

**Czech University of Agriculture in Prague
Faculty of Agrobiolgy, Food and Natural Resources
Department of Soil Science and Soil Protection**



**Temporal dynamics of chemical characteristics of
mountainous forest soils affected by acidification**

Master Thesis

**Author: Sabina Chovancová
Supervisor: RNDr. Václav Tejnecký, Ph.D.
Consultant: Ing. Ondřej Drábek, Ph.D.**

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Declaration

I hereby declare that this Master thesis with a title “Temporal dynamics of chemical characteristics of mountainous forest soils affected by acidification is a product of my own independent work under the supervision of RNDr. Václav Tejnecký, Ph.D. It does not contain other people’s work without this being stated and does not contain my previous work without being stated, and that the bibliography contains all the literature sources that I have used in writing the thesis.

April the 10th 2015

Signature

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Summary

The Jizera Mountains region was strongly affected by acid deposition in the last century. Natural soil acidification was accelerated and base cations were leached during the neutralization processes, soil pH decreased and toxic aluminum was released to the soil solution, sulfates and nitrates were accumulated in the soil. During the 1990s, emissions of acidifying compounds were reduced significantly but forest soils underlain by granite exhibit ongoing acidification. The aim of this thesis is to describe temporal changes in the forest mountainous soils under three different vegetation covers between 2008 and 2013.

Overall, soils were assessed as strongly acid. Organic horizons exhibited the lower pH than mineral horizons indicating that they are more sensitive to external factors such as vegetation cover, litter decomposition and atmospheric deposition. In the period 2008–2013, pH of atmospheric deposition did not change significantly. Nevertheless, throughfall pH in the beech forest exhibited higher values than the spruce forest and clear-cut area.

Soil sorption complex was primarily formed by soil organic matter that decreased with increasing depth. Mineral horizons were unsaturated by bases and aluminum was prevailing exchangeable cation in the sorption complex as a consequence of slowly weatherable granite bedrock with low content of base cations. In general, beech forest and clear-cut are exhibited better soil chemical characteristic compared to spruce forest. Significant increase in pH was observed in the clear-cut area. Spruce forest showed the lowest soil pH, base saturation, the Ca:Al ratio and the highest exchangeable acidity and the C:N ratio. With respect to changes between years of sampling, upward temporal trend in base saturation and decreasing exchangeable acidity occurred at each stand in organic horizons. The most significant changes in base saturation were determined in the clear-cut area and beech forest. On the contrary, mineral horizons showed declining trend indicating ongoing soil acidification and leaching of base cations. This was significantly pronounced in the spruce forest. Exchangeable acidity decreased in both organic horizons under the spruce forest whereas only in the upper organic horizon under the beech forest and clear-cut area. Changes in understory vegetation were attributed rather to changes in light conditions than changes of soil chemical parameters.

Key Words

Soil acidification, temporal changes, pH, cation exchange capacity, base saturation, exchangeable acidity, spruce forest, beech forest, clear-cut area.

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1 Introduction

Highly affected area in the northern part of the Czech Republic, along to borders with Poland and Germany, called “Black Triangle”, has experienced extremely high air concentrations of SO₂ and NO_x in the second half of the 20th century that contributed to severe massive forest diebacks. Historical loads of acids resulted in soil acidification that is henceforth present in forest ecosystem despite the fact that the major sources of sulfur and to a lesser extent nitrogen, have been cut. Forest ecosystems are considered to be sensitive to acid deposition since the canopy is highly capable to scavenge pollutants from the atmosphere.

Soils in terrestrial ecosystems play an important role in alleviating the effects of acid deposition. Affected regions suffer from long lasting soil acidification that gradually contributes to temporal changes in soil chemical parameters. Base cations, the important plant macronutrients, have been leached from the soil to surface waters during the neutralization processes. Soil pH decreased in the whole soil profile and inorganic, potentially phytotoxic, aluminum was released to the soil solution and thus get available to plant roots and subsequently washed out to streams and lakes. Despite the fact that emissions of acidifying compounds were reduced during 1990s, soils and surface waters are not fully capable to recover from the chronic acidification to the state prior to the air pollution. Besides the effect of acid deposition, the influence of tree species on soil chemical parameters is not negligible. However, nature-close beech forests were largely replaced by Norway spruce that has higher ability to scavenge pollutants and naturally acid litter.

2 Scientific hypothesis and objectives of work

Chemical composition of long-termly acidified mountainous forest soils is changing with respect to changes in the chemistry of atmospheric deposition and vegetation cover.

The major objects of this diploma thesis are:

1. Comparison of the influence of different vegetation covers on selected soil chemical parameters.
2. A comparison of selected soil chemical parameters of stands between 2008 and 2013.
 - Beech forest
 - Spruce forest
 - Clear-cut area
3. Changes of stand conditions according to understory vegetation between 2008 and 2013.

3 Literature Overview

The term soil acidification refers to a natural process when soil reaction decreases and soil sorption complex becomes significantly occupied by hydrogen and phytotoxic aluminum ions, whereas plant nutrients such as calcium, magnesium, potassium and sodium get depleted by leaching or by biota (Schaetzel and Andearson, 2005). Natural factors affecting soil genesis are generally determined by climate, parent material and species composition of the forest stand, topography and time (Jenny, 1941). With respect to that fact, soil acidification is considered to be an important soil forming process in the mountainous areas of the Czech Republic that has been accelerated by anthropogenic activities.

3.1 Natural soil acidification in the forest ecosystem

The vast majority of soils are acidic due to the leaching lasting over long periods in regions where precipitation exceeds evaporation (Fujii et al., 2012). Besides, rain is naturally acidic because of the presence of dissolved carbon dioxide, forming a weak carbon acid. Pure water in equilibrium with atmospheric carbon dioxide has a pH 5.6 while neutral water exhibits a pH 7.0 (Menz and Seip, 2004). Carbonic acid is thus a ubiquitous source of H^+ that removes base cations in leachate (Summer and Noble, 2003). Another factor affecting soil acidification in forest ecosystems is a vegetation cover since the litter quality regulates the process of litter decomposition and production of organic acids (Puhe and Ulrich, 2001). Equally important factor affecting the soil acidity is parent material. Soils developed on less weatherable rocks (quartzite, leucogranite, granite, gneiss, schist, mica) exhibit lower concentration of base cations and lower pH and thus they are more sensitive to acidification (Hruška and Krám; 2003; Krám et al., 2012). On the contrary, soils developed on more weatherable rocks (serpentinite, gabbro, calcareous granulite) are less prone to acidification. They exhibit higher buffering ability to neutralize incoming acids (Klimo et al., 2006; Krám et al., 2012). Parent materials with acid character prevail in the Czech Republic and on these rocks, under the interaction of all previously mentioned factors, soils being of acid reaction such as Podzols and acid Cambisols are developed (Klimo et al., 2006).

Podsolization

The occurrence of podzols in the area of the Czech Republic is mainly linked to hilly regions (except arenic podzols that are characteristic for lower altitudes), with poor parent material in base cations (Ca, Mg, Na, K) and Fe which are no longer able to buffer soil system against

acidification (Sauer et al., 2007). Climate conditions correspond to areas with relative low annual temperature and with high humidity and high annual precipitation rates (Schaetzel and Andearson, 2005). Development of podzols is typically under the vegetation of coniferous forest with slow decomposition of litter (Sauer et al., 2007). These conditions enable to accumulate substantial quantity of slowly degradable soil organic matter on the top of the soil profile. Soil profile morphology is characterized by organic surface horizon (O) that is rich in low molecular weight acids and fulvic acids. Due to the low pH, Al and Fe ions are released from primary minerals and clays and transported to deeper layers by organic acids as organo-metal complexes (Lundström et al., 2000; Sauer et al., 2007). Eluvial bleached horizon (E) consequently remains lack of Al, Fe and soil organic matter but enriched in minerals with slow weathering rate (quartz) (Lundström et al., 2000). Illuvial horizon (B) in which a part of the organo-metal complexes precipitate give rise to a spodic horizon (Duchaufour and Souchier, 1978). This horizon is composed of organic matter and Al, or of illuvial Fe (WRB, 2006). It is characteristic by brownish-black to reddish-brown color. (WRB, 2006). Relatively unaffected horizon (C) presents parent material, typically granite or sandstone (Lundström et al., 2000).

Brunification

Typically, products of brunification – cambisols occur in the middle altitude areas where there is an excess of precipitation, high accumulation of base-rich organic matter and Fe-rich parent material. In the forest ecosystems, quality of the litter is equal to mull or moder, most often under deciduous forest. Iron ion is released from lattices of primary silicates under conditions of higher pH and higher clay content which make leaching of base cations difficult in comparison with podsolization process. Released iron (potentially also Al) is thereafter oxidized and secondary minerals, such as goethite, are formed. Iron oxides are quickly tied up with organic matter and clay, forming immobile complexes in the upper solum with characteristic brownish coloring (Duchaufour and Souchier, 1978; Schaetzel and Andearson, 2005).

3.2 Anthropogenic acidification of forest ecosystems

Anthropogenic acidification is a very complex process that encompasses emissions of acidifying pollutants, their deposition and scavenging by forests canopy, chemical changes in soils, changes in nutrient cycling, nitrogen saturation and vegetation changes (Driscoll 2008). Although, major sources of emissions have been abated, manmade induced acidification is still a major problem in some terrestrial and aqueous ecosystems (Goss and Norton, 2008). It is necessary pointing out that not only airborne deposition is responsible for acidification in the forest ecosystems. Also adverse effects of forest management practices (biomass harvesting, choice of tree species) may contribute to anthropogenic acidification as well (Hruška and Ciencala, 2003).

3.2.1 Origin of major acid precursors

The term “acid precursors” refers to substances that react with atmospheric or terrestrial chemicals to form acids. Major chemical species of interest are SO_2 , NO_x and NH_3 .

Combustion of fossil fuels with high content of sulfur has been identified as a main source of SO_2 . When fossil fuels are burned, most of the sulfur contained is oxidized to form sulfur dioxide (Smith et al., 2001). In the Czech Republic, sources of the SO_2 emissions have roots in the development of heavy industry sector after the Second World War. Emissions have shown rapid increasing tendency since the 1950s. The maximum production of SO_2 , 800 kt per year was reached in the 1980s (Oulehle and Hruška, 2005) as a consequence of the new-built thermal power plants located in the northern part of the Czech Republic (Hruška and Kopáček, 2009). Positive qualitative and quantitative changes were observed in the 1990s as a result of the set of restrictions against the air pollution. Follow-up desulfurization of power plants caused that emissions of SO_2 were reduced over 85% and this decline belongs to the third highest one within the European Union, after Germany and Slovenia (Vestreng et al., 2007).

Further pollutants contributing to acidic deposition are nitrogen oxides (NO_x). Commonly used shortcut “ NO_x ” refers to the variable amount of nitric oxide (NO) and nitrogen dioxide (NO_2). Vast majority of NO_x are emitted as NO (Flagan and Seinfeld, 1988) which is quickly oxidized to NO_2 . Emissions of NO_x are attributed to the high-temperature oxidation of atmospheric N_2 . Hence, the crucial factor of emitted amount is a temperature of combustion (Flagan and Seinfeld, 1988). The most pronounced source of manmade NO_x seems to be road transport which contributed of 40% to emissions of NO_x in the European Union in 2011 (Figure 1).

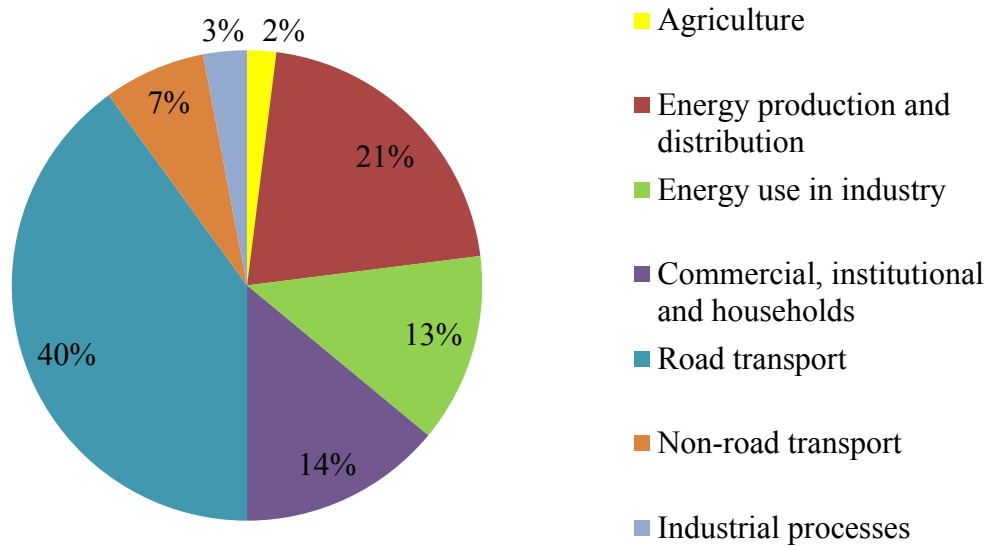


Figure 1: Share of NO_x emissions by the sector group in the EU-27 in 2011 (EEA).

Third just as important acidifying pollutant is ammonia (NH₃), largely coming to the atmosphere from agricultural activities, up to 94% of total in 2011 (Figure 2). Emissions are either derived from the decomposition of urea in animal wastes or from the usage of nitrogen fertilizers.

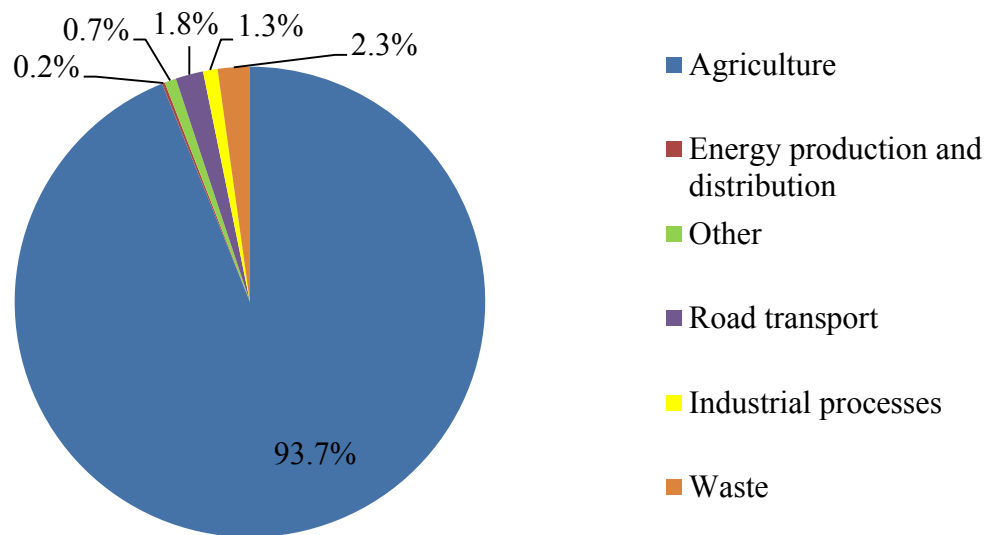


Figure 2: The contribution made by different sectors to emissions of ammonia in 2011 (EEA).

Precursors of “acid rain” are transported over hundreds of kilometers. Throughout the complex of photo-chemical reactions in the troposphere, these gaseous substances are transformed to acids according to the equations 1, 2, 3 (simplified):

- 1) $4 \text{SO}_2 + 4 \text{H}_2\text{O} + 2 \text{O}_2 = 4 \text{H}_2\text{SO}_4$
- 2) $4 \text{NO} + 2 \text{H}_2\text{O} + 3 \text{O}_2 = 4 \text{HNO}_3$
- 3) $4 \text{NO}_2 + 2 \text{H}_2\text{O} + \text{O}_2 = 4 \text{HNO}_3$

They can be found in rural areas downwind of industrial areas where there is any significant source of air pollution. The occurrence of long-range transport of acidic deposition precursors has been firstly recognized by Scandinavian researches in the middle of the last century who suggested that this phenomenon is connected to fish damages in surface waters. Several international agreements have been designed to reduce and control air pollution, including long-range trans-boundary air pollution in order to protect human health and environment. To abate acidification, eutrophication (...), Gothenburg Protocol was designed as a part of the Convention on Long-Range Trans-boundary Air Pollution from 1979 (UN, 2004).

3.2.2 Acid deposition

Transport of acidifying compounds from the atmosphere to the surface is termed deposition and it is distinguished into three types: wet, dry and occult deposition (Menz and Seip, 2004). Those processes in which precipitation is involved contribute to wet deposition, broadly called as “acid rain”. Those processes where sedimentation, turbulent and molecular diffusion, impaction and interception are involved, contribute to dry deposition (Tomlinson 1990). Dry deposition often dominates wet deposition in locations close to emission sources, urban and industrial agglomerations (Menz and Seip, 2004). In the Czech Republic, dry deposition exceeds wet deposition and it is generally considered as a crucial factor of acidification in forested areas (Hruška and Ciencala, 2003). Moreover, dry deposition is often influenced by a form of deposited compounds. Gaseous compounds (SO_2 , NH_3) are removed by canopy more efficiently than their particulate forms (SO_4^{2-} , NO_3^- , NH_4^+) (Tomlinson, 1990).

Finally, occult deposition is formed by pollutant gases with cloud droplets and can be divided into deposited (dew, white dew, hoar frost, soft rime) which condenses and sublimates directly on the plant surface, and collected (fog, cloud-water) which condenses in the atmosphere into a solid and liquid form and is transported by air to the surface (Tesař and Fottová, 2000).

This type of deposition, sometimes called wind-driven cloud water, is more common in high altitude areas (Driscoll, 2008) because of the higher frequency of fog and cloud situations that takes place over there.

In some areas, acidic input can be “neutralized” or made alkaline temporarily by the emissions of ammonia (Menz and Seip, 2004). Ammonia is capable of hydrogen bonding and it leads to formation of ammonium sulfates and ammonium nitrates. Partially, neutralization effect could be also ascribed to alkaline particles (Larssen and Carmichael, 1999) coming from wind erosion, forest and grasslands fires, traffic, combustion of fossil fuels as well as it can be result of land use management (Draaijers et al., 1997). For instance, Krejčí et al., (2001) compared chemical compositions of acid rime in the Ore Mountains between the winter 1985/1986 and 1995/1996. Air concentration were fairly similar and the winter 1985/1986 was even colder than winter 1995/1996. Nevertheless, severe damage of the forest was observed in the winter 1995/1996. Authors found that neutralization of acidic compounds was retrenched in the winter 1995/1996 because concentrations of sulfates were cut to half and concentrations of Ca were even 5 times lower compared to winter 1985/1986. Therefore, pH of precipitation decreased from 4.3 in the 1985/1986 to 3.08 in the 1995/1996. It indicates that such low pH destroyed epicuticular wax on the surface of needles that protects them from variety of effects.

3.2.3 Effects of acid deposition on forest soil and vegetation

Forest receives a much greater quantity of pollutants than does open land due to the filtering effect (Tomlinson 1990). Thus, forests belong to the most sensitive ecosystems threatened by acid deposition. Main factors influencing canopy capture are: tree species composition; the height, age of the forest stand (Stevens et al., 1994). Deciduous species collect less of pollutants than coniferous ones because of smaller specific leaf area index (LAI) and seasonal loss of foliage. Deposition of pollutants is approximately twice or three times larger in coniferous forest compared to deciduous forest and four times larger compared to clear-cut area (Augusto et al., 2002; Hruška and Kopáček, 2009). Oulehle and Hruška (2005) referred that atmospheric deposition of sulfur and nitrogen was 94% and 45% greater under spruce than in the beech forest as a result of enhanced dry deposition on the spruce canopy.

Both sulfur and nitrogen are macronutrients required by plants for growth. Certain amount of gases from air can be readily absorbed and metabolized by canopy due to physiological processes in the plant. Gases enter canopy via stomata since the cuticle is

permeable. Depending on the environmental conditions like temperature, humidity and light intensity, stomata are either closed or opened. These factors influence the rate of uptake of pollutants and the extent of possible injuries. High concentrations in the air and coincidence of abiotic and biotic factors as frost, drought, pests, may aggravate severe damages of assimilation apparatus or even massive forest diebacks of affected areas.

