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Klíčové faktory akumulace půdní organické hmoty

Key factors in soil organic matter accumulation

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Doctoral thesis

Supervisor: Prof. Mgr. Ing. Jan Frouz, CSc.

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Prohlášení:

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

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2. Abstract

Soil organic matter (SOM) is highly important for soil quality and the global carbon cycle. SOM content is influenced by a complex interplay of many different factors such as time, climate, parent material, vegetation, and others. The effect of time is often studied using the chronosequence approach. The effect of other factors can be studied by comparing two or more chronosequences. An important assumption of this approach is that the SOM quantification methods produce comparable results both among sites of each sequence and among different sequences. In this thesis, I explored the key factors in SOM accumulation and dealt with SOM quantification methods. I studied SOM accumulation in two model situations – in post-mining sites after open-cast coal and oil shale mining and in landslides in the Western Carpathians.

The key factor affecting the rate of SOM accumulation after a major disturbance is time. The accumulation rates found in the first 30 to 100 years in both post-mining sites and landslides are relatively high due to the low or zero initial SOM content of the newly exposed surfaces and high plant production. In the long term, the C storage attains a steady state and on the millennial time-scale, gradual loss of phosphorus controls the dynamics of C and N. Other important factors controlling SOM accumulation include climate and vegetation which interact together and affect the SOM inputs and outputs. Based on a methodological comparison, several methods that overcome the bias caused by fossil carbon of dominantly aliphatic character were identified as suitable for use in studies of SOM accumulation in post-mining sites.

This thesis provides further insight into the factors and mechanisms controlling SOM accumulation and provides a solution to a major methodological issue connected with the study of SOM accumulation in post-mining sites.

3. List of publications and manuscripts included in the doctoral thesis

Manuscript 1: Vindušková, O., Frouz, J., 2013. Soil carbon accumulation after open-cast coal and oil shale mining in Northern Hemisphere: a quantitative review. Environ. Earth Sci. 69, 1685–1698.

Manuscript 2: Vindušková, O., Dvořáček, V., Prohasková, A., Frouz, J., 2014. Distinguishing recent and fossil organic matter — A critical step in evaluation of post-mining soil development – using near infrared spectroscopy. Ecol. Eng. 73, 643–648.

Manuscript 3: Vindušková, O., Sebag, D., Cailleau, G., Brus, J., Frouz, J., 2015. Methodological comparison for quantitative analysis of fossil and recently derived carbon in mine soils with high content of aliphatic kerogen. Org. Geochem. 89–90, 14–22.

Manuscript 4: Frouz, J., Vindušková, O., (in press) Soil organic matter accumulation in post-mining sites: potential drivers and mechanisms. In: Munoz, M., Zornoza, R. (Eds.), Soil Management and Climate Change. Academic Press, p. 450.

Manuscript 5: Vindušková, O., Pánek, T., Frouz, J., (prepared manuscript) Soil development during last 13,000 years along a chronosequence of landslides in Central Europe.

Author's contributions

Manuscript 1: OV collected the literature data, performed most of statistical analyses and led writing of the manuscript.

Manuscript 2: OV performed all the laboratory as well as the statistical analyses and led writing of the manuscript.

Manuscript 3: OV performed the laboratory analyses except Rock-Eval, NMR and isotope analyses and performed the statistical analyses of data including those from Rock-Eval, NMR and isotope analyses and led writing of the manuscript.

Manuscript 4: OV contributed to writing of the manuscript and prepared figures for the manuscript.

Manuscript 5: OV performed the field work (soil sampling), sample preparation, total phosphorus analyses and statistical analyses and led writing of the manuscript.

The supervisor of the doctoral thesis and the co-author of all presented papers, Jan Frouz, fully acknowledges the contribution of Olga Vindušková as stated above.

Prof. Mgr. Ing. Jan Frouz, CSc.

4. General introduction

4.1. Introduction

Soil organic matter is an important soil component that **affects many soil properties** and functions. It increases soil cation exchange capacity (Helling et al., 1964) thereby increasing soil nutrient storage and retention of toxic substances (Kumpiene et al., 2008). It enhances soil structure leading to higher aeration, infiltration, water-holding capacity, and soil resistance to erosion (Bronick and Lal, 2005). It is a source of nutrients and energy to soil biota which is crucial to nutrient cycling (Carter, 2002). Soil organic matter content is therefore often used as an indicator of soil quality (Doran and Parkin, 1996) that can be greatly affected by soil management.

Moreover, soil organic matter (SOM) is an important **global carbon pool**. Soils store 1500–2400 Gt of carbon (C), which is 2 to 3 times more than C found as CO_2 in the atmosphere and 2 to 5 times more than C in living plant biomass (based on Ciais et al., 2013). Also the fluxes of C between SOM and other global C pools are significant. For example, the annual flux of CO_2 from soils to the atmosphere is estimated to 98 ± 12 g C yr^{-1} (Bond-Lamberty and Thomson, 2010) as opposed to 8 Pg C yr^{-1} (Ciais et al., 2013) released by fossil fuel combustion. Soil can represent a sink or a source of CO_2 based on the land-use and other environmental factors. Supporting C sequestration[1] in soils through soil organic matter accumulation has been proposed as a tool to mitigate the on-going increase of CO_2 in the atmosphere that is concurrently beneficial to soil quality (Lal, 2004).

Understanding SOM dynamics is crucial for prediction of future effects of climate change on ecosystems and the feedback from ecosystems to climate on various time-scales (Rustad, 2006) as well as for effective soil quality management.

4.2. Soil organic matter (SOM) – definition, chemistry, and stability

Soil organic matter (SOM) is a complex mixture of plant, faunal and microbial residues at various stages of decay. In the broad sense it includes litter, light fraction, microbial biomass, water-soluble organics, and more transformed organic matter (Stevenson, 1994). SOM is sometimes synonymously termed **humus** (*sensu lato*), although in some definitions humus (*sensu stricto*) does not include undecayed plant and faunal tissues and microbial biomass (Stevenson, 1994; Lehmann and Kleber, 2015).[2]

[1] The process of C capture in another geosphere than the atmosphere.

[2] Therefore, I avoid this term in my thesis except the part about "humus forms" which is an accepted term for the vertical arrangement of SOM in the top soil layers.

SOM consists of many different organic compounds ranging in complexity and degree of transformation; molecular structure of which has still not been completely described (Sutton and Sposito, 2005). Soil organic matter undergoes **decomposition** which is "a biological process that includes the physical breakdown and biochemical transformation of complex organic molecules of dead material into simpler organic and inorganic molecules" (Juma, 1999). The conversion of organic to inorganic compounds which is the final step of decomposition is known as **mineralization**. Whether soil organic matter formation involves also some synthesis reactions as proposed by the traditional humification theory is increasingly questioned (Piccolo, 2002; Lehmann and Kleber, 2015).

Soil organic matter content is often measured as **soil organic carbon** (SOC) content and one can be converted to the other based on the assumption that carbon represents 58 weight percent of soil organic matter, although this estimate is an average value for various organic compounds (Pribyl, 2010). Not only quantity but also **quality** of soil organic matter is important for its function. For example, although the forest floor horizons (litter, fermentation, and humification layers) are often included in the budget of C sequestered in soil (Guo and Gifford, 2002; Paul et al., 2002; Laganiere et al., 2010), such organic matter has certainly different impact on soil quality and fertility than SOM in higher degree of decay. Moreover, surface horizons provide less stable storage of C compared to the mineral soil. These reserves can be easily lost by fire, erosion or decomposition due to changes in microclimatic conditions (Jandl et al., 2007) or changes in pH (Oulehle et al., 2011). Therefore, the contribution of forest floor to total soil C stocks should be always reported separately (Vogel, 1981; Laganiere et al., 2010). Similarly, different fractionation techniques for separation of SOM fractions differing in physical or chemical properties provide better insight into the stability and potential function of SOM. For example, the traditional fractionation technique based on different solubility in alkali and acid separates the operationally defined “humic substances” into humin, humic acids, and fulvic acids where the latter two fractions may be further fractionated. The humic to fulvic acids ratio has been traditionally used as an indicator of SOM quality (Stevenson, 1994; Horáček et al., 2017). However, SOM function and **stability** (i.e., resistance against decomposition) is determined not only by chemical composition but also by physical protection (Oades, 1988). SOM may be either (1) physically protected inside (micro)aggregates where O_2 levels and access to microorganisms is low, (2) protected in organo-mineral associations with clay and silt particles or Al/Fe oxides (Kögel-Knabner et al., 2008), and (3) biochemically protected in chemically resistant (non-hydrolyzable) fraction (Six et al., 2002) which is increasingly assumed to be of microbial origin (Kallenbach et al., 2016; Paul, 2016). Therefore, many physical and physico-chemical fractionations techniques have evolved during the past 20 years (von Lützow et al., 2007; Zimmermann et al., 2007). These techniques separate SOM fractions based on one or more of these assumptions: 1) light SOM fraction is more labile than the heavy fraction associated with mineral particles 2) SOM occluded in aggregates is more stable than the non-occluded fraction 3) SOM in microaggregates is more stable than in macroaggregates 4) SOM more resistant to chemical or thermal oxidation is more stable. Apart from physical protection, other environmental constraints such as drought, flooding or freezing that decrease microbial activity also impede SOM decomposition.

4.3. Soil organic matter accumulation

The soil organic matter pool and its dynamics result from an **input-output balance**. Primary producers (plants) provide carbon input via leaf and root litter while the decomposers break down SOM in the process of decomposition producing CO_2 which determines the output, although methane production, leaching of dissolved organic matter (DOM) and erosion may also contribute to outputs (Davidson and Janssens, 2006). Soil organic matter accumulation then occurs when inputs exceed outputs and the opposite applies for soil organic matter loss. SOM accumulation typically occurs after different disturbances, land-use change or emergence of new surfaces typically in soils that have low or zero content of SOM. The disturbances may be either (1) natural – e.g., landslides, volcanic eruptions, fire, glaciation/ glacial retreat, or (2) human-induced – e.g., mining, agriculture, fire, clear-cutting.

The natural orderly process of community changes that follows a disturbance is termed **ecological succession** (Odum, 1963). **Primary succession** occurs on newly exposed surfaces with little or no biological legacy left by the pre-disturbance ecosystem (Walker and Shiels, 2013). Such surfaces are typically found on sand dunes, lava flows, or moraines after retreating glaciers. In contrast, **secondary succession** occurs after disturbance events that do not destroy the communities and abiotic conditions found in the ecosystem before the disturbance completely (Odum, 1963). Such disturbances include fire, clear-cutting, or cultivation. The extent and type of some disturbances such as landslides controls if they will be followed by primary or secondary succession because shallow (soil) landslides may leave islands of residual soil (Walker et al., 1996). In terms of SOM, the substrate in primary succession has typically contents close to zero, whereas secondary succession occurs on soil which already contains certain level of SOM.

Not only succession but also human-induced **land-use change** (e.g., afforestation) may lead to SOM accumulation if the input-output balance is shifted towards higher inputs and/or lower inputs. Land-use change may lead to both accumulation and losses of C from soil (Guo and Gifford, 2002). A typical land-use change inducing SOM accumulation is the change of agricultural land to grassland or forest which may proceed either by succession or planting (Post and Kwon, 2000). There is a large variability in the length of time and rate at which C accumulates that is related to productivity of the establishing vegetation and other factors (Post and Kwon, 2000; Guo and Gifford, 2002; Laganiere et al., 2010).

4.4. Factors affecting soil organic matter accumulation

Based on the earlier ideas of V. Dokuchaev (1846–1903), Jenny (1941) defined the state of soil to be a function of five independent soil-forming factors: climate, organisms, topography/relief, parent material, and time. However, already Jenny (1941) pointed out that although these factors *may* vary independently they also enter functional relationships among each other. For example, certain climate and/or parent material supports certain potential plant community composition. This makes the study of soil-forming factors challenging. However in the next chapters, the concept of soil-forming factors will be used to discuss factors and mechanisms that control SOM accumulation. For this purpose the "organisms" factor will be divided into: vegetation, soil biota, and human activities, as these differ greatly in their effects on SOM.

Figure 1 summarizes the key factors and mechanisms regulating soil organic matter content through an input-output balance. The main factors that influence the inputs are **net primary production (NPP)** and the fraction of NPP that is allocated to (both aboveground and belowground) **litter production** which together determine the overall litter input into soil. The main factors affecting the output, i.e. decomposition, is the **litter quality** (decomposability) and **microbial activity**. All the other factors influence SOM dynamics through changes in one or more of these main factors by different mechanisms. Factors increasing decomposition rates in turn increase nutrient availability that may support NPP if this is nutrient limited.

4.4.1. Climate

4.4.1.1. Temperature

The air temperature affects SOM accumulation both through inputs and outputs. It affects rates of both photosynthesis and (plant) respiration. Most models assume that there is a temperature optimum for the rate of photosynthesis (it is low at low and high temperatures) and that respiration is positively correlated (Šímová and Storch, 2017). Moreover, air temperature is correlated with the amount of photosynthetically active radiation (PAR) which is also an important driver of plant production. Above that, temperature increases evapotranspiration which together with precipitation govern the water balance. Altogether NPP generally increases with decreasing latitude (and increasing temperature) when water is not limiting (Šímová and Storch, 2017).

Air temperature is correlated with **soil temperature**, although vegetation cover may alleviate soil temperature fluctuations (Deardorff, 1978). Decomposition is accelerated by increasing soil temperature until an optimum of about 35°C after which the response becomes negative

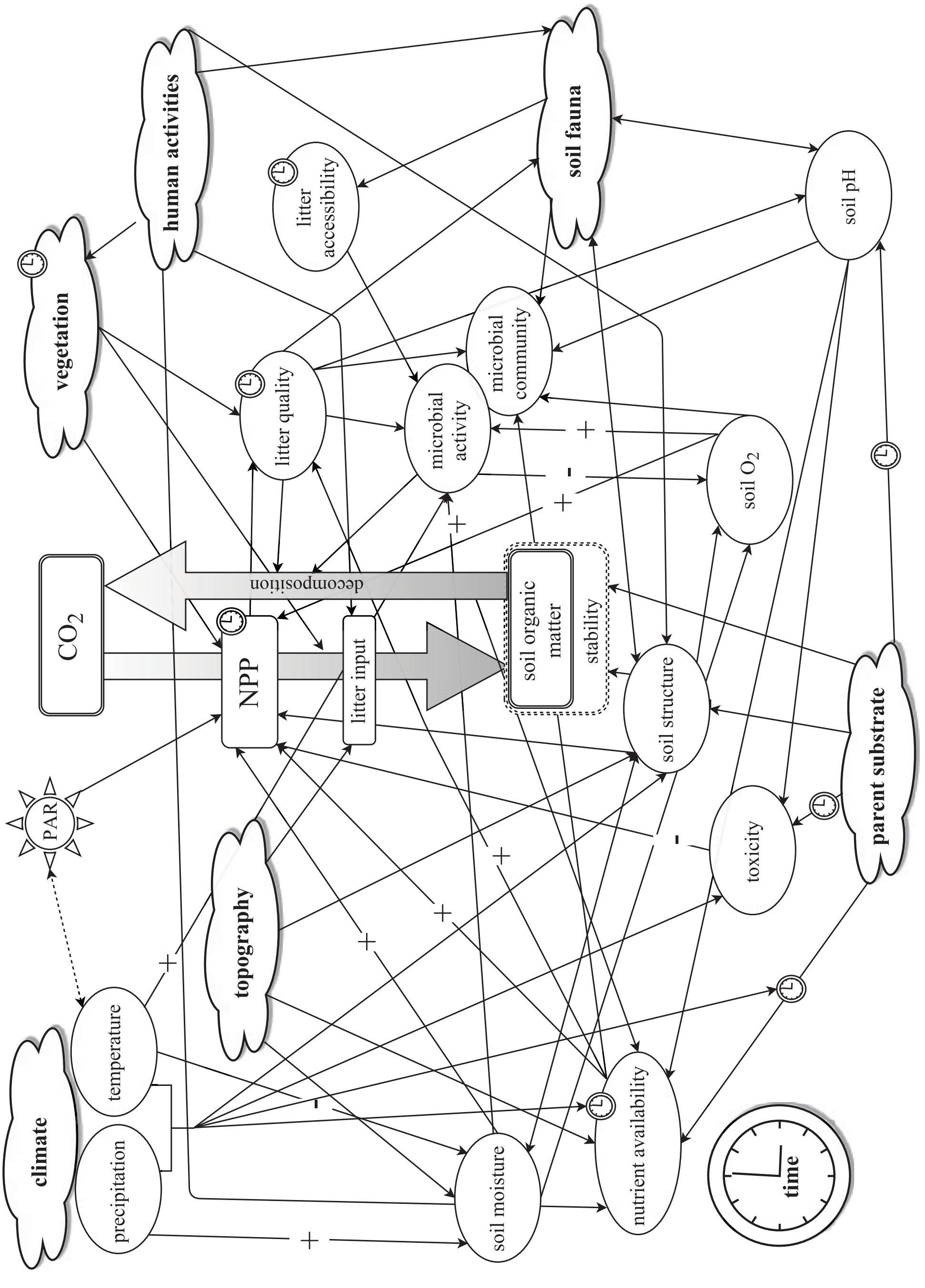

Fig. 1. Key factors and mechanisms regulating soil organic matter content through an input-output balance. Feedbacks from soil organic matter to factors such as soil moisture, nutrient availability, soil structure, fauna, etc. are not shown. NPP – net primary production

(Smith et al., 1997) which is typical of enzymatically driven reactions. This “intrinsic temperature sensitivity” of decomposition increases with increasing molecular complexity of

(Smith et al., 1997) which is typical of enzymatically driven reactions. This “intrinsic temperature sensitivity” of decomposition increases with increasing molecular complexity of

the substrate (Davidson and Janssens, 2006).However, temperature sensitivity of decomposition may be hindered by different environmental constraints, that limit microbial activity such as O$_2$-defficiency, drought or protection of SOM in organo-mineral complexes (Davidson and Janssens, 2006). Temperature together with precipitation also influences the rate of weathering and soil structure formation through wet-dry and freeze-thaw cycles.

On one hand, temperature is positively correlated with plant production. On the other hand, higher temperature may increase decomposition rates. Therefore, the overall effect of temperature on SOM accumulation is not clear. The soil C stocks in rather cold regions (tundra, alpine) and higher altitudes are higher than those of warmer regions (savannas and tropical forests) and lower altitudes (Schlesinger, 1977; Marková et al., 2016) suggesting that the soil C storage potential may be more output-driven. However, Post and Kwon (2000) observed a tendency for the SOC accumulation rates to increase from temperate to subtropical regions suggesting that the rates after land-use change are more input-driven. These contradictory observations may be driven by different methodologies and vegetation types, since Popleau et al. (2013) pointed out the soil C stocks are higher in colder regions if forest floor is included in the calculation and higher in warmer regions if only mineral soil is considered (**Question 3**).

4.4.1.2. Precipitation

Precipitation increases soil moisture and together with evapotranspiration determines the water availability which is crucial to plant production. The balance between precipitation and evapotranspiration also determines the direction of water movement in the soil profile and thereby the tendency for salinization or leaching. Precipitation altogether supports NPP, although extremely high precipitation impedes NPP via anoxia and nutrient leaching (Chapin et al., 2002).

On the other hand, soil moisture also affects decomposition – both low and high soil moisture content decreases microbial activity through low substrate diffusion and O$_2$ deficiency, respectively (Skopp et al., 1990). However, Post and Kwon (2000) found much lower SOC accumulation rates under arid conditions. This suggests that the effect of precipitation on inputs is stronger (**Question 3**).

4.4.2. Vegetation

Vegetation in terms of **plant community composition** depends on the potential natural vegetation, human management and time from disturbance. The potential natural vegetation depends on climate, topography and parent substrate (not shown in Fig. 1)

Plant community composition influences plant production, quantity of litter input, and litter quality (Binkley and Giardina, 1998). For example, some plant species may be deep-rooted and exploit water and nutrients better than other species leading to higher production (Chapin, 2003). Plant production and litter quality are inter-related. Plant species typical of productive environments (e.g. herbs and deciduous species) produce high quality litter that decomposes more rapidly compared to plant species typical of less productive environments (e.g. evergreens) (Hobbie, 1992; Wardle et al., 2004a). However apart from plant species, production and litter quality also depends on the **age of plant** (stand age) and nutrient availability (Waksman and Tenney, 1927). Establishment of vegetation during ecological succession or revegetation of agricultural soils increases plant production per area, litter inputs and therefore leads to SOM accumulation. Litter quality often decreases during soil development as a consequence of shift in dominant plant species (Melillo et al., 1982), or intraspecific changes in litter chemistry induced by aging and nutrient limitation (Northup et al., 1995) leading to lower decomposition rates, although also opposite trends have been observed (Wardle et al., 2004b).

Litter quality (decomposability) is given by the nutrient content and C quality of litter. The C:N ratio is often negatively correlated with the decomposition rate (Hobbie, 1992). However, Aerts (1997) showed that within the tropics and the Mediterranean region, lignin:N ratio is a better predictor of decomposition rates. Moreover, none of the investigated parameters (N and P content, C:N, C:P, lignin content, lignin:N, lignin:P) could predict decomposition rates in the temperate region (Aerts, 1997). In contrast, lignin and nitrogen content has been correlated with decomposition rates along a successional gradient in a northern hardwood forest (Melillo et al., 1982). Frouz et al. (2015c) did not find a significant difference in C lost by respiration over a 54-week incubation between litter of contrasting C:N ratio. Overall, it seems that C quality given by the concentration of recalcitrant and antibacterial compounds such as lignins or tannins/polyphenols (Derenne and Largeau, 2001) may be more important than stoichiometry (Hättenschwiler and Jorgensen, 2010). Litter quality alters soil pH, soil microbial community and soil fauna. Litter calcium content positively correlates with soil pH (Reich et al., 2005). High quality litter rich in nitrogen, low in phenol and lignin compounds supports low fungi to bacteria ratio (F:B), bacterial-based energy channel of soil foodweb and high densities of earthworms (Wardle et al., 2004a).

All of the above mechanisms lead to the development of three basic **humus forms**, i.e. the vertical arrangement of organic matter in topsoil horizons: mor, moder, and mull (Ponge, 2003). **Mor** (typical of coniferous forests) develops from low quality litter, which is slowly decomposed by a fungal-dominated microbial community and accumulates on the surface of mineral soil. **Mull** (typical of grasslands) develops from high quality litter, which is rapidly decomposed by bacteria and fragmented and mixed into the mineral soil by earthworms. **Moder** (typical of deciduous forests) develops from medium quality litter which is again decomposed mainly by fungi. However, fauna is more active here than in mor (although it is smaller and less abundant than in mull) creating a more gradual transition of the organic horizons into the mineral soil compared to mor. Although the plant community seems to be the key driver controlling the humus form, it has been shown that parent substrate (alkaline vs. acidic) and climate (cold vs. warm) are stronger predictors of the humus form in temperate forests than tree species, with mull associated with alkaline substrates and warm climate (Ponge et al., 2011). This suggests that nutrient availability and climatic factors controlling decomposition and weathering drive the nutrient cycling strategy of plants.

The overall effect of vegetation on SOC accumulation and storage can be partly inferred from carbon budgets of different biomes of comparable climate zone. For example, mean soil C stock for a temperate forest is 118 t ha^{-1} as compared to 192 t ha^{-1} of temperate grasslands (Schlesinger, 1977). However, such approach does not rule out the effect of climate and may be significantly influenced by other effects such as time, topography or substrate. The difference in SOM accumulation potential of grassland *vs*. forest is not clear. Post and Kwon (2000) found similar SOC accumulation rates for grassland and forest establishment after different land-use change that favors SOC accumulation. On the other hand, Li et al. (2014) found the SOC storage of grasslands to be two times higher than that of shrubland or forest after 15 years of reclamation in Inner Mongolia, China. A similar result was found by Zhang et al. (2016) in the Loess Plateau, China after 10–13 years after reclamation. They attributed the higher stocks found in grassland to higher input of root litter. Similarly, it is not clear if either coniferous or broadleaf trees support higher SOM accumulation. A meta-analysis of C changes after land-use change showed that broadleaf tree plantations placed onto prior native forest or pastures did not affect soil C stocks whereas pine plantations reduced soil C stocks by 12–15% (Guo and Gifford, 2002). Similarly, Laganiere et al. (2010) found that broadleaf trees have a greater capacity to accumulate SOC than conifers on afforested agricultural soils although they point out that afforestation by pine does not lead to overall C loss if forest floor is included in the C budget. However, common garden studies often report no whole soil profile differences in C storage between different tree species because higher forest floor C stocks (typically under conifers) are offset by larger mineral stocks under deciduous trees, although the differences in mineral stock are less consistent (Vesterdal et al., 2013).

Overall it is not clear which vegetation supports the highest C storage potential and even less is known about the dynamics of C storage under different vegetation (**Question 2**).

4.4.3. Soil biota

Soil biota may affect plant production through mycorrhiza, nitrogen fixation, herbivory and pathogeny (not shown in Fig. 1). These plant-soil biota interactions may play an important role in plant community changes during succession (Kulmatiski et al., 2008). However, soil biota influences SOM accumulation especially via decomposition. Soil microbiota plays the primary role in decomposition; however, its biomass and activity may be significantly modified by soil fauna.

Soil microbiota (bacteria, fungi, actinomycetes) account for 80 to 90 % of soil decomposer biomass and respiration (Chapin et al., 2002). **Microbial activity** is influenced by litter quality, litter accessibility, microbial community composition and environmental factors such as moisture, temperature and oxygen content. Different microbial communities have been shown to decompose the same litter at different rates (Strickland et al., 2009). A fungal-dominated microbial community shows lower respiration rates than a community with lower F:B ratio (Rousk et al., 2009), although litter quality has a stronger influence on the overall rate than the community (Cleveland et al., 2014). Fungal-dominated microbial community has been previously linked to C sequestration (Wardle et al., 2004a), although this may be a consequence of the relationship between microbial community and litter quality. **Microbial community** is strongly influenced by pH, litter quality and nutrient availability. At the field scale, acidic soils are often fungal-dominated (Rousk et al., 2010; Jozefowska et al., 2017) because low pH gives fungi a competitive advantage over bacteria (Chapin et al., 2002) and pH is also a key predictor of bacterial community (Fierer and Jackson, 2006). However, at larger scales, texture, nutrient availability or litter quality can be better predictors of the F:B ratio (de Vries et al., 2012) – substrates with low N and P content and high lignin content again give a competitive advantage to fungi over bacteria (Chapin et al., 2002).

Soil fauna modifies microbial activity especially through **fragmentation**, **aggregation**, **bioturbation,** and **predation**. Litter-feeding macrofauna (such as earthworms, woodlice, millipedes) fragment the litter thus making more litter surfaces accessible to microbes and thereby promote decomposition in the short term. However in the long-term, faeces of litter-feeding fauna decompose more slowly than litter from which they were produced (Frouz et al., 2015b). That means that even though fauna tends to speed up litter removal from the surface, this C becomes incorporated into mineral soil and the overall loss of C by mineralization is not increased by fauna (Frouz et al., 2015b). Fauna may even stabilize SOM in the long-term, e.g. by physical protection in earthworm casts (Angst et al., 2017) which contribute significantly to soil aggregation (Swaby, 1950). The process in which certain species of earthworms mix litter from the forest floor into the mineral horizons is referred to as bioturbation. Bioturbation is the key process behind the development of different humus forms. It is positively correlated with pH as most earthworms prefer neutral pH and cannot survive under pH < 4.5 (Edwards and Bohlen, 1996). Bioturbation by earthworms is also often negatively correlated with the fungi to bacteria (F:B) ratio which is explained by the vulnerability of fungi to soil disruption (Jozefowska et al., 2017). Bioturbation influences the exposure of the mixed organic material to moisture, temperature and other soil biota. The engineering effect of bioturbation has been well demonstrated by several studies on introduction of non-native earthworms into the North American forests, where earthworms lead to the removal of forest floor horizons with consequent changes in plant community (Bohlen et al., 2004). Most studies from North America have found an overall soil C loss following earthworm introduction (Bohlen et al., 2004), although case studies from other environments have shown that more intensive bioturbation is positively correlated with C storage (Frouz et al., 2006, 2007, 2013; Jozefowska et al., 2017). It seems that the effect of fauna on overall C mineralization depends on the history of soil – fauna may increase mineralization in soils previously unaffected by fauna but promote stabilization in soils that have already experienced soil fauna activity (Frouz, in press).

