

The Long-Term Effect of Slowly Dissolved Crushed Basic Rocks Amelioration on Metals Bioavailability in Soil

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Abstract Concentrations and bioavailability of Al, Fe, Cd, Pb, Cu, Zn, and Mn in mountain forest soil replanted with speckled alder (*Alnus incana* (L.) Moench) are explored 7 years after soil surface vs. planting hole application of amphibolite and dolomitic limestone mixture. The mechanisms of slow limestone dissolution are explained and discussed from broader systematic view. The aspects of soil pH and oxidable carbon and the cation exchange capacity changes as well as changes of water-soluble, total, and effective concentrations of tested elements in the amended soils are included. The soil amendment invoked the depletion of K (and slightly Zn) effective concentration. The total concentrations of Ca, Mn, Al, and partly Mg in soil were increased owing to the presence of these elements in the amendment; the water-soluble concentrations nor effective concentrations of Al, Mn, Zn, Cu, Cd, and Pb were

increased. Moreover, the effective concentration of Al in both amended variants decreased. The usual negative side effects of liming were not observed due to the slow dissolution of the amendment. Further, the surface application of the amendment is cheaper than the planting hole application, but there are some expected losses of the amendment by concurrent uptake by grass and by flushing.

Keywords Liming · Forest soil · Disturbed stand · Hazardous metals · Diffusive gradient in thin films

1 Introduction

The amelioration of forest soil with crushed basic rocks is a widely used procedure mainly on sites subjected to acidic air pollution. However, the impact of basic rocks amelioration is an intervention to the environmental system, and its results can be ambivalent.

The application of basic rocks is mostly disputable for nutrient-poor soils in harsh climate. The liming or applications of pulverised basic rocks in general may increase soil pH and temporarily, also, amount of bioavailable nutrients in soil. However, the application of soil amendment (liming in particular) may also cause some negative changes in soil chemistry (Kreutzer 1995; Misson et al. 2001; Podrázský and Ulbrichová 2003). It is supposed that mainly ion leaching (Lundell et al. 2001), organic matter losses (Nilsson et al. 2001), as well as an increase in bioavailability of hazardous metals (Bolan et al. 2003) belong to the negative

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impacts of soil amendments on the forest soil. It has to be noted that after liming, the depletion of the soil organic matter content in deeper horizons under conifers may be caused by longer decomposition time of needles litter after liming and its accumulation in the organic layer (Derome et al. 1986; Smolander et al. 1996).

In some cases (e.g., on most extreme sites), a localized application of slow-release soil amendments can expedite the regeneration phase of forest plantations and support their initial growth on harsh sites (Kiikkilä 2003; Kuneš et al. 2004, 2009; Vacek et al. 2009). Soil acidity and low content of nutrients, when counteracted, are mostly compensated by liming (Frank and Stuanes 2003). Extreme area (Jizerské Hory Mts.) selected for this purpose has been detrimentally influenced by air pollution (Křeček and Hořícká 2001, 2006) and the highly mineralized, acidified soil is nutrient poor (Fottová and Skořepová 1998; Kuneš 2003). The impacts of soil amendments have been examined in terms of soil chemistry including hazardous metals mobility.

Within the assessment of soil amendment interactions, it can be operated with three characteristics (levels) which may give complement information: total concentrations, water solubility, and effective concentration of focused element(s) in soil. The effect can be evaluated, e.g., according to availability changes of divalent cations in soil solution using diffusive gradient in thin films (DGT) technique as an additional point of view complement to pH changes, changes in organic matter content, change of cation exchange capacity (CEC), and others in soil and to the total concentration (amount) of nutrients in plant biomass.