Impact of acid deposition on forest soils is accompanied to temporal changes in soil chemistry. Many long-term studies of forest catchments (based on modelling or observation) confirmed common patterns providing the evidence of soil acidification such as pH decrease (Langan et al., 2009; Hédli et al., 2011), loss of base cations and accompanied decreases in base saturation, aluminum mobilization etc. (Bailey et al., 2005; Hruška et al. 2009, Hruška et al., 2012). With ongoing acid input, forest ecosystems become saturated by sulfur and nitrogen (Driscoll, 2008).

3.2.3.1 Acidification and buffering mechanisms in soil

Generally, the pH is used to indicate the acidity of soil. Soils are capable to resist changes in pH due to neutralization of acid load. Ulrich and Summer (1991) suggested that the nature of the specific minerals present in the soil, the reactions involved and their relative reaction rates can be derived from the soil reaction. If the given buffering mechanism is not capable to neutralize acid input completely, H^+ concentration increases, soil pH decreases and the current soil chemical state is no longer maintained. Ongoing acidification causes that base cations are leached to groundwater in association with a mobile acid anion (Majer et al., 2005). Subsequently, soil sorption complexes become largely occupied by potentially phytotoxic aluminum and hydrogen ions.

Table 1: Classification of the acid buffering reactions in forest soils

Buffering mechanism	pH range	Base saturation %	Example	Descriptive term
Carbonate	pH > 8 – 6.2	100	Loss of $CaCO_3$ as $Ca(HCO_3)_2$	Slightly alkaline
Silicate buffers	pH 6.2 – 5.0	100–70	Release of lattice cations, clay formation	Slidely acid to neutral
Cation exchange	pH 5.0 – 4.2	70–5	Decrease of base saturation, leaching of nutrients	Moderately acid
Aluminium range	pH 4.2 – 2.8	5–0	Destruction of clay minerals, aluminium mobilization	Strongly acid

Iron range	pH 3.8 – 2.4	0	Iron mobilization	Extremely acid
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Modified according to Ulrich and Summer (1991); Knaupi et al., (1986); Ulrich and Puhe, (1991) and Sparks (2003).

Carbonate buffer range (pH > 6.2) takes place if the dominant cation in the soil solution and at the exchange surfaces of the soil particles is the Ca^{2+} . The buffer capacity of soils in this range is proportional to the amount of CaCO_3 in the soil. (Kauppi et al., 1986; Ulrich and Summer, 1991). If there is no CaCO_3 in the fine earth fraction, the soil is classified as silicate buffer range. In this range the only buffer process taking place in the soil is the weathering of silicates and associated release of base cations from crystalline lattices of primary minerals and clay formation (Puhe and Ulrich, 2001). The dissolution of aluminous compounds is not significant until pH < 5.0 is reached (Ulrich and Summer, 1991; Tomlinson 1990). The rate of silicate weathering tends to be slow because of the resistance of silicate rock to decomposition and dissolution. However, buffering capacity is high. Weathering of silicates occurs throughout all buffer ranges. The switch to lower buffer ranges implies that weathering rate of silicates is not sufficient to buffer the acid stress completely (Kauppi et al., 1986; Ulrich and Summer, 1991).

The next buffering mechanism is cation exchange. The excess of H^+ ion is adsorbed at the exchange sites of soil particles and soil organic matter, thus displacing Mg, Ca, Na and K. The cation exchange reactions are fast. Hence, the buffer rate of soils in this range effectively counteracts any occurring rates of acid stress. The amount of available exchange surfaces is called cation exchange capacity – CEC (Ulrich and Summer, 1991). The base cation exchange capacity at any given time is quantified by base saturation, as the percentage of base cations of the total CEC. As long as the base saturation stays above 5–10%, the excess stress is buffered by the cation exchange reactions and the soil pH takes a value between 5.0 and 4.2 (Kauppi et al., 1986; Ulrich and Summer, 1991).

When pH drops below 5.0 and critical value of the base saturation under (0.05), soils are classified into the aluminum buffer range (Knaupi et al., 1986). In strongly acidic soils, “hexaaquaaluminum complex ion” $\text{Al}(\text{H}_2\text{O})_6^{3+}$, shortly as Al^{3+} , is released to the soil solution where prevails (Figure 3). With the increasing pH, aluminium ion forms the mononuclear species through repeated deprotonation AlOH_2^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$, soluble complexes with inorganic ligands such as sulfates and fluorides (AlF_2^+ , AlF_3^+ , $\text{Al}(\text{SO})_4^+$); and with organic compounds (humic and fulvic acids) (Krstic et al., 2012).

At the extreme stage of acidification, soils may be classified into the iron buffer range. The pH-value as low as 3.0 indicates that living organisms will severely suffer from toxicity and nutrient deficiency (Kauppi et al., 1986).

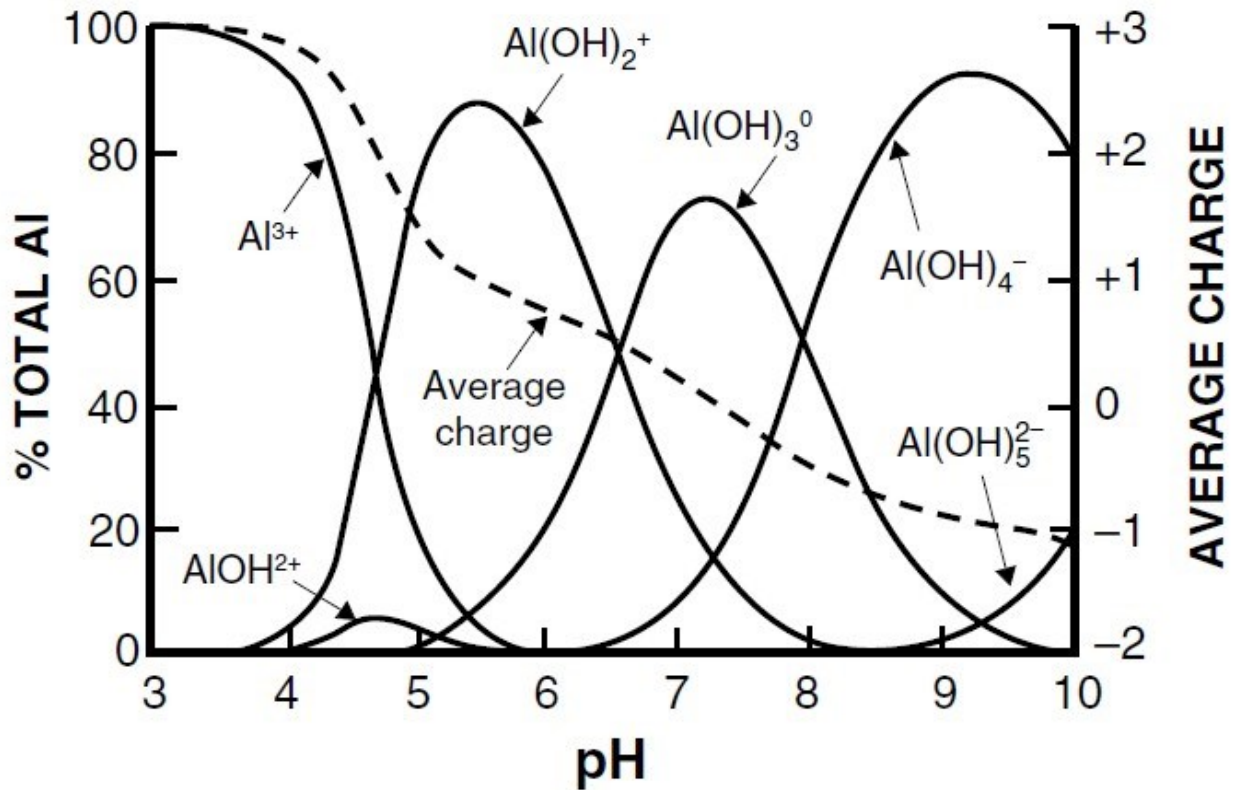


Figure 3: Relationship between pH and the distribution and average charge of soluble aluminum species (Marion et al., 1976 in Sparks 2003).

3.2.3.2 Retention of sulfates in soil

Sulfates may be absorbed electrostatically on positively charged sites in the soil sorption complex or organically cycled before being released to the soil solution (Alewell 2001). Organic matter has two different effects on the adsorption. Either there is a competition for adsorption sites between organic matter and sulfates resulting in blocking of the sites by soil organic matter (Mulder and Cresser, 1994) and thus adsorption is negatively related to organic matter concentrations or there is a formation of Al-Fe-humus complexes which substantially increase reactive surface and more sulfate anions can be hold in the soil (Alves and Lavarenti, 2004). Scherer (2009) reported that pH correlate to soil sulfate adsorption inversely. Adsorption of sulfates is also favoured by higher clay content that is more typical for older, well-weathered,

thick soils (Rice et al., 2014). With decreasing pH, sorption of sulfates on Fe and Al oxides is important type of sorption (Essington, 2004; Fisher and Binkley, 2013). Besides release of sulfates from decomposed soil organic matter in organic horizons, desorption seems to be driven by complex of processes like temporal and spatial changes in wet and dry conditions (Mitchell and Likens, 2011).

3.2.3.3 Nitrogen saturation of forest ecosystem

Nitrogen is an essential macronutrient that limits the plant growth and its capture by forest ecosystem is high (Tomlinson, 2003).

In natural forest conditions, most of the nitrogen input (1–2 Kg per hectare per year) is utilized by biota. Only little portion of nitrogen is leached, chiefly as organic nitrogen compounds, and slightly adsorbed on soil particles (Gundersen and Bashkin, 1994; Hogberg et al., 2000). High atmospheric deposition of NO_3^- may accelerate biological cycling, saturate previously N-limited ecosystems and thus diminish the retention of nitrogen inputs (Driscoll et al., 2001; Curtis et al., 2011). Aber et al., (1998) suggested that loss of mycorrhizal function, as mycorrhizal assimilation and exudation is the dominant process involved in immobilization of added nitrogen, could lead to exceeding of nitrogen retention capacity and enhanced nitrification and mobility of NO_3^- . Subsequently, acidification of soils and eventually surface waters may occur.

Nitrification is a two-step process consisted of oxidation of NH_4^+ to NO_2^- and subsequent oxidation of NO_2^- to NO_3^- (Bolan and Hedley, 2003). During these processes 2 cations of H^+ are generated when 1 cation NH_4^+ is processed via nitrification and thus the ambient environment may be acidified. Also plant uptake contributes partially to acidification (Puhe and Ulrich, 2001). When NH_4^+ is taken up by roots, the rhizosphere is acidified due to H^+ release, whereas when NO_3^- is taken up by roots either OH^- or HCO_3^- are released in exchange (Nasholm and Persson, 2000).

The carbon nitrogen ratio (C:N) is a key factor in the dynamics of nitrogen (Hogberg et al., 2000). The C:N ratio in the upper soil organic layers expresses the rate of retention of nitrogen in the forest soil solution and indicates how much of NO_3^- could be potentially leached from the ecosystem. The C:N ratio is influenced by broad scale of factors: from N-deposition, tree type, temperature, wet-dry conditions, along with soil pH, base cations storage (Hruška and Cienčala,

2003) to soil type, ecoregion or humus type (Cools et al., 2014). Lower C:N ratio indicates that the ecosystem is becoming saturated by nitrogen and thus leaching of NO_3^- may occur.

Coniferous forest soils on poorly weathered bedrock formed by granite are characterized by ratio C:N > 30 that indicates low biological activity, undecomposed litter layer and N-unsaturated ecosystem (Hruška and Ciencala, 2003). Larger pools of nutrients cycled via annual litterfall in deciduous forest positively influence C:N ratio and provide more favourable environment for microbiological activity (Cools et al., 2014; Evans and Nisbet, 2014).

Additionally, ecosystem in the stage of ecological succession is capable to saturate more nitrogen than ecosystems in the climax stage. This can be ascribed to forest ageing. Stevens et al. (1994) found that forest tend to have high N-demand during the early period of growth because larger amount of nitrogen is required for foliage that has low C:N ratio with respect to the mature stage when less N is required to form stem wood having higher C:N ratio.

3.2.3.4 Aluminum toxicity and indicators of aluminum stress

Mobilization of potentially toxic Al is mainly influenced by pH (Aksellson et al., 2013) and controlled by complexation with organic acids in highly acidic mineral soils that are undersaturated by gibbsite (Berggren and Mulder, 1995). Potential toxicity depends on the distribution of mobilizable Al species in the soil profile. High concentrations of Al^{3+} in the soil solution may cause deteriorating effects on biota as it is toxic to plants when occurred in soil solution with acidic soil reaction (Kochian, 1995). Negative charged plasma membrane is attracted by positively charged aluminum ions, providing binding sites. The affinity of Al^{3+} is about 500 times higher in comparison with Ca ions which have lower affinity (Vardar and Ünal, 2007). Thus, Al^{3+} can displace lower-valence cations from negatively charged plasma-membrane surface and block the normal uptake of nutrients. As a result, common plant symptoms of aluminum toxicity like inhibition of root growth development and changes in root morphology are observed (Kochian et al., 2004).

As an indicator of aluminum tree root damage in the forests ecosystems may serve the molar ratio of base nutrient cations (Ca, Mg, K, Na) to total dissolved aluminum in the soil solution of the rooting zone. When the ratio BC:Al is persistently below the one, Al toxicity to the tree roots may cause adverse effects from soil acidification to trees with the corresponding decline in growth and performance of the trees (Holmberg et al., 2001). In the case that the base saturation is less than 15 %, Ca:Al molar ratio is suitable substitution (Cronan and Grigal, 1995).

According to estimations if the ratio is lower than 1, there is 50% risk of adverse impact on tree grow, 75% risk if the ratio is lower than 0.5 and almost 100% risk of forest damage if the ratio is lower than 0.2 (Cronan and Grigal, 1995).

3.3 Recovery from soil acidification and temporal changes in soil chemical parameters

Moldan et al., (2013) studied catchments that were affected by long-term acidification in Sweden. These authors found that majority of lakes were recovering from acidification while nearly half of forest soils still exhibited symptoms of ongoing acidification. Although the emissions were reduced significantly in the Czech Republic (Figure 4) and acid deposition decreased over past 25 years as well (Figure 5), a recovery of soils continues very slowly owing to slow replacement of the base cations from weathering and/or deposition (Norton and Veselý, 2003).

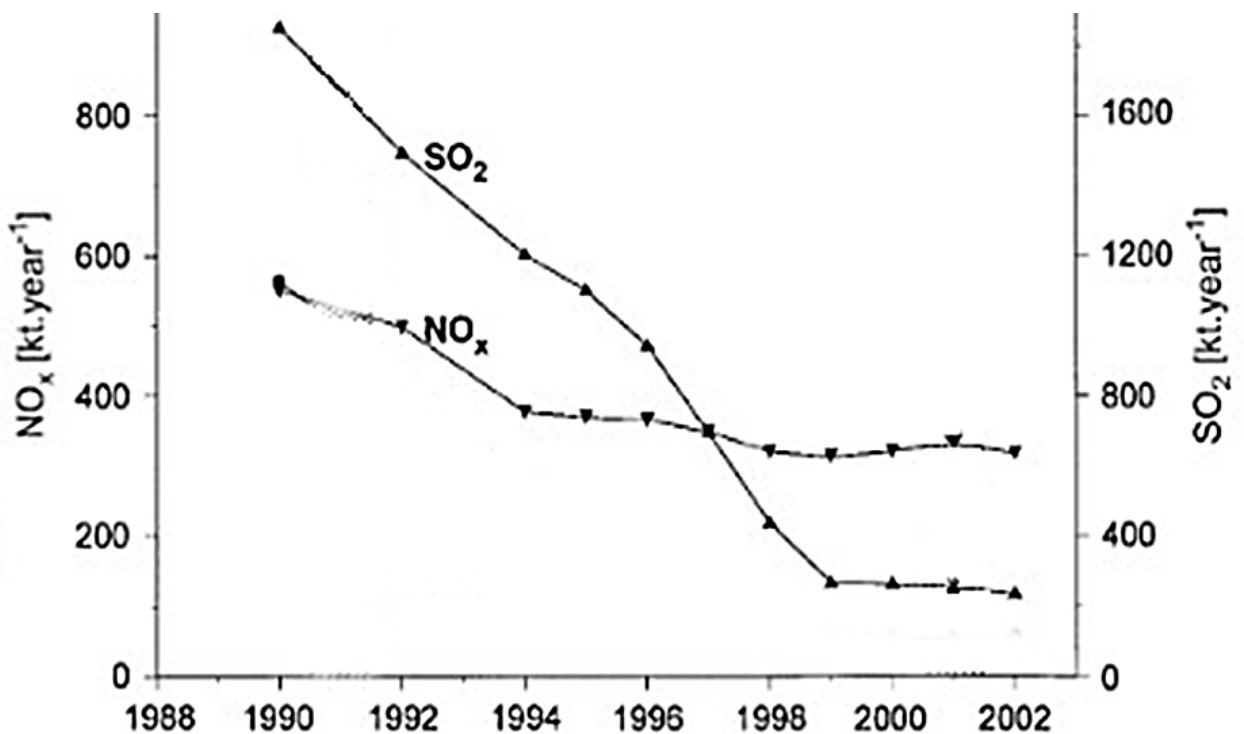


Figure 4: Total emissions of air pollutants (SO₂, NO_x) in the Czech Republic in 1990–2002 (Machálek et al., 2003 in Majer et al., 2005).

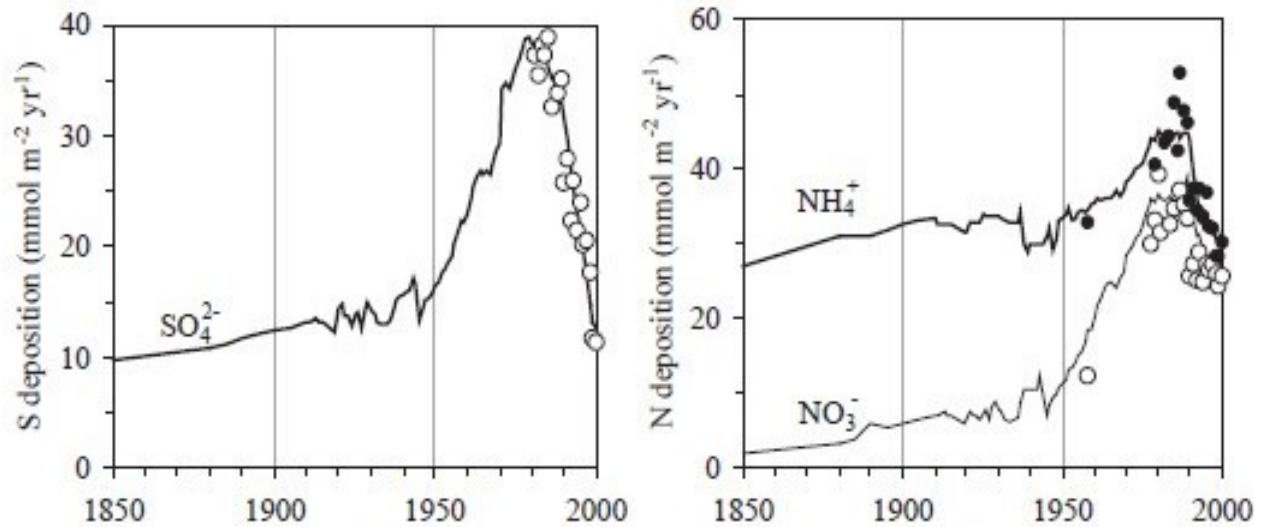


Figure 5: Reconstructed trends (lines) and observed data (circles) in wet-only S and N deposition in the Czech Republic over the period 1850–2000 (Kopáček and Veselý, 2005).

General patterns of recovery from soil acidification involve: increases in the soil pH and base saturation, concentrations of DOC (Evans et al., 2005), decreasing concentration of SO_4^{2-} and content of potentially toxic aluminum and in some part decreases in NO_3^- concentrations (Norton and Veselý, 2003). However, there are factors, varying from site to site, that limit the scale of recovery. For example inadequate reduction of acid deposition (Hrkal et al., 2006; Hruška et al., 2009), forest management practices (Hruška and Cienciala, 2003), ongoing desorption of SO_4^{2-} (Mitchel et al., 2011), increasing concentrations of DOC (Futter et al., 2014) etc.