Fungivorous, microbivorous and predatory micro- and mesofauna (such as protozoans, nematodes, mites, enchytraeids) can modify microbial activity through trophic interactions. It has been shown that both fungal and microbial-feeders can increase the rate of litter mass loss, CO_2 respiration and leaching of nitrate-N (Clarholm, 1985; Cragg and Bardgett, 2001). Respiration may be further increased by the presence of predators that feed on grazers suggesting that low-level grazing is more stimulating than high level of grazing (Hedlund and Ohrn, 2000).

It has been shown that soil fauna effect on decomposition is the highest in temperate and wet tropical climate where microbial activity is not constrained by environmental factors such as temperature, moisture and O_2 supply (Wall et al., 2008; Handa et al., 2014). Also the litter quality influences the effect of fauna on decomposition although the response is not clear. Two recent meta-analyses showed that the effect of fauna is either strongest with litter of intermediate quality (C:N 20–30) (Frouz et al., 2015b) or of the highest quality (low C:N, from an unknown range) (García-Palacios et al., 2013).

The soil fauna community composition and abundances changes during succession as a consequence of dispersal abilities, changing food resources and soil properties (Frouz et al., 2008). Both diversity and abundances of most faunal groups typically increase during succession (Kaufmann et al., 2002; Frouz et al., 2008). Earthworm colonization is often delayed compared to other faunal groups (Walker and Del Moral, 2003) and epigeic earthworms are better colonizers than deep-burrowing species of earthworms (Edwards and Bohlen, 1996) which is in accordance with observations that bioturbation is likely to occur in later stages of succession (Frouz et al., 2008).

4.4.4. Human activities

Human activities may affect SOM accumulation either directly by land-use and management or indirectly by pollution. **Management** influences vegetation type, production, litter input and quality through crop or tree species choice. Litter input and quality may be also manipulated by organic amendments or post-harvest residue management. Furthermore, soil disruption by tillage leads to lower physical protection of SOM and consequent SOM mineralization and release of nutrients. Tillage reduces abundance and diversity of soil fauna by mechanical stress but also by changing soil temperature, moisture variability and soil air composition (Hendrix et al., 1986). Pesticides and high doses of mineral fertilizers may influence soil fauna negatively. Heavy machinery used for agriculture operations may lead to compaction (Hamza and Anderson, 2005) and affect fauna negatively. Livestock density, fire suppression, and timber harvest may also affect plant production and SOM accumulation in managed ecosystems.

Pollution may affect both plant production and decomposition. For example, nitrogen deposition may have a fertilizing effect on N-limited ecosystems leading to higher productivity. At the same time, it may support SOM accumulation through reduction in decomposition (Janssens et al., 2010; Frey et al., 2014). The latter effect has been explained by decrease in belowground C allocation and consequent reduction in microbial activity and decomposition of more recalcitrant compounds, abiotic stabilization of SOM through incorporation of N into SOM, and acidification (Janssens et al., 2010). Indeed, it has been shown that systems recovering from acidification show decrease in SOM storage (Oulehle et al., 2011). Under certain conditions however (such as severe N-limitation, young forests, elevated CO_2), N deposition may lead to increased decomposition (Janssens et al., 2010).

4.4.5. Topography

Slope, shape and aspect of landscape are main features of topography. Higher slope leads to higher erosion, which constantly resets succession by nutrient loss and slower vegetation establishment (Walker et al., 1996) leading to lower litter inputs. Litter, fine particles and nutrients are transported from slopes downhill where they accumulate and potentially support plant production and SOM accumulation. Depositional areas such as base of slopes and valleys have typically higher moisture content than slopes but may suffer from poor drainage which impedes both plant growth and decomposition. Overall, the soil depth and C storage is higher in the lower slope positions than in the upslope soils (Chapin et al., 2002). The aspect of slope influences soil temperature and moisture supporting plant growth in dry climates while inhibiting decomposition in cold and wet climates on poleward-facing slopes (Chapin et al., 2002).

4.4.6. Parent substrate

Parent substrate affects SOM accumulation through both plant production and decomposition rates. Mineralogical composition of parent substrate affects pH (through acid neutralization capacity), nutrient availability (e.g. pH, weathering rate, base cation content, cation exchange capacity) and soil structure (through particle size distribution) which controls the amount of water available to plants as well as aeration and intensity of leaching. Clayey soils are often poorly drained and thus poorly aerated.

Mineralogy and particle size distribution has also important implications for the stabilization of SOM by protection in aggregates. Texture determines the maximum amount of C that can be protected by clay and silt particles thereby affecting the overall capacity of soil to store carbon (Hassink, 1997; Six et al., 2002). On average, clayey soils show slower decomposition rates than sandy soils (Veen and Kuikman, 1990).

Overall, clay-rich soils promote soil C stabilization but their effect on plant growth is not clear (nutrient retention capacity *vs*. waterlogging). A meta-analysis of afforested agricultural soils showed that clay-rich soils (33%) have a greater capacity to store carbon than soils low in clay content (Laganiere et al., 2010) (**Question 2**).

4.4.7. Time

During ecosystem development, different processes such as vegetation establishment, nitrogen deposition and fixation, weathering, etc. proceed at different rates leading to change of soil properties over time scales of years to millennia. Most importantly, both living and nonliving organic matter accumulates in the early stages of ecosystem development as gross production of ecosystem exceeds total respiration (P/R>1). Later, the accumulation ceases as production and respiration come to equality P=R (Odum, 1963). The **accumulation of SOM in time** is therefore not linear. Initially, the rates may be slow, because low plant biomass provides low inputs. However, as production increases during the first few years, the rate increases. Shrestha and Lal (2010) observed the highest accumulation rates already after 4 years under forest and 6 years under pasture on a 25-year chronosequence of mine soils. After maximum rates are reached they may remain more or less constant during the so-called progressive phase of ecosystem development which is characterized by a rapid accumulation of C and N, although some studies have observed nitrogen to accumulate more slowly than C, leading to a widening C:N ratio (Crocker and Major, 1955; Crocker and Dickson, 1957; Vitousek et al., 1983). This SOM accumulation may be linear and last decades (Bernasconi et al., 2011), centuries (Olson, 1958) or up to 3000 years (Schlesinger, 1990). After this progressive phase, the rates decrease significantly or approach zero when the C stock attains a steady state. The time at which this steady-state is attained is highly variable (see Table 1) and ranges from centuries (Bernasconi et al., 2011) to millennia (Syers et al., 1970; Merritts et al., 1991). Later on, accumulation rates may even come to negative values reflecting a decline in C stock (Protz et al., 1988; Schlesinger, 1990; Peltzer et al., 2010). This contradicts the classical concept of succession that both ecosystem and soil development head towards a steady-state (known as “climax”) that is then self-sustaining (Odum, 1963). However, it has been shown that in the absence of disturbances, ecosystems may enter a so-called retrogressive phase in which plant production and plant biomass decreases on millennial time-scales (Kitayama et al., 1997; Walker and Reddell, 2007; Peltzer et al., 2010; Chen et al., 2015; Turner and Laliberté, 2015). Less often, SOM accumulation may be “unexpectedly” reversed to SOM loss even on the time-scale of decades, due to e.g. emerged salinity problems (Yang et al., 2015). Generally in well-drained soils and on larger time-scale, SOM accumulation pattern reflects aboveground net primary productivity (Crews et al., 1995; Kitayama et al., 1997) although in the short-term (of decades) SOM accumulates slower than plant biomass (Walker et al., 1996) and the same may be assumed for its loss.

Many ecosystem properties that affect SOM accumulation change with time during both primary and secondary succession. The plant community is first dominated by species that are small, often herbaceous, short-lived r-strategist which produce litter with high quality which are later outcompeted by species of larger stature, more resistant tissues, long-lived, and more conservative in terms of nutrients which produce litter of poorer quality (Wardle and Peltzer, 2007).

Nutrient availability changes significantly over time during ecosystem development. This is because most of the processes that control nutrient inputs, outputs and availability are time-dependent. Nutrients may be lost from the ecosystem by leaching, erosion, denitrification, and harvest in managed ecosystems. In contrast, nutrients are introduced into the ecosystem nutrient cycles by weathering and external sources of nutrients which are mainly biological fixation, atmospheric deposition, lateral fluxes from erosion and fertilization in managed ecosystems. Accumulation of SOM and change in mineral composition may increase nutrient retention capacity over time. Also changes in pH may modify nutrient availability.

Nitrogen and phosphorus are regarded as two most common nutrients limiting terrestrial primary productivity. **Nitrogen** is commonly limiting to plant growth in young ecosystems since the parent material typically does not contain nitrogen and its main sources are atmospheric (N-fixation and deposition) which require some time to accumulate (Vitousek and Howarth, 1991). On the other hand, the main source of phosphorus is the parent rock, therefore it is relatively more available on younger, less weathered substrates (Vitousek et al., 2010). This may lead to a shift from N limitation in young ecosystems to P limitation in older ecosystems on millennial time-scales which has been confirmed by fertilization experiments in Hawaii (Vitousek and Farrington, 1997) and Jurien Bay, Australia (Laliberté et al., 2012) and inferred from stoichiometry and soil P status in New Zealand (Walker and Syers, 1976; Richardson et al., 2004), Arizona (Selmants and Hart, 2010) and Cooloola, Australia (Chen et al., 2015). However, P-limitation on young soils as well as persistence of N limitation in older ecosystems may also occur (Vitousek et al., 2010). According to the conceptual model of Walker and Syers (Walker and Syers, 1976), total phosphorus content as well as readily available forms of phosphorus decrease during soil development as a consequence of leaching, erosion and transformation of P in primary minerals into P bound in organic matter and secondary minerals. This concept has been tested in a few long chronosequences in humid tropics (Crews et al., 1995) as well as arid regions (Selmants and Hart, 2010; Chen et al., 2015; Turner and Laliberté, 2015) suggesting that phosphorus loss is much slower in arid regions. However, studies from temperate region have been restricted to the New Zealand chronosequences (Walker and Syers, 1976) with highly humid oceanic climate. Moreover, different parent substrates may differ in their intrinsic P content. Altogether, little is known about the joint effect of substrate and climate on the dynamics of total P decrease during ecosystem development due to lack of data over ranges of climate and substrates. Despite its importance for the C sequestration potential (Oren et al., 2001), the effect of nutrient limitation (especially that of phosphorus) is often not included in the models of primary productivity (Šímová and Storch, 2017) which represent one of the key uncertainties in earth system models that predict future climate change outcomes (Flato, 2011). Although the temperate forests have been traditionally regarded as N-limited (Vitousek and Howarth, 1991), it has been shown that this pattern is not as clear and that P limitation as well as N and P co-limitation may be equally important (Elser et al., 2007). Moreover, increasing human-enhanced N deposition has been suggested as a factor driving ecosystems towards P limitation (Vitousek et al., 2010).

Apart from nitrogen and phosphorus, also exchangeable base cations such as calcium or magnesium are important nutrients. These may accumulate in the short term (Walker et al., 1996) but decrease in the long term via leaching and erosion.

It has been long recognized that the time required by ecological succession depends on geography, climate, substrate, and other physical factors (Odum, 1963), although our understanding of these effects that would allow us to predict dynamics of ecosystem and soil development in various environments is far from complete. Typically different properties differ in the rate of change (Merritts et al., 1991). For example, soil nutrient pools recovered during 55 years of development on Caribbean landslides, but SOM recovered more slowly.

It is not clear whether primary succession (or similar land-use change on SOM-free soil) or secondary succession leads to higher SOM accumulation rates and total C sequestration. Already Odum (1963) stated that the rate of change is much more rapid, and the time required for the system to attain a steady state will be much shorter in secondary succession. This would imply that also SOM accumulation to a steady state level should proceed at higher rates. On the other hand, SOM-free soils are more distant from their C saturation capacity suggesting a higher sequestration potential.

Overall, the rate of SOM accumulation and its change over time after a major disturbance or land-use change is highly variable. The key factors determining the dynamics of SOM accumulation are not fully understood (**Question 1, 2, 9**). The same applies for the time required for recovery of different soil properties to pre-disturbance levels (**Question 3, 10**) or the time needed for SOM to attain a steady state and the size of the respective soil capacity to store C (**Question 9**). Phosphorus limitation has been suggested as an important driver of SOM dynamics in the long-term, but studies investigating this hypothesis on sedimentary bedrock in the temperate climate have been scarce (**Question 11**).

4.5. Study of soil development using the chronosequence approach

The use of chronosequences is an experimental approach that allows to study the independent effect of time on ecosystem and soil development (Jenny, 1941). A chronosequence is a set of sites differing in age with similar climate, parent substrate, topography, human impact and potential to be colonized by the same organisms (Chapin et al., 2002). A chronosequence may be formed in several ways but the classical examples include retreating glaciers or coastal sand dunes. A retreating glacier leaves behind newly exposed surfaces which are consequently colonized by vegetation and the age of ecosystem increases with the distance from the glacier. Similarly, accumulation of sand dunes along a shoreline creates new land, with the age of site increasing with the distance from the shoreline. Also a series of volcanic eruptions or landslides may create surfaces of different age in one region.

Apart from the effect of time, comparison of chronosequences differing in climate and other soil-forming factors may be used to draw general conclusions on the effect of other soil-forming factors (Stevens and Walker, 1970; Schlesinger, 1990; Wardle et al., 2004b; Walker et al., 2010). Even though the chronosequence approach needs to be used with caution (Walker et al., 2010), it is an irreplaceable tool for the study of soil development on millennial time-scales because it is difficult to determine age of most soils (Stevens and Walker, 1970). Unfortunately, the majority of the previous long-term chronosequence studies have been carried out in rather extreme climatic and/or parent rock environments, e.g. under extremely warm or cold climate, on volcanic substrates, etc. (Table 1). Chronosequences studies (>10,000 years) in temperate climate and on sedimentary parent material have been scarce and restricted to sand dunes (Franzmeier et al., 1963; Syers et al., 1970). Moreover, most studies focused on strictly natural ecosystems undisturbed by human use and it is questionable how can we extrapolate findings of these studies to biomes such as temperate forests, 99% of which have been affected by human use (Tyrrell et al., 2012). Some of the studies also reported only soil organic matter concentrations (in mass percent rather than stocks in mass per area) without bulk densities hampering the assessment of soil organic matter accumulation (Table 1).

Table 1 Chronosequences investigating SOM accumulation during primary succession extended after Schlesinger (1990) – time required to reach a steady state is listed for mineral soil C if not noted otherwise, conc. – concentration (mass percentage)

		Chronosequence Range					
Ecosystem Type	Soil Origin	min	max	Age Stage	Steady State Reached	Stock/ Conc. (%)	Reference
Alpine Tundra	Glacial Retreat	6	150	21	100	%	Bernasconi et al., 2011
Tundra	Glacier Retreat	8 000	115 000	4	no (max after 40 ka)	%	Evans and Cameron, 1979
Boreal Forest	Glacier Retreat	~10	~170	10	?170	stock	Crocker and Dickson, 1957
Boreal Forest	Glacier Retreat	~25	~200	9	?200	stock	
Boreal Forest	Storm Ridge	1 000	3 000	4	no (max 2 ka)	stock	Protz et al., 1988
Boreal Forest	Glacier Retreat	15	3 500*	4	no	stock	Chandler, 1943
Boreal Forest	Storm Ridge	<100	5 400+	6	no (max 3 ka)	stock	Protz et al., 1984
Temperate Forest	Volcanic Mudflow	55	1 200	4	no	stock	Dickson and Crocker, 1953; Sollins et al., 1983
Temperate Forest	Sand Dunes	25	2 375	20	140 (mineral)	stock	Lichter, 1998
					440 (total)	stock	
Temperate Forest	Sand Dunes	0	4 200	11	100	%	Burges and Drover, 1953
Temperate Forest	Sand Dunes	0	5 500	4	<3500	%	Bowman, 1987
Temperate Forest	Sand Dunes	0	6 500	6	<2500	%	Bowman, 1989
Temperate Forest	Sand Dunes	0	10 000	5	no	stock	Syers et al., 1970
Temperate Forest	Sand Dunes	3 000	11 000	5	?	?	Franzmeier and Whiteside, 1963
Temperate Grassland	Marine Terrace	3 900	330 ka	9	29 000	stock	Merritts et al., 1991
Subtropical Forest	Landslide	1	55	4	no	stock	Zarin and Johnson, 1995
Subtropical Forest	Sand Dunes	40	460 ka	6	no (max 130 ka)	stock	Chen et al., 2015
Tropical Forest	Volcanic Ash	52	142	2	no	stock	Crews et al., 2001
Tropical Forest	Volcanic Ash	110	3 400	3	no	stock	Raich et al., 1997
Tropical Forest	Lavaflow Pahoehoe	126	3 500	4	2 500	stock	Vitousek et al., 1983
Tropical Forest	Volcanish Ash	191	4 000	3	no	stock	Vitousek et al., 1983
Tropical Forest	Volcanic Ash	300	4 100 ka	6	20 000	stock	Crews et al., 1995

*age updated according to Crocker and Dickson (1957)

4.6. Post-mining soils

Mining represents a man-made disturbance and especially open-cast (surface) mining disturbs large areas world-wide. Open-cast mining affects much larger areas than the mining site itself because the excavated overburden (spoil) is deposited in heaps (also termed dumps, spoil tips, banks) outside the mining site. For example in Northern Bohemia, dumps after open-cast mining cover more than 8000 ha (Borůvka et al., 2012). Mining in China, which is the largest coal producer in the world, has disturbed an estimated area of 2 million ha and this number is increasing by an annual rate of more than 20 000 ha (Huancheng et al., 1989). Soils developing on heaps are termed post-mining or mine soils and are greatly influenced by reclamation practice. Reclamation practice defines the parent substrate, topography, initial SOM content, and vegetation of post-mining soils. Before and during the excavation, the mining operator decides which suitable substrates will be placed on the spoil surface through selective spoil placement (Sengupta, 1993). Heaping typically produces a wave-like topography which is later usually leveled (graded) by heavy machinery to stabilize the surface and facilitate future management of the site, e.g. by topsoil application, seeding, fertilizer application, etc. However, leveling may cause compaction and favor establishment of grass communities (Ashby, 1998).

After that, **topsoil** with SOM content may be applied on top of the SOM-free overburden. However, a sufficient amount of topsoil material may not always be available and therefore substantial part of mining areas are reclaimed without topsoil application typically in combination with reclamation to forest (Macdonald et al., 2015). Topsoil application improves the initial soil properties by providing organic matter, soil fauna and microorganisms, and plant propagules facilitating re-establishment of nutrient cycling and other soil functions (Borůvka et al., 2012) and it is necessary in agricultural reclamation. However, shallow topsoil application together with compaction of underlying overburden layers may decrease tree seedling survival (Ashby, 1997; Sweigard et al., 2007). Furthermore, leveling and topsoil application may lead to lower heterogeneity of the soil surface. The final step of reclamation is the seeding or planting of selected plant species based on the target land-use (agriculture, forestry). However, another possibility is to leave the sites to revegetate by spontaneous ecological succession. Succession often supports higher biodiversity than reclamation (Holec and Frouz, 2005; Mudrák et al., 2010; Hendrychová et al., 2012; Prach et al., 2013). Reclamation on the other hand may accelerate the establishment of vegetation cover and plant biomass accumulation (Gorman et al., 2001; Pietrzykowski and Krzaklewski, 2007), although this difference may disappear already after 20 years in Central Europe (Frouz et al., 2015a) which corresponds with the time required for establishment of woodland by spontaneous succession (Prach et al., 2013).

It has been suggested that **C sequestration potential** of post-mining soils is rather high and this could play an important role in mitigation efforts (Akala and Lal, 2001; Sperow, 2006;

Karu et al., 2009). However, a review that would discuss the sequestration potential of post-mining soils similarly to those dedicated to revegetated agricultural soils (Post and Kwon, 2000; Guo and Gifford, 2002; Paul et al., 2002; Laganiere et al., 2010) has been lacking (**Question 1**). Though many of the factors that affect SOM accumulation may be manipulated by the reclamation practice as explained above, the effect, relative importance and interaction of these factors is not fully understood. For example, the overall effect of **topsoil application** on C sequestration during post-mining soil development is not clear (**Question 2**). On one hand, topsoil application may accelerate the establishment of vegetation cover thereby supporting plant production. On the other hand, SOM-free overburden is more distant from its soil carbon storage potential which may lead to higher sequestration in soils without initial topsoil application. However, it may be assumed that topsoil application will accelerate the recovery of SOM content of post-mining soils to pre-mining levels. Studies investigating this hypothesis have been lacking and the usual time required for SOM content to recover to pre-mining levels has also not been investigated (**Question 3**). For example, Schwenke et al. (2000) estimated that it would take 33 years for the SOC content in Australian mine soils to reach that of an undisturbed native forest. Fifteen years of reclamation in Inner Mongolia (China) lead to soil carbon storage that was between 1/2 to 2/3 of the pre-mining stocks (Li et al., 2014). Cooke et al. (1999) concluded that more than 50 years is needed for forest ecosystem development in the USA after reclamation.

The parent substrate of post-mining soils (i.e. the overburden) may have some **extreme physical or chemical properties** compared to natural soils that will greatly influence the soil development by limiting plant growth. The physical texture may be very coarse or very fine and the nutrient content may be very low (Cooke, 1999). Post-mining soils may even suffer from toxicity (Fig. 1) caused by high salinity or by admixture of coal in the substrate – weathering of pyrite-containing coal leads to acidification which increases mobility of aluminum and other heavy metals (Dixon et al., 1982; Kubová et al., 2005; Moreno and Neretnieks, 2006). It is obvious that SOM accumulation will be greatly limited on such extreme substrates.

Post-mining sites are particularly well suited for the study of ecosystem and soil development using the chronosequence approach. The operating life of a mine can last several decades during which the excavated overburden is continuously deposited in different parts of a spoil heap or in different heaps creating a series of sites of different well-defined age on similar parent substrate. The limitation of post-mining sites when compared to other chronosequences is the relatively short time-scale (<100 years) which is given by the relatively short history of large-scale open-cast mining.

Post-mining sites in Sokolov mining district have been a subject of long-term ecosystem research focused on biodiversity and other ecosystem functions for more than 20 years. These sites provide great opportunity to study the effect of time and reclamation vs. spontaneous succession (e.g., Šourková et al., 2005; Frouz et al., 2008, 2015a), as well as the effect of different tree species on SOM accumulation and other ecosystem properties (Frouz et al., 2009). Such research expands our understanding of ecosystem development and also provides feedback on reclamation practices.

As indicated above, the chronosequence approach may be used to investigate the independent effect of time on SOM accumulation. Comparison of observations from two or more post-mining chronosequences may help identify the key factors influencing SOM accumulation. The independent effect of vegetation may be studied on a set of sites of similar age using the common garden approach. However, these approaches require that the methods used to quantify SOM give comparable results among sites of one chronosequence/common garden as well as among chronosequences.

4.6.1. Methodological issues in study of SOM in post-mining areas

The study of SOM accumulation in post-mining areas is complicated by the presence of fossil forms of carbon in the overburden. **Coal** is the most frequent form of fossil C in overburden of coal mining areas (Filcheva et al., 2000; Akala and Lal, 2001). Apart from coal which is rich in **aromatic** compounds, overburden may contain also other forms of fossil C such as **kerogen** which may be predominantly **aliphatic** (Kříbek et al., 1998; Karu et al., 2009).

Fossil C should not be included in the soil C sequestration estimate and its **contribution to soil quality** is also clearly different than that of recently accumulated SOM. On one hand, admixture of coal may lead to water repellency (Richardson and Wollenhaupt, 1983) and toxicity as discussed above. On the other hand, humic substances extracted from lignite have been studied and manufactured as a remediation amendment and fertilizer (Piccolo et al., 1997; Szczerski et al., 2013; David et al., 2014). However, it has been shown that humic substances extracted from compost sources significantly outcompete those from brown coals in terms of plant-growth promotion (Rose et al., 2014). Overall, the effect of fossil organic matter on soil quality is poorly understood, mainly because the quantification of fossil C remains a methodological challenge.

Fossil C in soils may lead to significant **bias** in the estimate of SOM accumulation and C sequestration if conventional methods such as dry combustion, loss-on-ignition or wet dichromate oxidation are used for SOM/SOC determination. All of these methods are based on oxidation which affects also fossil organic matter. Fossil C may contribute significantly to the measured organic carbon content. For example, it has been shown that lignite-derived fossil C accounts for 13–96 % of total organic carbon (TOC) in sites reclaimed without topsoil application (Rumpel et al., 2001). In mine soils in Ohio covered with topsoil, coal C contributed to TOC between 10 and 17 % (Jacinthe and Lal, 2007). In the Sokolov mining area, overburden contains 2–10, sometimes even 15 % C mainly from kerogen of Types I and II (Křibek et al., 1998). However, the bias from fossil C in Sokolov post-mining soils has been so far unknown (**Question 5**).

One of the ways to overcome the bias from fossil C is **repeated sampling** of the post-mining sites (Bartuška and Frouz, 2015). However, this is not feasible in the study of processes that span decades. Moreover, fossil organic matter may also undergo decomposition (Frouz et al., 2011; Jandová et al., 2017) and bring some unknown inaccuracy to this approach.

In another approach, fossil C is estimated as the **carbon content found in the C horizon** and this value is then subtracted from the carbon content of the A horizon to quantify recently accumulated SOC (Reintam et al., 2002; Frouz et al., 2009). However, the content of fossil organic matter in the soil profile may be variable again due to decomposition or stochasticity. The accuracy of this correction in Sokolov post-mining soils has not been explored so far (**Question 5**).

The only reliable method for separate quantification of fossil and recent C is **radiocarbon dating** which is based on the fact that ^{14}C activity of fossil C is zero (Rumpel et al., 1998; Karu et al., 2009). Unfortunately, this method is too expensive for routine use in the studies of SOM accumulation in post-mining soils. Other methods have been proposed in the literature for the separate fossil and recent C quantification, such as **near infrared spectroscopy coupled with partial least squares regression** (Chodak et al., 2007; Michel et al., 2009), **solid-state ^{13}C NMR** (Rumpel et al., 1998) or the **carbon stable isotope ratio method** (Chabbi et al., 2006; Ussiri and Lal, 2008). However, these methods have been tested only in soils containing coal or lignite. Applicability of these methods to soils where substantial amount of fossil C is present in aliphatic kerogen has been unknown (**Questions 4 and 6**). Moreover, Rock-Eval pyrolysis has been proposed as a cost-effective tool for organic carbon source determination (Carrie et al., 2012), although it has not been employed for the separation of fossil and recent C in mine soils so far (**Question 6**). This method originally developed for source rock characterization in oil and gas exploration (Espitalié et al., 1977) has been increasingly applied in soils and recent sediments (Disnar et al., 2003; Delarue et al., 2013).

Another issue in the study of post-mining soils is their spatial heterogeneity. Variable reclamation practice creates sharp discontinuities in soil properties (Rohošková et al., 2006). Soil mapping and assessment of post-mining soils may therefore require higher number of samples compared to other soils.

4.7. Conclusions

Soil organic matter is an important component of soil that is critical for soil quality as well as for the global carbon cycle. SOM content is a result of a balance between inputs and outputs and accumulation occurs when inputs exceed outputs. SOM accumulation is governed by a complex interplay of factors such as climate, vegetation, soil biota, human activities, topography, parent substrate, and time which through different mechanisms affect the SOM inputs, outputs, or both. Understanding the key factors and mechanisms controlling SOM dynamics is crucial for prediction of future feedbacks to climate change as well as for soil management.

Soils developing after major disturbances such as mining or landslides represent good model systems to study soil development and SOM accumulation using the chronosequence approach. Through similar studies we can study how quickly can the soil carbon pool and soil function recover to pre-disturbance levels and what is the potential of soils to sequester carbon. It has been suggested that post-mining soils have a high carbon sequestration potential but a quantitative review that would estimate this potential has been lacking. Comparison of observations from two or more chronosequences may help to identify the key factors influencing SOM accumulation. However, these approaches require that the methods used to quantify SOM give comparable results among sites and chronosequences. Unfortunately, post-mining soils often contain substantial amount of fossil carbon which may lead to significant bias in the estimate of SOM accumulation. Reliable and cost-effective method is needed to quantify recently sequestered carbon in post-mining soils.

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5. Aims of the study

- To review reported soil organic matter (SOM) accumulation rates and identify factors that control them in post-mining soils after open-cast mining in the Northern Hemisphere (**Manuscript 1**)
- To investigate the potential of near infrared spectroscopy for separate quantification of recent carbon (C), coal C and kerogen C (**Manuscript 2**)
- To compare the accuracy of different methods for quantification of recent carbon in the presence of dominantly aliphatic fossil organic matter (**Manuscript 3**)
- To summarize main findings of research on SOM accumulation carried out in post-mining sites (**Manuscript 4**)
- To investigate the effect of time on SOM accumulation, soil total phosphorus and other soil properties during 13 thousand years of soil development under temperate semi-natural forest on sedimentary bedrock (**Manuscript 5**)

6. Major questions and hypotheses

Manuscript 1

Question 1: What is the soil organic carbon (SOC) accumulation rate in post-mining sites of the Northern Hemisphere and how does it compare to that of revegetated agricultural soils?