DGT has been discovered in 1994 to determine an available portion of metal cations in waters (Davison and Zhang 1994), and, during almost two decades, it was developed to become a powerful tool for the determination of cations availability in more complicated environmental systems—soils and soil solutions (Davison et al. 1997; Jakl et al. 2009; Jaklová Dytrtová et al. 2008). The concentration of cations determined using DGT is sometimes called “effective” concentration, and it represents the element bioavailability in the soil given by the physicochemical properties of the soil as well as the chemical properties of all species (forms) of the element. Metals are adsorbed on the solid soil complex or in the soil solution create complexes (or salts) with organic matter and inorganic ions (Donisa et al. 2003; Jaklová Dytrtová et al. 2011b; Jones 1998; Tejnecký et al. 2010). The stability of the complexes

influences subsequent metals availability to plants or other organisms (bioavailability) as well as sorption to the surface of resin in the DGT device (Jaklová Dytrtová et al. 2009). There exist plenty of methods for the determination of metals complexation in solution and complexes kinetic properties (Jaklová Dytrtová et al. 2011a; Pesavento et al. 2009).

The main aim of this study is to characterize soil changes in the meaning of (hazardous) elements availability, risk of leaching, and others after two kinds of local soil amendment with a mixture of dolomitic limestone and amphibolites. The key hypothesis of the study is that the slow dissolution of the agent prevents negative side effects of the soil amendment.

2 Material and Methods

2.1 The Soil Amendment

The region on the Central Ridge in the Jizerské Hory Mts. (Northern Bohemia) belongs to the areas with increased (mainly wet) deposition of cadmium, lead, nickel, and also nitrogen and sulfur oxides; the average annual air SO₂, NO₂, and O₃ concentrations in the post-air-pollution period are 4 µg m⁻³ (2005–2008), 5 µg m⁻³ (2006–2008), and 102 µg m⁻³ (2003–2008), respectively (www.chmi.cz). Although the values are currently under the limit of direct forest damage, they are still high enough (in relation to the annual precipitation) to cause sneaking forest soil degradation.

The site is situated on the southwestern-facing slope of the ridge at an altitude of 950–960 m. The mean annual air temperature (1996–2007) at the site is 5.1 °C, and the mean annual precipitation (1994–2007) is 1,093 mm (Balcar and Kacálek 2008). The herbaceous vegetation on the site is dominated by *Calamagrostis villosa* (Chaix) J. F. Gmelin. The bedrock was determined as biotitic granite, soil as well-drained mountain humus Podzol (Placic Umbric Podzol according to the World Reference Base for Soil Resources (Food and Agriculture Organization of the United Nations) terminology).

The experimental soil amendment was established in May 2003. Inside a game-proof fence in the formerly clear-felled area, the pioneer species, speckled alder (*Alnus incana* (L.) Moench), as a 1-year old bare-rooted planting stock was planted. Apart from the (1) control treatment containing three replications, two

amended treatments were installed, each of which consisted of two replications. In the amended treatments, a mixture of 0.5 kg of crushed dolomitic limestone and 1.0 kg of pulverised amphibolite per tree (approx. $(2.5+5) \text{ t ha}^{-1}$) was applied. In the (2) surface treatment, the mixture was applied as a base dressing around alder seedlings in circles of 0.5 m in diameter, immediately after the trees had been planted. In the (3) planting-hole treatment, the same amount of the mixture was incorporated into the soil inside planting holes ($25 \times 25 \times 25 \text{ cm}$) during the planting of seedlings.

The crushed dolomitic limestone contained 93.5 % of particles smaller than 1 mm in diameter, and the pulverized amphibolite contained 45.5 % of particles smaller than 0.06 mm, 46.6 % of particles between 0.06 and 0.1 mm, 6.3 % of particles between 0.1 and 0.6 mm, and 1.6 % of particles larger than 0.6 mm in diameter (Kuneš et al. 2009). Mean concentrations of selected elements in the additives are mentioned in Table 1.