Many studies reported that during the recovery from acidification, rate of leaching of base cations from forest soils decreases (Skjelkvåle, 2003; Garmo et al., 2014) or remains stable (Hruška et al., 2009; Helliwell et al., 2013). Generally, sites with low base saturation and poor in base-parent material with low weathering rates are unable to balance leaching of acid anion from atmospheric deposition accumulated in soils over decades (Oulehle et al., 2006). Base saturation in the top soil horizons seems to recovery faster in comparison with mineral horizons where might be expected ongoing acidification (Navrátil et al., 2007). This finding is very important since the acidification is more intensive in the topsoil than in the subsoil (Hédl et al., 2011). Commonly, Vangelova et al., (2009) conducted a comprehensive study comparing chemical fluxes in time and found out that recovery of soil pH was evident but slow at sites with very low base saturation and weathering rates. Concurrently with this trend, decreases in dissolved

inorganic aluminum concentrations were detected. Consistently, Oulehle et al., (2006) noted decreases in aluminum concentrations in soil and soil solution related to reduce acid deposition. With declining deposition of acidifying pollutants, soil organic matter increases and soil is of better quality. For example, Futter et al., (2014) found that overall average DOC concentrations in study lakes in Sweden increased from 8.5 mg.L⁻¹ in 1988 to 14.5 mg.L⁻¹ in 2012. The same pattern, increasing release of DOC to stream waters, was observed by Hruška et al., (2009) in the Czech Republic.

Overall, SO₄²⁻ concentrations in freshwaters (lakes and streams) in the Europe and North America decreased significantly (Skjelkvåle, 2003; Garmo et al., 2014). Nevertheless, response of forest soils and catchments to reduced deposition of SO₄²⁻ is heterogeneous, reflecting soil adsorption capacity and mineralization of organically bound sulfur (Prechtel et al., 2001). For instance, decreases of SO₄²⁻ in soil water were lower than the reduction in deposition in Sweden (Akselson et al., 2013). However, Futter et al., (2014) reported that SO₄²⁻ concentrations decreased in lakes proportionally to decreases in atmospheric sulfur deposition.

Desorption of SO₄²⁻ from soil may result in delayed recovery and ongoing, excessive leaching of base cations from soils (Novák et al., 2000, Driscoll et al. 2001; Oulehle et al., 2006; Akselson et al., 2013) that is in contrary to the ability of soil to retain SO₄²⁻ anions from acid deposition that regulates leaching and mitigates the acidification of surface water.

Despite to consistent downward trend of SO₄²⁻ concentrations in the soil worldwide, NO₃⁻ have exhibited variable behavior (Skjelkvåle, 2003; Garmo et al., 2014). Factors that control concentrations of NO₃⁻ in soils are very complex. For example, it is illustrated by Veselý et al., (2002) who noted a rapid decreasing trend in mountainous catchments in the Czech Republic between period 1984–1986 and 1996–2000 that was greater than the decrease of N emission. It was suggested that it was a consequence of the increased plant uptake in the late 1990s due to the recovery from acidification, concurrently with enhanced mineralization in mid-1980s due to the large scale forest decline.

3.4 Influence of European beech (*Fagus sylvatica*), Norway spruce (*Picea abies*) and impact of deforestation on soil chemistry with respect to acid deposition and organic matter

It is generally accepted that the nature of litter reflects element content in plant tissues and determines the food quality for decomposers. Beech forests exhibit higher pH, better quality of litter (Augusto et al., 2002; Pavlů et al., 2007; Tejnecký et al., 2010) and thus more favourable conditions for soil fauna. Quality of humus determines the community of decomposers that are dependent on pH (Fisher and Binkley, 2013). If the soil is strongly acidified, most of fauna disappear and it leads to accumulation of a top organic layer. This is typical for spruce forest. However, widely accepted assumption that spruce litter is slowly decomposable due to inherent recalcitrance of needles was questioned by Berger and Berger, (2012) who concluded that retarded decomposition of spruce needles is rather caused by adverse environmental conditions that could be improved by beech admixture.

As was already mentioned, canopy of spruce significantly enhances the acid input in comparison with canopy of beech (Augusto et al., 2002; Oulehle and Hruška, 2005; Binkley and Fisher, 2013). This is especially important in highly polluted areas. Since the spruce canopy scavenges more pollutants than beech, it is expected that soils under spruce have higher content of atmospherically deposited SO_4^{2-} and NO_3^- in soil solution than beech forest (Rothe et al., 2002; Binkley and Fisher, 2013). In the case of NO_3^- , larger concentrations were found under spruce forest by (Oulehle and Hruška, 2005; Berger et al., 2009). On the other hand, Tejnecký et al. (2013) observed higher concentrations under the beech forest. Different findings could be explained by conditions varying from site to site depending on acid deposition (Binkley and Fisher, 2013) or different conditions for litter decomposition. With respect to distribution of SO_4^{2-} in the soil profile, beech forest showed the highest amount of SO_4^{2-} in the surface horizon and spruce forest in the spodic horizon (Tejnecký et al., 2013).

Speaking about aluminum and its toxic form, Tejnecký et al., (2010) did not confirm the influence of type of vegetation cover (beech vs. spruce vs. clear-cut area) on water extractable Al^{3+} . However, the influence of vegetation to other, potentially toxic water-extractable aluminum forms: $\text{Al}_{\text{H}_2\text{O}}$, $\text{Al}(\text{X})^{1+}$, $\text{Al}(\text{Y})^{2+}$ was evident. Moreover, concentrations of Al^{3+} in organic horizons were higher under the beech forest than under the spruce forest and clear-cut area. It indicates that aluminum under the spruce forest is bounded into less toxic forms due to the composition of complexing organic acids. Nevertheless, in the Ore Mountains, Oulehle and Hruška (2005) found

that in spite of higher concentration of DOC in organic soil solution under the spruce cover, organically bound aluminum contributed only 30% of total aluminum, whereas under the beech cover it account for 60% of total aluminum.

Generally, when the vegetation is disturbed or clear-cut, the internal N cycle is broken as there is comparably lower biological uptake. It leads to enhanced humus mineralization and nitrification (Norton and Veselý, 2003) due to changes in microclimate that favours the activity of microorganisms. Together with anions, base cations are leached, pH decrease and acidification is introduced to ecosystem. However, once a canopy is removed, light conditions improve. These conditions may introduce the acidophilous perennial grasses (Vacek et al., 1999; Wild et al., 2004) that become an important sink for atmospheric nitrogen pollution due to rapid and large accumulation in plant tissues and consequently acidification and losses of base cations (Fiala et al., 2005; Fiala et al., 2008). The soils, primarily organic horizons, under grass cover exhibit higher pH values and lower exchangeable Al content compared to adjacent surviving forest. Mobile Al species under the grass have larger proportion of non-toxic organic complexes (Drábek et al., 2007).

4 Materials and Methods

4.1 Study area

Study area “Paličnick” is located in the northern part of the Czech Republic, in the Jizera Mountains, along the borders with Poland (Figure 6). This region was extremely affected by acid deposition due to nearby coal-fired power stations (Hruška and Cienciala, 2003). In addition, a nature-close beech forests have been substantially replaced by spruce production forests since the end of 18th century (Šnytr, 2009). It induced, along with acid bedrock and high acid deposition loads, serious soil acidification with all symptoms that represent this term (e.g. Mládková et al., 2005; Borůvka et al., 2009, Tejnecký et al., 2013). Since the last devastating effects of SO₂ immissions with a combination of other stress factors in the winter 1995/1996, health conditions of young spruce forests has been improved (Šrámek et al., 2013).

4.1.1 Climate conditions

With respect to study area Paličnick, Balcar et al., (2012) observed annual precipitation on average around 1135 mm in the period of 1994 – 2010. The altitude of the observed locality is from 635 to 680 m (Tejnecký et al., 2013). Annual temperature varies about 4–7 °C (Správa CHKO Jizerské hory).

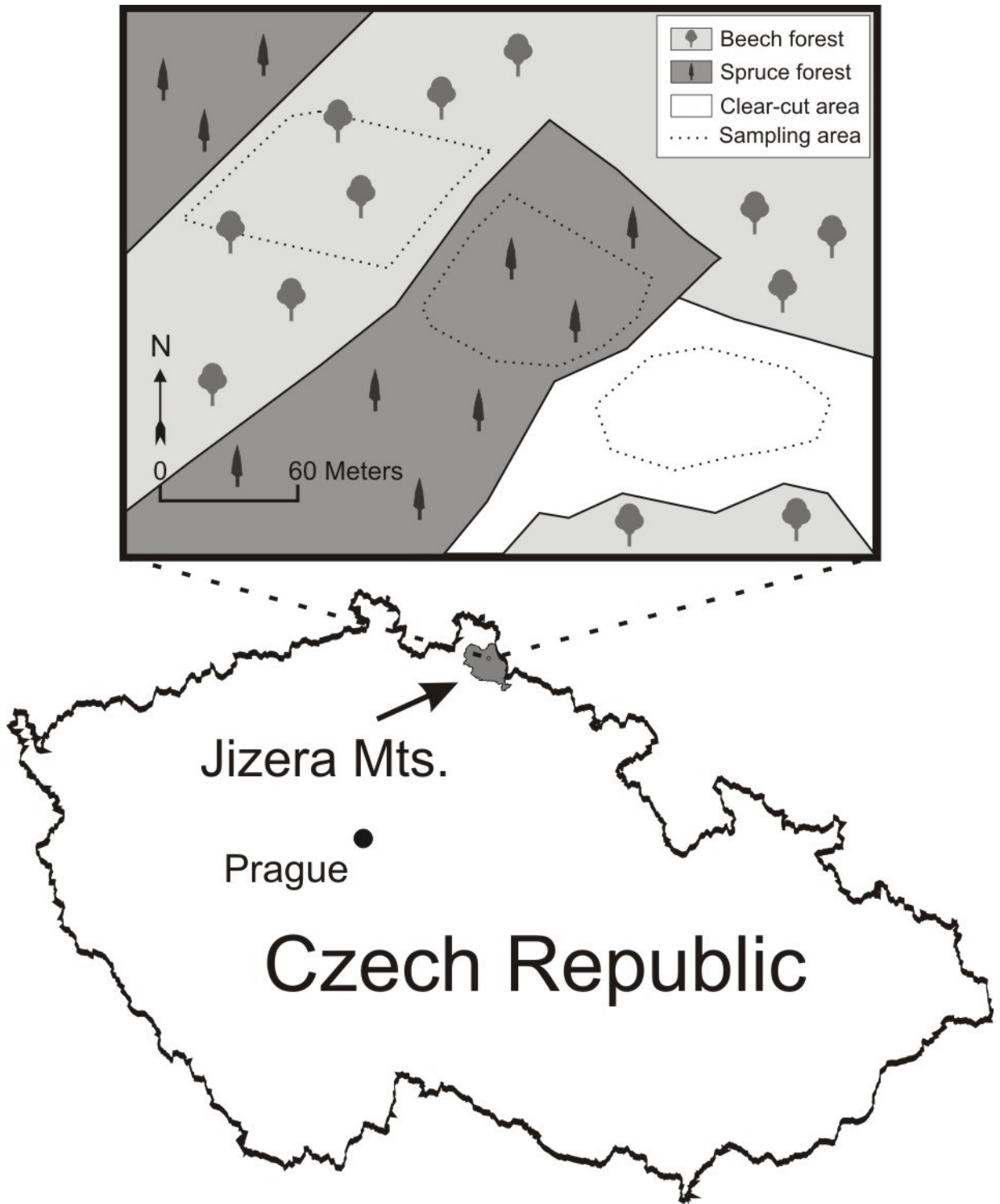


Figure 6: Location of sampling sites (top) over the area Paličnick and its location in the Czech Republic (down) (Tejnecký et al., 2013).

4.1.2 Vegetation

Study area Paličník consists of two single-tree species areas and one clear-cut area (Figure 6). Area consisted mostly of the European beech (*Fagus sylvatica*) is a residue of natural ecosystem with occurrence of perennial grasses in understory vegetation (*Calamagrostis arundinacea*, *Calamagrostis villosa*) (Figure 7). Spruce monoculture forest is a product of forest management activities. Norway spruce (*Picea abies* (L.) Karst.) is a dominant species along with perennial grasses (*Calamagrostis arundinacea*, *Calamagrostis villosa*) (Figure 8). Clear-cut area was chiefly invaded by grass, with prevailing species (*Calamagrostis villosa*). However, free-growing beech seedling and spruce coppices can be found there as well (Figure 9).



Figure 7: Beech forest and soil pit representing Dystric Cambisol (Author: Ondřej Drábek).



Figure 8: Spruce forest and soil pit representing Entic Podzol (Author: Ondřej Drábek).



Figure 9: Clear-cut area and soil pit representing Dystric Cambisols (Author: Ondřej Drábek).

4.1.3 Geological conditions and soils of the study area

The study area is located in petrologically homogenous area where medium-grained porphyric biotite granite to granodiorite (Chaloupský et al., 1989; Kratina et al., 2010) determines the development of soils with respect to vegetation cover and climate conditions. According to the World Reference Base for Soil Resources (2006), the main soil units were identified as Entic Podzols, Gleyic Podzols and Dystric Cambisols (Table 2). Color of cambic horizons was described as brown–dark brown (7.5 YR 4/4), spodic horizons were brighter, represented by light brown (7.5–10 YR 5/6) that might be a result of higher content of sesquioxides (Tejnecký et al., 2013).

Table 2: Soil units determined in the sampling areas with respect to the year of sampling and vegetation cover (WRB, 2006).

Vegetation cover	Year of sampling	
	2008	2013
Beech	Entic Podzols	Dystric Cambisols
	Dystric Cambisols	
Spruce	Entic Podzols	Entic Podzols
	Gleyic Podzols	
Clear-cut area	Entic Podzols	Dystric Cambisols
	Dystric Cambisols	

4.2 Soil sampling and soil sample treatment

Sampling was carried out in June 2008 and 2013. Three individual soil pits were dug at each single-species site (beech, spruce, clear-cut area).

Forest floor organic horizons O represented by both F horizon (intermediately decomposed, fermented organic matter) and by H horizon (highly decomposed, humified organic matter) were taken along with mineral horizons B (Bhs – spodic humusosquioxidic horizon, Bv – cambic horizon, Bvs – cambic horizon enriched with iron oxides, Bhsg – spodic humusosquioxidic horizon having gleyic patterns). If present, organo-mineral horizons A and eluvial horizons E (Ah – humic horizon, Ahe – bleached humic horizon, Epg – eluvial horizon having gleyic properties) were collected as well. Unfortunately, organo-mineral horizons were not of sufficient thickness or were absent in 2008. Organic litter horizons L were omitted. In total, 18 soil profiles were described and 72 samples collected. Samples were air dried and fine soil fraction was separated through 2 mm sieves and then archived for further analysis.

4.2.1 Sample analysis a procedures

4.2.1.1 Soil reaction

Soil samples were analyzed on exchangeable pH (pH_{KCl}) and active pH ($\text{pH}_{\text{H}_2\text{O}}$). For each sample, 2 replicates were prepared.

Active pH was determined in 1:2 (soil:water) suspension for mineral horizon and in 1:4 (soil:water) suspension for organic horizons. Deionised water was boiled prior to use in order to

remove dissolved CO₂. The suspension was placed at the shaker for 5 minutes and then pH was immediately measured by pH-metr inoLab pH Level 1 WTW, Germany.

Exchangeable pH was determined in 0.2 M KCl soil solution. Volume fraction was 1:2 (soil:solution) for mineral horizons and 1:4 (soil:solution) for organic horizons. The mixture was let to stand for 24 hours and then measured by pH-metr inoLab pH Level 1 WTW, Germany.

4.2.1.2 Exchangeable cations, exchangeable acidity and free H⁺ determination, CEC, base saturation

Total contents of exchangeable cations, exchangeable acidity (EA) and free H⁺ ions were determined according to the standard ICP Forest methods (Cools and De Vos, 2010).

Exchangeable base cations (Ca, Mg, Na, K) and the exchangeable acid cations (Al, Fe, Mn) were determined in the 0.1 M BaCl₂ extract of the soil by means of AAS (SpectrAA Varian 280FS, Australia). For each sample, 2 replicates were prepared.

Exchangeable acidity was determined by two ways. Firstly, by titration of 0.1 M BaCl₂ extract by 0.05 M NaOH solution to an endpoint of pH 7.8 or alternatively, by calculation of a sum of acid cations (units: cmol₍₊₎kg⁻¹) determined by spectrometry and free H⁺ ions determined by the German calculation method using the Ulrich/Prenzel factor for different pH values of BaCl₂ extract after leaching procedure.

Relationship between exchangeable acidity that was determined by titration (EA titration) and exchangeable acidity obtained as a sum of acid cations (EA sum up) was described by linear model of simple regression.

The equation of the fitted model is EA sum up = -0.413157 + 0.917275*EA titration. Analysis of variance ANOVA showed statistically significant relationship between the variables ($p < 0.05$). The R-Squared statistic indicates that the model as fitted explains 97.97% of the variability in EA sum up (Figure 10).

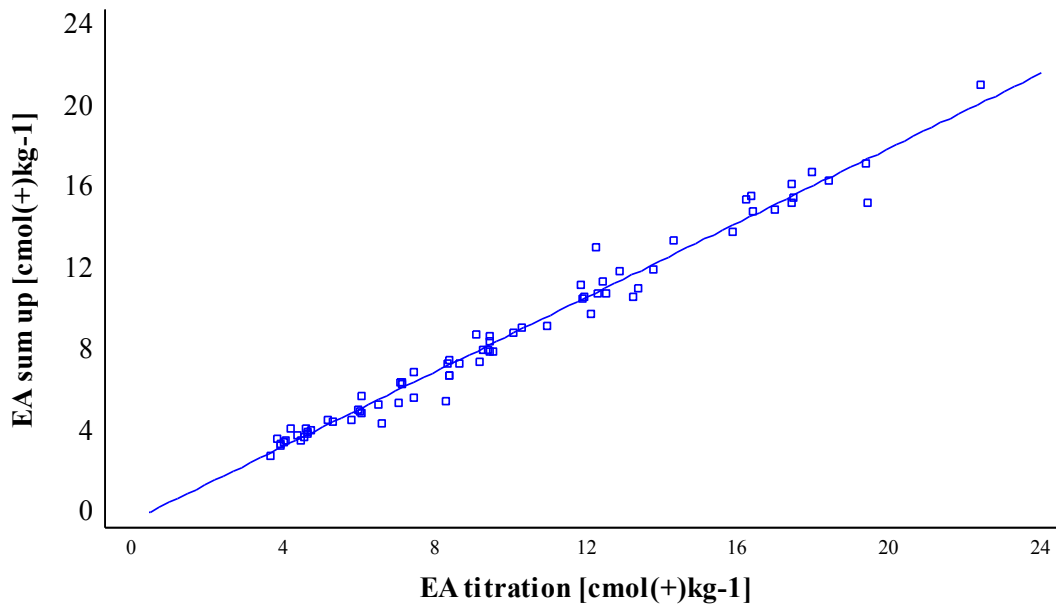


Figure 10: Simple regression of EA determined by titration (EA titration) and EA determined as a sum of acid cations (EA sum up).

However, results calculated from sum of exchangeable acid cations and free H^+ ions were chosen for further interpretation. The reason is obvious, concentrations of exchangeable cations measured by AAS are more precise than titration method that is more or less dependent on the subjective perception of the laboratory worker as well as on the accuracy of the used equipment.

Cation exchangeable capacity (CEC) was calculated as a sum of exchangeable cations (Ca, Mg, Na, K, Al, Fe, Mn, H). Base saturation (BS) was determined as the fraction of CEC associated with base cations (Ca, Mg, Na and K). The Ca:Al molar ratio was calculated from mean values of exchangeable Ca and Al in $cmol_{(+)}kg^{-1}$.

4.2.1.3 Determination of NCS

The determination of N, C, S in the organic horizons was carried out simultaneously and performed at the Elementary Analyzer Flash 2000 NCS (Thermo Scientific). Soil samples were properly homogenized in order to obtain sufficient amount of defined fine fraction (granularity of 100-200 μm). This has been performed by proper ball mills (Fritsch Vibratory Micro Mill pulverisette 0/sieve shaker analysette 3 SPARTAN). In order to ensure complete conversion of inorganic sulfur, up to 5 mg of vanadium pentoxide was added into every single tin container for small sample quantities. For each sample, 3 replicates were prepared. Using spatula, the amount of soil sample (5 – 10 g) was introduced into the tin container in three repetitions. Using two

spring tweezers, every filled container was carefully closed and the shape of pellet was obtained. The C:N ratio was calculated from mean values of C and N, as a percentage of weight.