H: *We expected that post-mining soils will have SOC accumulation rates comparable to those of agricultural soils.* On one hand, the initial SOC content of post-mining soils – especially without topsoil application – is lower and more distant from soil C saturation suggesting higher accumulation potential. On the other hand, the conditions for plant growth may be more harsh in some post-mining areas due to toxicity, unsuitable texture, or low SOC content which may hamper SOC accumulation in post-mining soils.

Question 2: How is SOC accumulation in post-mining sites affected by time, vegetation, climate, soil texture and application of topsoil?

H (time): *We expected the SOC accumulation rate to increase in the first stage, reach a maximum in the intermediate stage of soil development and then slowly decrease to approach zero in the long term.* The initial increase was expected because some time is required for the plant productivity per area to reach a maximum – plants need to establish at the site, grow and reach maximum litter fall. After that, competition between plants cause a decrease in primary production and a consequent reduction in litter inputs. Moreover, SOC accumulation may slow down as soil approaches its soil C storage potential.

H (vegetation): *We expected that soils under grasslands will accumulate more SOC than forests.* Temperate grasslands tend to store more soil carbon than temperate forests (Schlesinger, 1977).

H (climate): *We expected the SOC accumulation to be supported by higher precipitation* through higher primary production. *We expected the SOC accumulation to be supported by higher temperature* which is positively correlated with plant production.

H (texture): *We expected the SOM accumulation to be the highest in clay-rich soils* because clay supports SOM stabilization by microaggregation, organic-mineral interactions and clay-rich soils have highest cation exchange capacity supporting nutrient availability and plant production.

H (topsoil application): *We expected topsoil application to support higher rates of SOM accumulation* because better chemical and physical properties of topsoil compared to overburden may support plant production.

Question 3: **How quickly do SOC stocks recover to pre-disturbance levels and how is this affected by topsoil application?**

H: *We expected the SOC stocks to recover to pre-disturbance levels after 50 to 100 years. We expected this recovery to be accelerated by topsoil application* because topsoil contains already some SOM in contrast to the SOM-free overburden.

Manuscript 2

Question 4: **Can near infrared spectroscopy be used as a method for separate quantification of recent carbon (SOC), coal C and kerogen C in Sokolov post-mining soils?**

H: *We expected near infrared spectroscopy to be a good tool to distinguish recent C as well as different types of fossil C* because it has been used to quantify soil organic carbon in the presence of coal/lignite C (Chodak et al., 2007; Michel et al., 2009) and because kerogen C and coal C differ in their chemical composition which should be reflected in their infrared spectra (aliphatic vs. aromatic features).

Manuscript 3

Question 5: **What is the bias connected with the conventional methods of SOC quantification (dry combustion, wet dichromate oxidation, loss-on-ignition) and their correction by way of subtraction of subsoil C content from topsoil content?**

H: For all three methods, w*e expected the mean difference between the tested method and reference to be significant, comparable and higher than 2 % C. We expected the correction to remove the bias.*

Question 6: **Can the methods of recent and fossil C quantification proposed in the literature – ^{13}C isotope ratio method** (Chabbi et al., 2006; Ussiri and Lal, 2008) **and solid-state ^{13}C NMR** (Rumpel et al., 1998) **be used for quantification of recent C in a new situation where fossil C is dominantly aliphatic? Can Rock-Eval pyrolysis be used for this purpose?**

H: *We expected that all the three methods (^{13}C isotope ratio method, NMR, Rock-Eval) may be used to quantify recent and fossil C.*

Question 7: **Which is the most accurate method for the quantification of recently accumulated SOC in Sokolov post-mining soils?**

H: *We expected that the methods that provide insight into chemical composition of organic matter (such as NMR, near infrared spectroscopy, Rock-Eval) would outcompete the corrected conventional methods* because these measure only quantity of organic matter.

Manuscript 4

Question 8: **What are the main findings of research on SOC accumulation carried out in post-mining sites?**

H: *We expected that similarly as in other areas, SOC accumulation in post-mining sites is controlled by substrate, vegetation, soil biota, topography and time*. However in comparison with other areas*, the role of human activity is more pronounced in post-mining areas*, by the way the overburden material is dumped and by the reclamation measures taken. In contrary to natural conditions where vegetation is typically driven by substrate and climate, these three factors are often decoupled in post-mining sites and we can therefore observe combinations of these factors that otherwise do not occur in natural ecosystems.

Manuscript 5

Question 9: **How is SOC accumulation affected by time along a 13 thousand-year landslide chronosequence? What is the soil C storage potential of the landslide soils under semi-natural temperate forest on sedimentary parent substrate?**

H: *Similarly as in post-mining soils, we expected the SOC accumulation rate to increase in the first stage, reach a maximum in the intermediate stage of soil development and then slowly decrease to approach zero in the long term. We expect that the soil C storage will be within the range 50 to 100 t ha^{-1}* reported for forest soils in the studied region (Marková et al., 2016).

Question 10: **How quickly is SOC and other soil properties recovered to pre-disturbance levels?**

H: *We expected the SOC stocks to recover to pre-disturbance level after 50 to 100 years. We expected the other soil properties to recover to pre-disturbance level at different rates.*

Question 11: Can we observe soil phosphorus depletion on the millennial scale as predicted by the conceptual model of Walker and Syers (1976)?
H: *We expected to find lower total P stocks in the oldest landslides (>10 000 years)* as observed in some other long chronosequences world-wide.

7. Major findings

The results of this thesis are summarized in five manuscripts, more precisely in one book chapter accepted for publication and four papers. Out of the four papers, three have been published and one is prepared for publication in an international journal with impact factor.

Manuscript 1: Vindušková, O., Frouz, J., 2013. Soil carbon accumulation after open-cast coal and oil shale mining in Northern Hemisphere: a quantitative review. Environ. Earth Sci. 69, 1685–1698.

Manuscript 1 examined soil organic carbon (SOC) accumulation rates in post-mining soils after open-cast coal and oil shale mining and the effects of time, vegetation, climate, soil texture, and application of topsoil on these rates. Some of the data were also presented and discussed in a new perspective in Manuscript 4. The SOC accumulation rates found in post-mining soils were highly variable especially in the first 30 years. The rates decreased linearly with increasing site age with a value of 2.5 t ha^{-1} y^{-1}after 10 years and 0.9 t ha^{-1} y^{-1} after 40 years (Manuscript 1, Fig. 1). Most of the SOC accumulation rates found in post-mining soils were higher than typical rates reported after land use change from agriculture to grassland or forest (~0.3 t ha^{-1} y^{-1}; MS 4, Fig. 1) (Post and Kwon, 2000). This may be explained by the low or zero initial SOC content in post-mining soils which are therefore more distant from soil carbon saturation than agricultural soils. We did not observe the expected initial increase in the accumulation rates as reported elsewhere (Shrestha and Lal, 2006) probably because our dataset did not include sites <4 years which were often used for calculation of sequestered C in older sites.

When pooled across vegetation types and the age of sites that ranged from 4 to 65 years (MS 1, Fig. 1), meta-analysis did not show a significant effect of vegetation. However, the effect of vegetation was significant in the first 30 years of soil development – SOC accumulation rate was significantly lower under conifers (0.8 ± 0.4 t ha^{-1} y^{-1}) than under grassland (1.8 ± 1.6 0 t ha^{-1} y^{-1}) or deciduous trees (2.3 ± 1.0 t ha^{-1} y^{-1}) which did not differ significantly (MS 4, Fig. 2). Interestingly, the SOC accumulation rate followed different trends in the first 30 years under different vegetation – it decreased under deciduous forest, increased under conifers and did not change significantly under grassland. Therefore, the maximum rates were reached in the first 20 years in deciduous trees and after 30–40 years in conifers. These differences may be the reason behind the large variability of rates in the initial 30 years of post-mining soil development. The review also confirmed previous observations that deciduous trees support accumulation of OM in mineral soil compared to conifers. Deciduous trees stored 23 % of C in the forest floor compared to 62 % in conifers. However, forest floor represents a C stock more vulnerable to erosion, fire and decomposition under changed environmental conditions (Jandl et al., 2007). Therefore, deciduous trees or a mixture of deciduous trees and conifers should be preferred over conifers in reclamation of areas where broadleaf and mixed forests represent the potential natural vegetation.

The effect of temperature on SOC accumulation was vegetation-dependent – SOC accumulation was supported by warmer climate under grassland and by colder climate under conifers. This indicates that potential natural vegetation should be used in reclamation to support SOM accumulation, i.e., grassland should be established in warmer regions, coniferous forest in colder regions and deciduous forest in intermediate regions. Precipitation, texture, and topsoil application did not show a significant effect on SOC accumulation.

A large proportion of the sites reached pre-mining SOC stock within 20 years or less after reclamation (MS 1, Fig. 2) although we could not show that topsoil application would significantly accelerate this recovery. However, topsoil application is required by some countries while other use it preferentially for agriculture reclamation (Macdonald et al., 2015). It may be assumed that the effect of topsoil application will be greatly dependent on overburden substrate properties (such as texture and toxicity) and most likely also on other local factors such as climate, vegetation and management. Therefore, paired experiments should be used to investigate the effect of topsoil application on SOM accumulation.

The results suggest that time, vegetation, climate, and their interactions are the main factors controlling SOC accumulation in post-mining soils.

Manuscript 2: Vindušková, O., Dvořáček, V., Prohasková, A., Frouz, J., 2014. Distinguishing recent and fossil organic matter — A critical step in evaluation of post-mining soil development – using near infrared spectroscopy. Ecol. Eng. 73, 643–648.

In Manuscript 2, it was demonstrated that near infrared spectroscopy coupled with partial least square analysis (NIRS-PLS) has the potential to quantify both recently derived soil organic carbon and fossil C in Sokolov post-mining soils. Total amount of C and recent C could be successfully predicted in soils (MS 2, Table 2). Moreover, both coal and kerogen carbon (separately) could be successfully predicted in artificial mixtures (MS 2, Table 1); however, validation for soils was not possible as there is no reference method that could distinguish between these two forms of fossil C.

The advantage of NIRS-PLS is that large amount of samples can be processed rapidly at low per-sample cost. The disadvantage is that the method requires site-specific calibration with a relatively high (>100) number of samples measured by other method. In Sokolov post-mining soils, NIRS has the potential to become a rapid and cost-effective tool for soil mapping and long-term monitoring after further calibration with soil samples.

Manuscript 3: Vindušková, O., Sebag, D., Cailleau, G., Brus, J., Frouz, J., 2015. Methodological comparison for quantitative analysis of fossil and recently derived carbon in mine soils with high content of aliphatic kerogen. Org. Geochem. 89–90, 14–22.

In a methodological comparison for quantitative analysis of fossil and recently derived C in Sokolov post-mining soils (MS 3, Fig. 5), it was shown that using conventional methods for SOC determination in these soils leads to significant bias (8.2, 4.8 and 4.4 % C for loss-on-ignition at 550°C, dry combustion and wet dichromate oxidation, respectively). However, subtracting the C content of subsoil (50 cm deep) from the topsoil content provided an acceptable estimate of recent C. It is inappropriate to use these methods for soil quality or C sequestration assessment without such correction.

Furthermore, ^{13}C isotope ratio method provided acceptable estimates only when subsoil values were included in the calculation and therefore did not provide any advantage over conventional methods. Both ^{13}C NMR and Rock-Eval were found to be suitable for recent C determination in the presence of fossil organic matter and Rock-Eval was used for this purpose for the first time.

Of all the investigated methods, Rock-Eval proved to most accurately determine the actual recent C content. It is far simpler than ^{14}C dating or NMR, which require more sophisticated instrumentation. The accuracy of the investigated methods decreased in the following order: Rock Eval >^{13}C NMR > loss-on-ignition (LOI) at 550°C corrected > wet dichromate oxidation (C_{ox}) corrected >^{13}C isotope ratio method > dry combustion (TOC) corrected > LOI at 200°C > NIRS-PLS> C_{ox}> TOC > LOI at 550°C.

Manuscript 4: Frouz, J., Vindušková, O., (in press) Soil organic matter accumulation in post-mining sites: potential drivers and mechanisms. In: Munoz, M., Zornoza, R. (Eds.), Soil Management and Climate Change. Academic Press, p. 450.

Manuscript 4 is a book chapter that reviews the main findings of research on SOC accumulation carried out in post-mining sites and puts the findings of manuscripts 1, 2 and 3 into a wider perspective. First, we discuss the methodological issues of C sequestration studies on post-mining sites. These include variation of site history in the chronosequence approach and the presence of fossil organic matter and carbonates in the overburden. Then, the sequestration potential of post-mining soils is assessed. We discuss whether the decrease in sequestration rates after few decades of soil development is caused by soil C saturation or it reflects the decrease in primary production during ecosystem development. Results of a recent field transplant experiment (Frouz, 2016) suggest that the latter mechanism is more likely. Furthermore, we discuss the possible explanations behind the observation that under the same litter input, soils that have already accumulated some SOM are likely to sequester C more easily than soils low in SOM.

The major drivers of SOM accumulation in post-mining sites include the substrate and vegetation. Overburden substrates may have some extreme properties compared to natural parent substrates which may greatly limit SOM accumulation. We discuss why C sequestration in post-mining sites has not been observed to relate with clay content in contrast to non-mining soils. The reasons may include: masking by other factors such as toxicity, variable methodology of clay content determination, and decoupling of soil texture and chemistry. The possible effects of substrate heaping method, fossil organic matter, and topsoil application on C sequestration are also discussed.

Furthermore, we give examples of how vegetation and fauna influence soil C storage and its dynamics. Plant production and consequently C sequestration has different dynamics in sites reclaimed by alder and sites left to ecological succession. The effect of tree species is partly mediated by soil fauna which is more active under trees producing litter of lower C:N ratio and supports C storage by incorporating SOM into the mineral soil via bioturbation. Even though climate is assumed to have important effects on SOM accumulation, studies from post-mining sites investigating this issue are scarce. Our quantitative review of post-mining sites that covered only temperate and boreal zones showed that the effect of temperature is vegetation-dependent as discussed above. A study covering a wider climatic gradient is lacking.

Manuscript 5: Vindušková, O., Pánek, T., Frouz, J., (prepared manuscript) Soil development during last 13,000 years along a chronosequence of landslides in Central Europe.

A chronosequence of 26 landslides ranging in age from 4 to almost 13 thousand years located in Western Carpathians along the border of Czech Republic, Slovakia and Poland was studied for the first time. The study revealed that the most rapid SOM accumulation occurs in the first 100 years. During this initial phase, almost all of the soil carbon storage potential is reached (51 t ha^{-1} in mineral soil, 60 t ha^{-1} including the forest floor; MS 5, Fig. 4 and 5). This represents a rather high C sequestration rate (0.5 and 0.6 t ha^{-1} y^{-1}, respectively). The soil C storage capacity in landslides was found to resemble the median C stock of adjacent undisturbed sites (57 and 64 t ha^{-1}, respectively) and both were at the lower range of stocks reported for forest soils in the studied region (Marková et al., 2016). While SOC accumulation followed a sigmoid saturation trend, nitrogen stocks decreased slowly after reaching a maximum after about 350 years.

The rate of the recovery to pre-disturbance levels differed strongly among soil properties and ranged from decades to millennia (MS 5, Table S3).

A gradual loss of P from soil was observed (MS 5, Fig. 4) which may be attributed to leaching and erosion as predicted by the conceptual model of Walker and Syers (1976). The increasing soil N:P ratio suggests that ecosystem develops towards P limitation even though only fertilization experiment could confirm this hypothesis. The relatively humid climate and low initial contents of P in parent substrate of the chronosequence may have supported the relatively rapid development of P limitation which likely lead to tightening of nutrient cycling and decreased N availability. Historical wood harvest in the studied area probably added to the N and P losses from soil.

8. Conclusions

The key factor affecting the rate of soil organic matter (SOM) accumulation after a major disturbance is time. The accumulation rates found in the first 40 to 100 years in both post-mining sites and landslides are higher than those of revegetated agricultural soils. This may be explained by the low initial SOM content of post-mining and landslide soils. However, accumulation slows down during the 70 years of post-mining soil development and approaches zero after 100 years on landslides suggesting that SOM content attains a steady-state. Carbon stocks of most post-mining soils recovered to pre-disturbance levels during 20 years. Vegetation and climate interact and affect SOM accumulation in time. Accumulation was slower under conifers than under deciduous trees or grassland in the first 30 years. In this period, rates decreased under deciduous trees, increased under conifers and did not change under grassland. When averaged for all site ages, more C was stored in forest floor under conifers compared to deciduous trees suggesting that deciduous trees should be preferred over conifers in temperate broadleaf and mixed forest ecoregions in order to increase stability of soil C storage. The effect of temperature was vegetation-dependent suggesting that natural potential vegetation should be used in reclamation to support SOM accumulation.

Several methods have been proposed that may be used in studies of SOM accumulation on post-mining sites to overcome the bias caused by fossil carbon of dominantly aliphatic character listed in order of decreasing accuracy: (1) Rock Eval, (2) ^{13}C NMR, (3) correction of conventional methods by way of subtraction of the subsoil carbon content, (4) loss on ignition at 200°C, and (5) near infrared spectroscopy (NIRS). NIRS has a potential to become a cost-effective option after further calibration.

A unique 13 thousand-year landslide chronosequence provided insight into long-term soil development under temperate semi-natural forest on sedimentary bedrock. Several soil properties changed along the chronosequence and recovered to pre-disturbance levels after decades to millennia. While C attained a steady state after 100 years, soil nitrogen reached a maximum after 350 years and then decreased in older sites. Also total phosphorus was found to decrease, in accordance with the conceptual model of Walker and Syers (1976), as a consequence of erosion, leaching and harvest. The increasing soil N:P ratio suggests that ecosystem develops towards P limitation.

To conclude, this thesis provides further insight into the factors and mechanisms controlling SOM accumulation and provides a solution to a major methodological issue connected with the study of SOM accumulation in post-mining sites.

Manuscript 1

Vindušková, O., Frouz, J., 2013:

Soil carbon accumulation after open-cast coal and oil shale mining in Northern Hemisphere: a quantitative review

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ORIGINAL ARTICLE

Soil carbon accumulation after open-cast coal and oil shale mining in Northern Hemisphere: a quantitative review

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Abstract Meta-analysis and other statistical methods were used to evaluate how changes in soil organic carbon (SOC) content in post-mining soils are related to different factors; the data were obtained from 17 studies covering 93 temperate post-mining sites in the Northern Hemisphere that had been revegetated by forest or grassland either by reclamation or natural succession. Because many studies have failed to report any measures of variance, only part of the data were used for meta-analysis. According to the meta-analysis, the rate of SOC accumulation was unrelated to vegetation type. In a separate analysis that included all available data and in which rates of SOC accumulation at each site were used as individual entries, the rate of SOC accumulation differed depending on the age of the site and vegetation type. Under deciduous forests, the rate reached a maximum after 5–10 years and then decreased. Under coniferous forests, the initial SOC values were lower than under deciduous forests, but slowly increased with age and reached a maximum after 30–40 years. No significant temporal trend was found in grasslands, probably because the data set included only relatively young grassland sites. Based on data from sites younger than 30 years, sites with grasslands and deciduous forests accumulated SOC faster than sites with coniferous forests. The rate of accumulation was negatively correlated with temperature under coniferous forests, but positively correlated with temperature in grasslands. This suggests that carbon sequestration is favored by cold climates in coniferous forests, but by warm climates in grasslands. Deciduous forests were intermediate. Compared to conifers, deciduous trees may support SOC sequestration deeper in the soil profile, which may enhance SOC stability. A large proportion of post-mining sites reach the pre-mining SOC stock within 20 years or less after reclamation.

Keywords Soil carbon · Land use change · Sequestration · Meta-analysis · Mine soils · Reclamation

Introduction

Soil organic matter plays a principal role in many soil functions and processes. It increases the soil potential in storing both nutrients and toxic substances. It enhances soil structure and reduces the risk of erosion and compaction. It increases soil porosity, aeration, and water-holding capacity. Finally, soil organic matter represents a source of nutrients and energy for soil organisms and is therefore central to nutrient cycling (Carter 2002).

Mining substantially affects many ecosystem processes (Bradshaw 1983, 2000; Ricka et al. 2010). When deposited in the form of overburden (spoils), the post-mining soils have generally low or even zero content of recent soil organic carbon (SOC) (Bradshaw 1983, 2000). The overburden material itself lacks recent SOC (Rumpel et al. 2003; Fettweis et al. 2005), but in part of the reclamations topsoil with a recent SOC content is applied on top of this deposited overburden. The SOC content in such topsoil at the time of deposition is likely lower than in undisturbed soils due to losses from mineralization during manipulation and storage of topsoil (Abdul- Kareem and McRae 1984; Stahl et al. 2003; Shrestha and Lal 2011). Since soil organic carbon content is determined by the balance between inputs and outputs, the revegetation of spoils leads to SOC accumulation as a consequence of the increased carbon input from litter and belowground biomass.

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As explained above, SOC accumulation improves soil quality and hence is important for post-mining site restoration. Moreover, previous studies have indicated that accumulation of SOC in post-mining soils is rather high and these soils could play an important role in mitigation efforts (Akala and Lal 2001; Karu et al. 2009). In general, the rate at which SOC accumulates is greatly affected by many factors including vegetation, climate, drainage conditions, and soil texture (Carter 2002), but in post-mining soils it is also affected by reclamation practices (Bradshaw 1983, 2000). Selection of an effective reclamation practice for post-mining sites requires an understanding of how SOC accumulates in these sites.

Changes in SOC content also occur in agricultural soils after changes in land use. These changes have been discussed in a number of reviews, some of which used meta-analytical approach (Post and Kwon 2000; Guo and Gifford 2002; Paul et al. 2002; Laganiere et al. 2010). Similar studies devoted to post-mining soils are lacking.

The current study, using both meta-analysis and other statistical methods, attempted to determine how SOC accumulation in post-mining soils is affected by the following factors: type of vegetation, age of site, application of topsoil, soil texture, sampling depth, and climate. Other factors such as variation in reclamation technologies or using of amendments were also considered, but data in individual studies were too inconsistent to be compared. Because many types of mining activities exist with very different technologies and type of geological material, we focused exclusively on open-cast mining of coal and similar materials used for energetic purposes (coal, lignite, oil shales) due to the fact that geological mining conditions are alike in large geographical areas and also because open-cast mining causes expensive and large-scale disturbance of ecosystems.

Materials and methods

Data collection

The data collection was restricted to sites formed after open-cast mining of coal or similar organic materials. It was also required that all selected sites were located in upland conditions and thus well drained to avoid the effect of waterlogging on SOC accumulation. Data were extracted from 17 recent studies (published within the last 10 years) dealing with SOC accumulation in post-mining soils in the temperate zone of the Northern Hemisphere. Of these 17 studies, 15 were published in peer-reviewed journals and 2 in journals without peer review. These 17 studies contained data from 93 post-mining sites and 15 adjacent undisturbed sites (the latter sites were used as indicators of the pre-mining SOC content). For 54 sites, separate data were obtained for different horizons of the soil profile. In six cases, the authors were contacted and asked to supply unpublished data that were needed for the calculations (see “Acknowledgments”).

To be included in the data set, studies had to report either the rate of SOC accumulation (one study) or data that would enable calculation of this rate, i.e., age of site (number of years since reclamation or the dumping of overburden for unreclaimed sites) and the amount of recently sequestered SOC. Only two studies conducted repeated sampling and reported the SOC stocks of the sites at time zero (right after reclamation) (Nii-Annang et al. 2009; Shrestha et al. 2009).

Estimating the amount of recently sequestered SOC requires that the measured carbon content is reduced by the fossil SOC content in the dumped overburden. The proportion of recently sequestered and fossil SOC is measured either by radiocarbon dating using ^{14}C AMS (Morgenroth et al. 2004; Rumpel et al. 2003), which was done in three studies (Karu et al. 2009; Fettweis et al. 2005; Rumpel et al. 2003), or estimated once using a site-specific coal-correction equation developed by Amichev (2007) and used in Amichev et al. (2008). In three studies, the authors estimated the content of recently sequestered SOC by subtracting the C content of a deeper soil horizon from the total C content (Reintam 2004; Reintam et al. 2002; Frouz et al. 2009). For those studies that did not deal with correction for fossil SOC, recently sequestered SOC was estimated based on available data. One study (Sourkova et al. 2005) subtracted the C content of the dumped overburden from the total C content. The authors had estimated the C content of the dumped overburden based on a linear regression between the age of the plot and C content.

In four chronosequence studies (Akala and Lal 2001; Lorenz and Lal 2007; Chatterjee et al. 2009; Ganjegunte et al. 2009), the SOC stocks of reported sites were corrected by subtracting the SOC stock of the youngest available site (0–2 years old). This approach has been successfully used elsewhere (Shrestha and Lal 2010). In three studies (Sever and Makineci 2009; Keskin and Makineci 2009; Frouz and Kalčík 2006), a similar approach was used for the correction as in the studies described above, i.e., the C content of a layer in which SOC did not accumulate over time was subtracted from the total C content. This method is applicable only in sites without topsoil application and assumes that the soil profile of young post-mining soils is homogeneous, because the overburden material is mixed during heaping. This mixing is indicated by a general lack of SOC stratification in young sites (Chatterjee et al. 2009). Studies from which it was not possible to calculate the recently sequestered SOC in any of the ways described above were not included in the data set.

For studies that did not provide C data in terms of weight per area, the SOC stock (S_{SOC}, t ha^{-1}) was calculated as follows:

$$S_{\mathrm{SOC}} = \mathrm{SOC} \times \mathrm{BD} \times d \quad (1)$$

where SOC is the SOC concentration (g kg^{-1}), BD is bulk density (t m^{-3}), and d is the depth (m). If reported, organic matter content was converted to SOC based on the assumption that organic matter contains 58 % organic C (Nelson and Sommers 1996). Those studies that did not provide bulk density data were not included. Even though some authors of quantitative reviews have estimated bulk density based on its relation with SOC content (Post and Kwon 2000; Guo and Gifford 2002; Poeplau et al. 2011), others have avoided these estimations and emphasized that bulk density can be substantially influenced by land use change (Laganiere et al. 2010). Because the bulk density of post-mining soils is quite variable (Lal and Kimble 2001), estimation of bulk density based on SOC content could introduce substantial error.

Some studies reported data on SOC accumulation in surface organic layers (LFH or Oe horizon) and were compiled separately for further analysis. In the case of one study (Reintam et al. 2002), the SOC stock in the organic layer was calculated by using the bulk density of litter (pine needles) from another study (Frouz et al. 2009), as previously done by Fettweis et al. (2005).

For sites to be included in the analysis, the publication also had to provide data on: type of mined material (coal, 10 studies including 74 sites; lignite, 3 studies including 9 sites; oil shale, 3 studies including 10 sites), type of reclamation (with or without topsoil application), vegetation type (grassland, shrubland, or forest; in the case of forest—coniferous, deciduous, or mixed), soil sampling depth, and soil texture. Soil texture was given either as particle size distribution (in 4 studies) or as a texture class. If a texture class was not presented according to the USDA system, it was transformed to it. Sites were divided into three categories based on their clay content: low (<10 %), intermediate (10–35 %), and high (>35 %).

Optional characteristics of sites were: number of replicates (n), standard deviation of SOC accumulation rate, SOC stock of an adjacent undisturbed site, species composition of vegetation, information on amendments and management, mean annual temperature, mean annual precipitation, and geographic coordinates. Wherever possible, missing climate data (mean annual temperature, mean annual precipitation) were obtained from http://www.weatherbase.com using geographic coordinates or described location, as previously done by Poeplau et al. (2011).

Statistical analysis

Meta-analysis is a statistical approach initially introduced in medicine that enables evaluation of data from different studies accounting for different variability and number of replicates of each study (giving due weight to every mean value). In this study, the meta-analysis was used to explore the effect of vegetation type on the rate of SOC accumulation. The calculations were performed using MetaWin 2.0 (Hedges and Olkin 1985) as described previously, e.g., by Curtis and Wang (1998) or Liao et al. (2008). Generally, meta-analysis is based on the calculation of treatment effect size. There are several possibilites for calculating the effect size. The approach chosen in this study was the Hedges' d (also called the d-index) which is a standardized difference between an experimental and control mean. For this study, it was equivalent to SOC accumulation rate and was calculated as follows:

$$d = \frac{S_{\mathrm{SOC},x} - S_{\mathrm{SOC},0}}{x} \quad (2)$$

where $S_{\mathrm{SOC},0}$ (representing the control mean) is the SOC stock of the site at year 0 (just after dumping), $S_{\mathrm{SOC},x}$ (representing the experimental mean) is the SOC stock of a reclaimed site (one or more years after dumping), and x is the age of the site.