2.2 DGT Application

The DGT technique was used for the determination of bioavailable portion of metals. DGT units (DGT REsearch Ltd., GB) consisted of the Diffusive Gel Disc (0.8 mm) in 0.1 mol L^{-1} NaCl, the Chelex Gel Disc (0.4 mm) in deionised water (Millipore®), and the Tuffryn® Membrane Filter (25 mm, $0.45 \mu\text{m}$, Pall Corporation, USA). The detailed preparation followed the description in the technical manual (www.dgtresearch.com).

Table 1 Chemical composition of the additives used (mg kg^{-1} ; $n=3$)

Element	Limestone		Amphibolite	
	Mean	St.dev.	Mean	St.dev.
Al	5,121	291	49,293	2,428
Ca	227,038	2,936	79,402	2,226
Cd	0.125	0.005	1.35	0.00
Cu	1.76	0.03	156	3
Fe	1,108	75	69,660	399
K	1,629	85	1,909	
Mg	113,583	6981	44,082	3,376
Mn	396	4	1,850	39
Pb	4.41	0.06	9.52	0.59
Zn	46.9	0.1	111.6	1.7

The DGT units were placed on the site randomly on 50 cm radius from a stem, in 8 cm depth vertically, three times for each plot, in two replicates per tree ($2 \times 3 \times 2$ units or $3 \times 3 \times 2$ units for the treatment, respectively). The units were exposed for a defined time ($\sim 24 \text{ h}$, expressed in seconds; Eq. 1), and the exposure time and soil humidity were measured for each DGT unit separately. During the exposition, the average soil temperature was $8 \pm 2 \text{ }^{\circ}\text{C}$. After exposure, the DGT units were disassembled immediately on the site, and the Chelex gel discs (resins) were leached for 48 h (at $4 \text{ }^{\circ}\text{C}$) in 1.5-mL vials containing 1 mL of 2 mol L^{-1} HNO_3 (Jaklová Dyrtrtová et al. 2008) and kept in glass test tubes until analysis.

The bioavailable concentration of elements C_b ($\mu\text{g L}^{-1}$) was calculated by Zhang et al. (1998):

$$C_b = \frac{M \Delta g}{D t A} \quad (1)$$

where M (μg) is the element mass adsorbed on exposure area A (3.14 cm^2) within the time t (s), Δg (cm) is the thickness of diffusive layer (0.093 cm), and D (cm s^{-1}) is the diffusive coefficient of metal in the gel (www.dgtresearch.com).

The element mass M was calculated according to Zhang et al. (1998):

$$M = C_e \frac{V_g + V_e}{f_e} \quad (2)$$

where C_e is the measured element concentration ($\mu\text{g L}^{-1}$) in the 2 mol L^{-1} HNO_3 elution solution, V_g (L) is the volume of the resin gel, V_e (L) is the volume of elution solution, and f_e is the elution factor for each metal and elution reagent (typically for 1 mol L^{-1} HNO_3 $f_e=0.8$ (Zhang et al. 1998)). Other symbols were stated before.

2.3 Soil Sampling

The top soil samples were collected from 10 subsamples taken by single gouge auger ($d=30 \text{ mm}$; Eijkelkamp Agrisearch Equipment, Netherlands) in the 0.5-m circle distance around the tree, 0–10 cm depth.

2.4 Chemical Analysis

An aliquot (0.5 g) sample of the dried soil ($60 \text{ }^{\circ}\text{C}$, $<2 \text{ mm}$) or amendment was decomposed by the wet

decomposition procedure under high pressure and microwave heating in a mixture of 8 mL of HNO₃ (conc.), 3 mL of HCl (conc.), and 2 mL of HF (conc.) in Ethos1 (MLS) at 210 °C for 34 min. Each reaction mixture was then evaporated in 50-mL Teflon® beaker to dryness at 160 °C, and dissolved in 5 mL of *aqua regia*. The sample was then made up to 25 mL with deionised water and kept in glass test tubes until analysis. For the purpose of validation of analyses, certified reference materials WT-L (sewage sludge) and CMI 7003 (silty clay loam) were used.

