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IMPACT OF ACIDIFICATION ON SOIL ORGANIC CARBON AND PLANT BIOMASS PRODUCTION DURING THE SHORT-TERM POT EXPERIMENT

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Abstract

The aim of this study was to investigate the effects of simulated acid load on soil organic carbon and plant biomass production. A short-term pot experiment with spring barley was conducted on 6 different soil types (Chernozem, Fluvisol, Eutric Cambisol, Stagnosol, Dystric Cambisol, Podzol). Two treatments were applied (A: watering with distilled water of pH 5.4; B: watering with acid solution of pH 2.5). Due to the acid watering, a pH decreased in all six soil types. Acid load enhanced aboveground dry matter biomass production at all six soil types. TOC stock increased in both treatments in all soil types with the exception of Eutric Cambisol. Results of humic-fulvic acid ratio showed that acid load caused deterioration of organic matter quality in four soil types and improvement in two soil types.

Key words: *acidification, soil organic carbon, organic matter quality, pH*

Introduction

Soils contain the largest near-surface reservoir of terrestrial carbon. In terrestrial ecosystems the amount of carbon in soil is usually greater than the amount in living vegetation. The soil C pool comprises both organic (SOC) and inorganic (SIC) components. The SOC pool is more labile and dynamic than SIC pool, and is drastically influenced by anthropogenic activities (Post *et al*., 2000). There are two groups of factors that influence inherent organic matter content: natural factors (climate, soil parent material, land cover and/or vegetation and topography), and human-induced factors (land use, management and degradation) (Jones *et al*., 2004). Soil organic matter dynamics is controlled by climatic and physical factors, chemical like pH, C/N ratio, and resource quality (e.g. lignin and polyphenol contents) (Zech *et al*., 1997).

Most agricultural soils have lost 30% to 75% of their antecedent SOC pool or 30 to 40 t C. ha^{-1}. The magnitude of loss is often more in soils prone to accelerated

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erosion and other degradation processes (Lal *et al.*, 2007) including soil acidification.

The amount of C stored in a soil is determined by dynamic equilibrium between C inputs from primary biomass production and C outputs by mineralisation. Mineralization of organic carbon is inhibited by different stabilization processes. The interplay between these processes is very complex, requiring an understanding of chemical, physical, and biological interactions within the soil matrix (Kögel-Knabner *et al.,* 2008). Current soil organic matter (SOM) turnover models are not fully process-oriented and thus the simulation of ecosystem response to environmental changes such as management and the changing climate is still difficult (Parton, 1996). Mechanisms for C stabilisation in soils have received much interest recently due to their relevance in the global C cycle. Any change in the size and the turnover rate of soil C pools may potentially alter the atmospheric CO_2 concentration and the global climate. Recent analytical and experimental advances have demonstrated that molecular structure alone does not control SOM stability: in fact, environmental and biological controls predominate (Schmidt *et al.,* 2011). Acidification as a natural and human accelerated process plays an important role in organic carbon dynamics. The dynamics of soil pH in terrestrial ecosystems have recently received considerable attention, but the direction and magnitude of pH changes are highly variable among studies (Yang *et al*., 2012) and research need regional approach. The primary agents of acid deposition around the world are atmospheric sulphur dioxide (SO_2) and nitrogen oxides (NO_x). Deposition of sulphur compounds has declined considerably over the last 30 years in North America and Europe, however, this period has seen either no change or a slight increase in the deposition of N compounds (NEGTAP, 2001). Over the same period, S and N deposition have greatly increased in many areas of Asia due rapid industrialisation (Kim, Cho, 2003). The influence of many factors on soil carbon quantity and quality and biomass production has been well documented, but there remains uncertainty in the potential response of soil carbon dynamics to the increase in acidification caused by natural and human-induced factors.

In this study we analysed the impact of acid load on soil organic carbon quantity, quality, and biomass production in different soil types.

Material and methods

We made use of a short-term pot experiment in laboratory with grown plant of spring barley *Horedem sativum*, variety *Favorit,* cultivated at 6 different soil types, Chernozem (CH), Fluvisol (FL), Eutric Cambisol (CMeu), Stagnosol (ST), Dystric Cambisol (CMdy), Podzol (PZ) (Tab. 1) in four replications.