In the next step of meta-analysis, effect sizes from all studies are averaged into a weighted mean based on their sample size and measure of variance. Larger studies and studies with less random variation are given greater weight than smaller and less precise studies.

In our meta-analysis, weighted mean effect sizes as well as their confidence intervals (CI) were computed for each vegetation type for the comparison of their effect. If the 95 % CI would not overlap between the vegetation types, then the effect of revegetation on SOC accumulation would be significantly different between the vegetation types.

To include a study into the meta-analysis, it had to report the number of replicates (n) and measures of variance (SD or SEM) of one or both means. Only the variability of the experimental mean (reclaimed site) was considered, because the variability of the control mean (site just after dumping) was not reported in any of the studies. Many studies also lacked SD or SEM values for the reclaimed sites. The authors were contacted to obtain these data. In cases when the measures of variance were unavailable and the study contained a number of similar sites, the data from the sites were averaged (or were first divided into groups according to site age and then averaged) and the standard deviation of this newly formed mean was used as a measure of the variance. Data from one study (Sourkova et al. 2005) were treated this way (i.e., the mean and variance of sites grouped according to site age were used rather than data from each individual site), because including data from the individual sites of that study would have strongly influenced the analysis. For those studies that reported least significant differences rather than measures of variance, it was assumed that the SD was directly proportional to the mean and the SDs were calculated from the maximum possible confidence intervals that would still result in a significant difference.

Despite the described effort, it was possible to include only 87 sites in the meta-analysis. To use as much of the collected data as possible, an analysis of the entire data set using the rate of C accumulation at individual sites as individual entries was performed. In this analysis, the SOC accumulation rates among the different vegetation and soil texture categories were compared by one-way ANOVA followed by Fisher's least significant difference (LSD) post hoc test, and studied by linear regression between rate of accumulation and the age of the site, climate data, or depth of sampling. These calculations were performed using Statistica 10.0. In the major part of the analyses, sites with deciduous and mixed forest were considered as a single category, because the mixed forest sites represented only 10 % of all forest sites. Shrublands were assigned to (deciduous) forest sites for a similar reason.

To analyze how forest type influences the proportion of carbon sequestered in the organic layers compared to the mineral soil, SOC stocks were calculated separately for organic layers (LFH or O_e) and for mineral soil as in Eq. 1.

For the evaluation of SOC accumulation, SOC stock of the post-mining site was compared with that of an adjacent undisturbed site (forest, pasture). With this approach, we could estimate the rate at which SOC content recovered to the pre-mining level. For the calculation of this ratio, the total SOC stock was used for sites reclaimed with topsoil application. Thus, for this variable, SOC stock included also the SOC that was present in the topsoil applied during reclamation. In the sites reclaimed without topsoil application, the initial stock was subtracted from the total stock to correct for fossil carbon content.

Results and discussion

Rate of SOC accumulation in relation to site age and vegetation type

Revegetation of post-mining sites led to SOC sequestration in all but two sites (Table 1). Most of the rates of SOC accumulation were higher than typical rates for revegetated agricultural soils reported by Post and Kwon (2000).

The decrease in SOC on the two sites may have been an artifact caused by an overestimation of the initial carbon stock (e.g., due to heterogeneous coal residuals). The decrease could also have been real; because both sites were reclaimed by topsoil application and revegetation by trees or shrubs, the reclamation might decrease SOC stock in the applied topsoil layer similarly as reported in the first few years after afforestation on pastures (Paul et al. 2002). The applied topsoil layers have a relatively high default organic matter content compared to the overburden, which contains no recent organic matter. If the SOC is measured directly after the topsoil is spread on the spoil, part of the SOC in the topsoil may be lost because of intensive mineralization (Ingram et al. 2005), which is not compensated for by litter input in the first few years, just as litter input does not initially compensate for mineralization in afforested pastures. This explanation is consistent with the young age of the two sites (4–16 years old).

The rate of accumulation decreased linearly with increasing site age (Fig. 1). The variability in the rate also decreased with site age. The maximum rates occurred in young sites (<20 years old). In their chronosequence study of post-mining soils, Shrestha and Lal (2010) similarly reported that the maximum rates of accumulation occurred after 14 years under forest and after 6 years under pasture. Our data did not conform to the polynomial trend in their study, probably because our data set did not include sites younger than 4 years, which we have often used as reference for calculation of sequestered SOC in older sites. The average rate of accumulation was 2.46 t ha^{-1} y^{-1} after 10 years and 0.87 t ha^{-1} y^{-1} after 40 years. A somewhat higher but comparable rate (1.171 t h^{-1} y^{-1}) was found by Anderson et al. (2008) for a chronosequence of 13 post-mining sites that ranged in age from 11 to 26 years; this rate would have been reached after approximately 30 years based on our linear regression.

According to the meta-analysis, the rate of SOC accumulation based on effect sizes did not differ significantly according to the type of vegetation (data not shown). When we reduced the data set to include only sites younger than 30 years so as to include only clearly defined grasslands, coniferous, or deciduous forests (grasslands with shrubs and mixed forest were excluded), then the meta-analysis for the remaining 42 sites also failed to reveal a significant association between the rate of SOC accumulation and type of vegetation ($p = 0.079$). However, when we conducted a one-way ANOVA using the mean SOC accumulation rates (i.e., the accumulation rate averaged for all years, for which we can use also studies that do not provide any SD estimate and cannot be used to calculate effect sizes) from sites less than 30 years old, which once again meant that only clearly defined grasslands, coniferous forests, or deciduous forest were included ($n = 50$), the ANOVA model was significant ($p = 0.002$) and the accumulation rate was significantly lower in coniferous forests (0.81 ± 0.38 t h^{-1} y^{-1}, $n = 14$) than in grasslands (1.81 ± 1.55, $n = 21$) or in

Table 1 Rates of carbon accumulation in post-mining soils (mean ± SD) and other supporting data used for determining the accumulation rate reported in previous studies

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
Akala and Lal (2001)	5	27.20	17.00	2.4	1	Young site	Grassland	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	10	40.90	17.00	2.39	1	Young site	Grassland	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	15	54.90	17.00	2.53	1	Young site	Grassland	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	20	67.40	17.00	2.52	1	Young site	Grassland	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	25	93.20	17.00	3.5	1	Young site	Grassland	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	4	19.50	22.30	−0.70	1	Young site	Deciduous forest	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	10	31.30	22.30	0.90	1	Young site	Deciduous forest	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	15	46.00	22.30	1.58	1	Young site	Deciduous forest	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
	21	62.90	22.30	1.93	1	Young site	Deciduous forest	1020	11	Silty clay loam	Coal	No	SE Ohio, USA
Amichev et al. (2008)	47	48.60	N/a	1.3	1	Equation	Coniferous forest	1010	11	Silt loam	Coal	No	Indiana, USA
	34	34.10	N/a	1.00	1	Equation	Coniferous forest	1110	13	Sandy clay loam	Coal	No	Kentucky, USA
	39	25.00	N/a	0.64	1	Equation	Coniferous forest	1010	8	Sandy loam	Coal	No	Pennsylvania, USA
	28	33.90	N/a	1.21	1	Equation	Coniferous forest	970	11	Sandy loam	Coal	No	West Virginia, USA
	45	25.70	N/a	0.57	1	Equation	Mixed forest	1010	11	Silt loam	Coal	No	Indiana, USA
	38	28.40	N/a	0.75	1	Equation	Mixed forest	1110	13	Sandy clay loam	Coal	No	Kentucky, USA
	35	23.30	N/a	0.67	1	Equation	Mixed forest	1010	11	Sandy loam	Coal	No	West Virginia, USA
	27	40.70	N/a	1.51	1	Equation	Mixed forest	970	11	Sandy loam	Coal	No	West Virginia, USA
	47	22.70	N/a	0.48	1	Equation	Deciduous forest	1150	13	Silt loam	Coal	No	Illinois, USA
	44	39.70	N/a	0.90	1	Equation	Deciduous forest	1010	11	Silt loam	Coal	No	Indiana, USA

Table 1 continued

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
	35	22.80	N/a	0.65	1	Equation	Deciduous forest	1110	13	Sandy clay loam	Coal	No	Kentucky, USA
	50	24.10	N/a	0.48	1	Equation	Deciduous forest	930	10	Silt clay loam	Coal	No	Ohio, USA
Fettweis et al. (2005)	19	26.00	N/a	1.37	1	Radiocarbon	Coniferous forest	580	9	Loamy sand	Lignite	Ash	Cottbus, Germany
	19	22.00	N/a	1.16	1	Radiocarbon	Coniferous forest	580	9	Loamy sand	Lignite	Ash	Cottbus, Germany
	37	47.00	N/a	1.27	1	Radiocarbon	Coniferous forest	580	9	Loamy sand	Lignite	Ash	Cottbus, Germany
Frouz et al. (2009)	28	36.91	N/a	1.32 ± 0.72	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	31	38.03	N/a	1.23 ± 0.23	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	28	16.54	N/a	0.59 ± 0.27	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	27.8	4.39	N/a	0.16 ± 0.13	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	29.5	23.11	N/a	0.78 ± 0.17	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	27	9.32	N/a	0.35 ± 0.20	4	Deep layer	Coniferous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	22	9.70	N/a	0.44 ± 0.16	4	Deep layer	Coniferous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
Ganjegunte et al. (2009)	14	32.15	23.34	0.63 ± 0.32	4	Young site	Grassland	376	6.7	Loam	Coal	No	Wyoming, USA
	26	39.37	23.34	0.62 ± 0.19	4	Young site	Grassland	376	6.7	Loam	Coal	No	Wyoming, USA
	5	31.47	23.34	1.63 ± 0.97	4	Young site	Shrubland	266	7.4	Loam	Coal	No	Wyoming, USA
	10	27.78	23.34	0.44 ± 0.33	4	Young site	Shrubland	266	7.4	Loam	Coal	No	Wyoming, USA
	16	18.16	23.34	-0.32 ± 0.16	4	Young site	Shrubland	266	7.4	Loam	Coal	No	Wyoming, USA

Table 1 continued

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
Karu et al. (2009)	15	6.30	N/a	0.42 ± 1.13	3	Radiocarbon	Mixed forest	639	4.8	Sand	Oil shale	No	Narva, NE Estonia
	22	10.50	N/a	0.48 ± 0.32	3	Radiocarbon	Coniferous forest	639	4.8	Sand	Oil shale	No	Narva, NE Estonia
	37	44.60	N/a	1.21 ± 1.05	3	Radiocarbon	Coniferous forest	639	4.8	Sand	Oil shale	No	Narva, NE Estonia
Keskin and Makineci (2009)	17	33.90	21.48	0.73 ± 0.82	7	Deep layer	Deciduous forest	1049	14	Sandy clay loam	Coal	No	Istanbul, Turkey
	17	19.46	10.50	0.53 ± 0.80	5	Deep layer	Coniferous forest	1049	14	Sandy loam	Coal	No	Istanbul, Turkey
Chatterjee et al. (2009)	30	48.18	26.39	0.73 ± 0.34	3	Young site	Grassland	1039	10.7	Silt loam	Coal	NPK	Morgan, OH, USA
	9	56.70	26.39	3.37 ± 0.99	3	Young site	Grassland	1039	10.7	Silt loam	Coal	NPK	OH, USA
	11	48.90	26.39	2.5 ± 0.39	3	Young site	Mixed forest	1039	10.7	Silt loam	Coal	N/a	Noble, OH, USA
Lorenz and Lal (2007)	31	41.79	4.86	1.19 ± 0.44	9	Young site	Mixed forest	965	13	Loamy-gravel	Coal	No	Morgan, Ohio
Nii-Annang et al. (2009)	9	16.67	N/a	1.85 ± 0.70	3	Time shift	Deciduous forest	569	9.4	Loamy sand	Lignite	CaO, NPK	Lusatia, Germany
	9	18.54	N/a	2.6 ± 0.74	3	Time shift	Deciduousforest	569	9.4	Loamy sand	Lignite		Lusatia, Germany
	9	15.23	N/a	1.69 ± 0.75	3	Time shift	Deciduous forest	569	9.4	Loamy sand	Lignite		Lusatia, Germany
Reintam et al. (2002)	29	31.22	N/a	1.8	1	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	Sirgala, Estonia
	31	32.25	N/a	1.4	1	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	Sirgala, Estonia
	31	82.52	N/a	2.66	1	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	Sirgala, Estonia
	34	56.36	N/a	1.66	1	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	Sirgala, Estonia
Reintam (2004)	25	N/a	N/a	1.41	5	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	NE Estonia
	25	N/a	N/a	1.4	5	Deep layer	Coniferous forest	584	4.2	Sand	Oil shale	No	NE Estonia
	25	N/a	N/a	1.57	5	Deep layer	Deciduous forest	584	4.2	Sand	Oil shale	No	NE Estonia

Table 1 continued

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
Rumpel et al. (2003)	11	6.00	0.00	0.55 ± 0.25	2	Radiocarbon	Coniferous forest	580	9	Sand	Lignite	Ash	Lusatia, Germany
	17	12.20	0.00	0.72 ± 0.28	2	Radiocarbon	Coniferous forest	580	9	Sand	Lignite	Ash	Lusatia, Germany
	32	35.70	0.00	1.12 ± 0.29	2	Radiocarbon	Coniferous forest	580	9	Sand	Lignite	Ash	Lusatia, Germany
Sever and Makineci (2009)	17	30.38	23.35	0.41 ± 0.98	14	Deep layer	Coniferous forest	1049	14	Sandy loam	Coal	No	Istanbul, Turkey
Shrestha et al. (2009)	5	44.40	31.40	2.60 ± 0.36	3	Time shift	Grassland	934	9.8	Loam	Coal	CaO, NPK, mulch	Harrison, OH, USA
	5	36.70	32.90	0.76 ± 1.08	3	Time shift	Grassland	934	9.8	Clay loam	Coal		Noble, OH, USA
	5	54.10	50.60	0.70 ± 1.52	3	Time shift	Grassland	1070	9.2	Sandy clay loam	Coal		Belmont, OH, USA
	5	47.20	31.40	3.16 ± 0.36	3	Time shift	Grassland	934	9.8	Loam	Coal	CaO, NPK, mulch, chiseling	Harrison, OH, USA
	5	47.00	32.90	2.82 ± 1.08	3	Time shift	Grassland	934	9.8	Clay loam	Coal		Noble, OH, USA
	5	62.90	50.60	2.46 ± 1.52	3	Time shift	Grassland	1070	9.2	Sandy clay loam	Coal		Belmont, OH, USA
	5	45.00	31.40	2.72 ± 0.36	3	Time shift	Grassland	934	9.8	Loam	Coal	CaO, NPK, mulch	Harrison, OH, USA
	5	35.20	32.90	0.46 ± 1.08	3	Time shift	Grassland	934	9.8	Clay loam	Coal		Noble, OH, USA
	5	52.60	50.60	0.40 ± 1.52	3	Time shift	Grassland	1070	9.2	Sandy clay loam	Coal		Belmont, OH, USA
	5	47.70	31.40	3.26 ± 0.36	3	Time shift	Grassland	934	9.8	Loam	Coal	CaO, NPK, mulch, manure	Harrison, OH, USA
	5	45.40	32.90	2.50 ± 1.08	3	Time shift	Grassland	934	9.8	Clay loam	Coal		Noble, OH, USA
	5	61.10	50.60	2.10 ± 1.52	3	Time shift	Grassland	1070	9.2	Sandy clay loam	Coal		Belmont, OH, USA

Table 1 continued

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
Sourkova et al. (2005)	4	48.10	23.00	6.27 ± 6.01	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	5	50.57	23.00	5.51 ± 3.81	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	6	31.11	23.00	1.35 ± 2.30	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	6	41.42	23.00	3.7 ± 2.96	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	10	59.85	23.00	3.69 ± 2.69	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	13	59.15	23.00	2.78 ± 1.57	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	13	60.88	23.00	2.91 ± 1.86	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	14	70.19	23.00	3.37 ± 1.92	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	15	77.27	23.00	3.62 ± 1.77	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	25	59.39	23.00	1.46 ± 0.89	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	25	72.69	23.00	1.99 ± 1.17	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	26	70.34	23.00	1.82 ± 0.69	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	34	69.33	23.00	1.36 ± 0.86	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	34	80.75	23.00	1.70 ± 1.03	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	36	57.75	23.00	0.97 ± 0.61	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	36	48.66	23.00	0.71 ± 0.56	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	38	78.33	23.00	1.46 ± 0.85	3	Regression	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	64	62.87	23.00	0.62 ± 0.37	3	Regression	Deciduous forest	650	6.8	Gravel-sand	Coal	No	Sokolov, Czech Rep.
	65	82.81	23.00	0.92 ± 0.27	3	Regression	Deciduous forest	650	6.8	Gravel-sand	Coal	No	Sokolov, Czech Rep.

Table 1 continued

Reference	Age (y)	C stock (t ha^{-1})	Control C stock (t ha^{-1})	Accumulation rate (t ha^{-1} y^{-1})	n	Fossil c correction method	Vegetation type	MAP (mm)	MAT (°C)	Soil texture	Mined material	Amendments	Location
Frouz and Kalčík (2006)	11.3	N/a	N/a	0.24 ± 0.10	3	Deep layer	Shrubland	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	16.4	N/a	N/a	1.14 ± 0.24	5	Deep layer	Shrubland	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.
	29	N/a	N/a	0.62 ± 0.16	4	Deep layer	Deciduous forest	650	6.8	Clay	Coal	No	Sokolov, Czech Rep.

Fossil C correction methods, by which fossil C is subtracted from total C to determine recently sequestered C, included: radiocarbon dating (radiocarbon); subtraction of data obtained in a young site (young site), or a deep layer (deep layer); comparison between historical and recent contents at the same site (time shift); linear regression of content on age (regression), and a coal-correction equation developed by Amichev (2007) (equation). *MAP* mean annual precipitation, *MAT* mean annual temperature

deciduous forests (2.31 ± 1.02, $n = 15$), but was not significantly different in grasslands versus deciduous forests ($p < 0.05$, LSD post hoc test).

When SOC accumulation was regressed on the age of the site, the nature of the regression differed among vegetation types (Table 2). Because we obtained grassland data only for younger sites (0–30 years old), we compared grassland data with the data from the two forest types within this same age range. For this 30-year period, the rate of SOC accumulation did not change significantly in grassland sites, but significantly increased with age in coniferous forest sites and significantly decreased with age in deciduous forest sites (Table 2). When we compared forest sites using all available data, the relationship between SOC accumulation rate and age of site for coniferous forests was described by a polynomial equation in which accumulation rate reached a maximum of 35 years after reclamation (Table 2). In a similar analysis that used all available data, the relationship between SOC accumulation rate and the age of the site for deciduous and mixed forests reached a maximum after 10–20 years and then tended to decrease logarithmically (Table 2).

Effect of vegetation on the distribution of SOC in the soil profile

The vertical distribution of SOC in the soil profile differed among forest types. The contribution of SOC sequestered in the mineral soil (rather than in the surface organic layer) to the total SOC stock was significantly ($p < 0.05$, *t* test) higher in deciduous and mixed forests than in coniferous forests. The surface organic layer contained 23 % of sequestered SOC under deciduous and mixed forests and 62 % under conifers. This difference was more pronounced than that found in a meta-analysis of afforested agricultural soils and grasslands, which indicated that the percentage of SOC in surface organic layer was 57, 52, and 46 % for *Pinus* spp., deciduous species, and coniferous species, respectively, excluding *Pinus* spp. (Laganiere et al. 2010). The value for conifers was comparable in the two studies because *Pinus* was the most frequent coniferous species in the reclaimed sites of our data set. The lower value for SOC in surface layers under deciduous species in the current study versus Laganiere et al. (2010) may be associated with the high percentage of N-fixing species in our data set (at least 40 % of the deciduous trees in our data set were N-fixing species); N-fixing species produce litter that decomposes relatively quickly (Filcheva et al. 2000; Sourkova et al. 2005; Keskin and Makineci 2009). We cannot compare grasslands in this manner because none of the grassland studies mention a litter layer, fermentation layer, or any other kind of surface organic horizon, which indicates that the contribution of these layers to total SOC accumulation in grassland is low.

Although surface organic layers should be included in the calculations of sequestered SOC (Guo and Gifford 2002; Paul et al. 2002; Laganiere et al. 2010), SOC sequestered in the organic layer is less stable than that in the mineral soil because it is more vulnerable to loss by disturbance (fire, erosion, etc.). It follows that the contribution of organic layers should always be reported along with the total SOC stocks (Vogel 1981; Laganiere et al. 2010).

Recovery of SOC stock to pre-mining level

The degree to which the SOC stock of post-mining soils returned to pre-mining levels was highly variable. However, a large proportion of the sites reached pre-mining SOC stock within 20 years or less after reclamation. Topsoil application subset shows better correlation with time than no topsoil application data (Fig. 2). However, this may be mainly because the topsoil subset is more homogeneous, while no topsoil sites show high variability in the data set. The good chance of SOC recovery is consistent with Schwenke et al. (2000), who estimated that it would take 33 years for the SOC level to increase to the level of the undisturbed native forest in post-mining sites in Weipa, Australia, after topsoil application and the planting of native tree species. However, a general linear model with topsoil application as a categorical predictor and age as a continual predictor did not find any significant effect either for time or topsoil application ($p = 0.942$ for age and 0.808 for topsoil application), so we cannot conclude that topsoil application leads to faster recovery to pre-mining SOC stock.

Rate of SOC accumulation in relation to climate, soil texture, and sampling depth

The SOC accumulation rate was not significantly correlated with precipitation based on analysis of the whole data set or on analysis by vegetation type (data not shown). The rate of SOC accumulation, however, was significantly

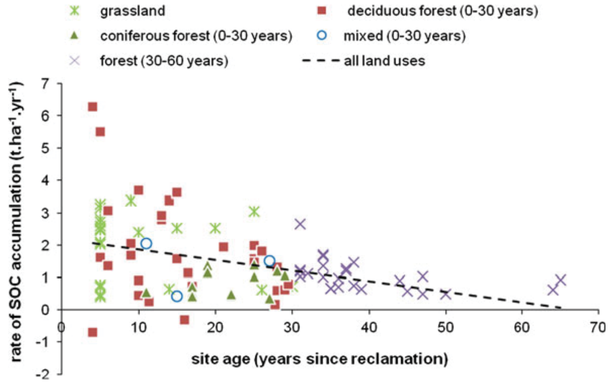

Fig. 1 Rate of SOC accumulation in post-mining soils in relation to vegetation type and the age of the site (all sites are in the temperate zone of the Northern Hemisphere). Regression equations and correlation coefficients for different categories are presented in Table 2

Table 2 Relationship between the rate of SOC accumulation (t ha^{-1} y^{-1}) and the age of the site (years since reclamation) for sites with different types of vegetation

Vegetation type	Regression
Grassland	ns
Coniferous forest, 0–30[a] years	$Y = 0.0436x - 0.0315$ ($n = 12$; $R^2 = 0.3689$; $p < 0.05$)
Coniferous forest, all ages	$Y = -0.0015x^2 + 0.1061x - 0.6575$ ($n = 22$; $R^2 = 0.1959$; $p < 0.05$)
Deciduous forest, 0–30 years	$Y = -0.0956x + 3.44682$ ($n = 27$; $R^2 = 0.281$, $p < 0.05$)
Deciduous and mixed forest, 0–30 years	$Y = -0.0724x + 2.8593$ ($n = 36$; $R^2 = 0.1672$, $p < 0.05$)
Deciduous and mixed forest, all ages	$Y = -0.8614\mathrm{Ln}(x) + 4.0325$ ($n = 50$; $R^2 = 0.2333$; $p < 0.05$)
Forest, 30–60 years	$Y = -0.023x + 1.9573$ ($n = 25$; $R^2 = 0.2403$; $p < 0.05$)
All vegetation types	$Y = -0.0329x + 2.2044$ ($n = 93$; $R^2 = 0.1589$; $p < 0.05$)

[a] Because data for grasslands were only available for younger sites (0–30 years old), we have included 0–30 years categories for forests to facilitate comparisons between sites with grassland and those with forest

related to temperature in sites with coniferous forest and grasslands, i.e., the rate decreased with increasing temperature for conifers and increased with increasing temperature in grasslands (Fig. 3). Deciduous forests show no significant correlation with temperature.

This relationship between temperature, SOC storage, and vegetation type corresponds with natural distribution of grassland, coniferous forest, and deciduous forest (Brown and Gibson 1983). This indicates that for reclamation of post-mining sites, the planted vegetation should be typical for the particular biome in which the post-mining site occurs. In other words, grasses should be planted at warmer sites, conifers at colder sites, and deciduous trees at intermediate sites.

These adverse trends in temperature dependence of SOC storage between coniferous forest and grassland may be related to two different mechanisms involved in the effect of temperature on SOC accumulation. Lower temperatures are associated with lower vegetation productivity resulting in deficient litter input (Karu et al. 2009; Laganiere et al. 2010). On the other hand, higher temperatures have accelerating effect on decomposition (Lal 2005).

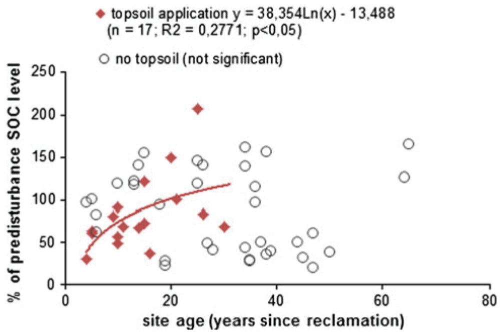

Fig. 2 Return of SOC levels to pre-mining levels in post-mining soils with or without topsoil application as a part of the reclamation practice (all sites are in the temperate zone of the Northern Hemisphere)

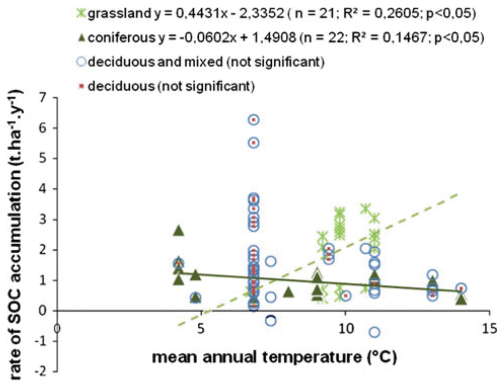

Fig. 3 Rate of SOC accumulation in post-mining soils as related to mean annual temperature and vegetation type (all sites are in the temperate zone of the Northern Hemisphere)

As mentioned earlier, most conifer litter accumulates on the soil surface, while substantial proportions of litter in grasslands accumulate in the mineral soil. In a meta-analysis of agricultural soils, Poeplau et al. (2011) report that accumulation is higher in colder sites if surface organic layers are included in the calculations, whereas the accumulation is higher in warmer sites when only mineral soil is considered. Results on post-mining soils are in agreement with these conclusions, considering that the SOC stocks of coniferous sites are largely formed by litter deposited on the soil surface, whereas the contribution of organic layers in grasslands is very low. This explains why under conifers the decomposability shows greater effect than the production of vegetation, whereas SOC accumulation in grasslands seems to be more input dependent.

Although some studies of agricultural soils have indicated that SOC accumulation may be influenced by clay content or soil depth (Laganiere et al. 2010), it was not related to soil texture or sampling depth in our analysis (data not shown).

Conclusions

This study is the first to summarize SOC accumulation rates in post-mining soils of the northern temperate zone. There are relatively few papers devoted to SOC accumulation and C sequestration in post-mining soils. In addition, comparison of the existing studies is difficult because of: (a) missing bulk density measurements; (b) missing or varying methods for fossil carbon assessment; (c) missing or varying methods for SOC content measurement in topsoil before reclamation; (d) missing or incomplete data on measures of variance (SD, SEM) and number of replicates (n). These factors should be taken into account by authors of future research of post-mining sites. In general, measures of variance and number of replicates should be automatically presented along with mean values in all studies to allow for their future interpretation.

