leaching steps. For example, the 1 N HNO_3 leach only partially dissolves biotite and subsequent, stronger leaches (e.g. concentrated HNO_3 and HF), are generally required to completely dissolve the mineral [as seen from dissolution results of mineral separates from Nezat et al. (2007)]

The sites were also characterized in terms of soil texture, bulk elemental composition and mineralogy. Particle size distribution was determined using the Horiba Partica LA-950 Laser Particle Analyzer. Because all samples had <2% C content, no pretreatment was needed to break down aggregates. Instead, sodium hexametaphosphate (4 mg per sample cell) and sonication for 1 min at level 7 were used on all samples for particle dispersion before measurement. Bulk elemental composition was determined on 32-mm-diameter fused beads prepared from a 1:4 soil:lithium tetra(meta)borate mixture heated at 1000°C for 18 minutes. An automated X-ray fluorescence Philips PW2440 spectrometer system with a Rhodium 60 kV end window X-ray source, operating at 3 kW, was used for analysis. The bulk elemental compositions were then used to assign elements to their respective minerals using the UPPSALA norms for soils (Sverdrup and Warfvinge, 1992). Similar to CIPW norms, UPPSALA is a normative back-calculation model for reconstructing empirical soil mineralogy from bulk elemental composition. It is based on the stoichiometric compositions of soil minerals of granitic origin (i.e., Swedish Precambrian Shield). The minerals are grouped based on similar composition and dissolution rates. Muscovite includes muscovite, secondary dioctahedral chlorite, and vermiculite of secondary weathered type. Chlorite is composed of trioctahedral chlorite, primary illite, trioctahedral vermiculite of primary type, and biotite, phogopite and glauconite. Also, hornblende includes all amphiboles (e.g. hornblende, glaucophane and tremolite), and epidote includes all epidotes (e.g. epidote, pyroxenes and zoisites). The UPPSALA norms are in the following order (the oxide and mineral units are in per cent, %):

$$\text{K-feldspars (KF)} = 5.88 \times K_2O - 0.588 \times Na_2O$$

$$\text{Plagioclase (PL)} = 11.1 \times Na_2O - 0.22 \times KF$$

$$\text{Apatite (AP)} = 2.24 \times P_2O_5$$

$$\text{Hornblende (HO)} = 6.67 \times CaO - 3.67 \times AP - 0.2 \times PL$$

$$\text{Muscovite (MU)} = 2.08 \times K_2O - 0.208 \times Na_2O$$

$$\text{Chlorite (CL)} = 3.85 \times MgO - 0.39 \times HO - 0.39 \times MU$$

$$\text{Epidote (EP)} = 0.1 \times HO + 0.03 \times OL - 0.3$$

$$\text{Calcite (CA)} = 1.79 \times CaO - 3.67 \times AP - 0.2 \times PL$$

$$\text{Quartz (QU)} = SiO2 - 0.63 \times PL - 0.68 \times KF - 0.38 \times MU - 0.33 \times CL - 0.45 \times HO - 0.42 \times EP$$

The sum of these minerals is then rounded to 100%. Semi-quantitative X-ray diffraction results and UPPSALA norms were compared by Houle et al. (2012) in Quebec. It was concluded that the UPPSALA norms apply well to the granitoid soils of Quebec.

2.3 Data analysis

The plantation setup allowed testing for the effect of time since poplar planting on soil characteristics. We therefore performed a series of analyses of covariance (ANCOVA) to test for differences in exchangeable and non-exchangeable cations between land use types, using time as a covariate. These analyses, however, did not reveal any significant differences ($p > 0.14$) between treatments. In this context, molar ratios (i.e. Ca/ΣAl+Fe, Mg/ΣAl+Fe and K/ΣAl+Fe) were tested, again using ANCOVA and time as a covariate, as an attempt to homogenize the soil data across the sites. Residuals were tested for normality and homogeneity of variances. The data were log or square-root transformed when necessary.

Exploratory analyses were also performed to identify potential changes in cation concentrations following leaches. Specifically, the direction and magnitude of change in cation concentrations were examined graphically using scatter plots as described in Ens et al. (2013). The thirteen sites included in this study represent a wide range of climatic conditions, parent material and soil texture, which affect cation concentrations with plantation establishment. The net effect on cation concentrations depends upon the initial conditions of the soil (i.e. initial concentration of Na, K, Mg, and Ca), the exchange capacity of the soil, and the ability of poplars to alter the soil (i.e. by uptake, weathering, biocycling, etc.). By using the control plots as proxies for initial cation concentrations, it was possible to represent change from plantation establishment as a function of initial conditions. We therefore produced scatter plots where initial concentrations of the control plots are on the *x*-axis and concentrations of the plantations are on the *y*-axis. Linear regression of the controls (*x*-axis) and plantations (*y*-axis) yields a line that can be visually and statistically compared to the 1:1 line (i.e. the control plots), with any deviation from the 1:1 line indicating a change resulting from plantation establishment. Differences in slope, tested against a slope of 1.0, also describe the nature of the change. A slope <1.0 means that there is more depletion at higher initial concentrations, whereas a slope >1.0 means that there is increased concentrations with high initial concentrations. A slope of one indicates that any change is independent of initial conditions.

Statistical analyses were performed using JMP 7.0.1 (SAS Institute, Cary, North Carolina).

3. Results and Discussion

3.1 Soil exchangeable and non-exchangeable cation concentrations

Scatter plots and slope analyses between the exchangeable and non-exchangeable cations in abandoned agricultural fields and those of plantations revealed an interesting response pattern of soils to land use change. Specifically, a higher non-exchangeable cation concentration in some abandoned agricultural field soils (*x* axis) was associated with a lower cation concentration in respective plantation soils. This was the case for Ca, Mg and Na with the HCl and HNO_3 leaches, and K with the HCl leach (Figs. 2 to 5).