Two treatments were applied, control treatment A: watering with distilled water of pH 5.4, and treatment B: watering with acid solution of pH 2.5. Acid solution was prepared as the mixture of sulphuric and nitric acid in 3:1 ratio added into the distilled water.

Table 1. *Basic characteristics*

Soil type	Substrate	Geomorfo-logical unit	Climate region	Yearly precipitation (mm)	Land-use category
Chernozem	Carbonate neogenic sediments	Podunajská Lowland	Warm, dry	550	Arable land
Fluvisol	Fluvial sediments	Podunajská Upland	Warm, mild dry	649	Arable land
Eutric Cambisol	Andesite	Krupina Plain	Mild warm, mild wet	649	Arable land
Stagnosol	Glaciofluvial deposits	Liptov Basin	Mild cold	754	Arable land
Dystric Cambisol	Slope deposits	Kremnica Mountains	Mild cold	852	Pastures
Podzol	Granodiorite	High Tatras	Cold mountain	944	Forests

Soil samples were collected from humic horizons where 5 soil samples were mixed from 1 plot of 10x10 m. Homogenised soil samples of 4 kg were placed in plastic flow containers with 4 dm^3 volumes. We seeded 100 grains of spring barley into two lines. After the plant emergence on the 11th day, we reduced the number of plants to 20 pieces per container (2 lines of 10 plants in every container). Two treatments were applied, control treatment A: watering with distilled water of pH 5.4, and treatment B: watering with strong acid solution of pH 2.5 with the aim to induce rapid changes in frame of short time pot experiment. Acid solution was prepared as the mixture of sulphuric and nitric acid in 3:1 ratio added into the distilled water. A volume of 200 ml was applied three-times per a week directly on the soil to avoid contact with growing plants. The pot experiment lasted for 88 days without any further fertilisation. The pretreatment of the soil samples excluded roots and other litter residues. Soil samples were air dried, homogenized, sieved on 2 mm sieves and characterized for soil pH ($CaCl_2$), pH buffering capacity (pHBC), total oxidizable organic carbon (TOC), total extractable carbon (TEC), carbon of humic acids (HAC), carbon of fulvic acids (FAC). At the end of the experiment, on 88th day we collected all above-ground biomass from each container, air dried and weighted.

The pH buffering capacity (pHBC) was measured using titration method as a single value for a particular soil, implying a linear relationship between pH and the amount of acid (HCl) or alkali (NaOH) added. Total oxidizable organic carbon (TOC) was determined according to Tjurin´s method in modification of Nikitin (Nikitin, Fishman, 1969) where potassium dichromate ($K_2Cr_2O_2$) and concentrated H_2SO_4 were used for rapid oxidation. To determine total extractable carbon (TEC), organic fractions as carbon of humic acids (HAC) and carbon of fulvic acids (FAC) were determined by accelerated method of Kononova – Belchikova (Kononova, 1966). Soil samples were extracted with 0.1 M $Na_4P_2O_7.10H_2O$ mixed with 0.1 N

NaOH. To determine organic matter quality the HAC:FAC ratio was calculated (Tab. 2).

Table 2 *Initial chemical soil properties*

Soil type	**pH $CaCl_2$**	**TOC** (% from soil mass)	**TEC** (% from soil mass)	**HAC** (% from soil mass)	**FAC** (% from soil mass)	**HAC: FAC ratio**
Chernozem	7.70	1.75	0.58	0.31	0.27	1.15
Fluvisol	6.77	1.46	0.51	0.20	0.31	0.64
Eutric Cambisol	6.34	2.28	0.78	0.32	0.46	0.69
Stagnosol	4.69	3.69	1.40	0.58	0.82	0.71
Dystric Cambisol	4.55	1.40	0.55	0.19	0.36	0.53
Podzol	4.43	6.20	1.98	0.76	1.22	0.62

Statistically we evaluated results by the Horn procedure of pivot measures because of small samples files. This is based on a depth which corresponds to the sample quartiles. The lower pivot is x_L and the upper is x_U. The estimation of the parameter of location is then expressed by the pivot halfsum $P_L = (x_L+x_U)/2$ and the estimate of the parameter of spread is expressed by the pivot range $R_L = x_U - x_L$ (Meloun *et al.*, 2001).

Results and discussion

Acid load significantly influenced soil parameters and thus affected organic matter quantity and quality as well as biomass production.

