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# Transformation of iron forms during pedogenesis after tree uprooting in a natural beech-dominated forest

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## ABSTRACT

Treethrow dynamics was revealed to be a key biomechanical effect of individual trees in soil formation in mountain temperate forests. The resulting pit–mound microtopography represents a specific pattern of microsites with a potential influence on the course of pedogenesis (Šamonil et al., 2010a). The aim of this study was to investigate the influence of tree uprooting on the transformation of Fe forms, as these forms indicate the degree of pedogenesis in Cambisols.

Soil samples originated from a Haplic Cambisols region in a natural fir–beech forest in the Western Carpathians, Czech Republic. Four pit–mound pairs of different ages – 20, 28, 180 and 191 years – as well as control, undisturbed profiles were sampled.

Iron forms were studied using the following two different approaches: (i) Fe forms (exchangeable, crystalline, and amorphous together with organically complexed Fe) were extracted by three specific extracting agents then subsequently determined by ICP-OES; and (ii) non-destructive methods such as Voltammetry of Microparticles (VMP) and Diffuse Reflectance Spectroscopy (DRS) were used.

The following Fe species were detected by VMP within individual microsites: ionic Fe(III), ferrihydrite, and poorly crystalline and crystalline Fe(III) oxides. Mn(III,IV) oxides were also detected. Goethite, hematite, $Fe^{2+}$–$Fe^{3+}$ pairs in Fe-bearing aluminosilicates (biotite, chlorite) and octahedral $Fe^{3+}$ (total $Fe^{3+}$ oxides and silicates) were quantified by means of the DRS technique.

Ferrihydrite and $Fe^{2+}/Fe^{3+}$ ratio were higher in soils from the pits compared to samples originating from the mounds and this ratio increased with increasing depth. Linear mixed effect (LME) models fitted by restricted maximum likelihood (REML) determined the relation between iron forms and other soil characteristics. Based on the development of Fe forms with time, we can conclude that tree uprooting significantly accelerates pedogenesis in the natural forest.

## 1. Introduction

As soil scientists have established already since the 1930s (e.g. Jenny, 1941) soil formation can be considered a function of many factors, particularly climate, topography, parent material, biota and time. Soil disturbances (e.g. due to tree uprooting) can be seen as specific dynamic soil forming factors connecting the effects of biota and time. The combination of aforementioned factors directly influences the genesis of Fe forms in soils. The formation and occurrence of $Fe^{2+}$ (reducing environment) and $Fe^{3+}$ (oxidizing environment) (oxy)-hydroxides are controlled by changes in the soil water regime. Biota – mainly in the form of microorganisms and soil vegetation cover – plays a key role in the creation of Fe-organo-mineral complexes (Kappler and Straub, 2005). Vegetation also significantly increases the amount of Fe in surface soil

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*Abbreviations:* ANOVA, analysis of variance; CEC, effective cation exchange capacity; Cox, oxidizable C; DBH, diameter at breast height (DBH = 1.3 m); DRS, Diffuse Reflectance Spectroscopy; Fe(III) (Mn(III,IV)), elements detected by VMP; $Fe^{2+}$ ($Fe^{3+}$), iron detected by DRS; $Fe_c$, crystalline forms of Fe ($Fe_d - Fe_{ox}$); $Fe_d$, crystalline together with amorphous and organically complexed Fe forms; $Fe_{ex}$, exchangeable Fe forms; $Fe_{ox}$, amorphous together with organically complexed Fe forms; $Fe_t$, total content of Fe in soils; H.G., homogeneous groups; ICP-OES, inductively coupled plasma optical emission spectrometry; LME, linear mixed effect models fitted by restricted maximum likelihood; LS mean, least significant mean; LS sigma, least significant sigma; $pH_{H_2O}$, active soil pH; REML, restricted maximum likelihood; SOM, soil organic matter; VMP, Voltammetry of Microparticles; XRD, X-ray diffraction analysis.

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and forest floor horizons by uplifting (Li et al., 2008). Bedrock influences the amount of soil Fe as it is the main source of Fe that is being replaced into a soil, mainly in the form of secondary minerals (Kappler and Straub, 2005). Changes of the different Fe forms have been successfully used for time ordering of soils developed on river terraces. The time of genesis of such soils ranges between hundreds and thousands of years, which is very similar to the genesis of tree uprooting (e.g. Šamonil et al., 2010a, 2013a). It was proven that the amount of crystalline Fe increases with increasing time (e.g. Alexander, 1974 and Arduino et al., 1984). Moreover, the detectable share of different Fe forms can be used for assessment of the degree of pedogenesis, including weathering of primary minerals (Bábek et al., 2011; Grygar et al., 2006; Richardson and Hole, 1979).

Iron forms are directly involved in the processes of pedogenesis such as podzolization (Lundström et al., 2000) and brunification (Schaetzl and Anderson, 2005), or processes of soil organic matter (SOM) binding and stabilization (Wagai and Mayer, 2007) in natural temperate forests. Iron forms also influence the fate and behavior of risk elements (e.g. Pb, Cd, Cu, Zn and As) in the soil environment (Komárek et al., 2013); moreover, Fe forms play a significant role in nutrient cycling (Anderson, 1988).

The different single-step extraction methods e.g. extraction by acid oxalate and by dithionate–citrate enable to assess the distribution of Fe forms in soils (Cornell and Schwertmann, 2007). However, the extraction methods do not provide a precise information regarding Fe mineral speciation. In contrast, non-destructive or micro-destructive methods, such as Voltammetry of Microparticles (VMP) and Diffuse Reflectance Spectroscopy (DRS), work directly on the soil sample and can be used for identification of Fe minerals. Mainly the soil Fe oxides and silicates containing $Fe^{2+}$ or $Fe^{3+}$ in their structure can be detected by these methods (Grygar et al., 2002, 2003). To our knowledge, these methods have not yet been used during the evaluation of soil formation processes in disturbed soils.