These results suggest that hybrid poplars are able to promote soil mineral weathering relative to plant species in abandoned agricultural fields. This ability, however, appears to be associated with soil characteristics. Indeed, a depletion of the pools of non-exchangeable base cations was observed only at sites where soils initially had high non-exchangeable base cation levels as represented by the abandoned agricultural field soils (Figs. 2 to 5). This is in agreement with the findings of Finzi et al. (1998) that trees induce greater soil mineral weathering on richer soils, but contradictory to those of Wallander and coworkers that trees induce soil mineral weathering on poor soils where base cation deficiencies may be a concern (Wallander and Nylund, 1992; Wallander and Thelin, 2009). Hence, our results suggest that induced soil mineral weathering and base cation release by hybrid poplar roots may be a mechanism that operates more efficiently on richer soils. Ste-Marie et al. (2007), in agreement with Bélanger et al. (2004), observed that nutrient demanding stands increased soil nutrient exchangeable pools even on poor sites. Our results suggest that the contribution of soil mineral weathering to the maintenance of exchangeable soil nutrient pools may be lower on poor than on rich soils.

In this study, the differences in non-exchangeable Ca, Mg, K and Na between the plantations and agricultural fields suggest that they were most likely released from more soluble minerals (e.g. calcite, apatite, epidote, hornblende, phyllosilicates such as biotite) rather than recalcitrant minerals (e.g. plagioclase feldspars, K-feldspars, muscovite) because the later minerals are not being efficiently attacked by the leaching treatments (Bélanger and Holmden, 2010; Nezat et al., 2007). The high amounts of non-exchangeable base cations measured in the richer abandoned agricultural field soils therefore indicate that Ca, Mg, K and Na containing minerals that are susceptible to weathering are more abundant in these soils (see Table 2 and Figs. 2 to 5). Because the *Populus* genera can produce acid root exudates with chelating powers (Qin et al., 2007), such minerals are therefore presumably more vulnerable to dissolution in the plantations relative to the abandoned agricultural field soils. Bulk elemental composition and UPPSALA simulations show a large range in soil chemical and mineralogical conditions across the sites, with some being more felsic than others (Table 2). The fact that trees induce greater soil mineral weathering on richer soils can be confirmed with the UPPSALA mineralogy (Table 2) and, in part, particle size distribution (Table 1). The site that showed the greatest difference between land use types is SHW, followed by NORM and SJG2 and finally SCH1 (Fig. 2 to 5):

(1) SHW — At that site, the lower non-exchangeable cation concentrations in the plantation, especially for Ca, can be explained by a soil mineralogy with high amounts of more easily weathered minerals such as apatite, epidote and hornblende, all of which contain large amounts of Ca. Moreover, this site has the highest clay content (52%). This translates into a greater area of reactive surfaces which is conducive to greater attack and

dissolution of minerals by acid root exudates. Because Ca is the dominant base cation in the HCl leachate (compare Fig. 5 to Figs. 2-4), calcite could also be an important source of Ca (Drouet et al., 2005). UPPSALA has been known to underestimate or even omit calcite where it is actually present and significantly releasing Ca into the soil solutions (Bélanger et al., 2012);

(2) NORM and SJG2 — These sites showed lower non-exchangeable Mg, and to a lesser extent Na, concentrations in the plantation. The NORM site has a low clay content (6%) relative to most other sites (average of 20%), whereas SJG2 is close to average at 23% clay. In either case, one has to turn to soil mineralogy to explain the impacts of afforestation of mineral weathering. Indeed, both sites have amongst the highest hornblende and epidote contents, which contain significant amounts of Mg (Note: with the UPPSALA classification, epidote also includes all ferromagnesian pyroxenes). The sites also have high plagioclase, which some species are rich in Na. Plagioclase minerals were shown to play a role in releasing base cations (notably Ca) to forest ecosystems, but the process is believed to be slow (Bailey et al., 1996), likely too slow to detect an effect induced by 22 years of afforestation or less;

(3) SCH1 — This sites showed lower non-exchangeable Mg concentrations in the plantation. It has relatively high clay at 31% and exhibits the highest MgO and chlorite content of all the sites. It is impossible to determine whether it is primary or secondary chlorite. Nevertheless, the combination of having high surface area due to high clay and the presence of a Mg saturated phyllosilicate mineral (chlorite) appears to have been conducive to trees promoting the release of non-exchangeable Mg.

It should be reminded that the UPPSALLA norms are based on bulk chemistry only and thus, the model yields a normative mineralogy for the bulk soil, not the clay fraction specifically. It would seem reasonable to think that the easily weathered minerals are clay sized for most sites. However, the relationship between soil texture and easily weathered minerals was not straightforward for the four sites showing a response to afforestation, i.e. SHW had the highest clay content, NORM had the lowest clay content, and SJG2 and SCH1 sites had average clay content. We therefore suggest that mineralogy (bulk) is the most useful variable explaining induced weathering by afforestation and that clay content interacts only at some sites.

The high productivity at SCH1 relative to most sites (Table 1) could have facilitated soil mineral weathering. However, the most productive STN site is an older site — yet, the accumulation of root biomass did not appear to induce soil mineral weathering more than the plants in the abandoned agricultural field. The more felsic nature of the STN soils (72.0% SiO_2 or 43.6% quartz) compared to those of SHW, NORM and SJG2 (59.6 to 63.4% SiO_2 or 16.4 to 27.6% quartz) could partly explain the lack of sensitivity of soil minerals to afforestation at that site (Table 2).