After decomposition, the total concentrations of elements in the soil samples were determined by inductively coupled plasma–optical emission spectrometer (ICP-OES; VARIAN VistaPro, Varian, Australia).

The concentration of elements in soil water-soluble fraction (1:10 w/v ratio, 2-h shaking, and centrifugation at 6,000 rpm (920×g) for 30 min, Hettich Universal 30RF, Germany) and the total elements concentration in digests (three times diluted) were determined by ICP-OES.

The oxidable organic carbon in soil (C_{ox}) was determined spectrophotometrically (Zeiss Spekol 221, Germany) after the oxidation of the organic matter by K₂Cr₂O₇ according to (Sims and Haby 1971).

Active pH (1:5 in H₂O) was measured using pH meter (pH 301i/SET, WTW, Germany). Cation exchangeable capacity of the soil samples was determined in solution (ICP-OES, pH meter) as the sum of cations (Ca, Mg, K, Na, H, Al, Fe, and Mn) displaced with 0.1 M BaCl₂ (Hendershot and Duquette 1986; ISO_11260 1994).

All chemicals were of analytical grade purity (p.a., Merck, Czech Republic), the deionised water was of ultrapure quality (>18.2 MΩ; Millipore Milli-Q).

2.5 Statistical Analyses

The quality assurance of analytical data is guaranteed by the control process using mentioned certified reference materials and certified methods of analyses. All statistical analyses (i.e., mean values, confidence intervals, standard deviations, and ANOVA test) and graphs were performed using OriginLab 8.0 (OriginLab Corp.) and STATISTICA 9.0 (StatSoft, Ltd.). Confidence intervals (CI) were calculated for 95 % probability and the mentioned number of replicates.

3 Results

3.1 Changes of Soil Active pH, Oxidable Carbon, and Cation Exchange Capacity After Liming

One of the basic factors, which determine elements mobility in soil, is soil pH as well as concentration of oxidable carbon in soil. Nevertheless, the increase in the soil-active pH and also changes in the organic (oxidable) carbon 7 years after liming were not significant (Table 2). This fact may consist in relatively high standard deviation of the control variant. Additionally, the soil active pH as well as concentration of oxidable carbon was practically the same before soil amendment and in control variant after 7 years of plantation.

After 7 years, soil cation exchange capacity in the control variant was 64±10 mmol kg⁻¹, in the surface application was 91±17 mmol kg⁻¹, and planting-hole application was 101±23 mmol kg⁻¹ of dry soil matter (*n*=12).

3.2 Evaluation of the Liming Effect on Elements Fractionation in Soil

As expected, the application of the mixture of dolomitic limestone and amphibolite (Table 1) caused elevation of the total concentration of several tested elements in soil (Fig. 1). This elevation was significant for Ca and Mn (for both amendments), Al (planting hole application), and Mg (surface application).

The water-soluble fraction gave the information about actual water solubility of elements related with the risk of possible leaching and mobilization in soil. Contrary to total, the water-soluble concentrations of focused elements in soil were not influenced significantly by the fertilization (Fig. 2).

In the meaning of metals bioavailability, the DGT technique revealed changes in the “effective” concentration of some elements (Fig. 3). In long-term, the soil

Table 2 Soil active pH and concentration of oxidable carbon in the soils

		Input	Hole	Control	Surface
pH(H ₂ O) (<i>n</i> =3)	Mean	4.60	4.85	4.55	4.81
	St.dev.	0.10	0.16	0.35	0.12
C _{ox} (%) (<i>n</i> =3)	Mean	6.46	6.26	6.48	6.41
	St.dev.	0.27	0.42	0.32	0.37