Although more studies are needed, we can report some useful preliminary findings based on our analyses of the studies published so far. In our meta-analysis of post-mining soils in the temperate zone of the Northern Hemisphere, the rate of SOC accumulation was not significantly related to vegetation type. However, further statistical analysis revealed that deciduous trees supported the accumulation of organic matter in the mineral soil, which stabilized the sequestered carbon. The maximum rates of SOC accumulation are reached after 30–40 years in sites with conifers and after 10–20 in sites with deciduous trees; the rates then decline as the sites get older. Accumulation is influenced by temperature. Accumulation decreases with increasing temperature in sites with conifers, but increases with increasing temperatures in grasslands. A large proportion of post-mining sites reach the pre-mining SOC stock within 20 years or less after reclamation.

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Manuscript 2

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Distinguishing recent and fossil organic matter — A critical step in evaluation of post-mining soil development – using near infrared spectroscopy

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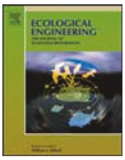

Short communication

Distinguishing recent and fossil organic matter — A critical step in evaluation of post-mining soil development – using near infrared spectroscopy

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ABSTRACT

Content of soil organic carbon (SOC) is an important parameter for monitoring of reclamation success. In coal mine soils, measurements of SOC are affected by fossil of organic matter in the overburden, such as kerogen and coal.

The objective of this study was to assess the potential of near infrared spectroscopy (NIRS) coupled with partial least square analysis (PLS) for quantifying recently formed and fossil organic matter in post-mining soils near Sokolov, Czech Republic. NIR data were acquired from soil samples ($n = 14$), where recent SOC was quantified by ^{14}C-AMS analysis, and from artificial mixtures ($n = 125$) of overburden, coal and material from fermentation (O_e) layer. 12 PLS analyses were performed on spectra, each separately calibrated to total C (C_{tot}), recent C (C_{rec}), coal C (C_{coal}) and kerogen C (C_{ker}). All models produced correlation coefficient of cross-validation RCV > 0.97. When validated using the independent validation set of soils, addition of soil samples into the calibration set improved soil predictions of C_{tot} and C_{rec} (obtained from cross-validation) considerably. All four models for C_{tot} and C_{rec} were classified as successful as indicated by root mean square error ranging from 0.74 to 1.11. Results showed no clear effect of grinding on predictive accuracy; thus, we conclude that particle size <2 mm is sufficient for NIRS. Our results demonstrate the ability of NIRS–PLS to quantify fossil and recent carbon in soils.

1. Introduction

Open pit coal mining has a severe impact on ecosystem. Overburden overlying the coal seam is removed and deposited in heaps leading to distribution of large areas (Bell and Donnelly, 2006). In many cases, overburden material becomes the parent substrate for soil development (Karu et al., 2009; Šourková et al., 2005). Soil organic carbon (SOC) is an important indicator of soil quality (Bodlák et al., 2012) and reclamation success (Courtney et al., 2013). It changes soil structure, sorption properties, affects porosity, water storage, and infiltration rates (Brady and Weil, 1999). Soil organic matter accumulation can lead to sequestration of carbon which can mitigate rising concentration of CO_2 in the atmosphere (Lal, 2004).

In mine soils, besides soil organic matter recently derived from plant residues also fossil forms of organic carbon such as coal or kerogen can be frequently found (Filcheva et al., 2000; Ussiri et al., 2014). Coal rich in aromatic compounds is the most frequent form of fossil organic carbon in coal mining areas (Vindušková and Frouz, 2013). However, the overburden may contain significant amounts of other organic compounds such as kerogen (Kříbek et al., 1998) which is predominantly aliphatic. Fossil organic carbon leads to overestimation of soil organic carbon sequestration. The lack of a generally accepted method for fossil and recent carbon determination severely hampers the evaluation of post-mining soil development, comparison of carbon sequestration among mine soils or comparison of mine soils and natural undisturbed soils (Mukhopadhyay et al., 2013; Vindušková and Frouz, 2013).

The only way to directly quantify recent and fossil carbon in post-mining soils is the radiocarbon (^{14}C-AMS) analysis, introduced by Rumpel et al. (1999), and applied in several studies (Karu et al., 2009; Morgenroth et al., 2004; Rumpel et al., 2003). Radiocarbon method is laborious and costly. There is a lack of a simpler and accessible method for quantifying fossil carbon (Karu et al., 2009).

Cost-effective, non-destructive and simple to use near infrared diffuse reflectance spectroscopy (NIRS) as well as younger mid-infrared spectroscopy (MIRS) has been applied on numerous

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materials such as forages, foods and also soil (Stenberg et al., 2010). When combined with multivariate chemometric techniques, such as partial least-squares (PLS) regression, NIRS can be used for prediction of sample properties based on interaction of particular chemical functional groups with near infrared radiation (Janik et al., 2007).

Soil organic matter has many characteristic absorptions in the NIR (Ben Dor et al., 1997 Michel et al., 2009; Stenberg et al., 2010) which allow estimation of total carbon (TC), as well as different carbon fractions (Janik et al., 2007). However, Pietrzykowski and Chodak (2014) showed that the accuracy of NIRS may be insufficient for the prediction of SOC content in a highly variable data set of mine soils if fossil C is not taken into account during calibration. There has been several attempts to distinguish coal from recent organic matter using NIR or MIRS (Chodak et al., 2007; Michel et al., 2009; Rumpel et al., 2001). No study has yet focused on NIRS application to soils where fossil carbon is found in two chemically different forms.

This paper describes the use of NIRS and PLS for the prediction of TC and recent carbon in soils and investigates the application of NIRS–PLS to distinguish fossil carbon derived from coal or kerogen.

2. Materials and methods

2.1. Geological setting

Study was performed in the Sokolov Brown Coal Basin (NW, Czech Republic) where overburden consists of Miocene lacustrine clay sediments forming the Cypris formation called after a leading fossil *Cypris angusta*. These sediments are characteristic of variable contents of organic matter (2–18% TOC), the bulk of which is kerogen of algal or mixed origin (Kříbek et al., 1998).

2.2. Samples and analytical procedures

A set of 14 composite soil samples were collected from 7 sites at Podkrušnohorská spoil heap (GPS: N 50° 14.234′ E 12° 39.55′). Soils were sampled at the top of mineral soil (0–10 cm) and the 40–50 cm depth. In addition, artificial mixtures were also produced by mixing different amounts of claystone, coal and partially decomposed litter (sampled from fermentation layer at one of the sites with organic carbon content (TOC) of 39.6%). Unweathered samples of coal (TOC = 62.4%) and two types of claystone differing in organic C content (C-poor/C-rich) were collected in a nearby abandoned mine, near intersection with Jiří mine (GPS: N 50°11.836′ E 012°40.199′), from a depth of 50–100 m. C-poor claystone (from the top of the lower part of Cypris formation) is a blue–gray kaolinite clay with a small admixture of siderite (TOC = 4.12%, TIC (inorganic carbon) = 0.51%). C-rich claystone (from the base of the upper part of Cypris formation) is a brown–gray illite–kaolinite claystone with a considerable admixture of siderite (TOC = 13.32%, TIC = 0.01%).

Soil samples were hand-picked to remove visible roots and non-clay rock fragments. Fermentation layer sample (O_e material hereafter) was sieved through a 2 mm mesh. Clay rock fragments and aggregates were crushed and left within the sample – samples were not sieved but crushed and homogenized to prevent underestimation of total soil C (Zabowski et al., 2011). The soil, claystone, coal, and O_e material samples were air-dried and coarse-ground in a IKA Analytical Grinding Mill A 11 and sieved through a 2 mm mesh. After the first NIRS measurement of coarse-ground samples, both soils and artificial mixtures were ball-milled to come through a 0.125-mm mesh (fine-ground hereafter) and measured again.

In studied sites, carbonate content was low (Šourková et al., 2005); therefore, samples were not pretreated to remove carbonates before NIRS. Conversely, carbonates were removed from samples before radiocarbon dating using the “rinse method” (Brodie et al., 2011).

For the artificial mixtures, the two types of claystone were mixed in 5 different ratios (1:0, 0:1, 1:3, 3:1, 1:1). After that, both O_e material and coal were added to each of these mixtures in ratios 0:100, 1:100, 2:100, 5:100 and 30:100; thus, 125 ($=5^3$) mixtures were made. The content of total organic carbon (C_{tot}) in mixtures was calculated as a sum of C_{rec}, C_{coal} and C_{ker} assuming all organic C in claystone was kerogen, all C in O_e was recent and all C in coal was coal. Total organic carbon (TOC) content in mixture materials and soils was calculated as a difference of total carbon (TC) and total inorganic carbon (TIC) determined using elemental analyzers ELTRA CS 530 and ELTRA CS 500 with a TIC modul, respectively.

^{14}C radiocarbon AMS analysis of soils was carried out in the University of Georgia’s Center for Applied Isotope Studies. Content of recent carbon in soils was calculated according Rumpel et al. (2003) as TOC multiplied by ^{14}C activity measured in samples divided by ^{14}C activity of recent organic matter for which 115 pMC was used as in earlier studies (Morgenroth et al., 2004; Rumpel et al., 1999).

2.3. NIRS

NIR spectra were recorded on an Antaris II FT-NIR spectrophotometer (Thermo Electron Corporation, Madison, USA), equipped with an interferometer, an integrating sphere working in diffuse reflection, plus an indium and gallium arsenide (InGaAs) detector. Approximately 30 g of each sample was placed in a 5 cm diameter spinning cup and scanned 64 times in a spectral range from 10,000 to 4000 cm^{-1} (equivalent to 1000–2500 nm) in 2 cm^{-1} intervals. The spectra were converted to absorbance units by ($A = \log$ [1/reflectance]). The 64 sub-scans were averaged to produce the final sample spectrum using software Omnic 7.3 (Nicolet Instruments Co., Madison, USA). No transformation of spectra was performed, since the untransformed spectra provided satisfactory calibrations.

Partial least square (PLS) regression was used to establish calibrations for C_{tot} (%), C_{ker} (%), C_{coal} (%), and C_{rec} (%). Separate models were developed for spectra collected after coarse and fine grinding. Where data for soils were available (C_{tot}, C_{rec}), separate models were developed using only the mixtures ($n = 125$) or including also the soil spectra ($n = 125 + 14 = 139$). For C_{coal} and C_{ker}, soils could not be included in calibration since their values in soils are unmeasurable. The calibrations were validated by full (hold-out-one) cross-validation. The optimum number of PLS factors used in calibration was determined using the prediction residual error sum of squares (PRESS) from the cross-validation procedure. Outliers, i.e., spectra different from the other spectra in calibration set, were identified as those with large residuals, i.e., differences between reference and predicted value (Michel et al., 2009).

All calibration models were described by a correlation coefficient (R), correlation coefficient of cross-validation (RCV), root mean square error of calibration (RMSEC), and root mean square error of cross-validation (RMSECV). To quantify the predictive capabilities of our models exclusively for soil samples, more indicators, i.e., RMSE(C)V, RPD, RSC and EF (described further) were calculated using only the predicted and measured values of C_{tot} and C_{rec} in soils. For these four parameters, negative predictions (<0) were converted to 0. Furthermore, in the calculation of these parameters, the soil outliers excluded from the calibration set were included again in order not to overrate the potential of NIRS.

Table 1
Model parameters of calibration and cross-validation.

Component	Calibration set	Grinding	Concentration range (%)	Region (nm)	Outliers	Calibration		Cross-validation		Factors
						R	RMSEC[a]	RCV	RMSECV[b]	
C_{tot} (%)	Mixtures	Coarse	4.12–20.86	1315–2455	0	0.998	0.24	0.997	0.27	7
	Mixtures	Fine	4.12–20.86	1315–2455	0	0.994	0.41	0.990	0.54	6
	Mixt. + soils	Coarse	4.12–20.86	1315–2455	4 soils	0.997	0.30	0.996	0.34	8
	Mixt. + soils	Fine	4.12–20.86	1315–2455	2 (1 soil)	0.994	0.44	0.992	0.52	8
C_{rec} (%)	Mixtures	Coarse	0–3.97	1315–2455	0	0.997	0.10	0.995	0.14	8
	Mixtures	Fine	0–3.97	1315–2455	1	0.997	0.12	0.987	0.24	10
	Mixt. + soils	Coarse	0–10.62	1937–2494	2 soils	0.998	0.25	0.984	0.30	10
	Mixt. + soils	Fine	0–10.62	1937–2494	1	0.989	0.13	0.977	0.37	8
C_{clay} (%)	Mixtures	Coares	3.29–13.32	1686–2455	0	0.999	0.11	0.998	0.18	9
	Mixtures	Fine	3.29–13.32	1686–2455	4	0.999	0.24	0.997	0.22	8
C_{coal} (%)	Mixtures	Coarse	0–6.25	1315–2455	0	0.994	0.23	0.991	0.30	8
	Mixtures	Fine	0–6.25	1315–2455	3	0.995		0.988	0.35	8

[a] Root mean square error of calibration.
[b] Root mean square error of cross-validation.

When calibration set included only mixtures and soils served as a validation set, RPD, i.e., ratio of standard deviation of the laboratory results (of validation set) to standard error of validation (Williams, 1987) was calculated. An RPD > 2.5 is usually considered good while a value between 2.5 and 2 is approximate and a value below 2 is insufficient (Bornemann et al., 2008). Where a validation set was not available, RSC (ratio of standard deviation of the laboratory results to standard error of cross-validation) was used as an alternative to RPD (Chang et al., 2001). An RSC > 2 indicates successful prediction and values >1.4 are considered satisfactory (Michel et al., 2009). Additionally, modelling efficiency (EF) was calculated (Loague and Green, 1990). The closer is the EF value to 1, the better is the model. A successful prediction is characterized by an EF value >0.90. An EF value >0.70 indicates satisfactory prediction (Michel et al., 2009). The best treatment (i.e., number of outliers excluded, spectral range) was chosen based on the highest EF by trial and error.

3. Results and discussion

3.1. NIRS

Parameters of calibration and cross-validation demonstrate a close relationship between measured and predicted values (R values higher than 0.9) (Table 1). Models based only on artificial mixtures produce better RCV values as the mixtures are likely to be more homogeneous than natural soils. The effect of fine grinding is inconsistent (Table 1).

However, in calculation of parameters in Table 1, predictions for artificial mixtures played a major role and thus could lead to overestimation of the potential of NIRS for soil analysis. To assess the performance of NIRS for soils alone, further parameters were calculated taking into account only predicted and measured values of soil samples (Table 2). Table 2 shows that models calibrated using only the mixtures provided poor predictions for C_{tot}. This is indicated by RPD values <2, low EF values and high error (RMSEV). For $C_{rec\text{-}fine}$, mixtures provided better calibration (EF = 0.60) and for $C_{rec\text{-}coarse}$ model produced already satisfactory results with EF > 0.70. For both C_{rec} and C_{tot}, addition of soil samples to calibration improved the performance of models considerably. When all soil samples were included in the calibration, all models yielded EF ≥ 0.70 indicating satisfactory predictions (Michel et al., 2009) and both $C_{tot\text{-}fine}$ and $C_{rec\text{-}fine}$ had already highly successful predictions with EF = 0.94 and EF = 0.95, respectively. After removing some of the soil outliers, the prediction of both C_{rec} and C_{tot} in coarse-ground samples was improved and both models could also be classified as successful according to EF. Again, no clear effect of fine grinding was detected – fine grinding produced comparable results for C_{rec}, but less accurate results for C_{tot}. It needs to be said that when included in the calibration set, almost all soil samples were detected as spectral

Table 2
Soil-based statistical parameters for evaluation of predictive accuracy. Parameters were calculated using soil values only (n = 14). For each component and grinding pretreatment, 3 models were compared differing in the size of calibration set.

Component	Grinding pretreatment	Calibration set	n	RMSEV[a]	RMSECV[b]	EF[c]	RPD[d]	RSC[e]	Mixture outliers	Soil outliers
C_{tot}	Coarse	Mixtures	125	10.04		−7.88	0.34			
C_{tot}	Coarse	Mixt. + all soils	139		1.43	0.82		2.36		
C_{tot}	Coarse	Mixt. + soils – ignored soil outliers	137		1.28	0.87		2.64		2
C_{tot}	Fine	Mixtures	125	7.64		−4.14	0.44			
C_{tot}	Fine	Mixt. – outliers + all soils	138		0.86	0.94		3.93	1	
C_{tot}	Fine	Mixt. – outliers + soils – outliers	137		0.85	0.94		3.97	1	1
C_{rec}	Coarse	Mixtures	125	1.69		0.73	1.93			
C_{rec}	Coarse	Mixt. – outliers + all soils	138		1.61	0.76		2.03	1	
C_{rec}	Coarse	Mixt. + soils – ignored soil outliers	137		0.74	0.95		4.41		2
C_{rec}	Fine	Mixtures	124	2.06		0.60	1.59		1	
C_{rec}	Fine	Mixt. – outliers + all soils	138		0.70	0.95		4.65	1	
C_{rec}	Fine	Mixt. + soils – ignored soil outliers	n/a		n/a	n/a		n/a		

[a] Root mean square error of validation.
[b] Root mean square error of cross-validation.
[c] Modelling efficiency.
[d] Ratio of standard deviation of the laboratory results (of validation set) to standard error of validation.
[e] Ratio of standard deviation of the laboratory results to standard error of cross-validation.

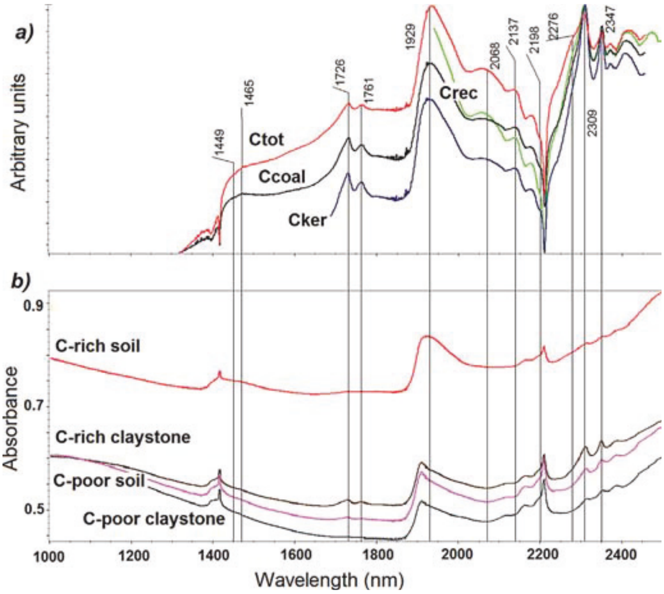

Fig. 1. (a) The first loading vectors of C_{tot},C_{rec}, C_{coal}, C_{ker} calibrations along with (b) an example of soil spectra and spectra of claystones. C_{rec} content of presented C-poor and C-rich soil is 9.67 and 0.09 wt%, respectively. Major bands are marked by line and wavelength (nm). Assignment of major bands can be summarized as follows (after Ben Dor et al., 1997; Stenberg et al., 2010; Michel et al., 2009): 1449 4ν of C=O, carboxylic acids; 1465 OH in water ($\nu_2 + \nu_3$); CH$_2$, cellulose/lignin/starch/pectin; 1726 and 1761 2ν of aliphatic C—H stretch, cellulose/lignin/starch/pectin/wax/humic acid; 1929 OH in water ($\nu_1 + \nu_3$), 3ν of —C=O and of —COOH, C=O of ketonic carbonyl, CONH$_2$, cellulose/lignin/glucan/pectin/wax/humic acid; 2068 and 2137 3ν of aromatic C=C, COO—hydrogen bond, C=O, cellulose/glucan/pectin; 2198 3ν of aromatic C=C, starch/lignin/wax/tannins; 2276 combination of O—H stretch and C—O of cellulose, combination of C—H stretch and CH$_2$ deformation of starch; 2309 3ν of aliphatic C—H, aromatic ring stretch, humic acid/wax/starch; 2347 3ν of aliphatic C—H, cellulose/lignin/glucan.

outliers, i.e., spectra distinctly different from an average spectrum. Although it is usually recommended to exclude spectral outliers from the calibration, we wanted to leave as many soils in the calibration set as possible. Since the spectra of mixtures represent the major part of calibration set, it is understandable that the minor soil spectra are detected as outliers. This effect would most likely be minimized if more soil samples were used in the calibration compared to mixtures.

To assess if they could also be predicted in soils, C_{coal} and C_{ker} were predicted by the models developed using the mixtures (data not shown). It was impossible to test if the predictions of C_{ker} and C_{coal} were reasonable, because their measured values were unknown. However, predicted values were at least compared with estimates of total fossil carbon calculated as the difference between C_{tot} and C_{rec} in soils. Realistic estimates were obtained only for C_{coal} in coarse-ground samples. In other cases, models lead to overestimation.

3.2. NIRS accuracy

Calibrations give a reasonable result considering the small number of calibration soil samples.

Our results are comparable to those reported by other authors who applied NIRS (Michel et al., 2009) or MIRS (Bornemann et al., 2008) on soils or similar materials to quantify different carbon pools. Compared to Michel et al. (2009), our results are slightly less accurate, but this well corresponds with their larger data set ($n = 432$) and larger number of excluded outliers (ranging 22–31). Above that, their data set includes only artificial mixtures and no soils leading to higher homogeneity. Our results as indicated by RPD and EF are comparable or better than those of Bornemann et al. (2008) who recommends MIRS to quantify black carbon with RPD values ranging from 1.64 to 2.31 and EF values ranging from 0.63 to 0.81. This can be again justified by higher heterogeneity of their data set that encompassed soil samples from different continents.

We want to emphasize that the great properties of predictions presented above can be well expected due to the local scale of calibration (Janik et al., 2007; Stenberg et al., 2010). Our model could not be as a whole transferable to e.g., other post-mining sites. Such application would require a separate calibration. Also, for regular use, further validation and calibration using a higher number of soil samples would be needed. Even though the models could not yet be used regularly, their parameters indicate that the method offers a good potential. This can be safely stated about C_{tot} and C_{rec}. In case of C_{coal}, and C_{ker} models developed using only the mixtures overestimated both components in soils. However, as similar predictions (by models developed only on mixtures) for C_{tot} and C_{rec} produced also poor results, we may hypothesize, that if also soil samples could be included in the calibration set, C_{coal} and C_{ker} could also be successfully predicted in soils. This, however, will remain unclear until a method that would be able to quantify coal and kerogen C in soils separately is developed.

3.3. Effect of particle size

The observed little effect of finer grinding on predictive ability of NIRS is in accordance with findings of Nduwamungu et al. (2009), who concluded that sample fineness of 2 mm was sufficient since finenesses of 0.2, 0.5, or 1.0 mm did not improve calibration accuracy. Similarly, Fystro (2002) observed no significant effect, even reporting slightly increased prediction error for ground (>0.5 mm) samples compared to sieved (4 mm) samples. Conversely, Barthès et al. (2006) received more accurate predictions after grinding compared to sieving (2 mm). They explained these contradictory results as an effect of different texture in studied soils – in their aggregated clay soils, grinding leads to better homogenisation of sample by crushing the aggregates. We can thus assume that in our soils, even though having high clay content, aggregates were already sufficiently crushed by low-intensity grinding.

3.4. Spectral characteristics

The first loading vectors were analyzed for each component (Bornemann et al., 2008). In the spectrum for C_{rec} (Fig. 1a), the two dominant doublets around 1700 nm (1726 and 1761 nm) and around 2300 nm (2309 and 2347 nm) are combinations and overtones of the C—H group which is characteristic of different organic substances, such as cellulose, lignin, starch, pectin, wax, and humic acids. The dominant peak around 1929 nm is associated with water, but also with —COOH and—C=O groups and its effect is also apparent in the spectra of a C-rich and C-poor soil (Fig. 1b). Additional major signals can be addressed to aromatic C=C, COO—H and C=O groups (2068 nm), starch and cellulose (2276 nm), water and CH_2 group (1465 nm), and carboxylic acids (1449 nm).

The loading spectrum for C_{coal} is dominated by the peak at 1900 nm, which is associated with water (OH $v_1 + v_2$) and also with —C=O in carboxylic group (—COOH), ketones and amides ($CONH_2$) (Ben-Dor et al., 1997). The importance of this band for coal C calibration has been already reported by Michel et al. (2009). Aliphatic C is again indicated by bands at 1726, 1761, 2309 and 2347 nm. The most intensive peak at 2309 nm is also positively related to vibration of aromatic ring. Signal at 2276 nm is also visible and was previously ascribed to polysaccharides in lignite (Michel et al., 2009). The lower influence of this peak in calibration of our coal corresponds with its higher rank compared to lignite.

In Fig. 1b, it is visible even to naked eye that the C-poor claystone has weaker peaks in the two aliphatic regions than the C-rich one. This is in accordance with previous findings that the studied lacustrine sediments have strong aliphatic character due to their algal origin (Kříbek et al., 1998). Also, the loading spectrum of C_{ker} correctly does not contain carbonate signals (2380, 2160, 1990, and 1870 nm) (Ben-Dor and Banin, 1990) and kaolinite signals that are apparent as doublets near 1400 and 2200 nm in the claystone spectrum (Stenberg et al., 2010). The spectrum for C_{tot} is similar to those of C_{rec}, C_{coal} and C_{ker}, except that 1900 and 2068 nm peaks are stronger indicating larger proportion of polysaccharides (Fig. 1a).

4. Conclusions

Near infrared spectroscopy coupled with partial least-squares regression has the potential to become a rapid and cost-effective tool for soil organic carbon measurement in monitoring and assessment of reclamation activities.

Total amount of C and recent soil organic carbon can be successfully predicted in soils. Adding a relatively small amount of soils to the calibration set of artificial mixtures improved predictions considerably. Both coal and kerogen carbon can be successfully predicted in artificial mixtures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2014.09.086.

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Methodological comparison for quantitative analysis of fossil and recently derived carbon in mine soils with high content of aliphatic kerogen

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ABSTRACT

In mine soil, quantification of soil organic carbon (OC) derived recently from biomass decomposition is complicated by the presence of fossil (geogenic) C derived from coal, oil shale, or similar material in the overburden. The only reliable method for such measurement is ^{14}C analysis (i.e. radiocarbon dating) using instrumentation such as accelerator mass spectrometry, which is too expensive for routine laboratory analysis. We tested two previously used and two new methods for recent C quantification and compared them with ^{14}C AMS radiocarbon dating as a reference using a set of soil samples ($n = 14$) from Sokolov, Czech Republic: (i) ^{13}C isotope ratio composition, (ii) cross polarization magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy, (iii) near infrared spectroscopy (NIRS) coupled with partial least squares regression and (iv) Rock–Eval pyrolysis. Conventional methods for OC determination (dry combustion, wet dichromate oxidation, loss-on-ignition) were also compared to quantify any bias connected with their use. All the methods provided acceptable recent carbon estimates in the presence of mostly aliphatic fossil C from kerogen. However, the most accurate predictions were obtained with two approaches using Rock–Eval pyrolysis parameters as predictors, namely (i) S_2 curve components and (ii) oxygen index (OI). The S_2 curve approach is based on the lower thermal stability of recent vs. fossil organic matter. The OI approach corresponded well with ^{13}C NMR spectra, which showed that samples rich in recent C were richer in carboxyl C and O-alkyl C. These two methods showed the greatest potential as routine methods for recent C quantification.

1. Introduction

Soil organic matter (SOM) has a significant positive impact on soil functioning by providing chemical energy and essential nutrients (Tiessen et al., 1994). It also contributes to soil cation exchange capacity, buffering capacity and influences soil structural properties, such as stability, water retention and thermal properties. Different pools of OM contribute differently to these functions (Baldock and Skjemstad, 2000).

In mine soil (Vindušková and Frouz, 2013) and some natural soils (Graz et al., 2011; Clouard et al., 2014), OM derived recently from vegetation is present with fossil OM in coal or kerogen. The contribution of such geogenic OC (fossil C hereafter) content to the above soil properties is poorly understood. The main reason is that quantification of fossil C remains a methodological challenge.

Moreover, an increase in soil C storage in mine soil has been studied as a potentially significant sink for atmospheric CO_2 (e.g. Sperow, 2006; Vindušková and Frouz, 2013). To assess soil quality development and the sequestration potential of mine soil properly, a reliable method for quantitative analysis of recently derived C in the presence of fossil C is needed. Also, the amount of fossil C reintroduced into the modern C cycle remains poorly quantified (Butman et al., 2014), again due to a lack of a reliable method for fossil C quantification in modern environments.