3.2 Elemental molar ratios and cycling of base cations

Average molar ratios (i.e. Ca/ΣAl+Fe, Mg/ΣAl+Fe and K/ΣAl+Fe) following the HCl and HNO_3 leaches were between 18.9 and 22.0% lower under plantations than abandoned agricultural fields, except for the K/ΣAl+Fe ratio of the HCl treatment with plantations having the highest ratios (Table 3). Some molar ratios (i.e. Ca/ΣAl+Fe of the HCl and HNO_3 leaches and K/ΣAl+Fe of the HNO_3 leach) were also marginally statistically lower ($p \leq 0.13$) under plantations than abandoned agricultural fields (Table 3). Because weathering indices are based on the principle that the ratio between levels of mobile (Si, Ca, Mg, K and Na) and immobile elements (Al, Fe, Zr and Ti) decrease with time due to more leaching (Birkeland, 1999; Chittleborough, 1991), these results partially reinforce the idea that the process of Ca, Mg and K removal/mobilization from the crystal lattice of minerals is more exhaustive under hybrid poplars than abandoned agricultural field. The lower molar ratios of the HCl and HNO_3 leaches under plantations could be due to a weathering "residue" that is impoverished in easily weathered minerals and thus enriched in recalcitrant aluminosilicates with high and low molar ratios, respectively (Munroe et al., 2007). A selective removal of Ca, Mg and K relative to Al and Fe through incongruent dissolution is a less likely mechanism. Such indices may be more sensitive variables than individual base cations to investigate the influence of afforestation on soil mineral weathering and should be considered for future studies.

All average molar ratios decreased in absolute terms in the order $BaCl_2$ > HCl > HNO_3 (Table 3). This reflects Al and Fe increasing in the order $BaCl_2$ < HCl < HNO_3 and Ca concentrations largely decreasing in the order $BaCl_2$ > HCl > $HNO_{3,}$ whereas Mg and K concentrations did not vary much across the leaches. As a whole, these trends suggest that, as the leach got stronger, aluminosilicates with lower leachable amounts of Ca (relative to the soil exchangeable complex) were being dissolved. On the one hand, this is indicative of a large long-term build-up of an exchangeable pool of Ca by plants (Jobbágy and Jackson, 2004) and that plants in these systems now rely heavily on that pool and its internal cycling to satisfy their nutritional demand. On the other hand, the more homogeneous Mg and K concentrations across the $BaCl_2$, HCl and HNO_3 leaches imply a larger role of soil mineral weathering on plant Mg and K nutrition for these systems.

Markewitz et al. (1998) showed that 34 years of tree growth (*Pinus taeda*) significantly decreased soil pH and effective base saturation in the surface soil at the Calhoun Experimental Forest. Soil exchangeable Ca and Mg depletions were also large, whereas exchangeable K depletions were negligible. The sum of Ca and Mg removals from immobilization in wood and the forest floor as well as net leaching (the latter being linked to acid deposition) were relatively well balanced with depletions, suggesting that mineral weathering and biocycling failed to match losses (Richter and Markewitz, 2001). Likewise, we speculate that the release of Ca from mineral weathering and biocycling was also outpaced by removals of Ca by the hybrid poplar plantations in our study. However, this inference is based on Ca/ΣAl+Fe ratios alone (i.e. non-significant decline of 15% following afforestation for the $BaCl_2$ leach, see Table 3) and not from individual exchangeable Ca, and therefore clearly implies that acidification of the Quebec soils due to afforestation is not as severe as Calhoun soils. The fact that Quebec soils were "recently" glaciated and contain fresh and unaltered minerals (Brais et al., 2009) could be one reason for the greater buffer capacity compared to Calhoun soils (kaolinite-dominated). Shorter tenure of the poplar trees (1 to 22 years) compared to pine at the Calhoun site (34 years) could be another. In the Canadian Prairies, Steckler et al. (submitted) built a complete nutrient budget to show no expected impact of hybrid poplar plantations on soil exchangeable Ca and Mg due to large Ca and Mg weathering fluxes of calcareous soils. The Ca and Mg budgets were slightly negative, neutral or positive, depending on site characteristics, growth rates and harvesting treatments. However, the weathering fluxes far surpassed weathering rates calculated for various soils in Quebec (Courchesne et al., 2002; Houle et al., 2012). *Populus* species generally have high Ca demand (Bowersox and Ward, 1977; Lamarche et al., 2004; Pinno et al., 2010; Zasada et al., 2001) and thus, the monitoring of soil exchangeable and foliar Ca levels may prove important in the long term in hybrid poplar plantations of Quebec.

Conversely, Quebec soils generally have a high content of Mg and K bearing minerals as they generally originate from granitoid rocks, rich in hornblende and chlorite, containing Mg, as well as biotite, illite and some more recalcitrant muscovite or alkali feldspars, containing K (Brais et al., 2009). This is supported by the relatively large concentrations of MgO and K_2O (relative to CaO) of the studied soils as well as their large estimated amounts of K-feldspars, muscovite, hornblende and chlorite (which contains illite and biotite according to UPPSALA classification) (Table 2). This data along with (i) the more homogeneous Mg and K concentrations across the $BaCl_2$, HCl and HNO_3 leaches compared to Ca and (ii) the lack of a decreasing effect of trees (relative to plants of the abandoned agricultural land) on Mg/ΣAl+Fe and K/ΣAl+Fe ratios of the $BaCl_2$ leach relative to Ca/ΣAl+Fe (Table 3) are consistent with soil systems where mineral weathering impacts Mg and K cycling more than Ca cycling.