4.2.2 Statistical analysis

Stratigraphics XVI.I Centurion and MS Excel were used for statistical analyses and graphical description. Multifactor analysis of variance (MANOVA) was done to test mean differences of basic soil characteristics between years 2008 and 2013, vegetation (beech, spruce, clear-cut area) and horizons (F, H, A, B) for the total dataset. Then one-way ANOVA was used in order to determine influence of horizon and year of sampling at each stand separately. However, organic horizons A from the year 2008 were not subject of one way ANOVA due to insufficient thickness or absence. Probability level of significance is shown as: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. The F-tests in the ANOVA identified the significant factors. For each significant factor, the multiple range tests using Fisher's least significant difference (LSD) procedure ($p < 0.05$) was performed in order to determine which means are significantly different from which others. Simple linear regression analysis was performed in order to evaluate the relationships between dependent and independent variables. Pearson product moment correlations were used in order to display the strength of the linear relationship between variables at the 95.0% confidence level.

4.3 Phytocenological research

Phytocenological research was conducted by Mgr. Tereza Klinerová in 2008 and Mgr. Ing. Zuzana Michalová in 2013. Mgr. Ing. Zuzana Michalová performed statistical analysis of dataset and provided obtained results.

The data on vegetation composition were taken using the modified Braun-Blanquet scale (Westhoff and Van der Maarel, 1978) post-transformed to percentage coverage using the median values of intervals and square-rooted prior to the analyses. In order to display the changes in vegetation composition, the non-metric multidimensional scaling (NMDS) approach was applied. NMDS was run for two-dimensional space, with 100 random starts, in order to find the global optimum (stable solution) and the product was subject to PCA to maximize the variability explained by the first canonical axis (standard setting of the meta MDS function). The shift in vegetation composition was addressed using the Bray-Curtis distance of vegetation records taken in years of 2008 and 2013. Ellenberg indicator values were used to define the changes in vegetation composition between the years 2008–2013, in terms of light, temperature, soil moisture, soil reaction, nutrient content and continentality. The influence of particular variables

on the vegetation composition was analyzed using permutation test with 999 repetitions with the “envfit” function. The 90% confidence interval envelopes were included in plots to illustrate the equivalent error bubble around most probable groups of stands (“Beech”, “Spruce” and “Clear-cut”). Ultimately, the between-year differences in Ellenberg values as proxy for environmental changes were addressed using the non-parametric Kruskal-Wallis analysis of variance (used because of low number of data points). The normality of distribution was controlled with the regression residual graphs. Median and inter-quartile point distribution is presented in the graphs. The computations were provided in R software (R Core Team 2013). Ellenberg values were obtained from JUICE software (Tichý 2002).

5 Results

The results of MANOVA described the effects of the three selected factors (year, vegetation and horizon) on soil parameters. Type of soil horizon had a statistically significant effect on all observed parameters with exception of S. Vegetation had a significant influence on the $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} , Na, Mn, Fe, H and BS (but not on the Ca, Mg, K, Al, CEC, EA, N and S). Year of sampling as a factor significantly contributed to changes in pH_{KCl} , Ca, Al, Mn, Fe, H, CEC, EA, BS but not to the other parameters ($\text{pH}_{\text{H}_2\text{O}}$, Mg, K, Na, C, N, S). (Table 3, 4)

Table 3: Multifactor analysis of variance (MANOVA) of basic soil parameters in all sampled horizons (n=72).

	pH _{H2O}	pH _{KCl}	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS
	F-RATIO												
Year ^a	0.06	4.37*	5.77*	0.54	0.01	1.19	29.7***	7.39**	33.3***	5.25*	15.7***	36.5***	11.9***
Vegetation ^b	10.2***	24.0***	1.14	0.88	2.6	7.31**	0.02	3.31*	7.20**	22.3***	0.83	2.62	3.25*
Horizon ^c	18.2***	57.2***	43.5***	91.0***	111***	38.0***	35.8***	18.8***	26.5***	35.0***	157***	54.3***	51.9***

Probability level of significance is shown as: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Indexes: a (2008, 2013), b (Beech forest, Spruce forest, Clear-cut area), c (F, H, A, B)

*71 samples in the case of manganese

Table 4: Multifactor analysis of variance (MANOVA) of nitrogen, carbon, sulfur content in organic horizons (n=36).

	N	C	S
	F-RATIO		
Year ^a	1.77	0.29	1.53
Vegetation ^b	1.43	3.78*	0.50
Horizon ^c	19.2***	14.2***	1.05

Probability level of significance is shown as: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Indexes: a (2008, 2013), b (Beech forest, Spruce forest, Clear-cut area), c (F, H)

Table 5: Basic statistical parameters of soil properties for the total set of soil samples according to the type of vegetation cover and results of multiple range test. Different letters (a, b) indicate significant differences between means at the 95.0% confidence level using the Fisher's least significant difference (LSD) procedure.

Beech forest

	pH _{H2O}	pH _{KCl}	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	N	C	S	
			mg.kg ⁻¹								cmol(+).kg ⁻¹		%				
Count	24	24	24	24	24	24	24	24	24	24	24	24	24	24	12	12	12
Average	4.02 b	3.38 b	428	43.6	114	13.0 ab	613	20.4 ab	85.1 a	0.73 a	10.9	8.08	18.4 ab	1.32	26.0 a	0.15	
Median	4.00	3.33	76.8	24.2	70.2	10.2	550	4.19	71.5	0.58	9.88	7.43	9.50	1.27	25.5	0.16	
SD	0.20	0.27	722	43.1	102	7.20	311	37.9	74.7	0.64	6.55	4.20	18.9	0.36	7.87	0.05	
Coef. of var.	5%	8%	169%	99%	90%	55%	51%	186%	88%	88%	60%	52%	102%	27%	30%	35%	
Minimum	3.64	2.86	6.64	5.33	13.9	5.19	235	1.30	3.88	0.10	2.95	2.79	5.49	0.68	12.5	0.03	
Maximum	4.39	3.88	2703	154	336	27.7	1301	145	266	2.78	25.7	16.3	75.5	1.91	41.1	0.21	

Spruce forest

	pH _{H2O}	pH _{KCl}	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	N	C	S	
			mg.kg ⁻¹								cmol(+).kg ⁻¹		%				
Count	24	24	24	24	24	24	24	23	24	24	24	24	24	24	12	12	12
Average	3.76 a	3.05 a	306	46.7	117	15.3 b	615	14.5 a	144 b	1.81 b	11.8	9.47	14.4 a	1.45	32.5 b	0.16	
Median	3.67	2.92	52.9	34.0	103	14.2	590	5.87	127	1.45	11.0	8.90	7.50	1.56	32.9	0.16	
SD	0.24	0.41	476	39.8	96.3	7.13	260	16.0	106	1.38	6.23	4.33	14.1	0.27	6.95	0.02	
Coef. of var.	7%	13%	155%	85%	82%	47%	42%	110%	131%	76%	53%	46%	98%	19%	21%	14%	
Minimum	3.51	2.55	4.27	4.09	8.86	3.52	277	1.31	5.57	0.13	3.44	3.27	3.53	0.96	22.6	0.10	
Maximum	4.33	3.94	1370	123	254	28.6	1164	57.2	381	4.39	23.3	17.2	47.8	1.74	41.7	0.19	

Clear-cut area

	pH _{H2O}	pH _{KCl}	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	N	C	S	
			mg.kg ⁻¹								cmol(+).kg ⁻¹		%				
Count	24	24	24	24	24	24	24	24	24	24	24	24	24	24	12	12	12
Average	3.86 a	3.32 b	467	51.3	140	10.6 a	606	37.3 b	99.0 a	0.89 a	11.5	8.30	21.5 b	1.49	28.8 ab	0.17	
Median	3.86	3.30	220	41.8	113	9.91	458	12.2	73.7	1.45	11.2	6.55	9.7	1.45	26.8	0.16	
SD	0.32	0.29	740	49.8	118	5.86	347	66.2	86.6	0.68	6.50	4.78	19.7	0.30	5.58	0.04	
Coef. of var.	8%	9%	158%	97%	84%	55%	57%	177%	88%	77%	57%	58%	92%	20%	19%	25%	
Minimum	2.92	2.77	0.00	5.34	18.5	3.79	136	1.22	11.5	0.10	3.87	3.39	3.89	1.11	22.6	0.11	
Maximum	4.37	3.87	3339	218	483	29.6	1520	233	300	2.51	24.0	21.1	85	1.96	37.7	0.24	

SD – standard deviation, *CEC* – cation exchange capacity, *EA* – exchangeable acidity. *a* represents the lowest mean.

5.1 Soil reaction

Active and exchangeable pH (H_2O , KCl) measured in the beech stand exhibited the highest values 4.02 ± 0.20 , 3.38 ± 0.27 , followed by lower values in the clear-cut area 3.86 ± 0.32 , 3.32 ± 0.29 and under the spruce forest 3.76 ± 0.24 , 3.05 ± 0.41 , respectively. The $\text{pH}_{\text{H}_2\text{O}}$ under the beech forest and the pH_{KCl} under the spruce forest differed significantly from other stands ($p < 0.05$). (Table 5)

5.1.1 Active $\text{pH}_{\text{H}_2\text{O}}$

Beech forest

The mineral horizon B exhibited persistently the highest ($p < 0.05$) $\text{pH}_{\text{H}_2\text{O}}$ in both years (4.26 ± 0.04 in 2008 and 4.27 ± 0.14 in 2013). The lowest $\text{pH}_{\text{H}_2\text{O}}$ was characteristic for organic horizons. For instance, in the year 2008, $\text{pH}_{\text{H}_2\text{O}}$ ranged from 3.91 to 3.97. (Table 6)

Spruce forest

The highest $\text{pH}_{\text{H}_2\text{O}}$ ($p < 0.05$) was observed in the mineral B horizon (4.13 ± 0.04 in 2008 and 4.12 ± 0.19 in 2013). Horizons (F, H) exhibited values varying about 3.62 ± 0.16 (F horizon, 2008) and 3.67 ± 0.13 (H horizon, 2013). There was no difference in pH between years of sampling. (Table 6)

Clear-cut area

The highest $\text{pH}_{\text{H}_2\text{O}}$ ($p < 0.05$) was observed in the B horizon (4.11 ± 0.27 in 2008 and 4.16 ± 0.02 in 2013). No significant change between years of sampling was determined. Only slight increase between 2008 and 2013 was evident in the surface F horizon in which the $\text{pH}_{\text{H}_2\text{O}}$ increased from 3.74 ± 0.17 (2008) to 3.97 ± 0.29 (2008) and in turn slight decrease in the H horizon 3.79 ± 0.23 (2008) and 3.68 ± 0.06 (2013). (Table 6)

5.1.2 Exchangeable pH_{KCl}

Beech forest

An exchangeable pH_{KCl} showed an increasing tendency ($p < 0.05$) with increasing depth in 2008. The lowest exchangeable pH_{KCl} experienced the F horizon 3.03 ± 0.21 and the B horizon showed the highest values 3.75 ± 0.02 . Similarly, in 2013, the average pH_{KCl} was the highest ($p < 0.05$) in the B horizon 3.77 ± 0.13 whereas the pH_{KCl} in organic horizons (F, H) did not vary significantly (3.23 ± 0.12 and 3.29 ± 0.14 , respectively). (Table 6)

Spruce forest

In 2008, the pH_{KCl} increased from very low 2.68 ± 0.20 in the F horizon, over 2.76 ± 0.22 , 2.98 ± 0.16 in the H to 3.66 ± 0.99 in the B horizon in which the pH_{KCl} was significantly highest

($p < 0.05$). In 2013, the pH_{KCl} similar pattern was observed. Mineral horizon B showed significantly ($p < 0.05$) higher pH_{KCl} values (3.73 ± 0.19) in comparison with the other horizons. No significant change between years of sampling was observed. (Table 6)

Clear-cut area

In both years, the highest pH_{KCl} ($p < 0.05$) was measured in the subsurface B horizon (3.55 ± 0.31 in 2008 and 3.76 ± 0.09 in 2013). The lowest value ($p < 0.05$) was measured in the F horizon (2.95 ± 0.12 in 2008) in which significant between-years change in pH_{KCl} was determined. The pH_{KCl} increased to 3.36 ± 0.04 in 2013.

Table 6: Mean soil pH values (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons B under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Horizon	Year	pHH ₂ O			pHKCl		
		mean	SD	HG	mean	SD	HG
F	2008	3.91	0.05	a	3.03	0.21	a
H	2008	3.97	0.14	a	3.26	0.17	a
B	2008	4.26	0.04	b	3.75	0.02	b
F	2013	3.96	0.20	ab	3.23	0.12	a
H	2013	3.87	0.22	a	3.29	0.14	a
A	2013	3.83	0.09	a	3.32	0.09	a
B	2013	4.27	0.14	b	3.77	0.13	b
F	2008	3.62	0.16	a	2.68	0.20	a
H	2008	3.62	0.13	a	2.76	0.22	a
B	2008	4.13	0.04	b	3.66	0.09	b
F	2013	3.63	0.12	a	2.75	0.07	a
H	2013	3.67	0.13	a	2.92	0.09	a
A	2013	3.62	0.05	a	2.92	0.04	a
B	2013	4.12	0.19	b	3.73	0.19	b
F	2008	3.74	0.17	a	2.95	0.12	a
H	2008	3.79	0.23	a	3.07	0.28	ab
B	2008	4.11	0.27	a	3.55	0.31	b
F	2013	3.97	0.29	ab	(3.36)	0.04	a
H	2013	3.68	0.06	a	3.21	0.14	a
A	2013	3.73	0.16	a	3.27	0.02	a
B	2013	4.16	0.02	b	3.76	0.09	b

SD – standard deviation. HG – homogeneous group, describes statistically significant differences between horizons at $p < 0.05$, a represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$.

5.2 CEC – cation exchange capacity

Cation exchange capacity showed decreasing trend in dependence on the depth (Figure 11). Major cations were Ca and Al. Cation exchange capacity was on average slightly higher in the spruce forest $11.8 \pm 6.23 \text{ cmol}_{(+)}\text{kg}^{-1}$, followed by clear-cut area $11.5 \pm 6.50 \text{ cmol}_{(+)}\text{kg}^{-1}$ and beech forest $10.9 \pm 6.55 \text{ cmol}_{(+)}\text{kg}^{-1}$ (Table 5).

Beech forest

Cation exchange capacity exhibited a decreasing trend with increasing depth in both years of sampling ($p < 0.05$). The highest CEC was measured in the organic horizon F ($21.6 \pm 3.55 \text{ cmol}_{(+)}\text{kg}^{-1}$ in 2008 and $18.5 \pm 1.83 \text{ cmol}_{(+)}\text{kg}^{-1}$ in 2013). The lowest CEC values were observed in the mineral horizon B ($4.10 \pm 0.35 \text{ cmol}_{(+)}\text{kg}^{-1}$ in 2008 and $3.64 \pm 0.62 \text{ cmol}_{(+)}\text{kg}^{-1}$ in 2013). (Table 7)

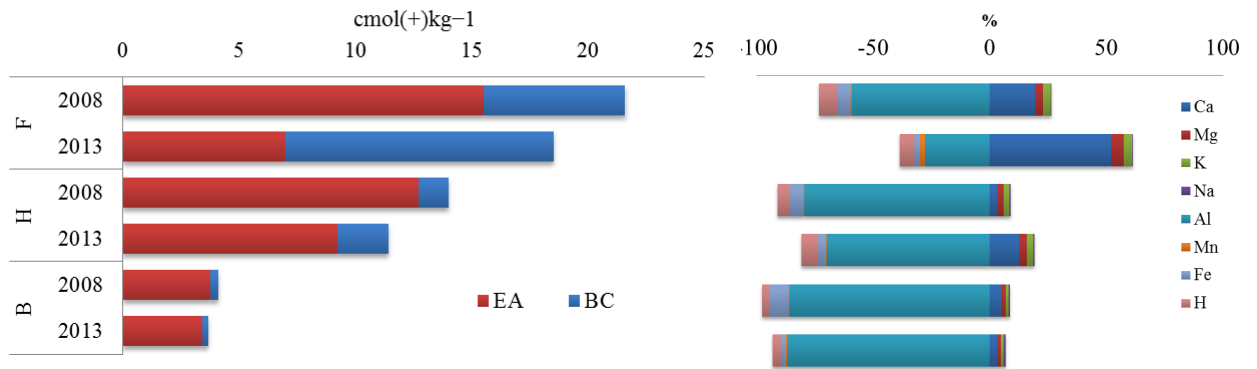
Spruce forest

Decreasing trend in CEC with increasing depth was identified in the spruce forest ($p < 0.05$). In 2008, cation exchange capacity in the F horizon was about $21.2 \pm 2.41 \text{ cmol}_{(+)}\text{kg}^{-1}$, in the B horizon about $4.43 \pm 0.36 \text{ cmol}_{(+)}\text{kg}^{-1}$. In 2013, cation exchange capacity in the F horizon was about $16.9 \pm 1.96 \text{ cmol}_{(+)}\text{kg}^{-1}$, in the B horizon about $4.22 \pm 0.68 \text{ cmol}_{(+)}\text{kg}^{-1}$. Temporal changes were observed in the organic horizon H in which the CEC significantly decreased ($p < 0.05$) from $17.7 \pm 2.72 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2008) to $12.8 \pm 0.61 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2013). (Table 7)

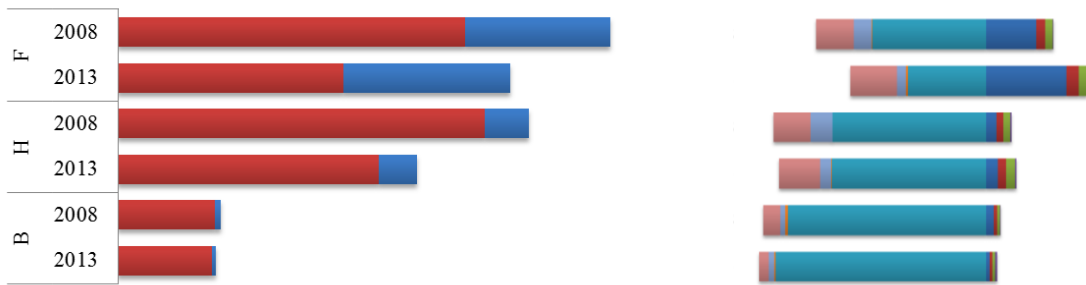
Clear-cut area

In both years of sampling, subsurface horizons commonly exhibited significantly lower ($p < 0.05$) CEC than organic horizons. In the year 2008, CEC reached $18.8 \pm 2.76 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $18.9 \pm 4.48 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the F and H horizons and $5.07 \pm 0.99 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the B horizon. In the year 2013, it reached $17.6 \pm 5.01 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $13.0 \pm 0.63 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the F and H horizons and $6.98 \pm 1.32 \text{ cmol}_{(+)}\text{kg}^{-1}$ and $4.35 \pm 0.58 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the A and B horizons respectively. (Table 7)

a) Beech forest



b) Spruce forest



c) Clear-cut area

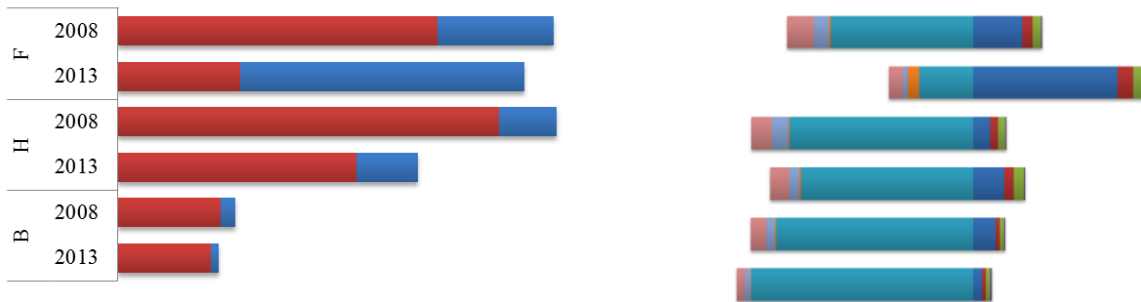


Figure 11: Cation exchange capacity (consisted of EA – exchangeable acidity and BC – sum of base cations) between years and horizons (F, H, B)) under different type of vegetation cover (left side) (n=3).