Several studies have indicated that acidification can cause changes in the soil chemical properties, the soil biota, the soil fauna and soil microbial biomass (Barak *et al.,* 1997, Monaghan *et al.,* 1998, Fenton and Helyar, 2002; Noble *et al.*, 2008; Mueller *et al.,* 2011). Due to the acid watering in treatment B a pH decreased in all six soil types (fig. 1). The biggest pH decrease expressed in hydrogen ion concentration was observed in Podzol (- 62 847.10^{-9}), the smallest in Chernozem (-4.10^{-9}). In the control treatment A pH increased in three (FL, CM_{eu}, ST) and decreased in three (CH, CM_{dy}, PZ) soil types.

However, to some degree, the magnitude of soil pH changes may depend on soil buffering capacity (Brady, Weil, 2008). Changes in pH are affected by dominated buffer systems in soil. Based on pH values, Ulrich and Sumner (1991) distinguished different buffer ranges for interpretation of pH values. Chernozem with active carbonate buffer system is the most resistant to acidification (fig. 2) and thus also to pH changes. On the other hand Podzol with the biggest pH decrease belongs to the aluminium buffer range weakly resistant to acidification.

There are many factors and processes that determine the direction and rate of change in organic carbon quantity and quality. The amount of soil C storage is controlled primarily by two fundamental factors: input by net primary production (its quantity and quality) and its decomposition rate. Decomposition of natural organic matter in soils is mainly microbially mediated, with about 10-15% of the energy of organic C utilized by soil animals (Wolters, 2000).

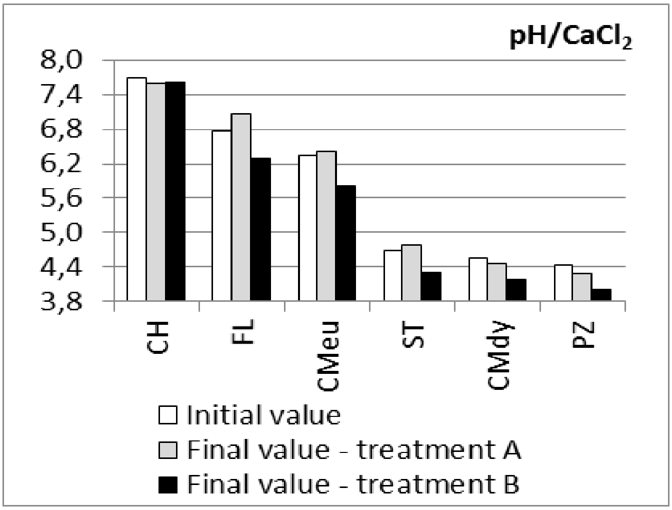

Figure 1
Changes in pH during the experiment

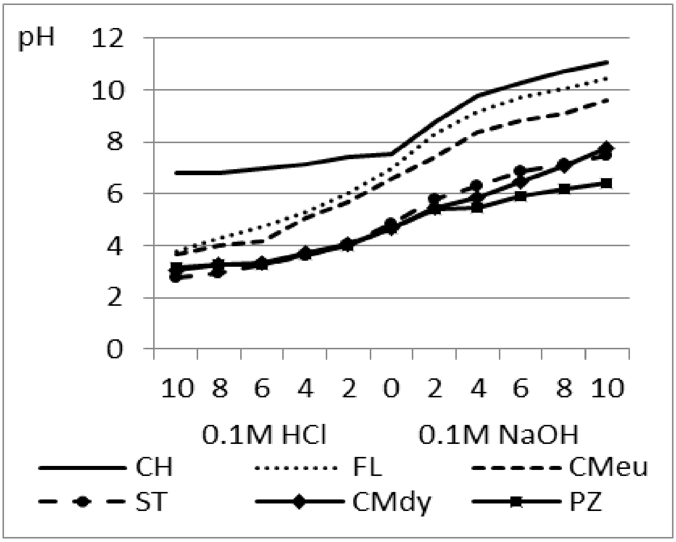

Figure 2
Buffer curves of soil types

In soils and soil horizons with differing texture and mineralogy, various stabilization mechanisms are operative, with differing importance. Turnover of stabilized organic matter is strongly dependents on environmental conditions and

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soil properties such as pH and mineralogy (Lützow et al., 2006, 2008). That is a reason why also our results concerning to initial TOC quantity and quality varies among the different soil types (Tab. 2).