Indeed, the generally higher concentrations of K in abandoned agricultural fields with the $BaCl_2$ and HCl leaches indicate that the K released from minerals can be efficiently cycled and retained by the hybrid poplar trees in surface soil. Potassium, which is found in very low concentration in wood (typically <0.1%), is highly mobile within trees and cycles rapidly in the plant-soil system (Likens et al., 1994; Maliondo et al., 1990; Ruark and Bockheim, 1988). The high K levels in foliage of *Populus* lead to high K returns to the soil via litterfall [as much as 30 kg ha^{-1} yr^{-1} according to Berthelot et al. (2000)] and can buffer a loss in exchangeable K at the soil surface because of high K demand by fast growing poplar trees (Camiré and Brazeau, 1998; Steckler et al., submitted). At the Calhoun Experimental Forest, for example, Richter and Markewitz (2001) attributed the negligible change in exchangeable K at the soil surface (despite large immobilization in pine biomass and forest floor) to a significant source of K from weathering of K-bearing minerals and effective biocycling by the pine trees. These authors also found that Mg sources and recycling better matched Mg removals from immobilization in the trees and forest floor as well as leaching than Ca, which could imply, like this study, a larger role of mineral weathering for Mg cycling. Finally, complex reactions involving K occurs in soils of cold temperate regions to form secondary (clay) minerals. The generally higher concentrations of K in abandoned agricultural fields with the HCl leach (Fig. 3) possibly indicate that the soil conditions are adequate for some K ions, brought about by hybrid poplars from mineral weathering and biocycling, to become structurally bound into secondary minerals (Wilson, 2004).

4. Conclusion

Both in Europe and North America, some tree species were shown to favor soil mineral weathering, thus increasing the availability of some nutrients for tree growth (e.g. Augusto et al., 1998, 2000; Bormann et al., 1998; Leyval and Berthelin, 1991; Quideau and Bockheim, 1997; Quideau et al., 1996). As tree species with high growth rates are generally accompanied by large nutrient uptake rates, those capable of releasing nutrients contained in soil minerals could be less vulnerable to nutrient depletion.

In our study, the main soil factors that can explain different site responses to hybrid poplar growth include soil particle size distribution, chemistry and mineralogical composition. Root growth and biomass, root exudate production and nutrient uptake rates, which are all linked to overall poplar productivity, are also important biological factors to consider. Improved base cation availability, notably Ca, can possibly support higher *Populus* yields, but also lead to faster depletion of the soil exchangeable complex. The overall regression results suggest that hybrid poplars are able to promote soil mineral weathering relative to abandoned agricultural field vegetation; this ability could well be related to *Populus*' high growth and nutrient uptake rates. Higher root biomass could lead to an increased production of acid root exudates, which was shown to enhance soil mineral weathering. However, our results also suggest a lesser role of soil mineral weathering on Ca cycling than Mg and K, which could lead to faster depletion of exchangeable Ca pools of the surface soil due to fast growth and high Ca demand by the poplars.

It is not yet fully elucidated why soil mineral weathering is favored relative to plants in abandoned agricultural fields only at some sites. Growth rates, nutrient demand, root exudates production, mycorrhizal associations, and differences in plant community composition could play a role, but the limited number of sites and interactions between soil productivity, plantation age and yields did not allow establishing a statistical relationship of these factors with soil mineral weathering. Only soil mineralogy and clay content could be linked to the dissolution of Ca, Mg and Na containing minerals. Our findings confirm Finzi et al.'s (1998) observation that trees induce soil mineral weathering on richer soils as well as Mareschal et al.'s (2012) suggestion that changes in soil chemistry induced by mineral weathering can be detected fairly rapidly (i.e. less than 20 years) following the establishment of the plantation.

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Table 1
Summary of study site features

Site	Age (yr)	Plantation type	Soil type	Particle size distribution (%)			Drainage	Mean annual increment (m^3 ha^{-1} yr^{-1})
				Sand	Silt	Clay		
AG2	1	Commercial	Glayed Regosol	20	62	18	Variable	0.2
FP7	2	Commercial	Orthic Gleysol	16	57	27	Poor	0.2
SCH4	4	Commercial	Podzol	29	46	25	Good	4.1
HPC	5	Commercial	Podzol	32	41	27	Good	4.3
SJG2	5	Commercial	Brown Podzolic and Podzol	34	44	22	Good to moderate	1.8
SCH2	6	Commercial	Podzol	36	53	11	Good	4.4
FP2[1]	6	Commercial	Orthic Gleysol	57	33	4	Poor	5.9
SCH1	7	Commercial	Podzol	26	43	31	Good	15.0
NORM[1]	10	Experimental	Podzol	48	37	6	Good	6.5
SHW	13	Experimental	Brown Podzolic	11	37	52	Good	6.3
PLA8	14	Experimental	Red-yellow Podzolic	34	56	10	Good to imperfect	8.3
STN	17	Experimental	Grey-brown Podzolic	27	52	21	Good to excessive	21.5
STH	22	Experimental	Grey-brown Podzolic	52	43	5	Good to excessive	11.5

[1] Particle size distribution does not sum up to 100% because of pebbles in the soil matrix