Figure 12: Proportion of exchangeable cations on the cation exchange capacity between years and horizons (F, H, B) under different type of vegetation. Acid cations are represented by negative values and base cations by positive ones (right side) (n=3).

5.3 Base saturation and base cations

Overall, base saturation reached the highest ($p<0.05$) mean values in the clear-cut area $21.5\pm 19.7\%$, slightly lower values were observed in the beech forest $18.4\pm 18.9\%$ and the lowest ($p<0.05$) saturation was determined in spruce forest $14.4\pm 14.1\%$. Calcium concentrations were the highest in the clear-cut area $467\pm 740 \text{ mg kg}^{-1}$, followed by the beech forest $428\pm 722 \text{ mg kg}^{-1}$ and the spruce forest $306\pm 476 \text{ mg kg}^{-1}$. Magnesium concentrations were the highest in the clear-cut area $51.3\pm 49.8 \text{ mg kg}^{-1}$, followed by the spruce forest $46.7\pm 39.8 \text{ mg kg}^{-1}$, and the beech stand $43.6\pm 43.1 \text{ mg kg}^{-1}$. Potassium concentrations decreased in the following order the clear-cut area $140\pm 118 \text{ mg kg}^{-1}$, the spruce forest $117\pm 96.3 \text{ mg kg}^{-1}$ and the beech stand $114\pm 102 \text{ mg kg}^{-1}$. No statistically significant differences in Ca, Mg, K concentrations between stands were found. Sodium concentrations were the highest in the forest stand $15.3\pm 7.13 \text{ mg kg}^{-1}$, followed by the beech forest $13.0\pm 7.20 \text{ mg kg}^{-1}$ and the clear-cut area $10.6\pm 5.86 \text{ mg kg}^{-1}$. Statistically significant difference ($p<0.05$) was found between clear-cut area and spruce forest. (Table 5).

Beech forest

In both years of sampling, the highest ($p<0.05$) base saturation was found in the upper organic horizon F (Figure 11a). It reached $26.6\pm 14.0\%$ in 2008 and $61.5\pm 12.2\%$ in 2013. This increase between years of sampling was statistically significant ($p<0.05$). (Table 7)

Concentrations of exchangeable Ca were significantly higher ($p<0.05$) in the upper organic horizons F than in other horizons. This was true for both years of sampling when concentrations reached $909\pm 762 \text{ mg kg}^{-1}$ (2008) and $1960\pm 656 \text{ mg kg}^{-1}$ (2013). No significant change between years of sampling was found. (Table 8)

Magnesium showed a decreasing tendency with increasing depth. The upper organic horizon F exhibited the highest ($p<0.05$) concentration in both years of sampling $90.6\pm 29.6 \text{ mg kg}^{-1}$ (2008) and $123\pm 35.5 \text{ mg kg}^{-1}$ (2013). (Table 8)

Potassium concentrations showed a decreasing pattern within organic horizons. However, significant differences between horizons diminished with increasing depth. The highest concentrations were determined in the upper organic horizon F ($268\pm 67.4 \text{ mg kg}^{-1}$ in 2008 and $255\pm 23.7 \text{ mg kg}^{-1}$ in 2013) and the lowest in the mineral horizon B ($21.1\pm 6.24 \text{ mg kg}^{-1}$ in 2008 and $15.9\pm 1.59 \text{ mg kg}^{-1}$ in 2013). No significant changes between years were determined. (Table 9)

In 2008, exchangeable Na followed decreasing pattern in dependence on the increasing depth. Higher amount of Na was found in organic horizons F, H in comparison with the subsurface horizon B in 2008 ($p<0.05$) and 2013. Statistically significant decrease at the 95.0% level of confidence was noted in the F horizon. Between years of sampling, Na declined from 24.7 ± 2.99 mg kg⁻¹ (2008) to 16.1 ± 3.61 mg kg⁻¹ (2013). (Table 9)

Spruce forest

On average, the highest ($p<0.05$) base saturation was identified in the F horizon in both years of sampling ($28.4\pm 13.5\%$ in 2008 and $42.8\pm 5.20\%$ in 2013) and declined with increasing depth (Figure 11b). In the mineral horizon B, statistically significant decrease was determined. The B horizon reached $6.18\pm 0.33\%$ in 2008 and only $4.62\pm 0.55\%$ in 2013. (Table 7)

Calcium under the spruce forest showed significantly higher ($p<0.05$) concentrations in the F horizons than in the remaining horizons (937 ± 637 mg kg⁻¹ in 2008 and 1135 ± 32.5 mg kg⁻¹ in 2013). Significant decreases ($p<0.05$) between years of sampling were determined mineral horizon B. Concentrations decreased from 28.3 ± 0.67 mg kg⁻¹ in 2008 to 12.5 ± 4.73 mg kg⁻¹ in 2013. (Table 8)

In both years, the spruce forest exhibited decreasing pattern of exchangeable Mg in dependence on increasing depth. The highest ($p<0.05$) concentrations of Mg were determined in the organic horizon F. The lowest concentrations were determined in the B horizon (7.97 ± 0.94 mg kg⁻¹ in 2008 and 5.64 ± 1.35 mg kg⁻¹). (Table 8)

Organic horizons (F, H) showed considerable higher ($p<0.05$) concentrations of K than subsurface horizons, varying from 239 ± 15.0 mg kg⁻¹ (F horizon, 2008) to 184 ± 24.3 mg kg⁻¹ (H horizon, 2013). (Table 9)

In both years of sampling, the highest ($p<0.05$) concentrations of Na were found in organic horizons, e.g. the H horizon (23.8 ± 5.07 mg kg⁻¹ in 2008 and 20.2 ± 5.51 mg kg⁻¹ in 2013). Statistically significant difference ($p<0.05$) between means was noted in the B horizon in which the content of Na increased from 5.38 ± 1.62 mg kg⁻¹ (2008) to 9.28 ± 0.50 mg kg⁻¹ (2013). (Table 9)

Clear-cut area

In 2008, the highest base saturation was determined in the F horizon and gradually decreased with increasing depth ($27.1\pm 5.37\%$, $13.2\pm 3.25\%$, $12.8\pm 6.19\%$ in F, H, B horizons, respectively).

Statistically significant ($p<0.05$) increment between years of sampling was observed in the F horizon. Base saturation increased up to $67.1\pm 15.8\%$. (2013). (Table 7)

The highest ($p<0.05$) concentrations of Ca were determined in the upper organic horizon F ($714\pm 150 \text{ mg kg}^{-1}$ in 2008 and $2086\pm 1103 \text{ mg kg}^{-1}$ in 2013) and the lowest in the B horizon ($90.1\pm 58.1 \text{ mg kg}^{-1}$ in 2008 and $32.1\pm 27.7 \text{ mg kg}^{-1}$). However, there was no statistically significant difference found between years of sampling. (Table 8)

Concentrations of Mg were significantly higher ($p<0.05$) in both organic horizons (F, H) in the year 2008 ($93.8\pm 24.5 \text{ mg kg}^{-1}$ and $66.6\pm 8.09 \text{ mg kg}^{-1}$, respectively) and only in the F horizon in the year 2013 ($134\pm 73.2 \text{ mg kg}^{-1}$). Generally, Mg continued declining with increasing depth. (Table 8)

Organic horizons showed noticeably higher concentrations of K than mineral horizons in both years of sampling. The highest amount was measured in the upper F horizon in 2013 in which the concentrations reached $282\pm 174 \text{ mg kg}^{-1}$. The lowest amount was on average noted in the mineral horizon B where the concentrations of K stayed stable ($\approx 30 \text{ mg kg}^{-1}$). (Table 9)

Overall, the largest pool of exchangeable Na was determined in organic horizons. For instance, Na reached $15.4\pm 4.35 \text{ mg kg}^{-1}$ (F horizon, 2013). Concentrations in the subsurface horizons varied between $8.26\pm 1.77 \text{ mg kg}^{-1}$ (A horizon, 2013) and $5.11\pm 0.93 \text{ mg kg}^{-1}$ (B horizon, 2008). (Table 9)

5.4 Exchangeable acidity and acid cations

Exchangeable acidity was the highest in the spruce forest $9.47\pm 4.33 \text{ cmol}_{(+)}\text{kg}^{-1}$, followed by the clear-cut $8.30\pm 4.78 \text{ cmol}_{(+)}\text{kg}^{-1}$ and the beech forest $8.08\pm 4.20 \text{ cmol}_{(+)}\text{kg}^{-1}$. Free H ions showed the same pattern (1.81 ± 1.38 , 0.89 ± 0.68 , $0.73\pm 0.64 \text{ cmol}_{(+)}\text{kg}^{-1}$, respectively).

Aluminum exhibited the highest values in the spruce forest $615\pm 260 \text{ mg kg}^{-1}$, followed by the beech forest $613\pm 311 \text{ mg kg}^{-1}$ and the clear-cut area $606\pm 347 \text{ mg kg}^{-1}$. No statistically significant difference between stands was found. Iron showed significantly higher ($p<0.05$) concentrations in the spruce forest $144\pm 106 \text{ mg kg}^{-1}$ as compared with the clear-cut area $99.0\pm 86.6 \text{ mg kg}^{-1}$ and the beech forest $85.1\pm 74.7 \text{ mg kg}^{-1}$. Manganese concentrations performed very high variability at overall. The highest content of Mn was measured in the clear-cut area $37.3\pm 66.2 \text{ mg kg}^{-1}$, followed by the beech forest $20.4\pm 37.9 \text{ mg kg}^{-1}$ and the spruce forest $13.9\pm 16.0 \text{ mg kg}^{-1}$. (Table 5)

Beech forest

In 2008, the exchangeable acidity measured in both organic horizons was higher ($p<0.05$) than in mineral horizons ($15.5\pm 0.76 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the F horizon and $12.7\pm 2.46 \text{ cmol}_{(+)}\text{kg}^{-1}$ in the H horizon). In 2013, the highest exchangeable acidity was found in the H horizon ($9.21\pm 1.43 \text{ cmol}_{(+)}\text{kg}^{-1}$). Statistically significant change between years was noted in the F horizon in which the exchangeable acidity decreased to $6.97\pm 1.67 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2013). (Table 7)

In 2008, the highest ($p<0.05$) concentrations of Al were found in the organic horizons. The F horizon reached $1114\pm 176 \text{ mg kg}^{-1}$ and the H horizon $999\pm 179 \text{ mg kg}^{-1}$. In the year 2013, the highest concentrations were observed in the H horizon $720\pm 116 \text{ mg kg}^{-1}$. Statistically significant difference ($p<0.05$) between years of sampling was identified in the F horizon in which the concentrations of Al decreased to $446\pm 181 \text{ mg kg}^{-1}$ (2013). (Table 10)

Generally, the largest concentrations of Mn were determined in the F horizon in both years. In addition, concentrations increased significantly ($p<0.05$) from $25.2\pm 19.5 \text{ mg kg}^{-1}$ (2008) to $112\pm 36.4 \text{ mg kg}^{-1}$ (2013) within the horizon F and from $2.89\pm 0.76 \text{ mg kg}^{-1}$ (2008) to $8.71\pm 2.72 \text{ mg kg}^{-1}$ (2013) in the H horizon. (Table 10)

Iron concentrations in the year 2008, similarly to Al, showed the largest ($p<0.05$) content in the organic horizons. The highest concentrations were found in the upper organic horizon F $225\pm 47.4 \text{ mg kg}^{-1}$ and the lowest ones were found in the mineral B horizon $12.0\pm 1.69 \text{ mg kg}^{-1}$. Statistically significant decrease ($p<0.05$) between years of sampling was determined in the F horizon in which Fe decreased to $153\pm 26.6 \text{ mg kg}^{-1}$ (2013). The amount of free H ions was the highest in the F horizon and decreased with depth in both years of sampling. (Table 11)

Spruce forest

Soil exchangeable acidity under the spruce forest in 2008 was the highest in both organic horizons and decreased ($p<0.05$) in dependence on increasing depth. In 2013, the highest ($p<0.05$) value was determined in the H horizon and the lowest ($p<0.05$) in the B horizon ($4.02\pm 0.66 \text{ cmol}_{(+)}\text{kg}^{-1}$). Statistically significant changes ($p<0.05$) were described in both organic horizons between years of sampling. Exchangeable acidity decreased from $15.0\pm 1.17 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2008) to $9.70\pm 2.01 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2013) in the F horizon and $15.08\pm 2.07 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2008) to $11.2\pm 0.57 \text{ cmol}_{(+)}\text{kg}^{-1}$ (2013) in the H horizon. (Table 7)

Overall, the highest ($p<0.05$) contents of Al within the soil profiles were found in both organic horizons in 2008 and only in the H horizon in 2013. With increasing depth, differences between horizons gradually decreased. Exchangeable Al measured under the spruce forest

showed significant decrease ($p<0.05$) between years in the H horizon. It decreased from 1016 ± 77.2 mg kg⁻¹ (2008) to 751 ± 66.2 mg kg⁻¹ (2013). (Table 10)

In total, Mn concentrations were higher in the organic horizon F (29.0 ± 14.1 mg kg⁻¹ in 2008 and 41.6 ± 13.7 mg kg⁻¹ in 2013, $p<0.05$). No statistically significant change was observed between years of sampling. (Table 10)

The concentrations of Fe decreased with increasing depth. There were significant decreases ($p<0.05$) between years in both organic horizons. In the F horizon, from 284 ± 17.1 mg kg⁻¹ (2008) to 112 ± 39.2 mg kg⁻¹ (2013) and in the H horizon, from 302 ± 78.8 mg kg⁻¹ (2008) to 114 ± 21.9 mg kg⁻¹ (2013). (Table 11)

Hydrogen decreased with increasing depth in both years of sampling. In the case of the F horizon, concentrations varied about 3.49 ± 1.53 cmol₍₊₎kg⁻¹ in 2008 and 3.25 ± 0.59 cmol₍₊₎kg⁻¹ in 2013. B horizon exhibited values ranging about 0.33 ± 0.27 cmol₍₊₎kg⁻¹ in 2008 and 0.17 ± 0.05 cmol₍₊₎kg⁻¹ in 2013. (Table 11)

Clear-cut area

In 2008, organic horizons exhibited significantly higher ($p<0.05$) exchangeable acidity than mineral horizons. In the year 2013, the highest exchangeable acidity was found in the H horizon (10.3 ± 0.47 cmol₍₊₎kg⁻¹). Statistically significant difference ($p<0.05$) between years of sampling was noted in the F horizon in which the exchangeable acidity decreased from 13.8 ± 2.73 cmol₍₊₎kg⁻¹ to 5.27 ± 1.72 cmol₍₊₎kg⁻¹. (Table 7)

In 2008, the highest concentrations of Al ($p<0.05$) were found in organic horizons whereas in 2013 the largest content ($p<0.05$) was determined in the H horizon. Positive quantitative change in Al concentrations between years was observed in the F horizon and significant differences ($p<0.05$) were found. Concentrations of Al in F horizon decreased nearly 3 times, 948 ± 213 mg kg⁻¹ (2008) and 297 ± 146 mg kg⁻¹ (2013). (Table 10)

Similar, statistically significant ($p<0.05$) trend of Mn in the most upper organic horizon in the beech forest has been reported in the clear-cut area as well. Concentrations increased from 36.9 ± 4.95 mg kg⁻¹ (2008) up to 202 ± 46.7 mg kg⁻¹ (2013). (Table 10)

In 2013, the H horizon exhibited the highest content of exchangeable Fe (96.2 ± 20.4 mg kg⁻¹). In 2008, the F horizon exhibited 2–3 times larger and statistically significant ($p<0.05$) content than in 2013 (216 ± 64.2 mg kg⁻¹ and 52.6 ± 8.75 mg kg⁻¹). (Table 11)

Concentrations of free H ion significantly ($p<0.05$) decreased in the F horizon (from 1.95 ± 0.19 $\text{cmol}_{(+)}\text{kg}^{-1}$ in 2008 to 0.95 ± 0.14 $\text{cmol}_{(+)}\text{kg}^{-1}$ in 2013). (Table 11)

5.5 Nitrogen, carbon and sulfur content

Nitrogen showed higher content (% percentage of weight) in the upper organic horizon F than in the H horizon at each stand, however differences between horizons (F, H) were significant ($p<0.05$) only in the spruce forest. In 2008, the largest amount was found in the clear-cut area 1.70 ± 0.29 % and the lowest in the beech forest 1.60 ± 0.36 %. In 2013, the highest nitrogen percentage of weight was observed in the spruce forest 1.69 ± 0.07 %. No significant changes between years of sampling were determined. (Table 12)

In the case of carbon, the highest content in the F horizon was determined in the spruce forest. In 2008, carbon reached 37.2 ± 5.23 % and 38.7 ± 3.66 % in 2013. In the clear-cut area, carbon did not varied significantly, 31.8 ± 4.88 % and 30.2 ± 6.54 % in 2008, 28.2 ± 7.46 % and 25.2 ± 3.57 % in 2013. Nevertheless, carbon varied significantly ($p<0.05$) between horizons in the year 2013 under the spruce forest. (Table 12)

Overall, mean sulfur percentage of weight ranged between 0.20% and 0.13%. No significant changes between sampled horizons or between years of sampling and between stands were found. (Table 12)

Table 7: Mean soil properties (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons B under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	CEC			EA			BS		
			cmol(+) kg ⁻¹		HG	cmol(+) kg ⁻¹		HG	%		
			mean	SD		mean	SD		mean	SD	
Beech											
	F	2008	21.6	3.55	c	15.5	0.76	b	26.6	14.0	b
	H	2008	14.0	2.81	b	12.7	2.46	b	8.95	0.97	a
	B	2008	4.10	0.35	a	3.73	0.33	a	8.90	1.43	a
	F	2013	18.5	1.83	d	(6.97)	1.67	b	(61.5)	12.2	b
	H	2013	11.4	1.19	c	9.21	1.43	c	19.3	6.75	a
	A	2013	6.57	0.72	b	6.03	0.59	b	8.18	1.78	a
	B	2013	3.64	0.62	a	3.39	0.55	a	6.94	1.53	a
Spruce											
	F	2008	21.2	2.41	b	15.0	1.17	b	28.4	13.5	b
	H	2008	17.7	2.72	b	15.8	2.07	b	10.6	2.48	b
	B	2008	4.43	0.36	a	4.16	0.34	a	6.18	0.33	a
	F	2013	16.9	1.96	d	(9.70)	2.01	bc	42.8	5.20	c
	H	2013	(12.8)	0.61	c	(11.2)	0.57	c	12.8	1.67	b
	A	2013	7.84	0.86	b	7.53	0.83	b	4.00	0.42	a
	B	2013	4.22	0.68	a	4.02	0.66	a	(4.62)	0.55	a
Clear-cut											
	F	2008	18.8	2.76	b	13.8	2.73	b	27.1	5.37	b
	H	2008	18.9	4.48	b	16.5	4.13	b	13.2	2.25	b
	B	2008	5.07	0.99	a	4.44	1.04	a	12.8	6.19	a
	F	2013	17.6	5.01	b	(5.27)	1.72	ab	(61.7)	15.8	b
	H	2013	13.0	0.63	b	10.3	0.47	c	(20.5)	3.18	a
	A	2013	6.98	1.32	a	6.33	1.04	b	8.90	3.59	a
	B	2013	4.35	0.58	a	4.02	0.49	a	7.45	3.11	a

CEC – cation exchange capacity, EA – exchangeable acidity, BS – base saturation, SD – standard deviation. HG – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, a represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$.