Different methods based on radiocarbon dating, spectroscopy and reactivity have been proposed, with a focus on coal C (reviewed by Ussiri et al., 2014). The only accurate and widely accepted method is ^{14}C analysis, such as accelerator mass

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spectrometry (AMS) radiocarbon dating; however, it is too expensive for routine use. The method is considered to be accurate for young mine soils developing from overburden material; analysis of mine soils on old stored topsoil material is more problematic. The contribution of fossil C to total organic carbon (TOC) content of mine soil can be substantial. Rumpel et al. (2001) reported that lignite-derived fossil C accounted for 13–96% of TOC in recultivated mine soil afforested without topsoil application. In mine soil in eastern Ohio, the fossil C contribution to TOC ranges between 10% and 17% with topsoil application (Jacinthe and Lal, 2007).

The situation in our study area – Sokolov, Czech Republic – is more complex since, in addition to small amounts of coal, the overburden contains a significant amount of sedimentary OM, most of which is kerogen of algal origin and is predominantly aliphatic, unlike aromatic coal (Křibek et al., 1998; Frouz et al., 2011). This kerogen C is finely dispersed in the parent rock and consequently also in the soil, so cannot be hand picked, in contrast to fragments of coal. It has different chemical and physical properties from coal C and so requires different treatment. This was shown for example by Hammes et al. (2007), who found that part of both coal and kerogen C can interfere with various black carbon quantification methods but each material interacts differently with each type of method. The amount of fossil C in our study area has been estimated as the carbon content of the C horizon (Frouz et al., 2009). The approach has been used elsewhere (Reintam et al., 2002), but the accuracy of such estimates is unknown.

Rock–Eval analysis is a pyrolysis method standardized for source rock characterization and evaluation in oil and gas exploration (Espitalié et al., 1977). Increasingly, it is being applied to soil (Disnar et al., 2003; Sebag et al., 2006; Hetenyi and Nyilas, 2014) and recent sediments (Marchand et al., 2008; Delarue et al., 2013; Siavalas et al., 2013) and has been proposed as a cost effective tool for bulk characterization of SOM, as well as for determination of OC source (Carrie et al., 2012) and biogeochemical stability (Saenger et al., 2013). However, it has not been applied for quantitative analysis of fossil and recent C.

In a previous short communication, we introduced the potential of near infrared spectroscopy (NIRS) for the quantification of recent and fossil C (Vindušková et al., 2014). The aims of the present study were to:

(i) Quantify the bias connected with soil OC determination methods (dry combustion, wet dichromate oxidation, loss-on-ignition) and their correction by way of subtraction of subsoil C content from the topsoil content.
(ii) Apply methods of recent and fossil C quantification proposed in the literature in a new situation where fossil C is dominantly aliphatic, i.e. ^{13}C isotope ratio method (Chabbi et al., 2006; Ussiri and Lal, 2008) and cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy (Rumpel et al., 1998) and test Rock–Eval pyrolysis for this purpose for the first time.
(iii) Compare the approaches, including near NIRS.

While a number of studies have focused on coal C, our study may be useful for situations where other sources of aliphatic fossil C similar to kerogen can be found. Such sites could typically be oil shale mines (Karu et al., 2009), coal mines with overburden containing sedimentary OM, and also soils, and fluvial or estuarine sediments formed by weathering of C rich rocks (Graz et al., 2011).

2. Geological setting

The study area consists of 7 sites at Podkrušnohorská mine spoil heap near Sokolov, Czech Republic (50°14′09 N, 12°39′05 E) covering reclaimed and unreclaimed sites 10–51 yr old. No topsoil had been applied after heaping the overburden; therefore, the overburden represents the parent substrate for all of the mine soils. In the study area, the overburden consists of tertiary clays rich in kerogen of algal origin (Types I and II) which is characteristic of a high aliphatic C content. They contain 2–10%, sometimes even 15% OC (Křibek et al., 1998).

3. Material and methods

Soil samples (n = 14) were collected from 7 sites and two depths – topsoil (0–10 cm) and subsoil (40–50 cm). In addition, model material (two types of claystone differing in TOC content, subbituminous coal and O_e material sampled from the fermentation layer at one of the sites) were also sampled and analysed to provide insight into the character of the fossil and recent OM. Details of the study site, sampling, sample preparation, TOC analysis and ^{14}C AMS analysis pretreatment are described by Vindušková et al. (2014). Briefly, soil samples were acid-washed to remove carbonate prior to both ^{14}C and ^{13}C/^{12}C analysis.

3.1. Total carbon (TC) and total nitrogen (TN)

TOC was calculated as the difference between TC and total inorganic C (TIC), both determined from dry combustion and dry combustion with a TIC module, respectively. TN was determined on dry samples using an elemental CN analyzer (EA 1108, Carlo Erba Instruments).

3.2. ^{14}C AMS radiocarbon dating

For ^{14}C AMS radiocarbon dating, the content of recent C in soils was calculated as follows:

$$C_{rec} = TOC \times (C_{rec}/TOC) \tag{1}$$

where C_{rec}/TOC is the proportion of recent C in the OC pool, calculated from Eq. (2; Rumpel et al., 2003):

$$C_{rec}/TOC = \frac{pMC_{TOC}}{pMC_{rec}} \tag{2}$$

where pMC_{TOC} is the ^{14}C activity and pMC_{rec} the ^{14}C activity of recent OM. For pMC_{rec}, an average value of 115 pMC was used as per earlier studies (Rumpel et al., 1999; Morgenroth et al., 2004; Fettweis et al., 2005).

3.3. Loss-on-ignition (LOI)

LOI is a widespread method due to its low cost and simplicity and allow larger amounts of samples to be tested than with the dry combustion method. However, its accuracy and OM to C conversion factors are controversial (Pribyl, 2010). It was performed by heating four 2 g sub-samples in a muffle furnace for 5 h, after which the weight of the residual ash was recorded. LOI was calculated as the wt% lost on ignition.

LOI for the four materials was measured at several temperatures (250, 350, 450, 550, 650, 750 and 850 °C). Soil samples were then analysed at lower temperature (150, 200, 250, 350 and 550 °C) since LOI of the model materials showed that the ideal temperature might lie near 250 °C. The mass of material lost was then converted to % carbon via a conversion factor 1.724 (Pribyl, 2010).

3.4. Wet dichromate oxidation (C_{ox})

C_{ox} (modified Tyurin method) is a wet chemistry method used in Central and Eastern Europe. It is similar to the Walkley Black method (Walkley and Black, 1934), but includes 45 min heating at 125 °C to facilitate the digestion of OC with dichromate. The excess dichromate is then measured titrimetrically by adding ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$]. Soil samples, model materials and coal were analyzed in triplicate, quadruplicate and septuplicate, respectively.

3.5. ^{13}C isotope ratio method

The sample $^{13}C/^{12}C$ ratio was measured using a stable isotope ratio mass spectrometer and expressed as:

$$\delta^{13}C(‰) = \left[\left(^{13}C/^{12}C_{\text{sample}} \div {}^{13}C/^{12}C_{\text{standard}}\right) - 1\right] \times 100$$

where the standard is Peedee belemnite. The error was < 0.1‰.

3.6. Solid state ^{13}C NMR

Solid-state ^{13}C NMR spectra were measured at 11.7 T using a Bruker Avance III HD 500 US/WB NMR spectrometer (Karlsruhe, Germany, 2013) in 7 mm ZrO_2 rotors at a spinning frequency of 5 kHz. The ^{13}C CPMAS spectra were measured with a CP contact time of 2 ms, TOSS (total suppression of spinning sidebands) sequence consisting of a set of 180° ^{13}C pulse of 8 s, repetition delay of 5 s, and the number of scans ranged from 2 to 15 k to reach acceptable signal/noise ratio. During the detection of the ^{13}C NMR signal the high power dipolar decoupling SPINAL-64 was applied. The frictional heating of the spinning samples (Brus, 2000) was mitigated by active cooling, and temperature calibration was performed with $Pb(NO_3)_2$. An external standard (glycine) was used to calibrate the ^{13}C scale (176.03 ppm – low field carbonyl signal).

For quantification, the spectra were integrated using Origin 8.5 software. The chemical shift regions 0–45, 14–110, 110–160, 160–220 ppm were assigned to alkyl C, O-alkyl C, aromatic C and carboxyl C, respectively (Wilson, 1987).

Schmidt et al. (1996) proposed the following signal intensity ratio as a fingerprint for brown coal particles in soil samples:

$$A = \frac{(\text{alkyl C} + \text{aromatic C})}{(\text{O-alkyl C} + \text{carboxylic C})}$$

We used an inverse ratio A'_1 that would be positively related to recent OM in our samples and, since fossil C in our area is assumed to be dominantly aliphatic (Kříbek et al., 1998), we also calculated a modified ratio A'_2 leaving out the aromatic C term:

$$A'_1 = \frac{(\text{O-alkyl C} + \text{carboxylic C})}{(\text{alkyl C} + \text{aromatic C})} \qquad A'_2 = \frac{(\text{O-alkyl C} + \text{carboxylic C})}{\text{alkyl C}}$$

Recent carbon relative content was then regressed against A'_1 and A'_2 ratios.

3.7. NIRS

Details of NIRS measurements are described by Vindušková et al. (2014). Briefly, spectra were acquired from 14 soil samples and 125 artificial mixtures of overburden, coal and O_e material. Two intensities of grinding were tested (coarse < 2 mm, fine < 0.125 mm). Partial least squares regression analysis was performed ($n = 125$ or $n = 139$) and calibrated to recent C content (wt %). Recent C values predicted from NIRS included in method comparison were obtained by leave-one-out cross validation.

3.8. Rock–Eval

Rock–Eval pyrolysis was performed using a Rock Eval 6 ('Turbo model', Vinci Technologies, France). A detailed description of the method is given by Espitalié et al. (1977), Lafargue et al. (1998) and Disnar et al. (2003). Briefly, it involves two successive steps. The sample is first subjected to pyrolysis under an inert (N_2) atmosphere with a temperature increase of 30 °C/min in a 200–650 °C range. The pyrolysis products are measured continuously – the free hydrocarbons (S_1) and hydrocarbons released during pyrolysis (S_2) are measured with flame ionization detection (FID; mg HC/g) and the oxygenated compounds (S_3CO_2 and S_3CO fraction, mg CO_2/g, mg CO/g, respectively) are measured with an IR detector. In the second step, the remaining sample is heated under an O_2 atmosphere to oxidize the residual carbon over a range of 400–850 °C. The evolved CO and CO_2 are measured (S_4CO and S_4CO_2) and, when integrated, represent the residual carbon (RC, wt%) fraction. Integration of S_3CO_2 and S_3CO curves gives pyrolysable carbon (PC, wt%). TOC is calculated as RC + PC. The temperature at the maximum in the S_2 curve is called T_{peak}.

The hydrogen index (HI; mg hydrocarbon/g TOC) is calculated as the amount of hydrocarbons generated during pyrolysis normalized to the amount of OC (Lafargue et al., 1998). Three oxygen indices are calculated as $OICO = S_3CO/TOC \times 100$, $OICO_2 = S_3CO_2/TOC \times 100$, $OIRE6 = [(16/26 \times OICO) + (32/44 \times OICO_2)]$. Here, OI refers to OIRE6.

The S_2 curves were integrated using R software, following the procedure described by Gillespie et al. (2014). The temperature regions 205–280, 280–340, 340–400, 400–460, 460–550 and 550–650 °C were assigned to F1a, F1b, F2, F3, F4 and F5, respectively. These indices are comparable to standard indices calculated from deconvolution used in previous studies (Sebag et al., 2006). A sum of the first four components of the S_2 curve (F1a + F1b + F2 + F3) was calculated and used to estimate recent C relative content using linear regression.

3.9. Method comparison

For the comparison of different methods for recent and fossil C quantification, we converted all approaches to recent C values (wt %) and compared them with recent C calculated from ^{14}C radiocarbon dating. The fossil C could be simply calculated as TOC – recent C values (wt%). Whenever regression was used to predict C_{rec}/TOC (^{13}C isotope ratio, NMR, Rock–Eval), leave-one-out cross validation was used in order to simulate the usage of the proposed regression on an unknown sample and not to overestimate the potential of the method. Negative predictions were converted to zero. Where any outlier was excluded from the calibration (^{13}C isotope ratio method), it was included again in biplots of measured and predicted values as well as in the *t*-test and root mean square error (RMSE) calculation in order not to overrate the method.

The calculated C_{rec}/TOC value was then used to calculate recent C content using Eq. 1. RMSE was used to assess accuracy of a method:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n}}$$

where y_i are values obtained from ^{14}C dating, $\hat{y}_i$ values predicted using the tested method and n is the number of samples.

Furthermore, a paired *t*-test was also performed for the values of tested and reference method to assess if there was any consistent bias (constant difference) between the methods (Smith et al., 1997).

4. Results and discussion

4.1. Total, recent and fossil carbon content, C:N ratio

Radiocarbon analysis showed that fossil C content varied among sites (Fig. 1). It accounted for 26–99% of TOC in the soils. In topsoil and subsoil samples it ranged from 26% to 99%, and from 93% to 99% of TOC, respectively. The absolute fossil C content for topsoil was 2.1–6.0 wt% C and 2.6–5.6 wt% for subsoil. However, fossil C content did not differ significantly between topsoil and subsoil at the same site (paired *t*-test, $p > 0.05$). This confirms previous assumptions that fossil C in topsoil can be estimated from the OC content of subsoil (Frouz et al., 2009). The accuracy of the approach is discussed in Section 4.8.

A negative non-significant correlation was found between C:N ratio (Table 1) and recent C relative content. Ussiri and Lal (2008) suggested that C:N could be an estimator for coal C content. They found that soils without coal C content had C:N ranging from 9.6 to 10.6, whereas the tested coal itself had a value of 50.7. Artificial mixing of coal with the soil caused a corresponding increase in the value. C:N could not be used as an estimator of relative recent C content of our samples, since it differed significantly between coal and claystone and even between the two types of claystone.

4.2. LOI

LOI of model materials at different temperature is presented in Fig. 2. This confirmed that, when it was performed at a temperature conventionally used for agricultural soils in the Czech Republic (550 °C; Zbíral, 2002), the weight of both coal and claystone changed considerably. The changes are most likely related to the oxidation of OM in both materials. Koide et al. (2011) also recognized that, with 550 °C, the organic portion of biochar is thermally oxidized and they used this fact to adapt LOI for biochar quantification in field soils. Moreover, the use of LOI is generally not recommended for clay-rich soil (Schumacher, 2002), because of the loss of structurally bound water from claystone during ignition. Moreover, loss of carbonate from the sample may also add to LOI values. However, for our samples, loss on ignition from coal and claystone was reduced significantly by decreasing the temperature to 250 °C.

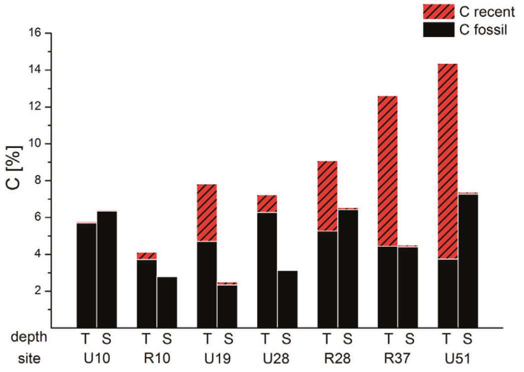

Fig. 1. Fossil and recent carbon (wt%) in mine soils near Sokolov, Czech Republic. Each column represents a soil sample. Samples were collected from seven sites at two depths – topsoil (T, 0–10 cm) and subsoil (S, 40–50 cm). Site names indicate reclaimed (R) and unreclaimed (U) sites and their age (yr since reclamation or overburden heaping at unreclaimed sites).

Amichev (2007) suggested that bituminous coal and recent OM can be distinguished by heating at 375 °C for 24 h (which oxidizes recent OM but not coal). Our results show that similar conclusions can be only site-specific and that thermal separation from recent OM is difficult for coals of low rank.

Measurement of LOI for soils at 150, 200, 250, 350 and 550 °C (Supplementary Fig. S1), showed that the closest estimate of recent C was obtained at 200 °C. However at this temperature, C-poor samples were overestimated and C-rich samples underestimated. Use of the conventional temperature (550 °C) led to an overestimation of recent C by > 8 wt%. Our findings correspond with a thermogravimetric study of Pallasser et al. (2013), who concluded that LOI is best constrained to temperatures from 200 to 430 °C, especially where clay content is high. When using LOI to separate recent and fossil C, neoformation of thermally resistant aromatic C from recent OM can be expected due to incomplete combustion, leading to overestimation of fossil C.

4.3. Wet dichromate oxidation (C_{ox})

Results from wet dichromate oxidation (modified Tyurin method) are presented in Table 1. For the model materials, C_{ox} values were similar to values from dry combustion (TOC), with somewhat higher C_{ox} values for O_e material and coal; however, this could be an effect of high error for C_{ox} with these samples. For soil samples, a paired *t*-test on the C_{ox} values and TOC measured from dry combustion showed that there was no significant difference in the means of the two sets of results ($p > 0.05$). However, for topsoil samples alone, paired *t*-test indicated that C_{ox} values were significantly lower than TOC (mean difference 0.65). For subsoil samples alone, C_{ox} was insignificantly lower. These results indicate that the wet dichromate oxidation probably did not react with the whole range of recent OM in the samples; this corresponds with a previous comparison of titrimetric Tyurin method and dry combustion (Jankauskas et al., 2006).

4.4. ^{13}C isotope ratio method

^{13}C isotope ratio values are presented in Table 1. The variability between C-rich and C-poor claystone was quite high, but fell into the range (−35‰ to −25‰) for kerogens of Type I reported by Whiticar (1996; −35‰ to −25‰). The $\delta^{13}C$ values for kerogens depend on the OM source and do not change from the time of their formation (Tissot and Welte, 1978; Meyers, 1994). The value for the coal (−26.9‰) fell into the range reported for coals (−22‰ to −27‰; Whiticar, 1996).

Even though it seems that C horizons are generally more depleted in ^{13}C than A horizons (an effect of dominance of lipid-rich Types I and II kerogen), the correlation between ^{13}C ratio and recent C relative content for all samples was rather poor (R^2 0.41). Most likely, ^{13}C ratio of fossil C in soil samples was variable among sites, just like it was between the two claystones as different sites were graded using different layers of the Sokolov formation. This is a source of variability which is not related to recent OM content and thus precludes the use of the $\delta^{13}C$ method for recent OM quantification only from the $\delta^{13}C$ value of topsoil sample.

An improvement in correlation was observed if a ratio of $\delta^{13}C$ for topsoil and of subsoil was used instead. This standardization removed the influence of variability among sites and brought quite good correlation with recent C relative content ($C_{rec}/TOC = -1135.1 \times (\delta^{13}C \text{ of topsoil}/\delta^{13}C \text{ of subsoil}) + 1146.1$, adj. R^2 0.82, $p < 0.05$) after removal of one outlier (site U10) indicated by Cook's distance > 1. When this relationship was used and final recent C content calculated, quite satisfying predictions could be obtained from full cross validation (Section 4.8). However, since

Table 1
Sample description and results from dry combustion, ^{14}C dating, ^{13}C isotope analysis and wet dichromate oxidation (C_{ox}). Age – yr since reclamation or overburden heaping at unreclaimed sites; R – reclaimed, U – unreclaimed sites.

id	Age (yr)	Type	Depth (cm)	TC (%)	TN (%)	TIC (%)	pMC_{TOC}	C_{rec}/TOC (%)	C_{rec} (%)	δ^{13}C (‰)	C:N	C_{ox} (%)	C from LOI 200 °C (%)
1	28	R	0–10	9.09	0.55	0.00	48.39	42.08	3.83	−29.5	16.6	8.29	1.58
2	28	R	40–50	6.62	0.27	0.08	2.16	1.88	0.12	−30.6	24.6	4.70	0.84
3	37	R	0–10	12.6	0.78	0.00	74.52	64.80	8.17	−28.1	16.2	12.46	1.95
4	37	R	40–50	4.71	0.21	0.22	2.31	2.01	0.09	−29.2	22.4	3.96	0.71
5	10	U	0–10	6.23	0.33	0.45	1.68	1.46	0.08	−30.7	19.2	5.30	1.02
6	10	U	40–50	6.84	0.33	0.44	0.92	0.80	0.05	−30.8	20.9	5.52	0.91
7	10	R	0–10	4.13	0.13	0.02	10.95	9.52	0.39	−28.3	31.7	3.16	1.05
8	10	R	40–50	4.95	0.26	2.12	1.9	1.65	0.05	−30.5	19.4	3.83	0.98
9	28	U	0–10	7.29	0.42	0.06	15.26	13.27	0.96	−30.5	17.2	6.46	0.97
10	28	U	40–50	4.98	0.25	1.82	1.96	1.70	0.05	−30.5	20.3	4.89	0.64
11	19	U	0–10	7.82	0.51	0.00	45.91	39.92	3.12	−29.0	15.4	6.91	1.51
12	19	U	40–50	2.78	0.14	0.26	7.59	6.60	0.17	−29.0	20.3	2.58	0.86
13	51	U	0–10	14.4	0.94	0.00	84.96	73.88	10.62	−28.6	15.2	13.90	2.75
14	51	U	40–50	7.53	0.44	0.15	1.75	1.52	0.11	−30.8	16.9	7.30	0.68
O_e				39.61[a]	1.84	0	104		35.82	−29.4	21.6	43.57	
Claystone (C-rich)				13.35[a]	0.57	0.01[a]	0.59		0.07	−32.4	23.3	12.76	
Claystone (C-poor)				4.63[a]	0.35	0.51[a]	3.77		0.13	−27.8	13.2	3.61	
Coal				62.44[a]	0.80	0	0.12		0.07	−26.9	78.2	78.27	

[a] Data from Vindušková et al. (2014).

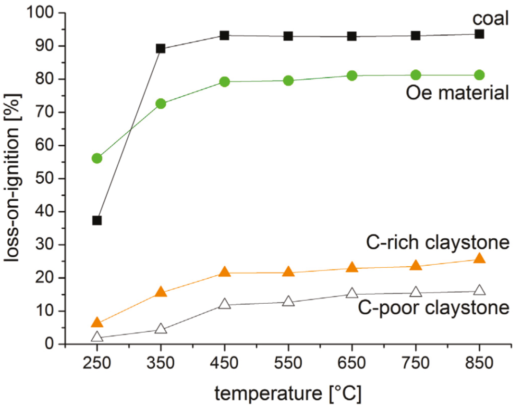

Fig. 2. LOI for model materials at different temperatures.

there is no good explanation for the outlying value of U10 site, the future applicability of the proposed model is questionable.

An opposite correlation between δ^{13}C ratio and ^{14}C activity was found in studies focused on the distinction of recent C and coal C (Chabbi et al., 2006; Ussiri and Lal, 2008). Chabbi et al. (2006) found a positive relationship between δ^{13}C and lignite content (R^2 0.95) and Ussiri and Lal (2008) found a similar, but less precise correlation (R^2 0.84) for bituminous coal. The opposite trend in our samples is most likely due to the different sources of fossil C in our study and the above studies. Fossil C from coal is relatively enriched in ^{13}C compared with recent OM, whereas fossil C in our study area has similar or lower ^{13}C content than recent OM due to its Type I kerogen origin.

4.5. NMR

Spectra from soil samples are shown in Supplementary Fig. S2 along with the recent C relative content of the respective samples. The distinct peak in the 0–50 ppm region, representing aliphatic carbon species was observed in all the spectra. This is in accord with a study of the claystones of the Sokolov Formation (Křibek et al., 1998), which demonstrated a dominating peak in the alkyl C region, a smaller peak in the aromatic carbon region and negligible peaks in the O-alkyl and carboxyl C regions.

Additionally, some of the samples showed a signal at 72 ppm, indicating the presence of polysaccharides. Furthermore, the signal at 56 ppm for samples 11 and 3 is characteristic of lignin. Both polysaccharides and lignin are typical plant litter compounds, indicating recently-derived SOM. The aromatic C region (110–160 ppm) did not show any clear peaks compared with spectra from lignite-rich soils (Rumpel et al., 1998; Clouard et al., 2014) and the relative intensity of aromatic C (Table 2) was even lower than reported for a claystone sample from the study area (29%; Křibek et al. 1998). This is most likely the effect of a greater relative importance of the other chemical shift regions. Clearly the relative intensity of the O-alkyl C and carboxyl C regions increases with recent C relative content. The effect was confirmed when inverse A ratios were calculated (Table 2). Considering the unclear signal in the aromatic C region, an adjusted A_2 ratio was calculated by leaving out the aromatic C term.

Both ratios showed comparable correlation with recent relative C, with $p < 0.05$ ($C_{rec}/TOC = 45.61 \times A'_1 - 12.3$, R^2 0.85; $C_{rec}/TOC = 82.82 \times A'_2 - 19.8$, R^2 0.83). The correlation is even slightly stronger than a similar correlation found by Rumpel et al. (2000) between lignite contribution to TOC and the A ratio (R^2 0.79). Use of the two ratios for recent C prediction is compared with other approaches in Section 4.8.

Rumpel et al. (1998) reported that the A signal intensity ratio was 1.4 and 1.5 for lignite and similar ratios were characteristic of soils samples dominated by lignite, whereas values for the forest floor material were well below 1. The corresponding ratio for our soils ranged from 1.0 to 6.2 and from 2.4 to 8.8 for the topsoil and subsoil, respectively. This corresponds well with the assumption that fossil C in our study area is dominated by kerogen of aliphatic character (Křibek et al., 1998).

4.6. NIRS

Detailed results from NIRS are described by Vindušková et al. (2014). Briefly, all models showed a close relationship between measured and predicted values ($R > 0.9$). Models calibrated using both mixtures and soils provided better predictions for soils than models based only on mixtures. For recent C content, coarsely ground samples (< 2 mm) produced better estimates than finely

Table 2
Relative intensity distribution (%) in solid state ^{13}C NMR spectra of soil samples and calculated A ratios. C_{rec}/TOC – recent C relative content measured with ^{14}C dating.

id	ppm	Alkyl C 0–45	O-alkyl C 45–110	Aromatic C 110–160	Carboxyl C 160–220	A[a]	A'_1[b]	A'_2[c]	C_{rec}/TOC
1		47	25	14	13	1.61	0.81	0.62	42.08
2		65	10	13	13	3.48	0.34	0.29	1.88
3		27	38	23	12	1.00	1.82	1.00	64.80
4		65	9	20	6	5.54	0.24	0.18	2.01
5		70	9	16	5	6.21	0.20	0.16	1.46
6		58	20	12	10	2.37	0.51	0.42	0.80
7		43	25	22	11	1.83	0.82	0.55	9.52
8		58	16	18	8	3.14	0.42	0.32	1.65
9		51	22	16	12	1.97	0.66	0.51	13.27
10		61	14	10	14	2.55	0.46	0.39	1.70
11		37	25	25	13	1.63	1.04	0.61	39.92
12		81	5	9	5	8.83	0.13	0.11	6.60
13		30	40	19	11	0.97	1.67	1.03	73.88
14		60	14	16	9	3.22	0.39	0.31	1.52

[a] (alkyl C + aromatic C)/(O-alkyl C + carboxyl C).
[b] (O-alkyl C + carboxyl C)/(alkyl C + aromatic C).
[c] (O-alkyl C + carboxyl C)/alkyl C.

ground samples (< 0.125 mm). Accuracy of this approach is discussed further in Section 4.8.

4.7. Rock–Eval

The Rock–Eval parameters are presented in Table 3. Plotting HI vs. OI allows interpretation of maturity and the origin of the OM (Fig. 3). Whereas claystone samples were characteristic with high HI and low OI values, the O_e material had low HI and high OI values. Soil samples then lay on a "mixing" curve between the claystone and O_e material regions and their position correlated with their recent C relative content. This may be interpreted as a transition between lipid-rich fossil OM to carbohydrate and lignin-rich recent OM – see Fig. 4 for comparison of our data with data from Carrie et al. (2012) who tested Rock–Eval 6 on a set of pure biochemicals and biological standards. It should be noted that this is a result of a site-specific situation where the source of fossil OM is mainly aquatic (algal lipid-rich) whereas the source of recent OM is terrigenous. Also, the coal had lower OI than the O_e material, in accord with the transformation undergone by OM during

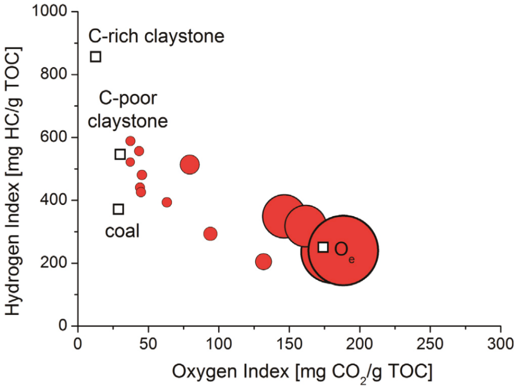

Fig. 3. HI vs. OI diagram for samples (O_e, fermentation layer sample). Bubbles represent soil samples and their size represents recent C relative content of soil samples.