Table 2
Soil bulk elemental composition and normative (UPPSALA) mineralogy

Site	Total chemistry								
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	MnO
	g kg^{-1}							mg kg^{-1}	
AG2	733	125	50,5	14,8	10,5	19,4	16,0	1485	1750
FP7	798	95,3	36,1	11,9	5,15	15,8	12,9	1070	300
SCH4	769	94,3	46,1	14,4	11,6	17,6	16,9	2725	955
HPC	769	94	46,1	14,4	11,6	17,6	16,9	2725	955
SJG2	690	156	49,2	17,3	7,3	10,7	30,2	1480	325
SCH2	740	102	61,3	16,8	11,6	17,6	17,8	2620	1695
FP2	720	127,1	40,2	9,40	24,4	26,4	25,3	1445	680
SCH1	750	93,6	50,1	29,0	11,5	17,2	17,4	1460	1060
NORM	634	156	63,1	24,4	31,1	31,5	25,4	2145	1125
SHW	596	170	64,3	28,4	44,2	33,0	30,4	2670	1030
PLA8	690	156	49,2	17,3	7,25	10,7	30,2	1480	325
STN	720	127	40,2	9,4	24,4	26,4	25,3	1445	680
STH	728	124	42,1	9,4	21,7	24,4	23,8	1710	800
	Mineralogy (%)								
	Quartz	K-Feldspar	Plagioclase	Muscovite	Hornblende	Chlorite	Apatite	Epidote	Calcite
AG2	58,1	9,27	22,1	3,28	2,06	4,28	0,37	0,53	0,00
FP7	68,3	7,24	17,4	2,56	0,00	3,97	0,26	0,20	0,00
SCH4	60,9	9,60	19,0	3,40	2,10	3,83	0,66	0,46	0,00
HPC	19,5	11,6	37,7	4,10	23,2	0,00	0,45	3,13	0,30
SJG2	24,7	17,5	31,5	6,20	15,4	1,76	0,79	2,15	0,00
SCH2	58,3	10,5	19,3	3,70	2,25	4,85	0,66	0,47	0,00
FP2	69,4	8,50	16,9	3,01	0,00	1,67	0,29	0,19	0,00
SCH1	55,4	9,77	18,1	3,46	3,24	9,18	0,35	0,55	0,00
NORM	27,2	14,1	34,6	5,00	13,5	2,90	0,52	2,07	0,00
SHW	16,0	16,9	35,0	5,97	21,9	0,73	0,63	2,92	0,00
PLA8	56,2	20,1	9,45	7,13	2,36	4,11	0,39	0,17	0,00
STN	41,4	13,9	27,6	4,93	10,2	0,00	0,34	1,54	0,00
STH	45,7	13,3	25,8	4,72	8,70	0,00	0,41	1,32	0,00

Table 3
Means (± 1 S.E.) of molar ratios and results of ANCOVAs using time as a covariate

Variable	Extraction treatment					
	$BaCl_2$		HCl		HNO_3	
	Abandoned	Plantation	Abandoned	Plantation	Abandoned	Plantation
Ca/ΣAl+Fe	210.1 (86.7)	178.9 (39.9)	0.452 (0.128)	0.355 (0.069)	0.025 (0.006)	0.020 (0.004)
	p = 0.43		p = 0.09		p = 0.13	
Mg/ΣAl+Fe	19.4 (6.7)	23.7 (9.9)	0.069 (0.016)	0.056 (0.010)	0.051 (0.013)	0.041 (0.009)
	p = 0.89		p = 0.17		p = 0.23	
K/ΣAl+Fe	3.0 (1.2)	2.7 (0.7)	0.012 (0.002)	0.015 (0.002)	0.009 (0.002)	0.007 (0.001)
	p = 0.54		p = 0.23		p = 0.07	