Table 8: Mean content of exchangeable Ca and Mg (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons B under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	Ca			Mg				
			mg kg ⁻¹		HG %	mg kg ⁻¹		HG %		
			mean	SD			mean		SD	
Beech										
	F	2008	909	762	a	19.6	90.6	29.6	b	3.41
	H	2008	99.0	39.2	a	3.45	42.1	8.61	a	2.48
	B	2008	41.7	3.55	a	5.11	8.70	2.92	a	1.74
	F	2013	1960	656	b	52.1	123	35.5	c	5.45
	H	2013	285	153	a	12.8	44.3	18.6	b	3.13
	A	2013	56.5	39.7	a	4.11	15.3	2.54	ab	1.96
	B	2013	26.5	17.6	a	3.43	6.32	0.37	a	1.46
Spruce										
	F	2008	937	637	b	21.1	101	27.1	c	3.87
	H	2008	159	93.5	a	4.29	64.2	16.4	b	2.96
	B	2008	28.3	0.67	a	3.20	7.97	0.94	a	1.48
	F	2013	1135	32.5	c	33.8	103	14.3	c	5.13
	H	2013	131	17.7	b	5.07	53.5	12.4	b	3.42
	A	2013	10.4	5.30	a	0.69	14.4	4.77	a	1.49
	B	2013	(12.5)	4.73	a	1.54	5.64	1.35	a	1.09
Clear-cut										
	F	2008	714	150	b	19.4	93.8	24.5	b	4.05
	H	2008	260	69.9	a	6.83	66.6	8.09	b	2.97
	B	2008	90.1	58.1	a	9.02	9.68	0.33	a	1.60
	F	2013	2086	1103	b	56.7	134	73.2	b	6.09
	H	2013	321	70.5	a	12.3	60.1	14.6	a	3.78
	A	2013	56.9	49.5	a	3.72	19.2	5.26	a	2.23
	B	2013	32.1	27.7	a	3.63	7.70	3.08	a	1.42

SD – standard deviation. *HG* – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, *a* represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$. Contribution to the cation exchange capacity is given in %.

Table 9: Mean content of exchangeable K and Na (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons B under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	K			Na				
			mg kg ⁻¹		HG %	mg kg ⁻¹		HG %		
			mean	SD			mean	SD		
Beech										
	F	2008	268	67.4	c	3.16	24.7	2.99	b	0.50
	H	2008	135	26.4	b	2.47	17.9	6.01	b	0.55
	B	2008	21.1	6.24	a	1.31	7.05	1.61	a	0.74
	F	2013	255	23.7	c	3.55	(16.1)	3.61	a	0.38
	H	2013	131	62.8	b	2.86	15.3	8.91	a	0.59
	A	2013	40.6	11.6	a	1.63	7.31	2.91	a	0.48
	B	2013	15.9	1.59	a	1.13	7.36	1.66	a	0.92
Spruce										
	F	2008	239	15.0	c	2.93	22.7	2.43	b	0.47
	H	2008	193	37.6	b	2.79	23.8	5.07	b	0.59
	B	2008	17.0	4.38	a	0.97	5.38	1.62	a	0.52
	F	2013	219	28.8	b	3.38	18.8	2.08	b	0.47
	H	2013	184	24.3	b	3.66	20.2	5.51	b	0.69
	A	2013	35.7	11.5	a	1.16	12.1	2.60	a	0.67
	B	2013	17.3	7.44	a	1.02	(9.28)	0.50	a	0.97
Clear-cut										
	F	2008	250	57.7	b	3.37	14.2	3.33	a	0.33
	H	2008	211	53.8	b	2.94	16.5	11.4	a	0.42
	B	2008	33.2	3.09	a	1.72	5.11	0.93	a	0.44
	F	2013	282	174	c	3.89	15.4	4.35	c	0.41
	H	2013	204	54.1	bc	3.99	12.7	2.48	bc	0.43
	A	2013	65.7	12.9	ab	2.41	8.26	1.77	ab	0.53
	B	2013	30.1	11.6	a	1.73	6.46	0.36	a	0.66

SD – standard deviation. *HG* – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, a represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$. Contribution to the cation exchange capacity is given in %.

Table 10: Mean content of exchangeable Al and Mn (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons B under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	Al			Mn		
			mg kg^{-1}		HG %	mg kg^{-1}		HG %
			mean	SD		mean	SD	
Beech								
	F	2008	1114	176 b	59.2	25.2	19.5 a	0.40
	H	2008	999	179 b	79.7	2.89	0.76 a	0.08
	B	2008	316	27.5 a	85.9	4.87	3.57 a	0.42
	F	2013	(446)	181 a	27.7	(112)	34.6 b	2.19
	H	2013	720	116 b	70.0	(8.71)	2.72 a	0.28
	A	2013	476	36.0 a	80.8	2.28	0.76 a	0.13
	B	2013	284	43.9 a	86.8	4.77	3.60 a	0.53
Spruce								
	F	2008	885	249 b	47.8	29.0	14.1 a	0.49
	H	2008	1016	77.2 b	64.5	6.20	3.42 a	0.12
	B	2008	331	8.42 a	83.3	15.8	19.6 a	1.29
	F	2013	508	216 a	32.7	41.6	13.7 b	0.92
	H	2013	(751)	66.2 b	65.0	6.47	2.08 a	0.18
	A	2013	513	66.4 a	72.7	2.66	2.05 a	0.13
	B	2013	336	51.9 a	88.6	6.66	4.53 a	0.58
Clear-cut								
	F	2008	948	213 b	55.6	36.9	4.95 b	0.73
	H	2008	1224	273 b	72.0	12.7	2.42 a	0.26
	B	2008	350	51.0 a	77.1	5.62	7.00 a	0.47
	F	2013	(297)	146 a	21.1	(202)	46.7 b	4.57
	H	2013	786	46.5 c	67.5	17.8	8.02 a	0.51
	A	2013	493	84.2 b	78.9	3.81	0.42 a	0.20
	B	2013	339	38.1 ab	86.8	3.39	1.20 a	0.28

SD – standard deviation. *HG* – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, *a* represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$. Contribution to the cation exchange capacity is given in %.

Table 11: Mean content of exchangeable Fe, H (n=3) in the organic horizons F, H, organo-mineral A (if present) and mineral horizons (B) under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	Fe			H		
			mg kg ⁻¹		HG %	cmol(+) kg ⁻¹		HG %
			mean	SD			mean	
Beech								
	F	2008	225	47.4 b	5.65	1.81	0.96 b	8.12
	H	2008	153	58.9 b	5.79	0.78	0.32 ab	5.48
	B	2008	12.0	1.69 a	1.57	0.13	0.01 a	3.27
	F	2013	(153)	26.6 a	2.26	1.20	0.41 c	6.37
	H	2013	72.1	59.1 a	3.37	0.79	0.12 bc	6.97
	A	2013	60.8	20.1 a	4.91	0.40	0.09 ab	5.96
	B	2013	14.2	11.4 a	1.99	0.14	0.03 a	3.71
Spruce								
	F	2008	284	17.1 b	7.25	3.49	1.53 b	16.1
	H	2008	302	78.8 b	9.07	2.82	0.97 b	15.6
	B	2008	16.3	2.87 a	1.97	0.33	0.27 a	7.25
	F	2013	(122)	39.2 b	3.82	3.25	0.59 d	19.7
	H	2013	(114)	21.9 b	4.75	2.22	0.45 c	17.2
	A	2013	142	24.2 b	9.67	1.05	0.12 b	13.5
	B	2013	18.3	12.9 a	2.21	0.17	0.05 a	3.98
Clear-cut								
	F	2008	216	64.2 b	6.06	1.95	0.19 b	10.5
	H	2008	231	82.2 b	6.62	1.58	0.90 b	7.96
	B	2008	34.1	38.9 a	3.23	0.35	0.31 a	6.39
	F	2013	(52.6)	8.75 b	1.74	(0.95)	0.14 b	5.53
	H	2013	96.2	20.4 c	3.96	0.99	0.41 b	7.51
	A	2013	68.0	18.4 b	5.18	0.47	0.02 a	6.83
	B	2013	18.5	6.07 a	2.26	0.14	0.04 a	3.23

SD – standard deviation. *HG* – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, *a* represents the lowest mean. Numbers in parenthesis indicates statistically significant difference between years of sampling at $p < 0.05$. Contribution to the cation exchange capacity is given in %.

Table 12: Mean content of nitrogen, carbon, sulfur and C:N ratio (n=3) in organic horizons F, H under the beech forest, spruce forest and clear-cut area with respect to the year of sampling (2008, 2013).

Species	Horizon	Year	N		C			S			C:N ratio	
			%		%			%				
			mean	SD	HG	mean	SD	HG	mean	SD		HG
Beech												
	F	2008	1.60	0.36	a	28.8	7.73	a	0.15	0.11	a	18.0
	H	2008	1.06	0.19	a	21.2	3.95	a	0.14	0.02	a	19.9
	F	2013	1.52	0.22	a	32.2	8.27	a	0.16	0.03	a	21.1
	H	2013	1.11	0.38	a	21.9	8.19	a	0.14	0.05	a	19.6
Spruce												
	F	2008	1.68	0.08	b	37.2	5.23	a	0.17	0.02	a	22.2
	H	2008	1.31	0.21	a	28.8	5.88	a	0.15	0.01	a	22.0
	F	2013	1.69	0.07	b	38.7	3.66	b	0.17	0.01	a	22.9
	H	2013	1.14	0.16	a	25.5	2.56	a	0.14	0.03	a	22.4
Clear-cut												
	F	2008	1.70	0.29	a	31.8	4.88	a	0.20	0.05	a	18.7
	H	2008	1.52	0.19	a	30.2	6.54	a	0.19	0.03	a	19.9
	F	2013	1.43	0.45	a	28.2	7.46	a	0.13	0.04	a	19.7
	H	2013	1.30	0.18	a	25.2	3.57	a	0.14	0.01	a	19.4

SD – standard deviation. *HG* – homogeneous group describes statistically significant differences between horizons at $p < 0.05$, *a* represents the lowest mean.

6 Discussion

Soil chemical parameters of forest mountainous soils underlain by granite are strongly influenced by type of vegetation cover and type of soil horizon. It was necessary to differentiate these factors in order to determine potential changes between years of sampling. Soil samples were taken in 2008 and 2013 and that is, for example, in comparison with study comparing soil parameters between 1967 and 1997 conducted by Bailey et al., (2005) or by Oulehle et al., (2006) who compared soil chemical parameters over the years 1997–2005, short period.

Most of the studies compare changes in soil parameters with respect to reduced or enhanced atmospheric deposition (Oulehle et al., 2006; Navrátil et al., 2007; Hédl et al., 2011, Hruška et al., 2012, etc.). In the study area Paličnick, pH of the atmospheric deposition showed no statistically significant trend in the period of the monitoring (Figure 13). That is in accordance with total emissions of acidifying pollutants in the Czech Republic that remained constant (SO_2 and NO_x) or changed slightly (NH_3) over the period of concern (Figure 14) (Czech Hydrometeorological Institute). Vašát et al., (2015) used dynamic models: the Very Simple Dynamic Model (VSD) and the Model of Acidification of Groundwater in Catchments (MAGIC) in order to describe historical loads of acidifying pollutants in the Jizera Mountains region that reached the maximum in 1970s. It was predicted that until 2100, status of soil chemical parameters will not recovery prior to state before the main pollution era. For instance, pH 5.5 will not be reached if there is no change in present chemical composition of deposition. During the period 1993–2010, Šrámek et al., (2013) observed positive changes in health state of young forest stands (defoliation, year annual increment, chemical composition of needles) and, in parallel, poor nutrient status of soil that could subsequently affect future development and growth of spruce forests in the region. Soil parameters determined in this study show high variability, especially in the organic horizons. However, high variability of selected soil parameters through the soil profile in the study area Paličnick was also observed by Pavlů et al., (2007). Between-years changes in organic horizons were more characteristic for the beech forest and clear-cut area. Spruce forest, in turn, exhibited noticeable between-years changes in mineral horizons. Some temporal trends in NO_3^- and SO_4^{2-} concentrations were already observed by Tejnecký et al., (2013) during the period 2008–2010. Ellenberg indicator values were used to define changes in vegetation composition between 2008–2013, in terms of light, temperature, soil moisture, soil reaction, nutrient content and continentality.

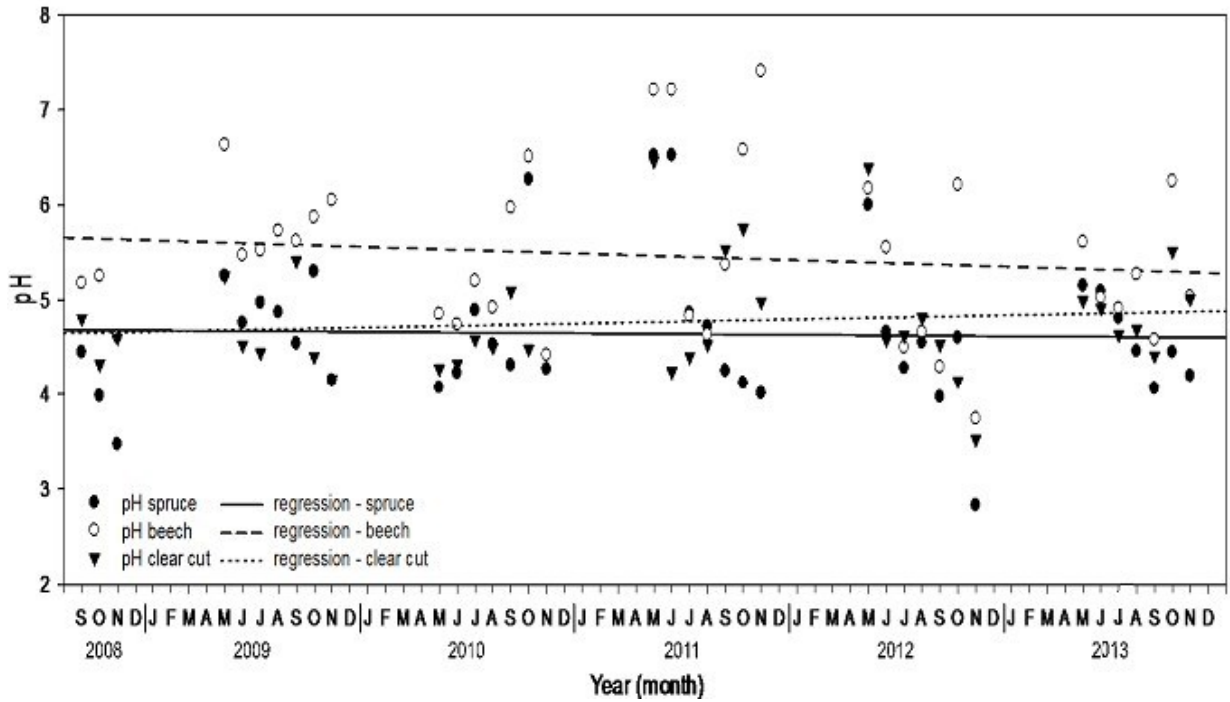


Figure 13: Simple linear regression of the pH of atmospheric deposition in the beech forest (throughfall), spruce forest (throughfall) and clear-cut area (bulk precipitation) in the period 2008–2013 (Bradová et al., under review).

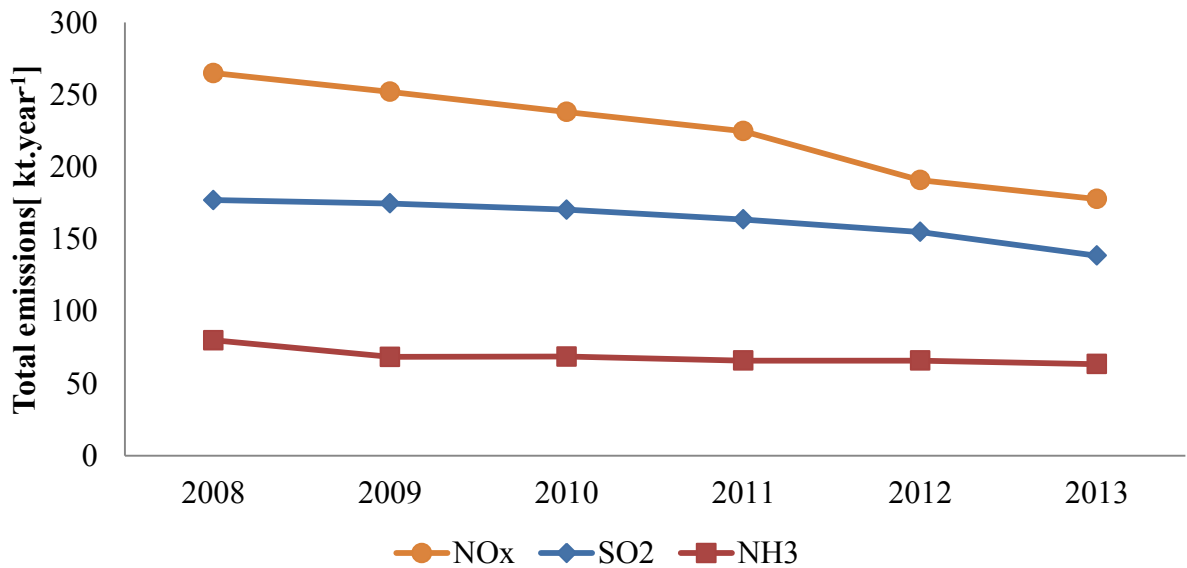


Figure 14: The development of total emissions of SO₂, NO_x and NH₃ for 2008–2013 in the Czech Republic (Czech Hydrometeorological Institute).

Table 13: Correlation coefficients of the relationships between soil chemical properties in the beech forest (n=24), CNS in organic horizons (n=12). CEC – cation exchange capacity. EA – exchangeable acidity. BS – base saturation.

	pHH ₂ O	pHKCl	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	C	N
pHKCl	0.78***														
Ca	-0.22	-0.51*							***	p < 0.001					
Mg	-0.31	-0.64***	0.91***						**	p < 0.01					
K	-0.41*	-0.72***	0.78***	0.95***					*	p < 0.05					
Na	-0.24	-0.67***	0.51*	0.69***	0.78***										
Al	-0.49*	-0.65***	0.004	0.33	0.56**	0.70***									
Mn	-0.09	-0.31	0.94***	0.86***	0.67***	0.35	-0.14								
Fe	-0.59**	-0.78***	0.24	0.50*	0.70***	0.64***	0.86***	0.06							
H	-0.47*	-0.85***	0.70***	0.78***	0.84***	0.74***	0.53**	0.47**	0.75***						
CEC	-0.50*	-0.83***	0.74***	0.89***	0.96***	0.84***	0.68***	0.59**	0.78***	0.90***					
EA	-0.53**	-0.75***	0.16	0.47*	0.68***	0.76***	0.98***	-0.004	0.92***	0.67***	0.79***				
BS	-0.22	-0.47*	0.98***	0.90***	0.77***	0.49**	-0.03	0.96***	0.17	0.62**	0.70***	0.12			
C	0.32	-0.47	0.77**	0.87***	0.77**	0.52	-0.36	0.70**	0.03	0.68*	0.69*	-0.17	0.74**		
N	0.30	-0.49	0.65*	0.85***	0.92***	0.59*	-0.09	0.55	0.26	0.74**	0.80**	0.10	0.60*	0.92***	
S	0.20	-0.40	0.37	0.53	0.53	0.23	-0.25	0.32	0.15	0.55	0.34	-0.10	0.37	0.72**	0.72**

CEC – cation exchange capacity. EA – exchangeable acidity. BS – base saturation.

Table 14: Correlation coefficients of the relationships between soil chemical properties in the spruce forest (n=24), CNS in organic horizons (n=12).

	pHH2O	pHKCl	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	C	N
pHKCl	0.94***														
Ca	-0.43*	-0.55**							***	p < 0.001					
Mg	-0.61**	-0.76***	0.88***						**	p < 0.01					
K	-0.58**	-0.74***	0.68***	0.93***					*	p < 0.05					
Na	-0.55**	-0.69***	0.45*	0.74***	0.87***										
Al	-0.54**	-0.63***	0.11	0.46*	0.67***	0.78***									
Mn	-0.18	-0.33	0.81***	0.70***	0.51*	0.24	-0.13								
Fe	-0.74***	-0.80***	0.34	0.61**	0.66***	0.72***	0.84***	0.09							
H	-0.72***	-0.84***	0.80***	0.96***	0.89***	0.74***	0.52**	0.56**	0.71***						
CEC	-0.70***	-0.84***	0.72***	0.92***	0.92***	0.85***	0.75***	0.45*	0.83***	0.93***					
EA	-0.69***	-0.80***	0.39	0.70***	0.83***	0.86***	0.94***	0.11	0.92***	0.77***	0.92***				
BS	-0.42*	-0.55**	0.97***	0.90***	0.74***	0.48*	0.09	0.85***	0.27	0.80***	0.70***	0.36			
C	-0.47	-0.79**	0.88***	0.97***	0.74**	-0.17	-0.50	0.86***	0.17	0.85***	0.65*	-0.13	0.87***		
N	-0.34	-0.68*	0.84***	0.93***	0.81**	-0.11	-0.37	0.84***	0.23	0.71**	0.68**	-0.05	0.82**	0.96***	
S	-0.67*	-0.75**	0.73***	0.87***	0.63*	-0.32	-0.44	0.69***	0.22	0.82**	0.56	-0.08	0.71**	0.88***	0.85***

CEC – cation exchange capacity. *EA* – exchangeable acidity. *BS* – base saturation.