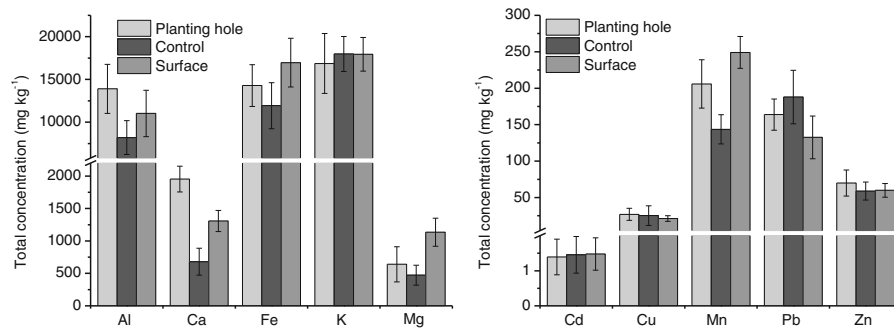


Fig. 1 Total concentration of the elements in soil (\pm CI mg kg^{-1} dry weight, $n=6$)

amendment decreased bioavailability of Al and K in both the amended treatments significantly.

4 Discussion

Typically, the mineralization rate (and thus decrease of soil carbon) is considered to be enhanced by the increase of soil pH (Curtin et al. 1998). It may be expected that the soil pH increases after the basic cations addition (Frank and Stuanes 2003; Saarsalmi et al. 2011); however, after 7 years of the treatments, the increase of pH of both treated treatments was not significant and the pH ended up on the same value as before the treatment. Moreover, the treatment with crushed basic rocks did not cause a long-term decrease of oxidable carbon concentration in soil. The unchanged concentration of oxidable carbon of both amended treatments comparing to the control can be also caused by losses of dissolved inorganic C by CO_2 (degassing) during the handling technique or during centrifugation, which is typical for noncalcareous soils (Dahlgren et al. 1997). Moreover, the decrease of oxidable carbon in the soil samples can

be also caused by conversion of low-molecular-weight organic acids to CO_2 which was observed under laboratory conditions in solution during oxalic acid interaction with phospholipids membranes as well in the gas phase under mild ionization conditions (Parisová et al. 2013).

The amendment caused the increase of Ca, Mn, and Mg (only in surface application) total concentration in soil. This increase is caused by the presence of Ca, Mg, and Mn in applied crushed basic rocks. However, the increase of total concentrations of these metals (Ca, Mg, and Mn) had no long-term effect on the increase of water-soluble concentration of these metals. This fact in case of Mg corresponds very well with the concept that in the surface application, the amendment decomposes slightly faster than in the planting hole (Fig. 4). Moreover, it is expected CaCO_3 dissolves faster (solubility in water is 1.3 g L^{-1} (Patnaik 2003)) than MgCO_3 (solubility in water is 10.6 mg L^{-1} (Patnaik 2003)). It means that in the planting-hole amendment, the major part of MgCO_3 remained undissolved in soil, which resulted in almost unchanged total concentration, water-soluble concentration, as well as effective concentration of Mg comparing to the control. In contrast, the

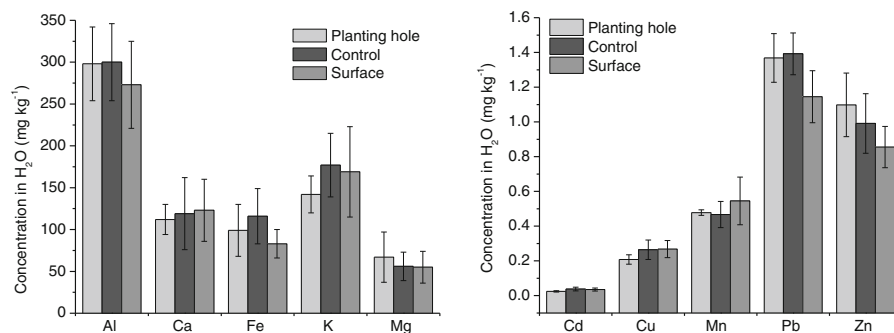


Fig. 2 Water-soluble portion of the elements in soil (\pm CI mg kg^{-1} dry weight, $n=6$)