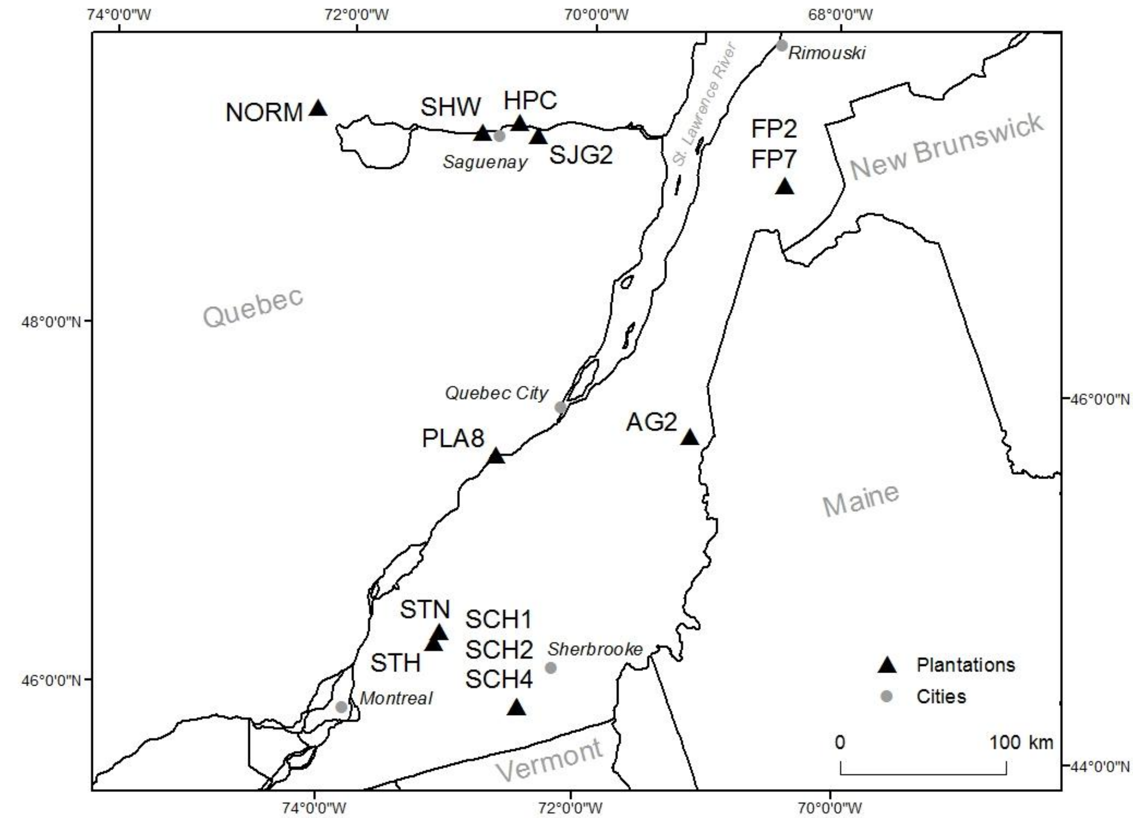

Fig. 1. Location of study sites

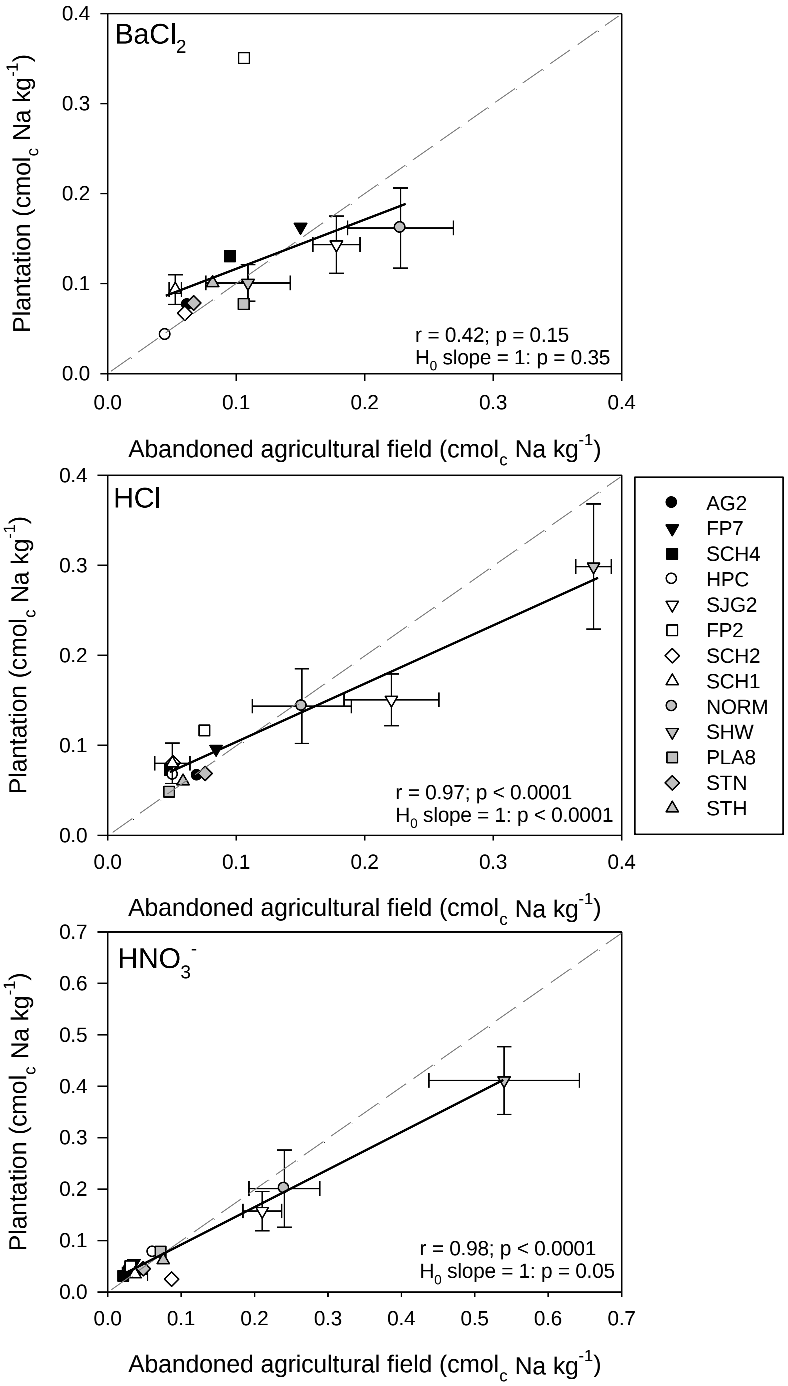

Fig. 2. Relationship for leached (i.e. $BaCl_2$, HCl and HNO_3) soil Na concentrations between abandoned agricultural fields and plantations. The grey dashed line is the 1:1 line. Standard deviation along the *x* and *y* axes are given only for the four sites showing an effect of afforestation, i.e. SJG2, SHW, NORM and SCH1. Black symbols denote plantations that are <5 years-old; open symbols denote plantations that are ≥5 and <10 years-old; grey symbols denote plantations that are ≥10 years-old