Table 15: Correlation coefficients of the relationships between soil chemical properties in the clear-cut area (n=24), CNS in organic horizons (n=12).

	pHH2O	pHKCl	Ca	Mg	K	Na	Al	Mn	Fe	H	CEC	EA	BS	C	N
pHKCl	0.48*														
Ca	0.16	-0.16							***	p < 0.001					
Mg	0.01	-0.47*	0.89***						**	p < 0.01					
K	-0.06	-0.57**	0.76***	0.96***					*	p < 0.05					
Na	-0.10	-0.41*	0.36	0.60**	0.66***										
Al	-0.39	-0.77***	-0.17	0.23	0.40	0.40									
Mn	0.08	-0.05	0.76***	0.61**	0.44*	0.37	-0.23								
Fe	-0.37	-0.82***	0.02	0.39	0.53**	0.57**	0.88***	-0.11							
H	-0.49	-0.86***	0.29	0.58**	0.66***	0.37	0.76***	0.12	0.81***						
CEC	-0.22	-0.76***	0.62**	0.86***	0.90***	0.60**	0.66***	0.40	0.74***	0.85***					
EA	-0.41*	-0.83***	-0.06	0.33	0.49*	0.44*	0.99***	-0.13	0.92***	0.84***	0.75***				
BS	0.16	-0.13	0.96***	0.84***	0.71***	0.42*	-0.20	0.86***	-0.01	0.24	0.57**	-0.09			
C	0.09	-0.62*	0.29	0.60*	0.74**	-0.03	0.30	-0.19	0.56	0.70*	0.91***	0.39	0.10		
N	0.22	-0.50	0.29	0.64*	0.79**	0.17	0.22	-0.24	0.51	0.56	0.79**	0.29	0.10	0.93***	
S	-0.22	-0.78**	-0.17	0.20	0.38	0.02	0.67*	-0.53	0.74**	0.74**	0.73**	0.72**	-0.36	0.83***	0.85***

CEC – cation exchange capacity. *EA* – exchangeable acidity. *BS* – base saturation.

6.1 Influence of vegetation and temporal changes

As was already described, study area was strongly affected by acid deposition that caused soil acidification that is characteristic by leaching of base cations together with deposited acid anions, decreases in soil pH, increasing content of exchangeable Al etc. Between-years changes revealed some temporal trends in organic horizons as well as in mineral horizons.

Studied forest mountainous soils can be assessed as strongly and very strongly acid. In all cases, $\text{pH}_{\text{H}_2\text{O}}$ was slightly higher than pH_{KCl} because $\text{pH}_{\text{H}_2\text{O}}$ refers to the acidity of the soil solution and pH_{KCl} to the acidity of adsorbed acid cations on soil sorption sites. Differences in pH values were apparent between organic and mineral horizons. Both active and exchangeable pH gradually increased with increased distance from the soil surface. The same pattern was observed for example by Drábek et al., (2007). On the base of these findings, it could be inferred that acidification is more intensive in organic horizons than in mineral horizons. Hédl et al., (2011) also observed that differences in acidification patterns were more distinct between surface and subsurface horizons. The surface horizons are exposed to external factors such as acid deposition, litter decomposition, liming etc. Decreases of exchangeable acidity in organic horizons and declines of base saturation in mineral horizons indicate that the influence of vegetation is apparent in organic horizons and influence of parent material and soil-forming processes plays significant role in mineral horizons (Anderson, 1988; Penížek and Zádorová, 2012). Exchangeable Ca and Mg were the highest in the surface horizons indicating that biological cycling of Ca and Mg is of great importance in nutrition in acids soils (Van der Heijden et al., 2013).

6.1.1 Soil reaction

The highest mean pH values were determined in the beech and the lowest in the spruce forest. That is in accordance with findings that were published by Oulehle and Hruška, (2005); Mládková et al., (2006). Values of pH_{KCl} in the clear-cut area were analogous to the beech forest. It corresponds to the amount of exchangeable acid cations bounded in the soil sorption complex that was comparable for both stands. Spruce forest exhibited the lowest pH due to the nature of litter and roots producing low molecular organic acids that substantially decrease the soil pH Augusto et al., (2002). Additionally, coniferous forests have higher ability to scavenge pollutants than broadleaved species (Hruška and Kopáček, 2009). Giving perception, the average pH of the throughfall was 4.63 in the spruce forest, 5.46 in the beech forest and bulk precipitation reached

4.77 in the clear-cut area over the period 2008–2013 (Figure 15). However, one should keep in mind that precipitation chemistry is often altered as it passes through the canopy due to dry deposition, canopy uptake and leaching (Bhat et al., 2011) and thus bulk precipitation and throughfall precipitation may significantly differ from each other.

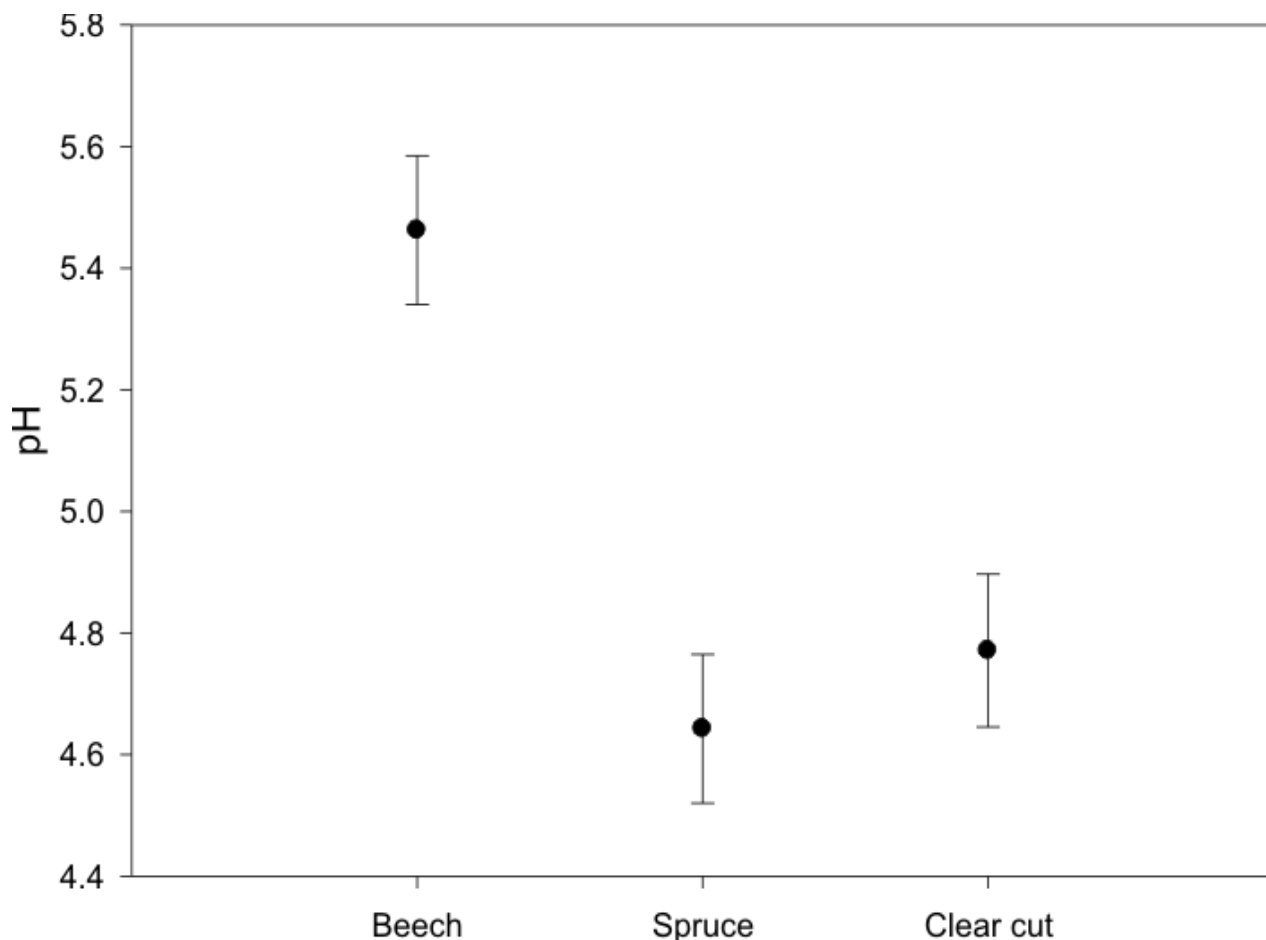


Figure 15: Means and 95.0 percent LSD intervals of the pH of the atmospheric deposition with respect to different vegetation cover (Bradová et al., under review).

Between-years changes in the pH were apparent in organic horizons. Beech and clear-cut area showed increasing tendency. However, changes were the most pronounced in the clear-cut area where significant increment in pH_{KCl} in the F horizon was observed. This is partially in congruence with Ellenberg indicator values according to which, soil pH exhibited increasing, trend (not significant) between years in the beech forest whereas clear-cut area with spruce forest exhibited downward tendency (Figure 16).

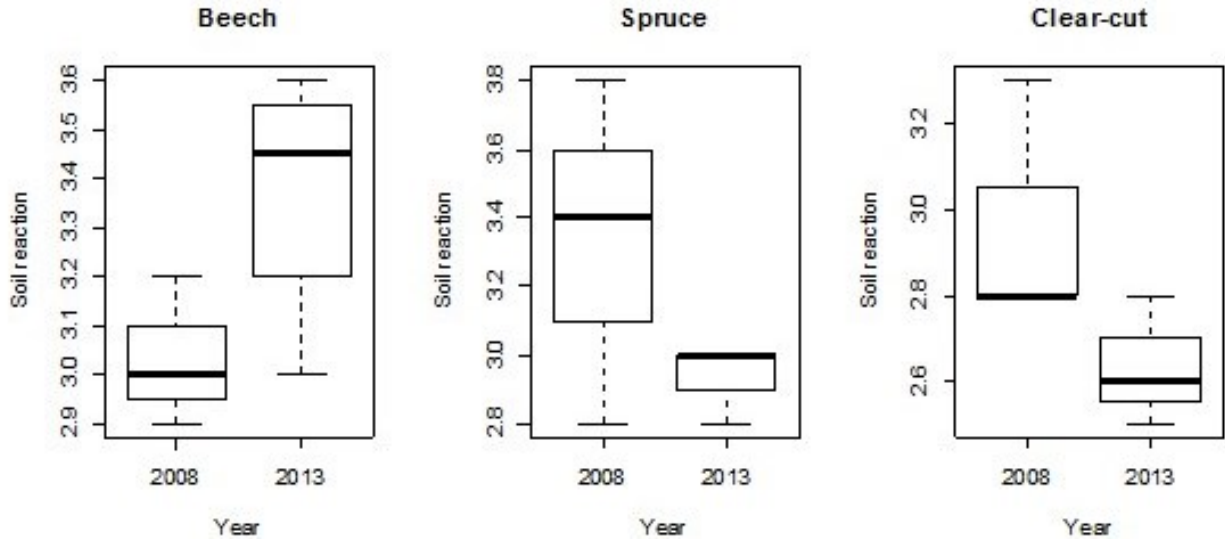


Figure 16: Median and inter-quartile point distribution of soil reaction between years for beech and spruce forest and clear-cut area separately according to Ellenberg indicator values.

6.1.2 Cation exchange capacity

Cation exchange capacity was on average quite low and did not vary significantly between stands. Higher CEC was in organic than in mineral horizons. Cation exchange capacity correlated with the content of C in organic horizons (Figure 17) since the soil organic matter consists of all of the carbon containing organic substances (Binkley and Fisher, 2013). Gruber and Mulder (2015) stated that the slope of the regression determines the number of negatively charged sites of soil organic matter (SOM). They found the smallest number for hornbeam and oak, and largest for spruce and pine soils. Our results showed that the slope of the regression of CEC to C content increased in the following order: spruce forest < beech forest < clear-cut area. It indicates that SOM plays a decisive role in the soil sorption complex in organic horizons with the highest influence in the clear-cut area and the lowest in the spruce forest.

No changes between years of sampling in CEC were found with exception of spruce forest in which significant decrease was apparent in the H horizon (Figure 11). This was accompanied by slight decreases in C content and decreased concentrations of exchangeable Fe. Additionally, despite the fact that concentrations of exchangeable Al in the horizon H quantitatively decreased, relative distribution on CEC did not change markedly (64.5% in 2008 compared to 65.0% in 2013) (Figure 12).

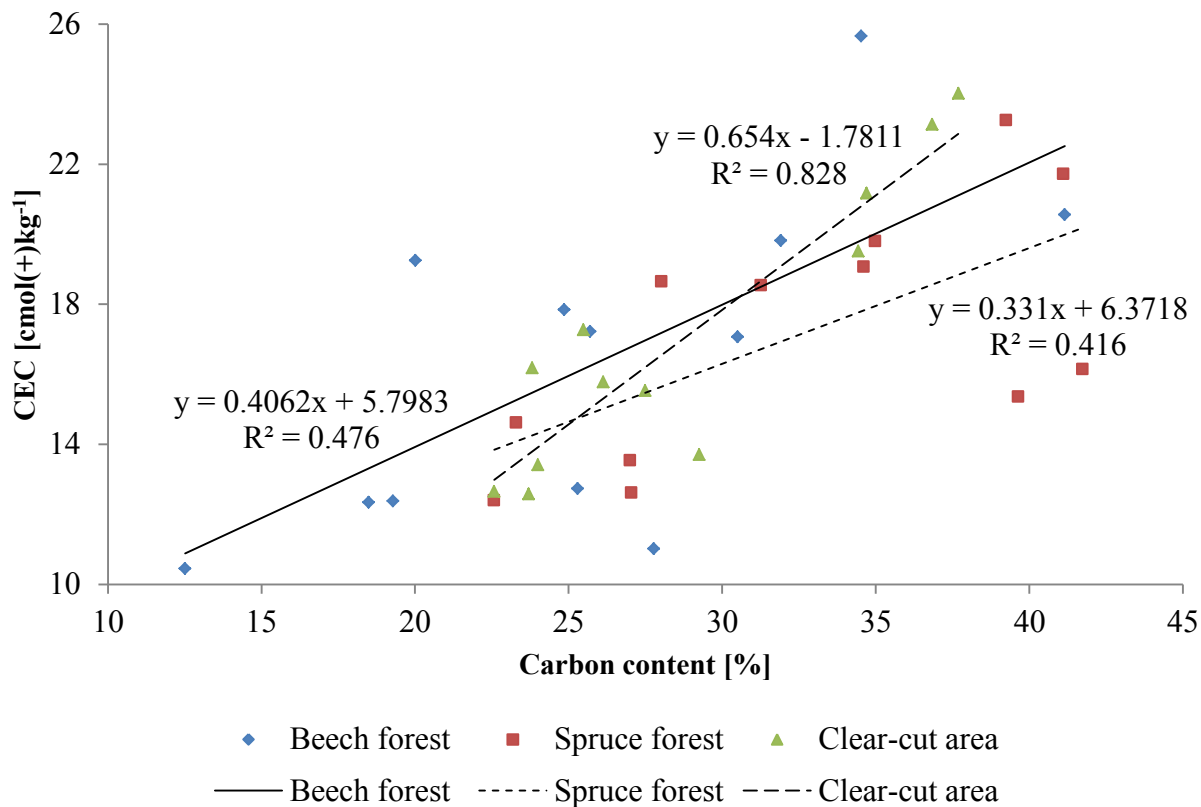


Figure 17: Simple linear regression of CEC and C under different type of vegetation cover in organic horizons. (n=12). Confidence levels are listed separately for beech, spruce forest and clear-cut area in Tables 13, 14, 15, respectively.

6.1.3 Base saturation and base cations

The storage of base cations expressed as base saturation was on average well below the 20% at each stand. Spruce forest represents a stand with the lowest base saturation and the highest exchangeable acidity. Similar values of base saturation in the spruce forest were observed by Šrámek et al., (2014). For example, ICP Forests monitoring plot Jizerka exhibited BS = 12.9% in the 0–10 cm depth and 6.4% in the 10–20 cm depth. Base saturation correlated to Ca content in the soil and also to CEC. Strong relationship was determined in the spruce and beech forest ($r^2 = 0.70$; $p < 0.0001$) and moderately strong relationship in the clear-cut area ($r^2 = 0.57$; $p < 0.01$). As cation exchange capacity decreased in dependence on increasing depth, so did basic saturation. Same pattern was for example observed by Oulehle et al., (2006). Soil organic matter is a main sink and source of plant nutrients that are held on cation exchange sites or bound in the organic matter itself and released during the decomposition processes. Cation exchange capacity of soil organic matter is commonly 50–300 $\text{cmol}_{(+)}\text{kg}^{-1}$ and it increases with increasing soil pH (Sparks, 2003; Binkley and Fisher, 2013).

Despite the fact that concentrations of base cations in organic horizons under the clear-cut area did not show significant trend between years of sampling, relative distribution of the major base cation on CEC increased from 19.4% and 6.83% to 56.7% and 12.3% in the F and H horizons, respectively (Figure 12). This improvement can be partially described by the influence of vegetation cover. Ability of grass cover to ameliorate acidified soils due to production of humus of better quality (C:N = 19.4), higher nutrient turnover was studied by Fiala et al., (2005); Drábek et al., (2007); Fiala et al., (2008). In parallel, base saturation in the beech forest increased in organic horizons and changes were apparent especially in the F horizon due to increases in exchangeable Ca and Mg. It confirms the importance of biological input.

Base saturation in mineral horizons decreased between years of sampling at each stand. Changes were significant under the spruce forest primarily as a result of decreases of exchangeable Ca and Mg. Decreases in Ca budget were also observed by van der Heijden et al., (2013) over the period 2003–2008. This could be attributed to the leaching of base cations together with acid anion due to ongoing acidification. Large amounts of base cations have been already depleted during the last 50 years and soils are not able to neutralize acid inputs despite the main sources of pollutants were reduced (Hruška and Krám, 2003; Vašát et al., 2015). Additionally, large portion of S from acid deposition is stored in soil. For example, Novák et al., (2000) stated that the amount of S stored in the soil (Dystric Cambisol) in the Ore Mountains, Czech Republic is enough to supply the seepage flux for next 60 years.

6.1.4 Exchangeable acidity and acid cations

Decreasing content of organic matter and increasing influence of parent material was displayed in A and B horizons having lower CEC than organic horizons. Moreover they were enriched by Al and, in turn, poor in Ca. Average fraction of Al on CEC varied between years of sampling in the range 85.9–86.8% (beech forest), 83.3–88.6 % (spruce forest), 77.1–86.8% (clear-cut area) in the B horizons (Figure 12). Gruba et al., (2013) observed similar fraction of exchangeable Al in A and B horizons (78 % and 88 %, respectively) in acid soil (pH_{H2O} range 3.3–5.4) in Southern Poland. It could be concluded that low CEC is caused by low cation exchange capacity of Al-Fe (hydro)oxides that occurs in the soil. Essington (2004) stated that poorly crystalized Al(OH)₃ has CEC reaching 10–100 cmol₍₊₎kg⁻¹. Content of Al-Fe (hydro)oxides can be estimated from the soil colour by means of Munsell's color chart (Scheinost and Schwertmann, 1999). Spodic horizons

were brighter, containing higher amount of Al-Fe (hydro)oxides (7.5–10 YR, 5/6) than cambic horizons (7.5 YR, 4/4) (Tejnecký et al., 2013).

Exchangeable acidity remained relatively stable in mineral horizons between years of sampling. However, there was identified decreasing tendency in F horizons at beech forest and clear-cut area and even in the H horizon in the spruce forest. Similarly, Tamminen and Derome, (2005) confirmed decreasing exchangeable acidity and Al concentrations in organic horizons in Southern Finland and no changes in mineral horizons.

Despite the fact that Al concentrations did not show any significant differences between stands, Tejnecký et al., (2010) found that type of vegetation in the study area Paličník influences less toxic species¹ Al(X)^{1+} , Al(Y)^{2+} of water extractable aluminum but not phytotoxic Al^{3+} . Spruce forest exhibited higher content of mono and divalent Al species than beech forest and clear-cut area. Determination of water soluble and exchangeable Al forms should be the object of the future research.