The TOC increased in both treatments in all soil types with the exception of Eutric Cambisol. In comparison of treatment A and treatment B, acid load in treatment B caused higher increase of TOC in Chernozem, Dystric Cambisol and Podzol. Distilled water watering in treatment A caused higher increase of TOC in Fluvisol and Stagnosol (Tab. 3). The TOC changes were more remarkable at soil types with lower buffer capacity (PZ, CMdy, ST) than in soils with higher buffer capacity. The highest TOC increase (from 6.2 to 9.6 %) was observed in the treatment B induced by acid load in Podzol. It can be consequence of high organic matter stock that is in case of Podzol rich in lignin.

Table 3. *Changes in Cox (%) during the experiment*

Treatment	Statistical characteristic	CH	FL	CMeu	ST	CMdy	PZ
Initial values		1.75	1.46	2.28	3.69	1.40	6.20
Final values							
A	**Pivot halfsum (P_L)**	1.82	1.62	1.88	4.23	1.49	6.50
	Pivot range (R_L)	0.18	0.11	0.32	0.14	0.15	0.90
B	**Pivot halfsum (P_L)**	1.91	1.61	1.79	4.19	1.95	9.60
	Pivot range (R_L)	0.07	0.04	0.09	0.30	0.08	1.28

Simultaneously with TOC changes, acid load induced changes in organic matter quality expressed by humic and fulvic acid carbon content (Tab. 4 and 5).

Table 4. *Changes in humic acid carbon content (% from soil mass) during the experiment*

Treatment	Statistical characteristic	CH	FL	CMeu	ST	CMdy	PZ
Initial values		0.31	0.20	0.32	0.58	0.19	0.76
Final values							
A	**Pivot halfsum (P_L)**	0.34	0.19	0.25	0.54	0.17	0.89
	Pivot range (R_L)	0.03	0.02	0.01	0.00	0.02	0.10
B	**Pivot halfsum (P_L)**	0.36	0.21	0.24	0.52	0.21	1.67
	Pivot range (R_L)	0.01	0.01	0.02	0.06	0.02	0.08

Table 5 *Changes in fulvic acid carbon content (% from soil mass) during the experiment*

Treatment	Statistical characteristic	CH	FL	CMeu	ST	CMdy	PZ
Initial values		0.27	0.31	0.46	0.82	0.36	1.21
Final values							
A	**Pivot halfsum (P_L)**	0.30	0.36	0.43	0.64	0.40	1.22
	Pivot range (R_L)	0.03	0.02	0.01	0.00	0.02	0.10
B	**Pivot halfsum (P_L)**	0.31	0.37	0.44	0.67	0.47	2.08
	Pivot range (R_L)	0.01	0.01	0.02	0.06	0.02	0.08

Results of humic-fulvic acid carbon ratio (Fig. 3) showed that acid load caused deterioration of organic matter quality at four (Chernozem, Fluvisol, Dystric Cambisol, Eutric Cambisol) and improvement at two soil types (Stagnosol and Podzol) staying in the aluminium buffer range. In addition Podzol organic matter rich in lignin offers good material for humic acids formation. According to the some theories (e.g. Kononova, 1966) humic acids as aromatic compounds have a lignin origin. Lignin significantly contributes to the soil humic acid composition (Adani *et al*., 2007).