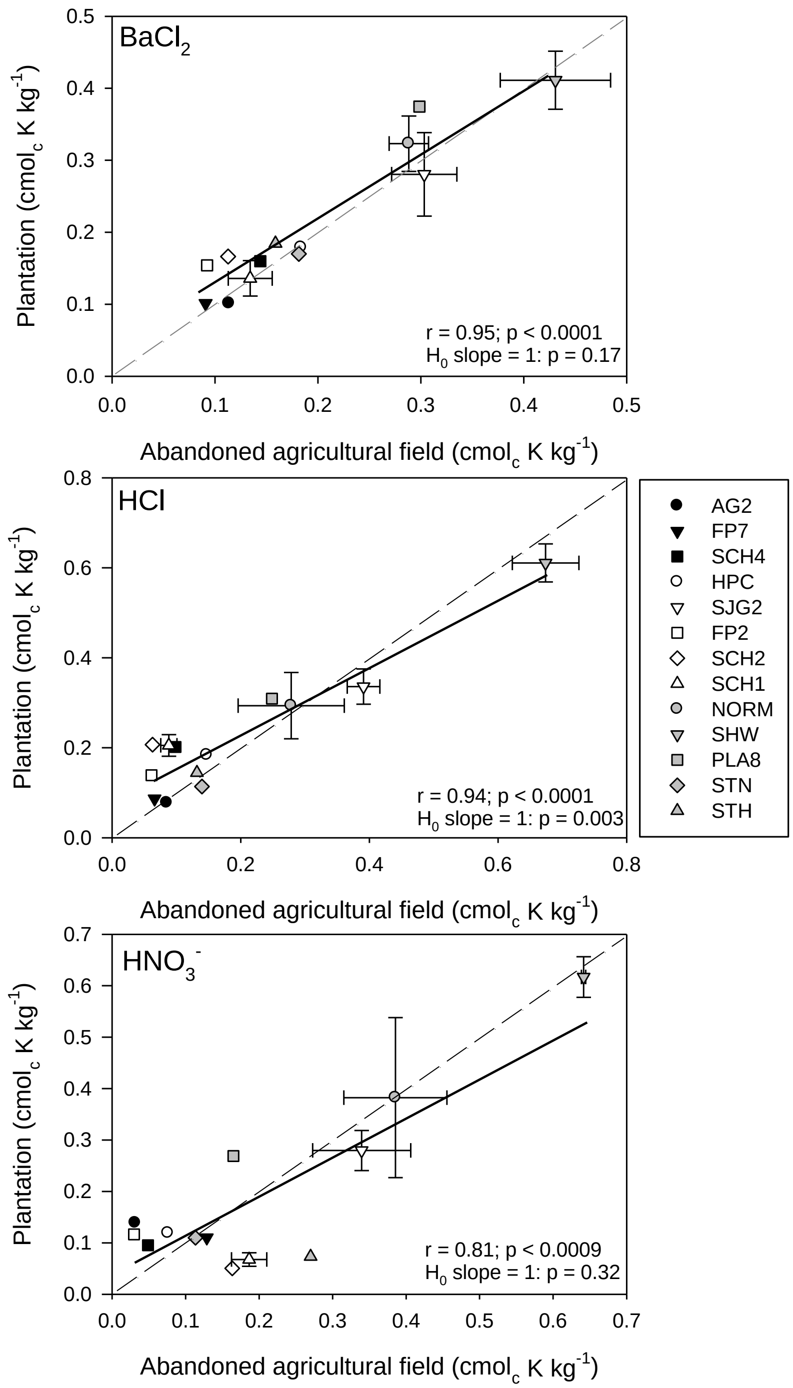

Fig. 3. Relationship between abandoned agricultural field soil K concentration and plantation soil K concentration. The grey dashed line is the 1:1 line. Standard deviation along the *x* and *y* axes are given only for the four sites which are discussed in further details, i.e. SJG2, SHW, NORM and SCH1. Black symbols denote plantations that are <5 years-old; open symbols denote plantations that are ≥5 and <10 years-old; grey symbols denote plantations that are ≥10 years-old