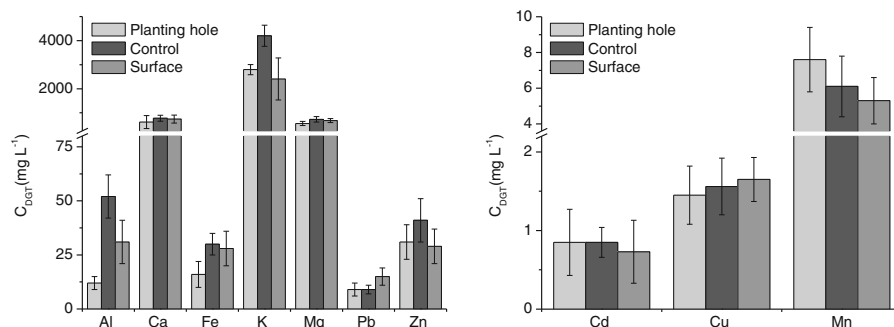


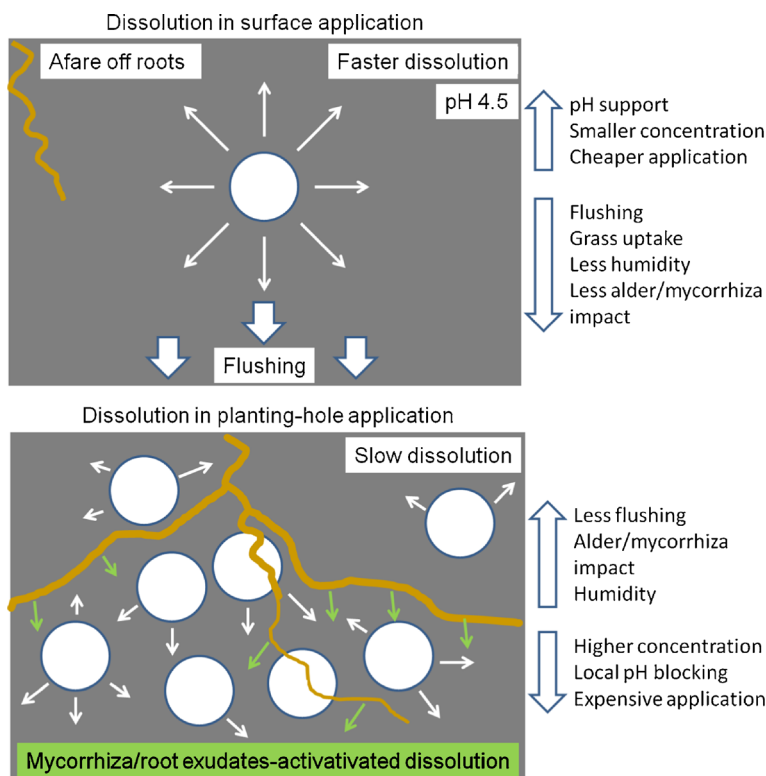
Fig. 3 Bioavailable portion of the elements in the soil determined by DGT, expressed in milligrams per liter (mean \pm CI, $n=6$) of the soil solution

total concentration of Ca in both treatments increased comparing to the control due to faster dissolution of limestone. However, the water-soluble as well as the effective concentration of Ca was the same as in the control variant. This was implied from the physiological growth demands (Lambers and Poorter 2004) of alder. As expected (Kuneš 2003; Kuneš et al. 2004), the growth of alder planted in both amended soils was enormously higher than in the non-amended soil (Kuneš et al. 2009); the higher growth of biomass is related with higher uptake of nutrients (Ca and others)

from soil, where their available forms (presented by effective and water-soluble concentration (Jaklová Dyrťová et al. 2008)) are preferred. Consequently, both, the water-soluble and effective concentrations of Ca, were finally equilibrated to the similar value in all variants. The same trend is remarked for Mg and Mn.