Table 3
Rock–Eval pyrolysis parameters.

Sample	PC (%)	RC (%)	TOC (%)	MINC (%)	HI (mg HC/g TOC)	OI (mg CO_2/g TOC)	T_{peak} (°C)	F1a + F1b + F2 + F3
Soil								
1	2.54	5.18	7.72	1.03	348	146	434	42
2	2.10	3.00	5.09	0.88	481	46	434	32
3	2.62	8.05	10.66	1.28	236	181	429	58
4	1.11	2.11	3.22	1.23	393	63	432	40
5	1.91	2.12	4.04	1.91	556	43	434	34
6	2.00	2.51	4.51	2.07	522	37	434	34
7	0.61	2.34	2.95	1.23	205	132	434	39
8	1.15	1.88	3.03	1.79	441	44	436	31
9	2.56	3.15	5.71	1.39	513	79	434	33
10	1.15	1.99	3.13	1.67	426	45	433	32
11	2.09	4.70	6.79	0.80	318	162	432	46
12	0.58	1.58	2.16	0.56	293	94	433	38
13	3.37	10.07	13.44	0.90	240	188	430	59
14	2.93	2.95	5.87	1.00	588	37	434	33
Model material								
O_e material	9.48	27.64	37.12	1.51	250	174	321	76
Claystone (C-rich)	7.64	3.06	10.70	1.24	856	13	438	29
Claystone (C-poor)	1.10	1.28	2.38	2.04	546	30	434	42
Coal	19.53	41.93	61.46	0.81	371	29	412	60

coalification. Diagenesis leads to loss of functional groups and an increase in aromaticity (Tissot and Welte, 1978).

Fig. 3 highlights the possibility of using OI and HI for the estimation of recent C relative content. Testing of OI and HI as single or combined predictors showed that OI is a sufficient predictor of relative recent C and HI does not bring further significant improvement of the prediction. Recent C relative content could be well predicted from OI by exponential regression ($C_{rec}/TOC = 1.041 \times e^{0.023 \times OI}$, R^2 0.95, $p < 0.05$). This approach is discussed further in Section 4.8. It corresponds well with findings of Carrie et al. (2012), who concluded that the S_3 signals (CO/CO_2 ratios: OICO, $OICO_2$ and $OIRE_6$) are the best discriminants for the source of OM as terrigenous plant matter typically has much higher OICO values than aquatic biota, proteins and lipids.

A significant negative correlation (Spearman's r −0.59, p 0.025) was found between T_{peak} and recent C relative content. This corresponds with the lower T_{peak} (320 °C) for the O_e material and higher values measured for the C-poor and C-rich claystone (434 and 438 °C, respectively) and generally with the interpretation of T_{peak} as an indicator of maturity (Disnar et al., 2003).

T_{peak} for the O_e material was at the lower limit of the range reported (Disnar et al., 2003) for Ol, Of and some of Oh horizons (320–390 °C) and even lower when compared with Sebag et al. (2006) who found a T_{peak} of 350 °C for forest litter horizons. They observed a T_{peak} between 380 °C and 400 °C for humic (Oh, O/A) layers and above 400 °C for organo-mineral (A) horizon samples. T_{peak} for the coal lay, however, somewhere between those of O_e material and claystone and may cause the variability that impaired the prediction of recent C relative content of soil samples from T_{peak} values.

The relative contribution of six components to the S_2 curve is given in Supplementary Table S1. A strong correlation was found between recent C relative content and a sum of the first four components given in Table 3 ($C_{rec}/TOC = 2.6 \times (F1a + F1b + F2 + F3) - 83.9$; adj. R^2 0.88). Use of this relationship for recent C quantification is discussed in Section 4.8.

Carrie et al. (2012) suggested that the shape of the S_2 pyrogram (S2a/S2b ratio) could be used as an indicator of the dominant OM source in fresh material with higher values (> 2) indicative of aquatic biota and smaller values (< 0.3) indicative of terrigenous plant material. Conversely, in our study, the mean S2a/S2b ratio [calculated as (F1a + F2a + F3)/(F4 + F5)] for C and A horizons was 0.08 and 0.27, respectively, suggesting that terrigenous OM in our soils led to a higher ratio, i.e. relatively more hydrocarbons were released during pyrolysis below 400 °C. This may be explained by the greater thermal stability of the OM present as kerogen than recent soil OM. We also conclude that factors other than OM source affect the shape of the S_2 pyrogram and conclusions from the analysis of fresh material should be transferred to soils and sediments with caution. Copard et al. (2006) found that the F1 and F6 clusters from S_2 deconvolution were present in bedrock but absent from litter and proposed their use as markers of fossil OM (FOM) in modern environments. The integration method used in their study was slightly different (F1 and F6 were defined as clusters with T_{peak} 250 and 550 °C); however, we found no signal from a labile FOM fraction corresponding to their F1 cluster in our samples of unweathered claystone. On the other hand, their proposed refractory F6 cluster was in our study represented by F4 and F5 (460–550 °C and 550–650 °C, respectively). The strong correlation between the sum of the F1 to F3 components and recent C relative content fully complements the conclusion that F4 and F5 are indicative of FOM. Again, this is due to the fact that relatively more hydrocarbons are released during thermal cracking at lower temperatures (< 460 °C) from recent (less-altered) OM than from FOM, as can be seen also in the F4 + F5 values for the O_e material and claystones (pure recent and fossil OM, respectively). Also, according to previous studies, the latter two components are relatively scarce in soils compared with fossil sediments (Sebag et al., 2006).

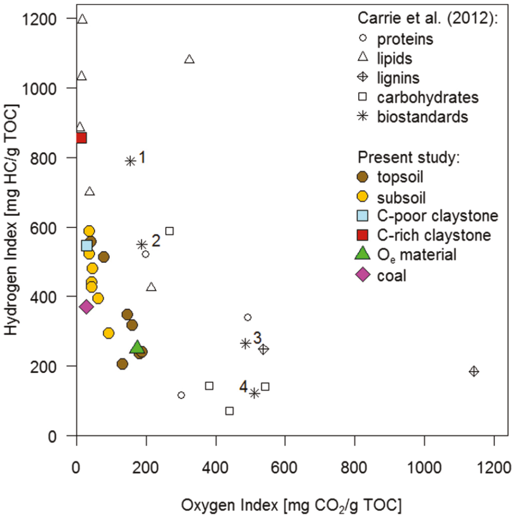

Fig. 4. HI vs. OI diagram for samples measured here and samples of pure biochemicals and biological standards measured by Carrie et al. (2012). Biostandards: 1, copepods; 2, phytoplankton; 3, needles; 4, bark.

We have shown that, apart from the OI, S_2 pyrogram parameters can also be used for quantitative estimation of recent (or fossil) OM in the study soils.

4.8. Method comparison

Estimates obtained from twelve methods are plotted against recent carbon obtained from ^{14}C dating in Fig. 5. The lines in the biplots are lines of equality on which all points would lie if the tested method gave exactly the same results as ^{14}C dating.

Biplots for TOC, C_{ox} and LOI 550 °C indicate that all of these three conventional methods used for soil OC determination in agricultural soil lead to overestimation, with the highest error for LOI 550 °C (RMSE 8.70). Its extent is clearly evident when plotted as the mean difference between the tested method and reference (called bias when significant; Supplementary Fig. S3). The mean bias was 8.23, 4.75 and 4.39% C for LOI, TOC and C_{ox}, respectively. However, as shown in the second column of biplots, a correction for these three methods with acceptable level of accuracy was obtained by subtracting subsoil content from topsoil content. This time, corrected LOI 550 °C showed the greatest accuracy (RMSE 1.21) followed by C_{ox} (RMSE 1.62) and TOC (RMSE 2.07). The mean difference was reduced to 0.06, 0.16 and −0.37 for LOI, TOC and C_{ox}, respectively, and was then not significant for any of the three methods (paired t-test, $p < 0.05$). However, laborious and costly, sampling and analysis of the subsoil is required for such correction with subsoil content.

Another way to adapt the conventional methods is to decrease the heating temperature for LOI to 200 °C. Such a modification produces acceptable but less accurate results (RMSE 2.64) vs. subsoil corrected methods; however, sampling of subsoil is not required. Regression based on $\delta^{13}C$ topsoil/subsoil ratio gave estimates with accuracy similar to the subsoil corrected conventional methods (RMSE 1.73). Since application of this method also requires subsoil

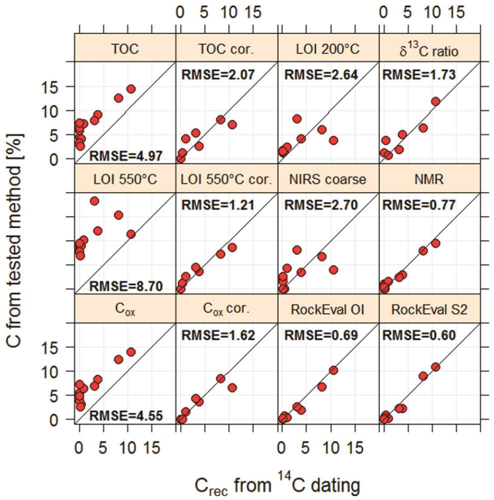

Fig. 5. Comparison of C from tested methods with recent C (C_{rec}) obtained from radiocarbon method. TOC, dry combustion; LOI, loss-on-ignition; C_{ox}, wet dichromate (modified Tyurin) method; δ^{13}C ratio, regression based on topsoil/subsoil δ^{13}C ratio; NIRS, near infrared spectroscopy after coarse grinding; cor., correction by subtraction of subsoil from topsoil; OI, regression based on oxygen index; S_2, regression based on F1a + F1b + F2 + F3 components of S_2 curve. Data for NIRS are from Vindušková et al. (2014).

sampling and – in addition – is more costly, we cannot recommend it as an alternative to conventional methods.

NIRS of coarsely ground samples produced estimates with accuracy similar to LOI 200 °C (RMSE 2.70). On the other hand, NIRS of finely ground samples leads to significant overestimation (paired *t*-test, $p < 0.05$, mean difference 1.48, see Supplementary Fig. S3). Like LOI 200 °C, NIRS does not require subsoil sampling and may be a cost effective tool for analysis of a large number of samples.

NMR was used to estimate recent carbon as follows. Recent C relative content was calculated from inverse *A* ratios using linear relationships described in Section 4.5 and then used to produce estimates of recent C from Eq. 1. Prediction using the A'_2 ratio that does not account for an aromatic C term yielded more accurate results (RMSE 0.77; Fig. 5) than the A'_1 ratio (RMSE 0.89, data not presented). This may indicate that the aliphatic structure of kerogen is the major source of fossil C in our samples and the contribution from coal is not that significant.

Rock–Eval OI was used to estimate recent C as follows. Recent C relative content was calculated from OI using the exponential relationship described in Section 4.7 and then used to produce estimates of recent carbon from Eq. 1. This approach produced the second most accurate predictions (RMSE 0.69).

Similarly, a sum of first four components of the S_2 curve (F1a + F1b + F2 + F3) was used to estimate recent C, first by using a linear relationship (Section 4.7) to calculate recent C relative content and then estimating recent carbon from Eq. 1. This approach produced the most accurate predictions (RMSE 0.60).

Based both on *t*-test results and RMSE, both Rock–Eval approaches were the most accurate. Even though NMR gave also very precise predictions, it is a laborious and costly method, requires long measurement times and highly specialized instrumentation and is therefore not suited to routine analysis of mine soil samples. Rock–Eval on the other hand is relatively simple and rapid. Use of the OI as an indicator of recent OM is in accord with the NMR analysis, which confirmed that recent OM is rich in carbohydrates and lignin, while fossil OM contains predominantly aliphatic and aromatic structures. Use of the Rock–Eval S_2 curve is based on lower thermal stability of recent OM than fossil OM.

Finally, we would like to highlight that, due to lack of data from additional sites, truly independent evaluation was not possible. It is also important to note that the regression equations used for NMR and Rock–Eval are specific to the type of fossil OM in our study area. Therefore, to apply such an approach in other areas, a site-specific equation would need to be developed.

5. Conclusions

Fossil carbon accounted for 13–99% of TOC in study soil samples, which is equivalent to 2–6% C content. Subtracting the C content of subsoil (50 cm deep) from the topsoil content provided an acceptable estimate of recent C. This could be applied to C content from dry combustion, wet dichromate oxidation and LOI (550 °C). In the study area, it is inappropriate to use these methods for soil quality or C sequestration assessment without such correction.

Of all of methods, Rock–Eval proved to most accurately determine the actual recent C content of each soil sample over a wide range of recent C concentration. It is far simpler than other methods such as ^{14}C dating or NMR, which require more sophisticated instrumentation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orggeochem.2015.10.001.

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Supplementary Data

Table S1

Contribution of components to S2 curve (% of whole signal).

Sample	F1a	F1b	F2	F3	F4	F5
	205-280	280-340	340-400	400-460	460-550	550-650 °C
Soil						
1	0.60	3.36	9.50	28.93	55.34	2.27
2	0.39	0.90	3.81	26.98	66.16	1.76
3	1.27	8.09	18.25	30.55	38.20	3.63
4	0.47	1.23	5.96	32.39	57.94	2.00
5	0.38	0.92	4.17	28.62	64.21	1.70
6	0.43	0.95	4.02	28.35	64.52	1.73
7	1.13	1.98	6.72	28.91	57.07	4.19
8	0.57	1.15	3.57	25.37	67.16	2.18
9	0.36	1.22	4.42	26.69	65.58	1.73
10	0.56	1.20	3.81	26.83	65.72	1.88
11	0.60	3.57	10.44	31.13	51.69	2.58
12	0.77	1.78	6.82	28.62	59.11	2.89
13	1.64	9.55	19.01	28.80	37.68	3.32
14	0.22	0.77	4.31	28.14	65.16	1.39
Model material						
O_e	3.59	18.61	27.13	26.28	20.32	4.07
Claystone (C-rich)	0.15	0.49	3.06	25.09	70.40	0.82
Claystone (C-poor)	0.80	1.60	5.97	33.37	56.71	1.55
Coal	1.37	4.08	13.17	41.66	35.79	3.93

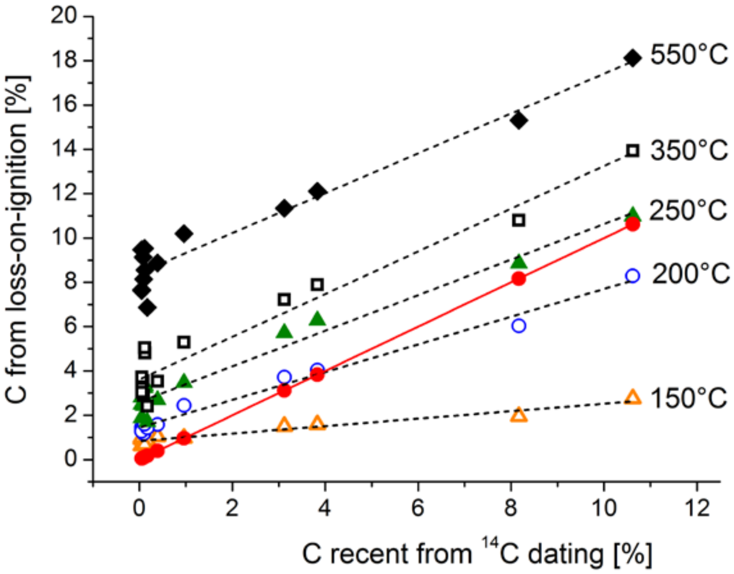

Fig. S1. LOI converted to C content (conversion factor 1.724) in comparison with recent C content determind from ^{14}C radiocarbon dating. True values from ^{14}C dating are represented by full circles and solid regression line (y=x). Different LOI temperatures are indicated by different symbols and respective dashed regression lines.

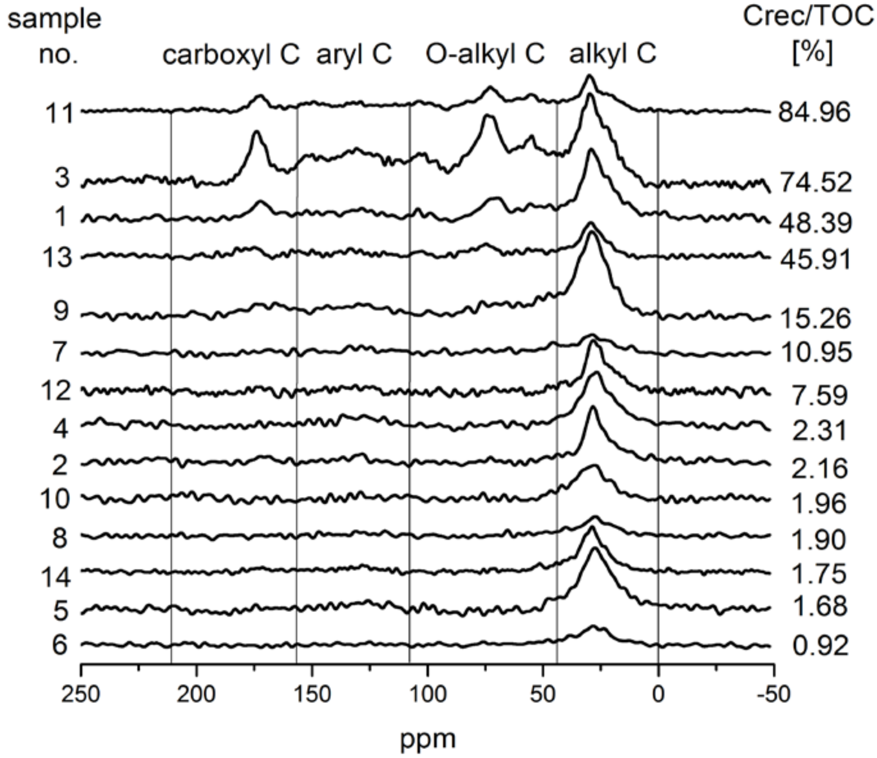

Fig. S2. ^{13}C CPMAS NMR spectra of soil samples sorted according the recent C relative content measured with ^{14}C dating.

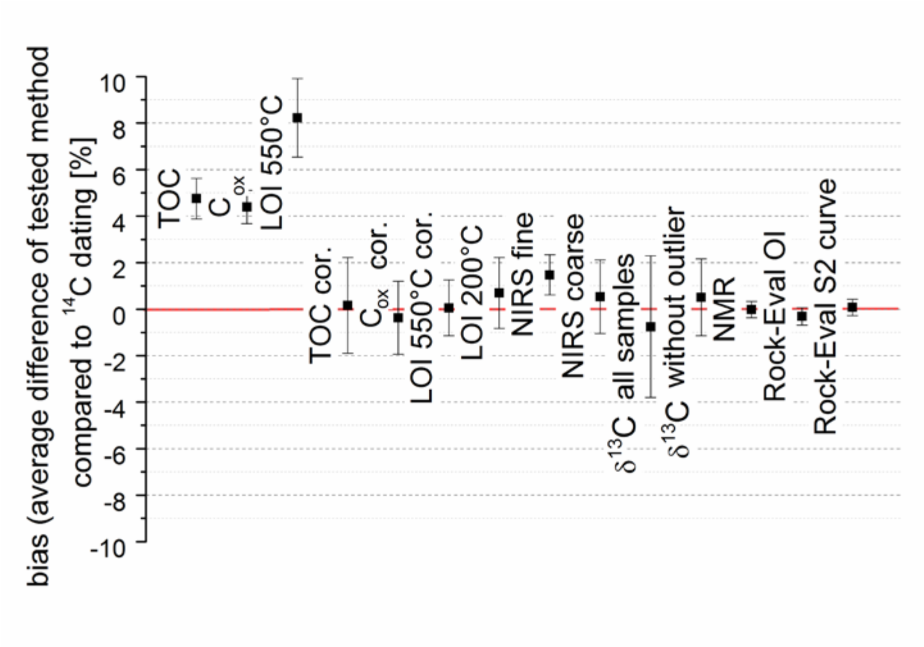

Fig. S3. Mean difference for C measured with tested methods vs. recent C determined with reference ^{14}C dating method (= 'bias') (wt%). Error bars ca. 95% CI. TOC, dry combustion; C_{ox},wet dichromate (modified Tyurin) method; LOI, loss-on-ignition; cor., correction by subtraction of subsoil from topsoil; NIRS, near infrared spectroscopy; coarse/fine, type of grinding.

Manuscript 4

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Soil organic matter accumulation in post-mining sites: potential drivers and mechanisms.

Soil organic matter accumulation in post-mining sites: potential drivers and mechanisms

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Abstract

Surface mining causes disturbance of large areas. Material excavated from above the mined deposit is transferred elsewhere and new ecosystems are reconstructed here either with help of technical reclamation or by natural processes. We present the main findings of research carried out in these post-mining sites with a focus on carbon sequestration in soil. We shortly discuss methodological issues of C sequestration studies in these soils. Further, we focus on the potential and dynamics as well as the main driving factors of C sequestration. Rates of soils carbon accumulation in post mining soils are higher than the typical rates for revegetated agricultural soils (~0.3 $t.ha^{-1}.yr^{-1}$), however, the rate of C sequestration decreases with increasing site age (2.5 $t.ha^{-1}.yr^{-1}$ after 10 years and 0.9 $t.ha^{-1}.yr^{-1}$ after 40 years). Substrate and type of vegetation belong to major drivers. In average soil C storage is significantly lower in coniferous forests than in grasslands or in deciduous forests. Rate of C sequestration responds positively to site temperature in grassland and negatively in conifers.

1. Introduction

Mining provides substantial part of raw materials used by modern industrial society. At the same time, mining and open-cast mining in particular cause extensive destruction of ecosystems. Reconstruction of soils and whole ecosystems is necessary for socioeconomic recovery of affected areas (Bradshaw, 1997; Macdonald et al., 2015). In this contribution, we will focus on open-cast mining of energetic materials such as coal, lignite, and oil shales. These materials cover substantial part of electricity consumption in many countries. During open-cast mining, overburden layers lying above the mined deposit have to be removed and they are partly stored inside the mining pit and partly outside. Overburden usually substantially differs from recent soils and in some cases weathering of overburden material can bring serious ecological problem such as acidification and acid mine drainage produced by pyrite weathering (Bradshaw, 1997; Sample and Suter II, 2002; Frouz et al., 2005). As a consequence, ecosystems in large areas are completely erased, either excavated or buried. Excavation and burial or recent soils may result in reduction of carbon (C) stock as was demonstrated for C stored in peat deposits in case of oil shale mining (Rooney et al., 2012). However, experience with sediment burial actually indicates the buried soil may effectively contribute to C storage (Chaopricha and Marín-Spiotta, 2014), but this aspect has not been considered in context of mining.

Previous studies indicate that accumulation of soil organic carbon (SOC) in post-mining soils is rather high and that these soils could play an important role in efforts to capture CO_2 (Akala and Lal, 2001; Šourková et al., 2005b; Shrestha and Lal, 2010). Proper land restoration alone could off-set 16 Tg CO_2 in the USA annually (Amichev et al., 2008). However, C stock in post-mining soils has been reported to be lower than in natural soil in surroundings (Fettweis et al., 2005). There is, however, still little understanding about the major drivers and underlying mechanisms that determine soil C storage in post-mining soils.

Certain biogenic elements such as carbon and nitrogen gradually accumulate during ecosystem development due to plant activity and gradual accumulation of soil organic matter (Šourková et al., 2005b). In contrary to other elements such as phosphorus, which originate from geological substrates, N and C can gradually become more and more available to plants during ecosystem development, but they can, as a consequence, become increasingly bound in plant biomass, so their stock in the soil gets gradually depleted (Šourková et al., 2005b). Changes in the pools of available biogenic elements in the ecosystem are among important determinants of organism populations and communities including various biotic interactions such as mycorrhiza. Moreover, C sequestration in soil given by accumulation of soil organic matter is closely related to soil formation, development of soil horizons and changes of other soil properties such as pH, adsorption, water retention, soil structure etc. (Brady and Weil, 1999). In this chapter we briefly summarize major methodological challenges in the study of C sequestration in post-mining soils, describe sequestration potential and its changes over time and effect of major environmental factors that can modify C sequestration in post mining soils. Finally, we will explore effect of C sequestration on other soil properties.

2. Methodological approaches in study of C sequestration in post-mining soils

Post-mining sites are very well suited for the study of soil C dynamics using the so-called chronosequence approach. This approach allows us to study development of a system over time using space-for-time substitution. The principle of the technique is that we select sites of different age which presumably have identical or very similar history. By comparing various sites of different age at one time we can get an idea how an individual site develops over time. Using this approach, we can study development of ecosystem over a time span, study of which would be otherwise unpractical or inaccessible by direct observation. As already mentioned, post-mining sites are ideally suited for space-for-time substitution as mining of one deposit often takes a long period of time and during this period similar overburden layers are excavated and deposited in similar manner. Consequently, set of similar sites of various ages is often available in individual post-mining areas (Frouz and Nováková, 2005; Šourková et al., 2005a, 2005b; Baldrian et al., 2008; Frouz et al., 2008; Helingerová et al., 2010).This approach has several pitfalls, namely the history of individual sites may vary due to variation in initial conditions and due to various stochastic events and researchers have typically only very limited control over site history. This can be improved by revisiting of the individual sites along a chronosequence (Bartuška and Frouz, 2015; Mudrák et al., 2016). This allows us to measure the changes in the system of individual sites over time and compare these changes for systems of various ages. In this way, time-driven changes can be partly separated from the variation between individual sites.

One of the major methodological problems in the study of C sequestration in post-mining sites, namely in sites after mining of coal or oil shales, is the presence of fossil organic matter in the overburden. Some overburden may contain substantial amount of fossil organic matter in the form of coal or kerogen which may vary between sites (Kříbek et al., 1998; Rumpel et al., 1998; Frouz et al., 2011a; Vindušková and Frouz, 2013; Vindušková et al., 2015). Common laboratory techniques used for soil C measurement are not able to distinguish between recent and fossil organic matter. The major problem in estimation of fossil carbon is that fossil carbon may occur in chemically very variable form from coal with high aromaticity to kerogen which can be mostly aliphatic (Kříbek et al., 1998; Vindušková et al., 2014). There are several approaches to tackle this problem. The most accurate method to estimate the proportion of recently sequestered and fossil SOC is radiocarbon dating using ^{14}C-AMS introduced by Rumpel et al. (1999), and applied in other studies (Morgenroth et al., 2004; Karu et al., 2009; Vindušková et al., 2015). However, this method is rather costly for proper C sequestration monitoring which requires high number of soil samples to be analyzed.

Amichev (2007) came with the idea that bituminous coal and recent soil organic matter (SOM) can be separated by heating at 375 °C for 24 h (which oxidizes recent SOM but not coal). However, such thermal separation may be difficult for coals of low rank and a site-specific oxidation temperature should be found for this approach (Vindušková et al., 2015).

Near infrared spectroscopy can be used for quantification of recent C in the presence of coal and kerogen in a large number of samples (Vindušková et al., 2014). However, a site-specific calibration model needs to be calibrated and validated using a rather high amount of samples, in which recent and fossil C has been determined by other method (e.g., ^{14}C-AMS).

Other approaches such as ^{13}C isotope ratio method (Chabbi et al., 2006; Ussiri and Lal, 2008; Vindušková et al., 2015), solid state ^{13}C NMR spectroscopy (Rumpel et al., 1998) and Rock–Eval pyrolysis (Vindušková et al., 2015) can also work well but need to be tested and calibrated for the specific type of recent and fossil organic matter and require specialized instrumentation.

Some studies have used simple subtraction of the C content of a deeper soil horizon from the total C content in the topsoil (Reintam et al., 2002; Frouz et al., 2009). A comparison with ^{14}C data showed that this approach provides an acceptable estimate of recent C and it can be applied to C contents measured by dry combustion, wet dichromate oxidation or loss-on-ignition method (Vindušková et al., 2015).

Another methodological problem with C content determination may be carbonates. Of course, carbonates are common also in natural soils outside the mining area. However, the most common carbonates found in natural soils are calcite and dolomite. In post-mining soils, also different (and otherwise rare) forms of carbonates such as siderite or ankerite can be found. Siderite is a diagenetic mineral typical for coal-bearing sequences around the world, because coal-forming depositional environment is also favorable for the formation of siderite. Siderite is much less detectable by standard tests on carbonates and difficult to remove by standard procedures used to remove calcite or dolomite (Larson et al., 2008). Moreover, the content of siderite can be highly variable throughout the overburden material. Therefore, soils in post-mining sites should be analyzed for mineralogical composition by powder X-ray diffraction and treated by a specific procedure before SOC analysis when containing siderite.