The most stable and abundant soil $Fe^{3+}$ oxides are goethite ($\alpha$-FeOOH) and hematite ($\alpha$-$Fe_2O_3$); while ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) and particularly feroxyhyte ($\delta'$-FeOOH) occur less often in the soil environment, because they are less thermodynamically stable (Bigham et al., 1991; Schwertmann and Taylor, 1989). Generally, it was found that higher proportions of non-crystalline (amorphous) Fe forms are mainly present in surface organo-mineral A horizons (Pai et al., 2004). Higher occurrence of crystalline Fe forms was determined in basal B–C horizons. Moreover, the evolution of Fe forms in podzolized soils has been studied in detail (e.g. Giesler et al., 2000; Sauer et al., 2007); in contrast, the evolution of soil Fe forms in the Cambisol environment has not yet been satisfactorily studied.

Tree uprooting represents a specific biogeomorphic process affecting – through feedbacks to tree regeneration and impact in soil and biodiversity formation – whole forest ecosystem dynamics in the natural (or close to natural) temperate forest environment (see reviews by Šamonil et al., 2010a; Pawlik, 2013). New gaps in the forest canopy are created by tree uprooting. Pits, mounds and fallen tree trunks resulting from an uprooting event are unique niches for tree regeneration (Simon et al., 2011; Šebková et al., 2012), as well as for herbs and mosses (von Oheimb et al., 2007). Different microclimate conditions occur within pits and mounds (Schaetzl, 1990; Beatty, 1984). With the exception of during snowy seasons, mounds are generally warmer and drier than respective pits. Flat, undisturbed neighboring sites show close to average microclimate values. Unique microclimate conditions cause changes in trajectories of pedogenesis. (Šamonil et al., 2010a).

Šamonil et al. (2010b) used multidimensional statistical methods to determine the soil depth and the microsite of tree uprootings as factors with the highest impact on soil properties in the Cambisol region.

Specific ecological and erosion–sedimentation processes of the microsite of uprooted trees lead to the transformation of soil Fe forms and species. This transformation process can be an important part of the pedogenesis of Cambisols (Šamonil et al., 2010b). The period of tree uprooting turnover (how often an area equivalent to the entire study area is disturbed, see Pickett and White, 1985) in a natural Central European spruce–fir–beech forest was calculated as 1250–1390 years; in specific cases it is even less than 1000 years (Šamonil et al., 2009, 2013a). The description of pedogenesis in a small number of microstands of tree uprooting might significantly help to better understand the general principles of pedogenesis of Cambisols, including the previously discussed retrograde evolution.

The questions are: Is it possible to use non-destructive or micro-destructive methods for the determination of Fe forms (species) in soils, and thus assess (or describe) the pedogenesis? How do treethrow processes affect the pedogenesis of Cambisols; as described by the distribution of soil Fe species?

## 2. Material and methods

This work closely continues and extends published results concerning the soil chemistry and morphology that is influenced by tree uprooting events (Šamonil et al., 2008b, 2010b, 2015). In this work new results are presented, which can help to clarify the process of pedogenesis in natural beech-dominated forest in a Cambisol region. We present results from the study of soil Fe species in detail.

### *2.1. Locality and soil samples collection*

Soil samples were collected from the natural fir–beech forest Razula (Western Carpathians, Czech Republic). The bedrock is composed of flysch rocks: sandstones, claystones and argillaceous shales. Skeletic and particularly Haplic Cambisols predominated in the locality (according to FAO, 2006).

The field survey was conducted in 2006 and included all identifiable single treethrows (single uprooted trees and pit–mound microtopographical pairs already without uprooted tree trunk) occurring in the geomorphologically homogeneous part of Razula (10.8 ha). The minimum height of a mound, and/or depth of a pit (related to the contour line), was 0.05 m (treethrows with small dimensions) and 0.2 m (treethrows with bigger dimensions). A total number of 1562 treethrows represented 14.3% of the area (Šamonil et al., 2008a, 2008b). Of this, 9.8% consisted of mounds and the remaining 4.5% of pits.

The course of soil formation in the natural forest was studied for the 14 dated pit–mounds and in adjacent, currently undisturbed surroundings (for limitations of the space-for-time substitution in chronosequencing, see Phillips, 2015). A longitudinal excavation with a minimum depth of 100 cm was dug through each pit–mound in the direction of the tree fall. The entire profile was examined for soil morphology (layering of soil horizons, character of soil texture and orientation, the location of skeleton, argillans, root and trunk remains, etc.). From this excavation, soil samples were taken from the upper A mineral horizon (depth 0–10 cm, on average 5 cm) as well as from the depths of 15, 30, 50 (B-horizon) and 100 cm (BC- or C horizon) at the pit and mound positions. Variables of data collection: sampling depth, microsite and age after tree uprooting event were all independent of each other. Samples from a control profile on a currently non-disturbed and flat spot in the vicinity of the pit–mound were taken in a similar manner.

### *2.2. Site selection criteria*

In order to effectively utilize the dendrochronological dating, a suppositional gradient of age was constructed on the basis of directly measured characteristics (thickness of A-horizon on mound, steepness of mound, etc., Šamonil et al., 2009). Pit–mound features designated for dating were then chosen regularly along this gradient; this sampling scheme allowed us to obtain a representative selection of pit–mound pairs of various age.