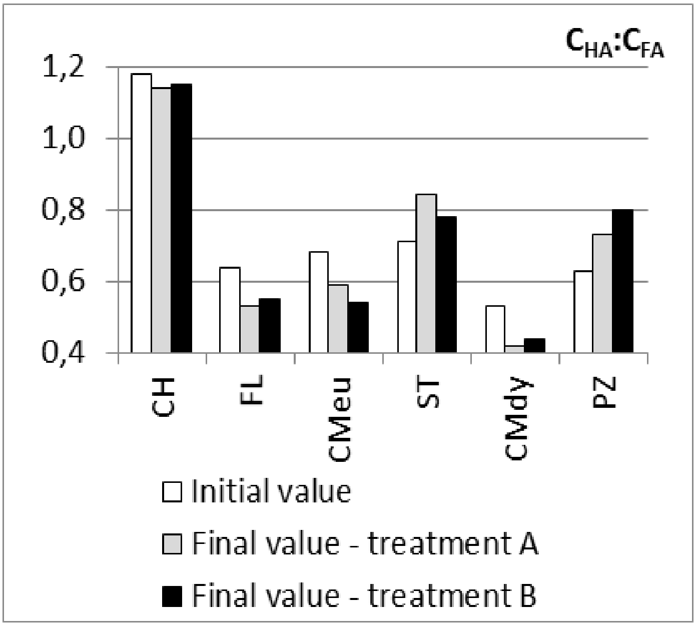

Figure 3
Changes in humic-fulvic acid ratio during the experiment

Acidification is also important factor in mineralization processes. The mineralisation is mainly determined by the quality of soil organic matter (Tian *et al*., 2013). Persson *et al*. (1989) found out that strong acidification reduced C mineralisation. Similarly Ravenek (2009) found out that high acidity reduces C mineralization and also N mineralization. Other studies have shown that acidification can at least temporarily stimulate N mineralization (Tamm, Wikladnder, 1980). Such processes of mineralization as many other processes can affect biomass production. And therefor it is difficult to assess only direct effects of the acidification on plant growth. During the experiment, acid load enhanced aboveground dry matter biomass production at all six soil types. Thus the aboveground biomass production was higher at all soil types in treatment B than in control treatment A (Fig. 4).

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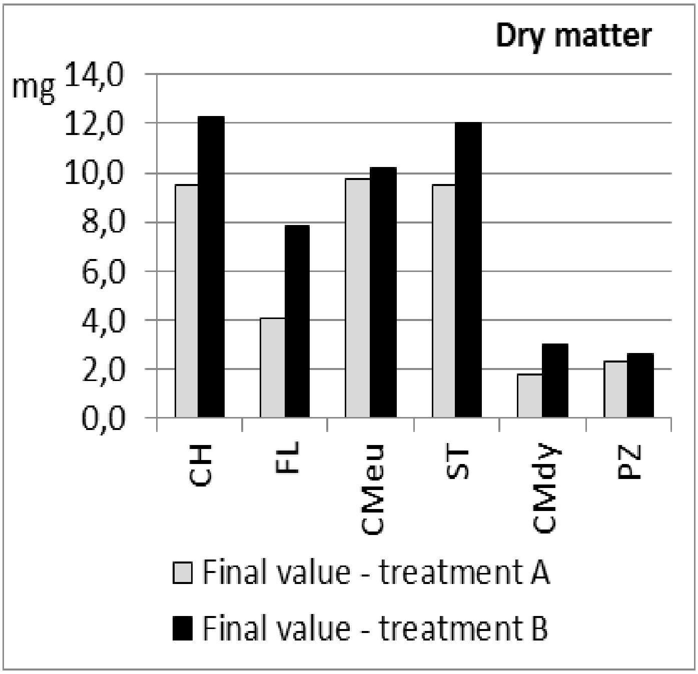

Figure 4
Changes in the aboveground biomass during the experiment

The effect of higher plant production in treatment B with acid load can be connected with N input (acid solution was prepared as the mixture of sulphuric and nitric acid) what is partially in line with suggestions by Högberg *et al*. (2006), Holland (1997). They showed, but in frame of long term experiments, that N-load led to an additional plant C sequestration.

Higher biomass production was recorded at the soil types (CH, FL) more resilience to acidification where small pH decrease could stimulate nutrients availability. Low aboveground biomass production at PZ and CMdy is consequence of low pH values. At low soil pH values, Al, Mn, and other mineral elements may be present in toxic concentrations, and the availabilities of essential elements, particularly Ca, Mg, P, Mo and Si may be suboptimal. In most acid soils Al and Mn toxicities are more important than H ion toxicity in limiting the growth of plants (Kochian *et al*., 2004; Marler, Cruz, 2001).

Conclusion

This study provides new insights into the impacts of acidification caused by acid load on the soil and biomass production. The results demonstrated that simulated acid load causes pH decrease and thus increase soil acidification. We recorded that N-load has generally positive effect on plant biomass production wherein plant biomass quantity depends on genetic soil type and pH. Acidification also affected soil carbon quantity in dependence of individual soil type characteristics, and induced changes in organic matter quality.

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