The Ca:Al ratio (between exchangeable Ca and Al) was very low (<0.1) in mineral horizon B indicating high risk of Al toxicity (Figure 18). Organic horizons in the clear-cut area exhibited Ca:Al ratio higher than 1. However in the case spruce forest it was equal to 0.45 ± 0.25 (Figure 19). The Ca:Al ratio below 0.5 indicates that there is 75% risk of Al toxicity. However, one should keep in mind that this assessment is valid for Ca:Al ratio determined in the soil solution (Cronan and Grigal, 1995).

¹ Al(X)^{1+} refers to Al(OH)_2^+ , $\text{Al(SO}_4)^+$, AlF_2^+ , $\text{Al(org.)}_{\leq 1}^+$, etc.,
 Al(Y)^{2+} refers to Al(OH)_2^{2+} , $(\text{AlF})^{2+}$, etc. (Drábek et al., 2005).

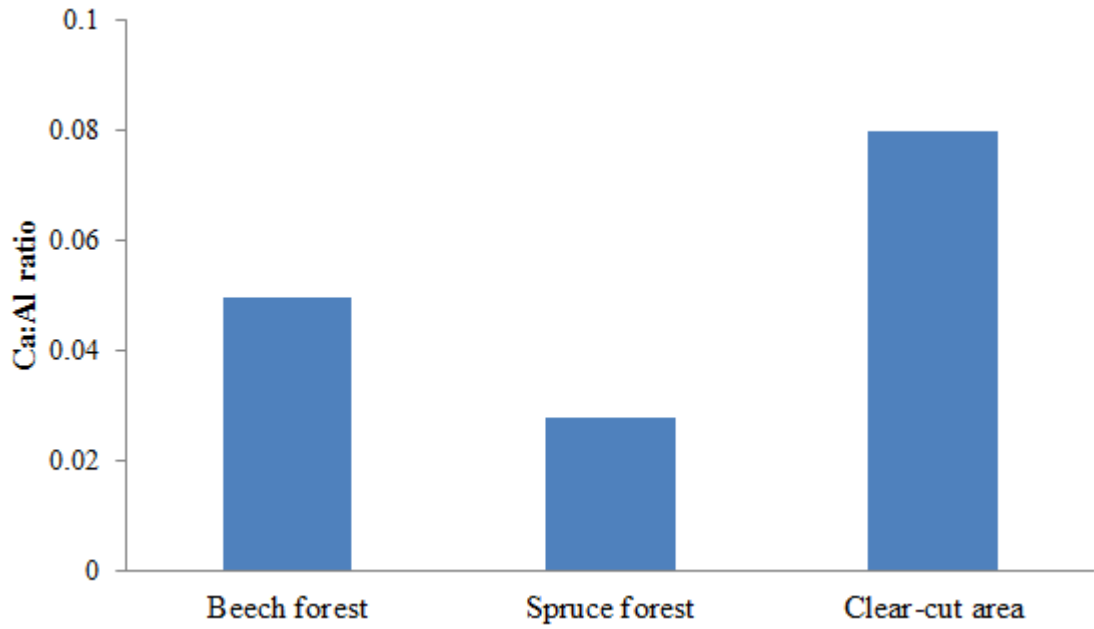


Figure 18: Mean Ca:Al ratio in the mineral horizon B separately for different type of vegetation (n=6).

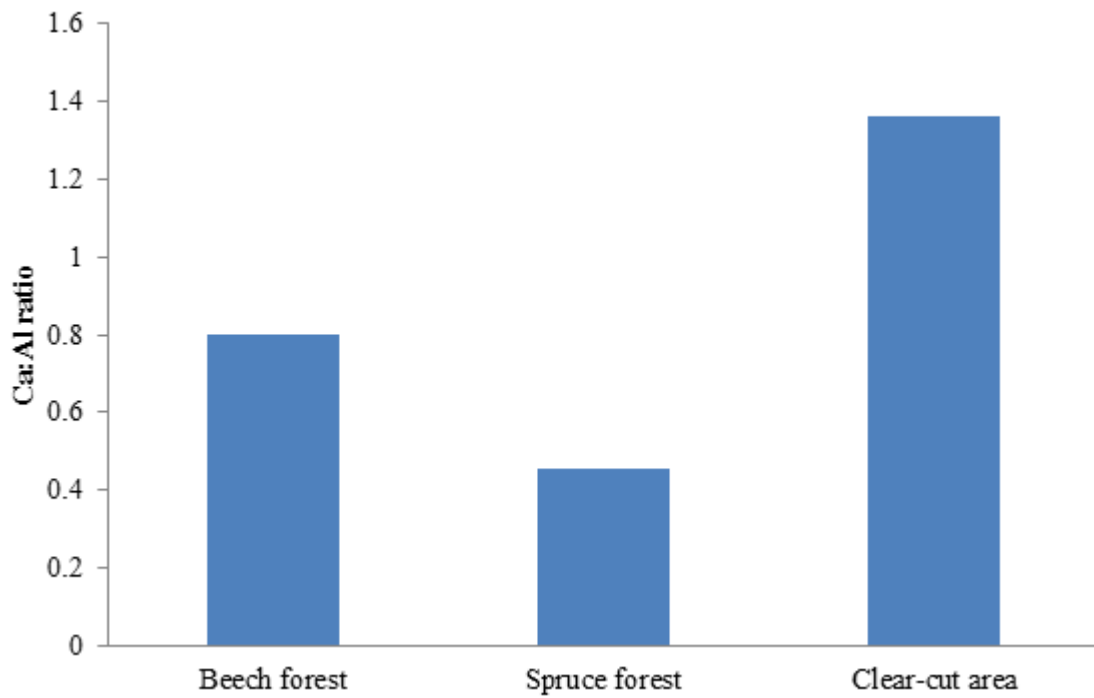


Figure 19: Mean Ca:Al ratio in organic horizons (F, H) separately for different type of vegetation (n=12).

The highest concentrations of exchangeable Fe were determined in the spruce forest and the lowest in the beech forest. Content of exchangeable Fe and free H ions in the organo-mineral horizon A of the spruce forest was about 2 times higher than in the case of the beech forest and clear-cut area whereas F and H horizons exhibited comparable values. In parallel, exchangeable pH showed very low values (2.92 ± 0.04) and base saturation reached only $4.00 \pm 0.42\%$. It could mean that the prevailing buffering mechanism is mobilization of Fe from Fe (hydro)oxides (Kauppi et al., 1986; Puhe and Ulrich, 1991).

Moreover, in contrast to beech and spruce forest, correlation between S content and Fe, Al, H was found in the clear-cut area. This could be explained as the impact of the soil unit – Gleyic Podzol that was observed in the year 2008. Gleyic properties refer soils that show signs of chemical reduction due to water stagnation that occurs temporarily. In soils that contain large amount of sulfates and Fe, formation of pyrite may occur under reductomorphic conditions. Under reducing conditions, FeS is formed but it is eventually transformed to FeS₂. In the presence of oxygen, FeS₂ is unstable and it can be transformed to dissolved Fe²⁺ and SO₄²⁻, to jarosite or even goethite (van Breemen and Buurman, 2002).

Both Al and Fe exhibited similar pattern between years of sampling. For example, horizon F in the clear-cut held lower amount of exchangeable Al and Fe in 2013 compared to 2008. Al decreased from $948 \pm 213 \text{ mg kg}^{-1}$ (55.6%) in 2008 to $297 \pm 146 \text{ mg kg}^{-1}$ (21.1%) in 2013. In case of the beech forest, decline was from $1114 \pm 176 \text{ mg kg}^{-1}$ (59.2%) in 2008 to $446 \pm 181 \text{ mg kg}^{-1}$ (27.7%). Regard to increased pH, this could be evidence of the decreasing acidity trend in organic horizons at both stands (Tamminen and Derome, 2005).

Intriguing pattern was observed in Mn concentrations that were higher in the clear-cut area and beech forest than in the spruce forest. Manganese also exhibited strong correlation to Ca, Mg, K. Manganese correlated also to carbon content in the beech forest and also to nitrogen and sulfur content in the spruce forest. Differences were significantly pronounced in organic horizons and between years of sampling. Navrátil et al., (2007) observed that about 70 % of Mn input to the forest ecosystem comes from litterfall. Content of exchangeable Mn increased compared to 2008 nearly 3-5 times in both organic horizons under the beech forest and nearly 5-6 times in the case of the F horizon under the clear-cut area. This is very much contrary to expectations. According to the literature concentrations of Mn from litterfall are about three times higher in the spruce

forest than in the beech forest due to higher accumulation of Mn in needles and higher input of litterfall mass in the spruce forest (Navrátil et al., 2007).

6.1.5 Nitrogen, carbon, sulfur content

Content of nitrogen, carbon and sulfur was only determined in organic horizon because mineral horizons were expected to have much lower content and thus they were omitted in this study.

Generally, content of C in organic horizons is related to the accumulation of litter. Higher carbon content was found under the spruce forest than in the beech forest and clear-cut area where better litter quality is expected due to faster decomposition related to more favourable environment for microbiological activity (Fiala et al., 2005; Drábek et al, 2007). This assumption is supported by comparison of C:N ratios according to which the type of humus can be derived (Table 13).

Table 13: Type of humus according to the C:N ratio.

	C:N
Mull	16
Mull-moder	18
Moder	20
Mor	23

Taken from Duchaufour and Souchier, (1978).

Results show that higher nutrient turnover is expected under the beech forest and clear-cut area with moder humus type (19.7, 19.4, respectively) than spruce forest with mor humus type (22.4) (Figure 20). Similarly, Berger et al., (2009) observed that on nutrient poor bedrock (Molasse), the C:N ration declined from spruce to beech. Moreover, when the C:N ratio is on average well below 30, it could be suggested that there is a risk of nitrate leaching (Hruška and Cienciala, 2003). Considering the above mentioned, Tejnecký et al., (2013) observed slight increases of water extractable NO_3^- in the under the beech and spruce forest in the period 2008–2010. However, more observations need to be done in order to determine whether or not there is an increased nitrate leaching. In the case of the clear-cut area quickly invaded by grass and with occurrence of free-growing young spruce and beech trees, low C:N ratio could be associated to the ecological succession stage of this stand because larger amount of nitrogen is required by tree foliage in the early period of grow (Stevens et al., 1994). In addition, Fiala et al., (2008) proved

the importance of grass swards that retain and immobilize substantial amount of nitrogen in areas that were clear-cut.

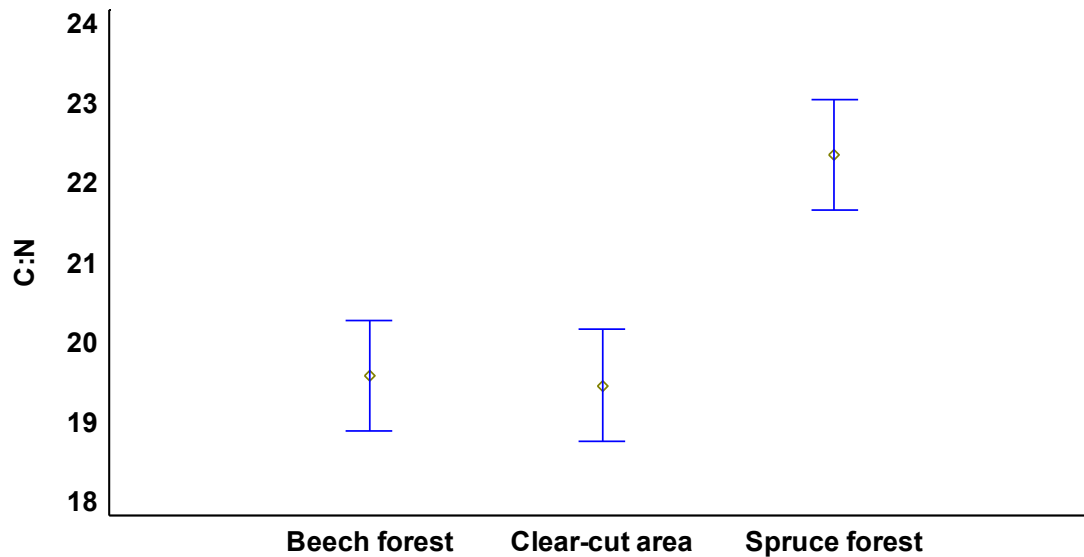


Figure 20: Means and 95 % LSD intervals for C:N ratio for each stand in organic horizons (F, H) (n=12).

6.2 Is the understory vegetation composition changing with respect to soil chemical parameters?

Increasing abundance of nitrophilous acid soil tolerant perennial grasses (*Calamagrostis villosa*, *Calamagrostis arundinacea*) was observed in the spruce forest between years of sampling. For example, Van Doben and de Vries (2010) found a small but significant shift towards nitrophytic species at high N-deposition sites in the European network and towards acidophytic species at high S-deposition sites in the Dutch network. This indicates that enhanced nitrogen loads could give rise to changes in the vegetation composition towards nitrophilous species. Vegetation composition in the study area Paličník was subject of phytocenological research between the years 2008 and 2013 in order to display changes in understory vegetation.

According to the Ellenberg indicator values beech forest experienced significant decrease ($p=0.0019$) in light conditions between years of sampling. Spruce forest exhibited significant decrease in temperature ($p=0.008$) and increases in the light conditions ($p=0.02$) (Figure 21). Clear-cut area did not experience any significant changes between years of sampling. However, it seems to have higher irradiation than both the beech and spruce forest. Changes of irradiation in the spruce forest are ascribed to reduced canopy cover most likely due to forest thinning. For

example, Vacek et al., (1999) concluded that increased defoliation is associated to changes in the forest understory. Similarly, Wild et al., (2004) who observed vegetation changes in climax spruce forest, stated that changes are related to decreases in tree canopy cover. It could be concluded on the ground of Ellenberg indicator values that composition of understory vegetation is rather influenced by light conditions than changes in the soil chemical parameters.

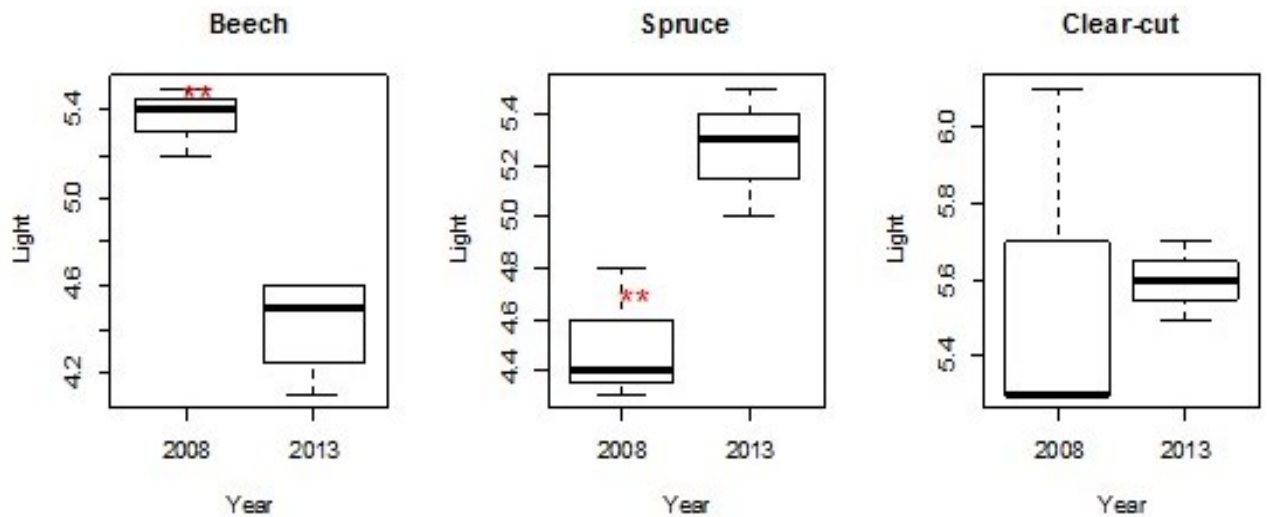


Figure 21: Median and inter-quartile point distribution of light between years for beech and spruce forest and clear-cut area separately according to Ellenberg indicator values. Significant results are marked with the asterisks.

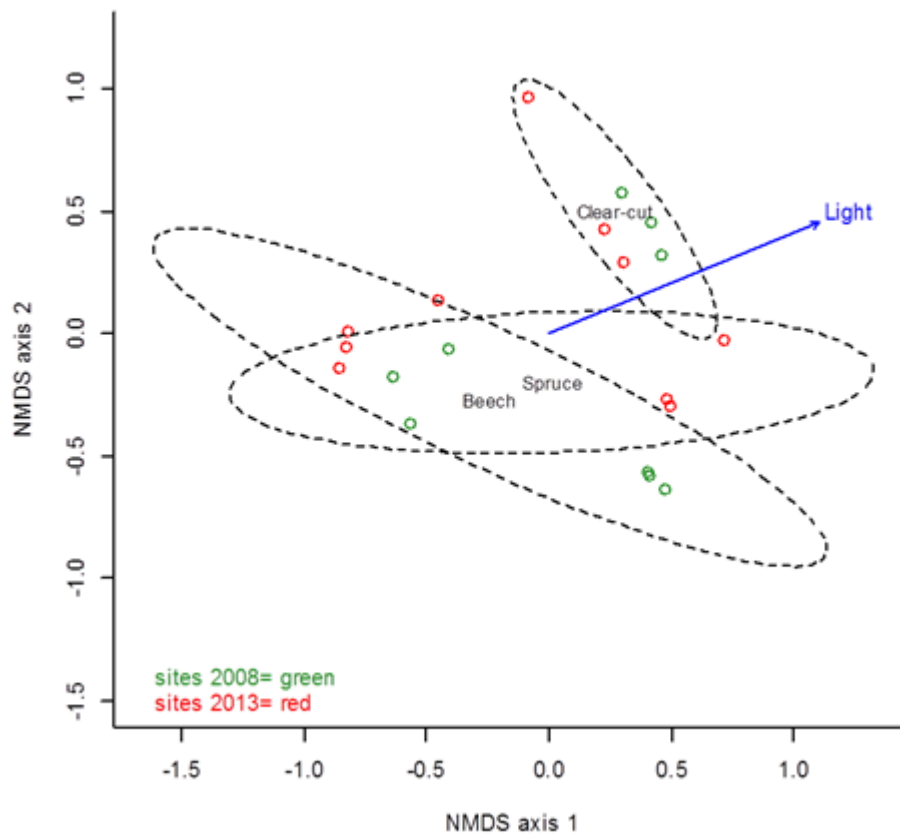


Figure 22: Changes in understory composition between stands and years of sampling (2008–2013) based on Ellenberg's indicator values.

7 Conclusions

It was shown that forest mountainous soils are strongly acid. Soil sorption complex strongly correlated to carbon content in surface horizons. Lower pH values were determined in organic horizons compared to mineral horizons indicating that acidification is more intensive in surface horizons. Cation exchange capacity in mineral horizons was extremely unsaturated by bases and exhibited high saturation of exchangeable Al. The Ca:Al ratio between exchangeable Ca and Al is very low at each stand in mineral horizons and only clear-cut area exhibits Ca:Al ratio higher than 1 in organic horizons.

The lowest mean soil pH as well as pH of throughfall was determined in the spruce forest. Enhanced decomposition of soil organic matter was found in clear-cut area and beech forest compared to spruce forest. However, the C:N ratio was lower than 30 at each stand and it could be expected that there is risk of nitrate leaching. Concentrations of exchangeable Al did not vary between stands whereas concentrations of exchangeable Fe and free H ions were 2 times higher in the spruce forest. Differences were especially apparent in the A horizon. On the base of findings it could be concluded that main buffering mechanisms was Fe mobilization.

Changes between years of sampling were more pronounced in the organic horizons reflecting the influence of vegetation cover. Clear-cut area exhibited significant increment in pH_{KCl} , base saturation and significant decrease of exchangeable acidity in organic horizons. Base saturation also increased and exchangeable acidity decreased in the beech forest. Spruce forest exhibited decreases in exchangeable acidity in both organic horizons and in parallel, significant decreases in base saturation in the mineral horizon B suggesting ongoing leaching of base cations during neutralization processes.

According to Ellenbergs indicator values, it was not proved changes in understory vegetation are connected to changes in soil chemical parameters because the occurrence of understory vegetation is rather influenced by light conditions.

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