An interesting effect of plant (mycorrhiza) activity on speciation of unpleasant elements was demonstrated on the case of Al. Its total concentration was increased in both amended variants owing to its presence in the fertilizer. Nevertheless, its water-soluble and effective

Fig. 4 Schematic presentation of positive and negative factors influencing amendments decomposition and dissolution in soil after different treatments



concentration was similar or even smaller than its concentration in the control variant. The decrease of Al bioavailability might have a positive impact on the alder stand and is supported by the evidence that liming increases Al adsorption in soil (e.g., (Mora et al. 1999)). This positive effect can be seen on the better fitness of alders growing in the amended soils (Kuneš et al. 2009).

The soil amendment decreased potassium effective concentration by almost 45 %, comparing the value for the control ($4,202 \text{ mg L}^{-1}$) to the values of the amended treatments ($2,407 \text{ mg L}^{-1}$ for the surface treatment and $2,796 \text{ mg L}^{-1}$ for the planting-hole treatment, respectively). Nevertheless, this might be a result of higher K uptake by faster growing alders in the amended soil, which consumes the most available portion first. The decrease of K was not observed in its total concentration, but it was slightly visible in water-soluble concentration. It may indicate future growth depletion caused by K unavailability and high energetic demands related with K uptake from less available portion.

The total concentration of Fe was slightly elevated by the treatment; however, its water-soluble concentration as well as effective concentration decreased. This effect might be related with extensive alder growth observed after the treatment. In the future, while maintaining the current growth trend, the Fe deficit might be observed. This trend is now visible on relatively low effective concentration of Fe in planting-hole amendment. Fe is mostly present in the amphibolic amendment in the forms of less soluble or insoluble ferro-oxides and silicates (Hawthorne and Oberti 2006).

From the methodological point of view, the determination of the total concentration of elements in soil is crucial in the evaluation which amount of each element is in the soil physically present and might be potentially released into more available species. Advantageously, the information, which part of the total amount exists in more available species (water-soluble part and effective concentration), might be helpful in more complex evaluation of the situation. It can be pointed out that, despite the total concentration of a hazardous element (Al) is elevated, its available portion remains unchanged and is not promptly harmful. The water-soluble concentration gives the information which part of the total concentration can be released into the available forms if the soil moisture is high (e.g., during spring snow melt). Also, the water-soluble concentration helps to estimate the risk of leaching. On the other hand, the effective

concentration is the available concentration for biota; it includes nonbounded or slightly bounded elements of organic/inorganic part of soil whereas the effective concentration has not included the local effect of plant/mycorrhiza exudation.

5 Conclusion

Soil amendment (after 7 years) with the mixture of amphibolite and dolomitic limestone applied in either planting hole or surface application had mostly positive impact on alders vitality and growth as well as soil properties. Values of pH and oxidable carbon did not change among variants or from their initial values. On the other hand, the cation exchange capacity of both amended variants were extended about one third comparing to the control variant. The most positive impact of such kind of soil amendment might be demonstrated on the lack of usual negative effect related with liming such are an increase of hazardous metals availability, nutrient leaching, an increase of organic matter decarboxylation, etc. None of these negative side effects were observed. Moreover, the effective concentration of Al and partly Zn decreased, and the effective concentration of other hazardous elements (Cu, Cd, and Pb) remained unchanged. This positive evidence might be attributed to the slow dissolution of utilized amendment given by the original soil properties, climate, and the way of its application.

From the long-term point of view and more rentable investment to the reforestation, the planting-hole application seems to be better than the surface application. The main reason lies in the rate of the amendment dissolution and losses. The dissolution rate of the amendment in the planting-hole application and the losses by concurrent grass uptake and by flushing are smaller owing to its concentration in soil volume and short distance from the tree root system. In initial growth, both the amendment applications served well for tree establishment, and 7 years after application, the particles of amphibolites were still visible and might serve as future depots.

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