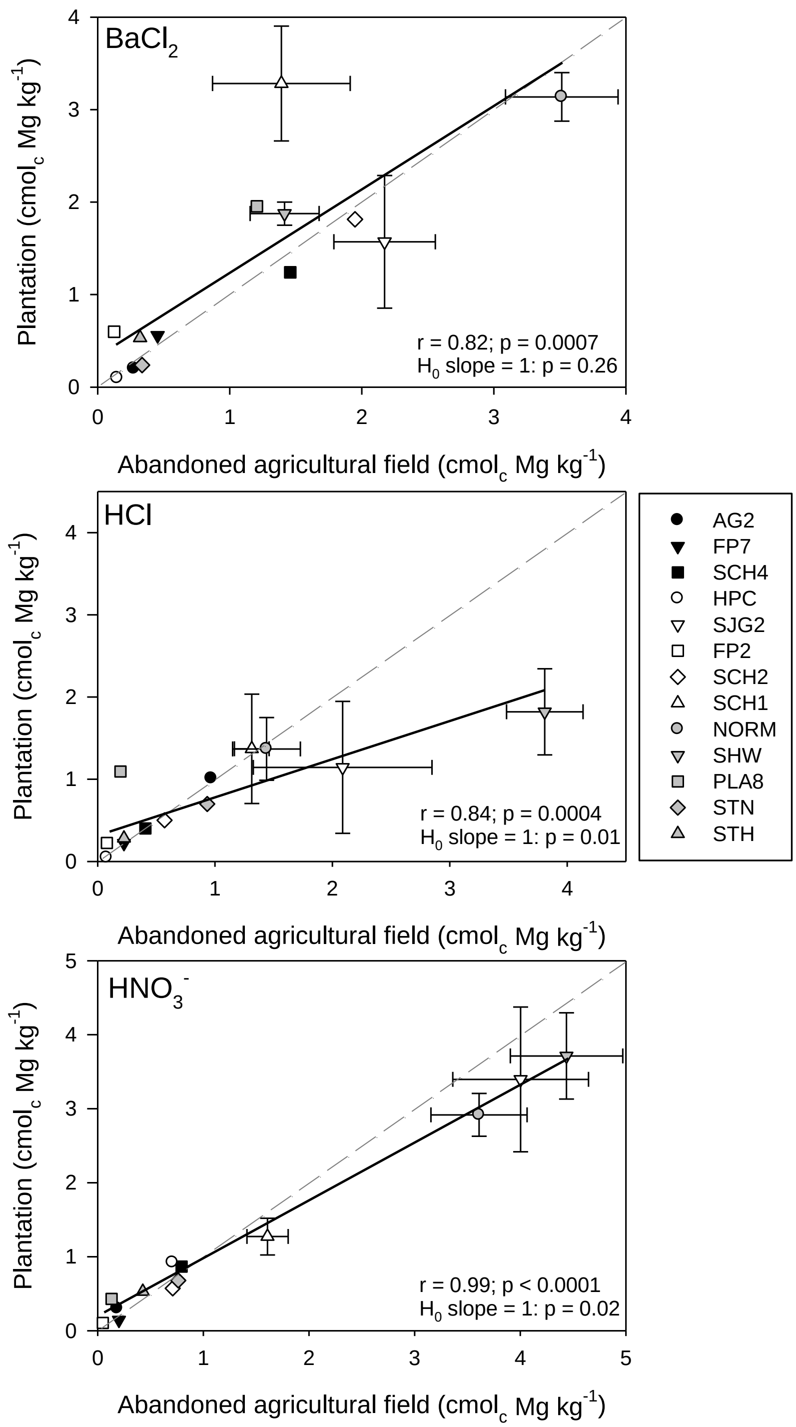

Fig. 4. Relationship between abandoned agricultural field soil Mg concentration and plantation soil Mg concentration. The grey dashed line is the 1:1 line. Standard deviation along the *x* and *y* axes are given only for the four sites which are discussed in further details, i.e. SJG2, SHW, NORM and SCH1. Black symbols denote plantations that are <5 years-old; open symbols denote plantations that are ≥5 and <10 years-old; grey symbols denote plantations that are ≥10 years-old

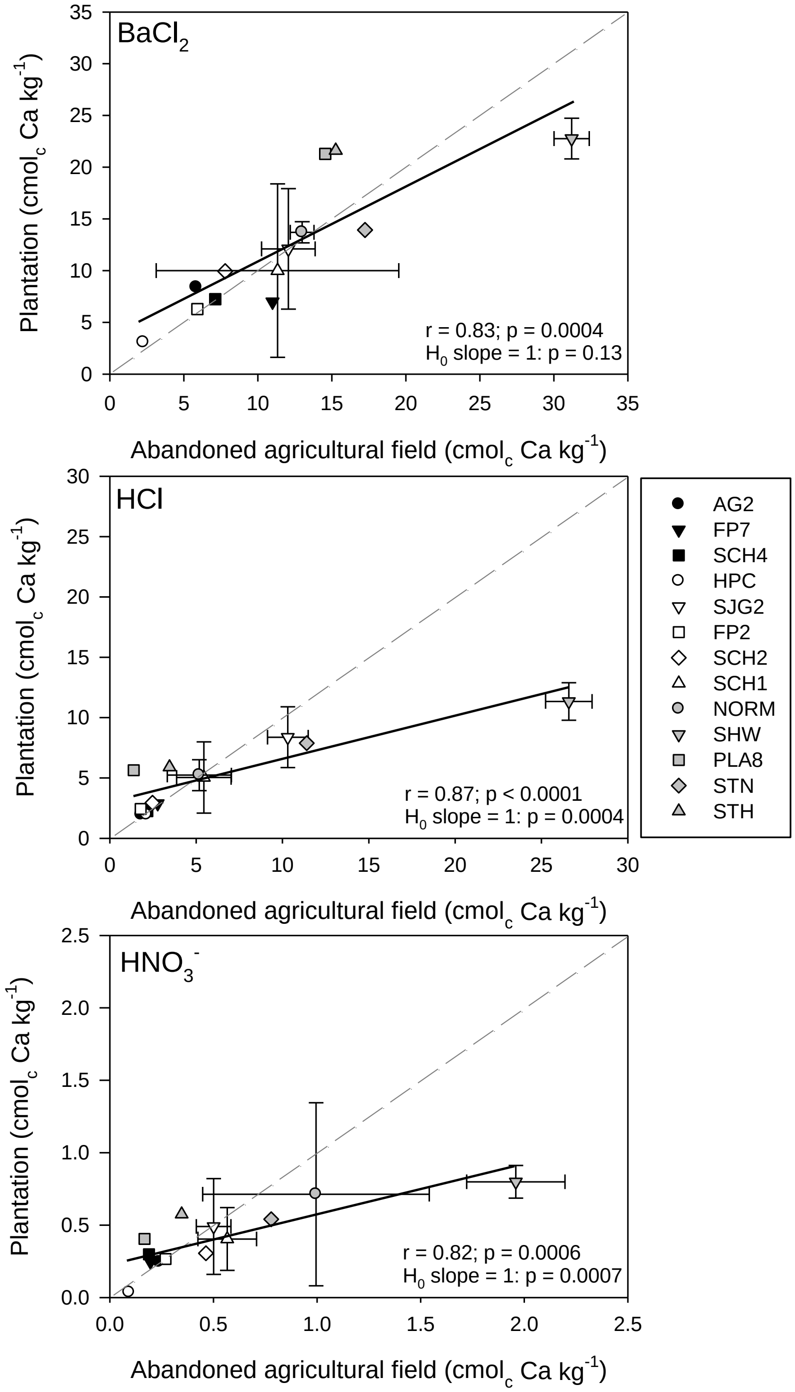

Fig. 5. Relationship between abandoned agricultural field soil Ca concentration and plantation soil Ca concentration. The grey dashed line is the 1:1 line. Standard deviation along the *x* and *y* axes are given only for the four sites which are discussed in further details, i.e. SJG2, SHW, NORM and SCH1. Black symbols denote plantations that are <5 years-old; open symbols denote plantations that are ≥5 and <10 years-old; grey symbols denote plantations that are ≥10 years-old