3. Potential of C sequestration in post-mining sites and its dynamics over time

Several studies (Shrestha and Lal, 2010; Šourková et al., 2005ab) have reported that post-mining soils have very high rates of C sequestration. In an extensive meta-analysis that dealt with soil C accumulation in post-mining soils of the temperate zone of the Northern Hemisphere (Vindušková and Frouz, 2013), it was also shown that most of the rates of SOC accumulation were higher than the typical rates for revegetated agricultural soils reported by Post and Kwon (2000) (see Figure 1 for comparison of sequestration rates from both studies). The mean value for agricultural soils converted to grassland or forest reported by Post and Kwon (2000) was 0.34 $t.ha^{-1}.yr^{-1}$. In post mining soils however, the rate of C sequestration decreased linearly with increasing site age. It was 2.46 $t.ha^{-1}.yr^{-1}$ after 10 years and 0.87 $t.ha^{-1}.yr^{-1}$ after 40 years. A somewhat higher but comparable rate (1.17 $t.ha^{-1}.yr^{-1}$) was found by Anderson et al. (2008) for a chronosequence of 13 post-mining sites, which ranged in age from 11 to 26 years. Similar results were obtained by Bartuška and Frouz (2015) who re-sampled sites previously studied by Šourková et al. (2005b). Such repeated sampling allowed to measure C sequestration rate for individual sites of different ages. This study showed that rate of C sequestration decreased with increasing site age

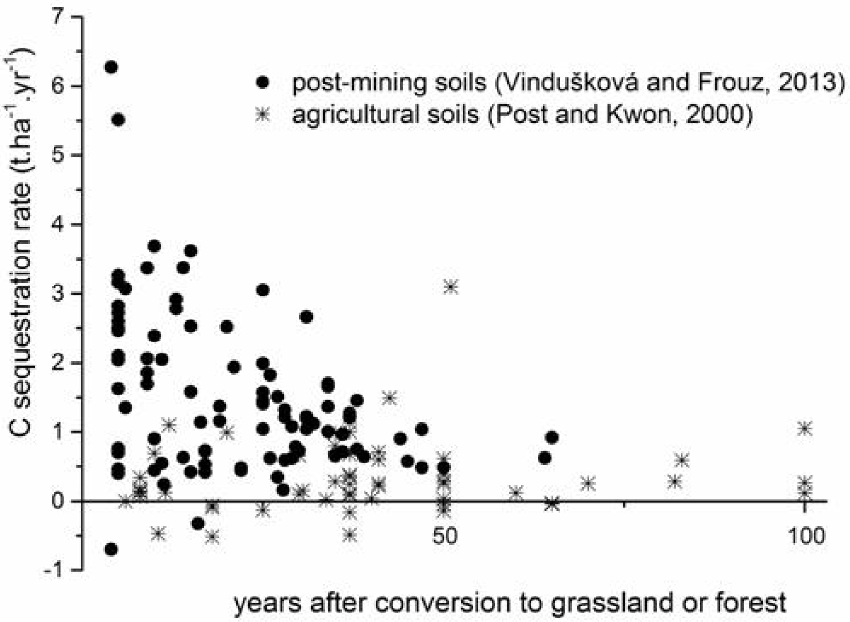

Fig. 1. C sequestration rates in soils after conversion to grassland or forest. Only data on agricultural soils (<=100 yrs old) describing land use change to grassland or forest were included from Post and Kwon (2000) (n=56). All post-mining sites were included from Vindušková and Frouz (2013) (n=93).

being about 2.3 t.ha^{-1}.yr^{-1} in 10-year-old sites and close to zero in 40-year-old sites. The question is how much is this decrease in C sequestration rate indicative of C saturation of post-mining soils and how much is this driven by other forces namely by decrease in primary production. Particularly in the study of Bartuška and Frouz (2015) who studied alder plantations, this may be the case as biomass production and litter input in 25-year-old or older plantations stagnate or even decrease in comparison with younger sites.

SOM represents a wide array of compounds, from fragments of litter to largely transformed humic substances. SOM can be divided into several pools that differ in their chemical composition as well as in their degree of stabilization. Stabilization may result from changes in chemical structure of SOM, the incorporation of SOM into aggregates (i.e. physical protection) and the adsorption of SOM to mineral surfaces. The latter two mechanisms of stabilization reduce bioaccessibility of SOM to microorganisms and therefore reduce its decomposability (Six et al., 2004; Zimmermann et al., 2007). SOM pools are measured by various fractionation methods, which are based on at least one of three principles. First, SOM in smaller soil aggregates is assumed to be more recalcitrant than SOM in bigger soil aggregates. Second, SOM bound in microaggregates is assumed to be more protected than SOM bound in macroaggregates or than SOM that is not bound in aggregates at all. Third, the heavier fraction of SOM is assumed to be more tightly bound to mineral soil and consequently more protected than the lighter fraction of SOM (Sohi et al., 2001; Six et al., 2002, 2004; Zimmermann et al., 2007). Long-term experiments have documented a lower level of additional SOM sequestration in high-C than in low-C soils (Campbell et al., 1991). These results suggest that there is a limit to the quantity of added C that a soil can sequester, i.e., soils can become saturated with C (Six et al., 2002; Stewart et al., 2007). Frouz (2016) used a soil transplantation experiment to answer the question whether the decrease in C sequestration in post-mining soils described by Vindušková and Frouz (2013) and Bartuška and Frouz (2015) results from C saturation or from an external factor such as a change in the quantity or quality of C that enters the soil. In soils exposed to the same level of litter input and bioturbation no difference in bulk C sequestration has been found which suggests that external forces namely litter input contribute to this decrease. Detailed observation in individual pools showed that changes in a given pool plotted against the initial content of those pools were well described by bell-shaped curves. This suggests that in highly unsaturated conditions, soil that has already accumulated some of the C will have a greater ability to accumulate additional C. Although signs of C saturation were observed in some of the SOM pools, the soils from the post-mining sites in the current study seem to be far from C saturation even after 50 years of soil development (Frouz, 2016). This is consistent with previous results of Frouz et al. (2014a), who showed that soils in which some organic matter had been already incorporated by bioturbation tended to sequester more C than soils that were exposed to bioturbation for the first time. Mechanisms behind these phenomena remain unclear but may involve interactions between various C pools. During soil formation at the studied post-mining sites, humic substances form rapidly (Abakumov et al., 2013). Humic substances may increase soil organic C sequestration through hydrophobic protection of SOM (Spaccini, 2002). Another plausible mechanism may involve an interaction between dissolved organic C (DOC) with clay surfaces and sesquioxides that may affect surface charge (Tombácz et al., 2004) and aggregate formation in soil (Piccolo et al., 1997), which may in turn affect the amount of particulate organic carbon (POC) bound to soil aggregates, and the strength of that binding. In this way, exposure of the clay substrate to DOC during the formation of soil from pristine claystones may affect the ability of the young soil to form aggregates and to bind POC to such aggregates.

The transition between pools may be affected by reclamation technology and vegetation. Bartuška et al. (2015) observed faster accumulation of POC and namely POC bound in soil aggregates in reclaimed than in unreclaimed sites which corresponds with lower CN ratio of litter in reclaimed alder plantations that in spontaneous regrowth and consequently higher level of bioturbation in reclaimed sites which promotes faster POC accumulation. However overall, only small fraction of POC was bound in soil microaggregates, most seemed to be loosely bound in macroaggregates or occur between aggregates (Bartuška et al., 2015). This is in agreement with Abakumov et al. (2013), who studied the same sites and reported that humic acids increase with site age and that humic acids, which are usually associated with clay minerals in the heavy fraction of organic matter, represent only a small percentage of the total SOM. Abakumov et al. (2013) also observed larger proportion of humic acids in reclaimed sites while soils with spontaneous regrowth were typically dominated by fulvic acids.

3.1. Post-mining substrates and their effect on C sequestration

Post-mining soils may develop directly on overburden, or overburden can be supplied by various amendments and finally one or more layers of topsoil or both topsoil and subsoil can be spread on top of overburden and these layers then serve as medium for soil development.

Overburden substrates can be highly variable ranging from substrates highly suitable for plant growth, such as loess deposits, to substrates that show toxicity to plants. Overburden differs from recent soils (Bradshaw, 1983, 1997) in many aspects. Overburden typically does not have soil aggregates as we know them from recent soils, they often have extreme texture (e.g., too much sand and gravel or too much clay, clays are often cemented by carbonates or fossil organic matter in claystones or shales), substrate can repel water (be hydrophobic) and may be toxic for plants and soil biota for various reasons. One of the reason for overburden toxicity can be pyrite weathering, which decreases pH. Low pH increases mobility of some heavy metals, as well as other toxic elements in the soils (Jenner and Janssen-Mommen, 1993; Bradshaw, 2000; Sample and Suter II, 2002; Frouz et al., 2005). The high content of salts is another reason for toxicity of post-mining sites (Frouz et al., 2005). Quaternary substrates are generally more likely to be free of the adverse chemical conditions described above than are geologically older substrates (Frouz et al., 2005). Overburden toxicity can be estimated using biological tests or chemical analysis of the soil. The pH value is a useful and affordable parameter to measure to indicate toxicity: sites with a pH below 3.5 are very likely to be toxic; sites with pH below 5.5 should be tested for potentially toxic elements (As, Se, etc.). Sites close to a neutral or slightly alkaline pH are usually suitable but should be checked for conductivity to exclude salinity problems (Frouz et al., 2005). In some cases, toxicity problems such as high salt content may not appear in freshly excavated overburden but can occur later with weathering of the substrate.

Overburden can effect C sequestration in two principal ways. By effect on primary production and by effect on soil organic matter stabilization in soil. Despite several studies comparing effect of various substrates on plant growth and soil development exist (Dixon et al., 1982; Martínez-Ruiz et al., 2001; Šourková et al., 2005a; Finkenbein et al., 2013), it is difficult to find simple universal relationships between overburden properties, plant growth and soil development. The overburden materials that support soil development include loess and loess loams, bentonite, kerogen-rich tuffitic claystones with illite, smectites and admixture of carbonates, and sandstone (Rojík, 2004, 2014). Materials that decrease reclamation potential include toxic materials such as acid clays containing coal debris, pyrite and marcasite, kaolin and kaolinic clays (Rojík, 2004, 2014).

3.1.1. Clay-rich substrates

If not toxic, clay-rich substrates support the most vigorous plant growth and the highest ecosystem C storage (Pietrzykowski and Krzaklewski, 2007). On the contrary, development of ecosystems has been reported to be particularly slow on substrates consisting of slowly weathering stones and gravel (Rydgren et al., 2013). Clay soils may suffer from poor drainage and unsuitable soil structure (Scullion and Malik, 2000). However, most clay-rich spoils are in the form of shales or claystones, where the clay is more or less consolidated and impregnated either with carbonates or various types of organic matter such as kerogen (Křibek et al., 1998). As a consequence during the weathering of such spoils, only a small fraction of the material disintegrates into physical clay. The bulk of the claystones disintegrates into fragments with the sizes of silt, sand, or gravel, which are only very slowly broken down. Therefore, the texture of such soils can be quite suitable for plant growth.

Relationships between clay content and soil organic matter storage often reported in non-mining soils (Nichols, 1984; Kleber et al., 2007) have not been found in post-mining soils (Lorenz and Lal, 2007; Vindušková and Frouz, 2013). This does not necessarily mean that clay content has no effect on C sequestration in post-mining soils. It rather means that correlation between SOM sequestration and clay is masked by many confounding factors such as toxicity described above. Another reason lies in methodology of clay content determination. Kuráž et al. (2012) showed that different method of sample preparation for soil texture measurement yields substantial difference in measured clay content of post-mining soils. As already mentioned, clays in post-mining soils may be cemented by organic matter and carbonates and effectively behave as grains of larger size. Consequently, much higher clay content was measured if the soils were prepared using the FAO methodology developed for tropical soils then when more gentle preparation techniques, typically used in temperate soils, have been applied (Kuráž et al., 2012). Variability in preparation techniques may be one of the reasons why no correlation between clay content and C sequestration rate has been found when various studies were compared (Vindušková and Frouz, 2013). Moreover in common soils, both chemical properties and texture are products of long-term weathering and leaching (Brady and Weil, 1999) which is not the case in post-mining sites. As a consequence, there are combinations of texture and soil chemistry in post-mining overburden which could not be found in common soil. Some clay soils may not be suitable because of high salt content or acidity (Rojík, 2004, 2014; Miller et al., 2012; Zipper et al., 2013). This decoupling of texture and chemistry may be another reason for the lack of correlation between SOM sequestration and clay content. The relationships between overburden properties and soil development is clearly complex and should receive more attention. Among the most important factors affecting the substrate's reclamation potential are mineralogical composition, nutrient availability, organic matter content, concentration of potentially toxic elements, cation exchange capacity, pH, texture and structure, and the degree of weathering prior to exposure by mining operations.

3.1.2. Substrate heaping method

Method of excavation, transport and re-deposition as well as manipulation after deposition such as leveling also affect the overburden reclamation potential. Leveling by earth-moving machinery is one of the most widespread reclamation techniques. The aim of leveling is to make the site more homogeneous and to enable the use of the machinery during and after reclamation. In many cases, post-mining sites are heaped in such a way that results in a very irregular terrain, typically with a wave-like appearance. These waves promote spatial heterogeneity in soil physical and chemical properties, e.g. by washing clays and ions downhill (2011b). Heterogeneity can also promote specific microsites with faster soil development (Topp et al., 2001). Frouz et al. (2011b) who studied vegetation development and soil chemistry in wave-like unleveled overburden concluded that local transportation processes within individual waves play the principal role at the investigated sites. Leaching of materials from the wave tops and their deposition at the wave bottoms may explain why the highest contents of available Ca, K, and Na were found at the bottom of the waves. Similarly, the high C content at the wave bottom was caused by accumulation of litter at these locations. Litter accumulation at wave bottoms caused a significant decrease in pH in this microhabitat, and this heterogeneity in pH might have affected other parameters such as P availability, as shown above. Local transportation processes resulting from parallel row heaping were found to be important also in other studies (Buczko et al., 2001). Leveling is a common reclamation operation and it may improve access to the site but it may also cause soil compaction, which may tend to support grasses and suppress the growth of trees (Ashby, 1997).

3.1.3. Fossil organic matter

As already mentioned, overburden may contain substantial amount of fossil organic matter. Most studies on C sequestration consider this fossil organic matter as inert material that can affect determination of C content. There is little data on how fossil organic matter may affect changes in the overall C stock during ecosystem development. There are several studies showing that fossil organic matter can be subject to microbial decomposition (Frouz et al., 2011a). As a matter of fact, most of microbial activity in some freshly dumped post-mining soil may be supported by fossil organic matter (Frouz et al., 2011a). As a consequence, C sequestration in post-mining soils is affected by accumulation of recent organic matter and decomposition of fossil organic matter. It is well known that coal and kerogen can play important role in sorption of organic compounds and affect their bioaccumulation and biodegradation (Cornelissen et al., 2005). However, the potential effect of fossil organic matter on sorption of DOC is another underexplored aspect of SOM dynamics in post-mining soils. Finally fossil organic matter may affect activity of soil biota and plant growth both positively and negatively. Frouz et al. (2005) showed significant positive correlation between coal content and overburden toxicity. On the other hand, coal and coal-derived products are used as a soil amendment to improve soil quality and promote plant growth (Pandey and Singh, 2010).

3.1.4. Organic amendments and topsoil application

In some reclamation approaches, various organic amendments are used to promote plant growth and ecosystem development. It can be various waste products (composts, lignohumates, organic waste, municipal biosolids or compost) or salvaged materials (sod or umbric horizons) (Sydnor and Redente, 2002; Van Rensburg and Morgenthal, 2003; Mercuri et al., 2006; Perminova et al., 2006; Brown and Naeth, 2014). These amendments usually decompose over time. For example, Abakumov and Gagarina (2006) show that about two third of added turf decomposed over 20 years. Therefore, the role of these amendments is to improve initial soil conditions and promote plant growth (Brown and Naeth, 2014; Brown et al., 2014) rather than increase the overall soil C stock directly.

The application of topsoil substitutes, or even more complex covers consisting of several layers instantly improves the soil conditions and allows for a rapid establishment of highly productive vegetation (Rohošková et al., 2006; Borůvka et al., 2012). Topsoil spreading is a costly operation, and besides the clear advantages mentioned above it may also bring some disadvantages; soil spreading may promote soil compaction and the release of nutrients. Compaction may also negatively affect the rooting of plants, especially trees (Ashby, 1997, 1998). The release of nutrients may support grasses and promote the competition of grasses over trees (Ashby, 1997). Compaction caused by leveling and topsoil application can be compensated by ripping which may improve tree growth (Ashby, 1997, 1998). However, ripping may also promote soil respiration which may result in lower overall C storage in ripped compared to standard topsoil application (Jacinthe and Lal, 2007). Application of topsoil or topsoil substitutes is irreplaceable in restoring agricultural land or in restoring extreme, specific toxic substrates. In this case, the more complex cover is often used with the bottom layer consisting of clay or gravel, which separates the toxic layer from the fertile topsoil placed upon the top.

The effect of topsoil may be closely connected with the technologies used, which may vary from direct transfer of undisturbed soil blocks, including associated vegetation, to removing topsoil, stockpiling and then spreading it. Transfer of undisturbed blocks gives excellent results in ecosystem recovery, but it represents an extremely costly and logistically complex operation (Boyer et al., 2011). Other techniques are associated with the disturbance of the soil structure during soil handling (Boyer et al., 2011). Furthermore, the stockpiling of topsoil causes the formation of anaerobic conditions in the pile, which may lead to eradication of soil fauna and changes in the soil microbial community. Changes in the microbial community during stockpiling and spreading may lead to loss of organic matter and future degradation of the soil structure (Ingram et al., 2005; Wick et al., 2009).

3.2. The effect of vegetation on C sequestration

To illustrate plant production and soil organic matter sequestration dynamics over time, let us consider data from two chronosequences located on post-mining heaps near Sokolov, Czech Republic. The first chronosequence is a set of alder plantations (a mixture of *Alnus glutinosa* and *Alnus incana*). The second chronosequence is on unreclaimed land (i.e., land covered with spontaneous vegetation from natural colonization) dominated by birch (*Betula* spp.), willow (*Salix caprea*) and aspen (*Populus tremula*) (Šourková et al., 2005b; Frouz and Kalčík, 2006; Frouz et al., 2008).

Frouz et al. (2015a) showed that biomass of young (5 to 10-year-old) reclaimed sites was significantly higher that biomass of unreclaimed sites, whereas in older sites (25-year-old or older) the difference between reclaimed and unreclaimed sites disappears or even unreclaimed sites show higher biomass of woody vegetation than reclaimed ones. This is in agreement with Zeleznik and Skousen (1996) as well as with Wick et al. (2007) who measured woody biomass production at various sites in the eastern United States and found slightly higher biomass at unreclaimed sites compared to reclaimed ones. On the other hand, Pietrzykowski and Krzaklewski (2007) found substantially larger tree biomass of pine in reclaimed sites compared to sites developing by succession in an open-cast sand quarry. This may have two reasons, one may expect that effect of reclamation namely any kind of nutrient input, would be larger in more oligotrophic sandy soils. Another reason may be the age of forest stands studied because, as already mentioned, in younger sites reclamation is likely to reach higher biomass than succession which may not be true in older sites (Frouz et al., 2015a).

Input of litter onto the soil surface results in accumulation of carbon in the soil. The total C stock including carbon both in the fermentation layer of the forest floor (Oe) and in the mineral soil (A horizon) at the depth of 0–10 cm below the litter or fermentation layer increased significantly at both reclaimed and unreclaimed sites (Šourková et al., 2005b; Frouz and Kalčík, 2006) . Based on slopes of regression lines between C stock and time, we can estimate the rates of C accumulation to be 646 $kg.ha^{-1}.yr^{-1}$ in reclaimed sites and 927 $kg.ha^{-1}.yr^{-1}$ in unreclaimed sites (Šourková et al., 2005b; Frouz and Kalčík, 2006). However in reclaimed sites, the C sequestration appears to be the fastest in younger sites and then it slows down in the 25-30 year old sites, while an opposite pattern has been observed in unreclaimed sites which have lower rate of C sequestration in younger sites and then it speeds up in older sites (Šourková et al., 2005b; Frouz and Kalčík, 2006). This is consistent with the pattern of primary production in these sites as described above (Frouz et al., 2015a). Beside differences in temporal pattern, reclaimed and unreclaimed sites differ also in distribution of C between individual soil horizons. While in reclaimed alder plantations most of C is stored in A horizon of mineral soil, substantial part of C stock of unreclaimed soils is stored in fermentation (Oe) layer (Šourková et al., 2005b; Frouz and Kalčík, 2006). This pattern is given by various intensities of bioturbation at the two sites. At reclaimed sites, soil invertebrates (namely earthworms), which take significant part in bioturbation, occur even at young sites, most likely due to unintentional colonization associated with tree planting. Unreclaimed sites, by contrast, are colonized by earthworms only later (at site age of about 25 years), and intensive bioturbation starts after that (Frouz et al., 2007a, 2008). This results in gradual disappearance of C from the forest floor and its mixing into the mineral soil.

To better explore the role of individual tree species in carbon storage in the soil and in aboveground tree biomass, Frouz et al. (2009, 2013) studied sites afforested with different tree species (spruce, pine, larch, oak, lime and alder) and unreclaimed sites left to natural regeneration on the same heap as described above. No topsoil was applied at these sites, so carbon accumulation resulted solely from *in situ* soil development. The aboveground biomass of trees was estimated by allometric equations as described in Frouz et al. (2009). Furthermore, carbon stock in the fermentation layer and in the A horizon was estimated. To correct for fossil C, soil samples were taken from the depth of 70 cm, and the C content of these samples was subtracted from the C content of the A layer. Carbon storage in the aboveground tree biomass ranged from 17.0 ± 5.9 to 67.6 ± 5.9 $t.ha^{-1}$, and the rate of C sequestration in biomass increased from 0.60 ± 0.09 to 2.31 ± 0.23 $t.ha^{-1}.yr^{-1}$ in the following order: natural regeneration < pine < spruce < oak < lime < alder < larch. Carbon storage in soil organic matter varied from 4.5 ± 3.7 to 38.0 ± 7.1 $t.ha^{-1}$, and the rate of C sequestration in soil increased from 0.15 ± 0.05 to 1.28 ± 0.34 $t.ha^{-1}.yr^{-1}$ at the sites in the following order: natural regeneration < spruce < pine < oak < larch < alder < lime.

Carbon storage in the soil was positively correlated with aboveground tree biomass. Soil carbon was equivalent to 98.1% of the carbon found in aboveground tree biomass at lime-dominated sites, but only 21.8% of that found at sites with natural regeneration. No significant correlation was found between C storage in the soil and aboveground litter input. However, total soil carbon storage was correlated positively and significantly with earthworm density and the occurrence of earthworm casts in the topsoil, which indicates that bioturbation plays an important role in soil carbon storage.

The density of earthworms was higher under trees producing easily decomposable litter such as alder or lime. Not only restoration of wood production but also recovery of the soil community is therefore critical for C storage in the soil and the whole ecosystem. Bioturbation can be also one of the reasons why is C stored more under trees that produce easily decomposable litter with a low C:N ratio than under trees producing litter with a high C:N ratio, which is decomposed at a lower rate (Frouz et al., 2009, 2013). Worm bioturbation can promote incorporation of organic matter into mineral soil but also protection of soil organic matter in soil aggregates (Bossuyt et al., 2005; Frouz et al., 2011c).

Extensive meta-analysis of post-mining sites from Northern Hemisphere showed that the rate of C storage was significantly lower in coniferous forests (0.81±0.38 $t.h^{-1}.yr^{-1}$) than in grasslands (1.81±1.55) or in deciduous forests (2.31±1.02), but it did not significantly differ between grasslands and deciduous forests (Vindušková and Frouz, 2013). In agreement with observation made before by comparison of individual tree species (Frouz et al., 2013), vertical distribution of SOC in the soil profile differed between deciduous trees and conifers. The surface organic layers contained 23% of sequestered SOC in deciduous forests and 62% under conifers (Vindušková and Frouz, 2013), for sites younger than 30 years the difference was even more pronounced with only 17% of SOC sequestered in organic layers of deciduous forest. In Figure 2, we used these proportions to divide the mean C sequestration rates for grasslands, coniferous and deciduous forests to present the potential vulnerability of the sequestered C to loss by disturbance such as fire or erosion.

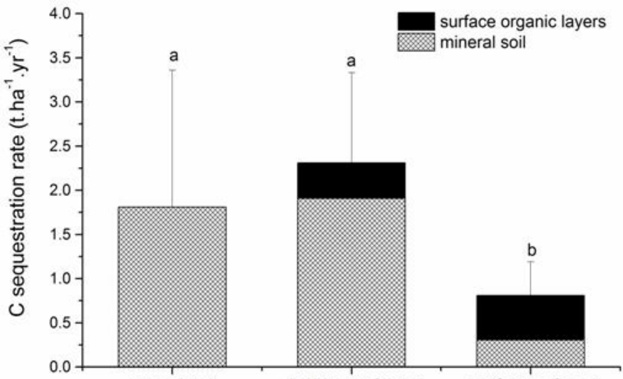

Fig. 2. Mean C sequestration rates in post-mining soils (<=30 years old) under different vegetation types combined with mean relative contributions of surface organic layers and mineral soil to C storage based on data from Vindušková and Frouz (2013)

3.3. The effect of soil fauna on C sequestration

Above-mentioned results from a common garden experiment (Frouz et al., 2013) show that higher incorporation of organic matter under trees producing litter with lower C:N ratio corresponds with higher macrofauna density and activity. Soil carbon is positively correlated with earthworm abundance and amount of earthworm casts in the soil profile. This suggests that the effect of trees on soil may at least partly be mediated by soil fauna (Frouz et al., 2013). Fauna change organization of topsoil layer, leading to different so-called humus forms, which in turn affects rate of decomposition and C sequestration. In soil supplied with litter that has a high C:N ratio, bioturbation effect of fauna is small. As a consequence, most litter is decomposed on the soil surface and a *mor* type of humus develops. Most decomposition under these conditions is done by fungi, the fungal to bacterial ratio (F:B) is high. The activity of soil fauna is more pronounced in soil supplied with easily decomposable litter with a low C:N ratio, resulting in the incorporation of a substantial part of the litter into soil and in the formation of a moder or mull type of humus (Ponge, 2003, 2013). More intensive bioturbation has been shown to correlate positively with C storage and microbial biomass and negatively with microbial respiration and F:B ratio (Frouz et al., 2013). The observation that fauna may support C storage in soil may appear to contradict the litterbag experiments which show much larger mass loss from fauna-accessible bags than from bags non-accessible to soil fauna. However, extensive meta-analysis of Frouz et al. (2015b) showed that fauna promotes removal of organic matter from litter layer (or litter bags) but this organic matter is then largely stored in the mineral soil. Study of soil microstructure showed a substantial role of soil fauna in the formation of the A horizon in these post-mining soils (Frouz et al., 2007b). A detailed study on chronosequences of reclaimed and unreclaimed sites showed a clear effect of earthworm colonization on soil microstructure, soil microbial properties, namely fungal to bacterial ratio and carbon storage (Frouz et al., 2008). Field and laboratory manipulation experiments supported the hypothesis about significant effect of soil fauna bioturbation on carbon storage (Frouz et al., 2006, 2007a). Laboratory experiment showed that incorporation of litter into soil by earthworms results in stronger carbon storage than mechanical mixing of soil or no mixing (Frouz et al., 2014b) which may be related to protection of soil organic matter in soil aggregates (Bossuyt et al., 2005; Frouz et al., 2011c, 2015c).

3.4. The effect of climate on C sequestration

Climate is assumed to have several sometimes contradictory effects on soil C sequestration. On one hand, organic matter inputs depend on primary production, which increases with moisture and temperature. On the other hand, both moisture and temperature increase the decomposition rate (except in waterlogged soils where decomposition is oxygen-limited). Post and Kwon (2000) pointed out that in revegetated agricultural land, there is a tendency for rates of SOC accumulation to increase from temperate regions to subtropical regions. They concluded that this may indicate that inputs (productivity) rather than outputs (decomposition) determine the rate of SOM accumulation.

There is little data about comparison of C sequestration in post-mining soils among biomes. In the already-mentioned extensive meta-analysis of Vindušková and Frouz (2013), who compared post-mining sites only in temperate and boreal climate, no effect of rainfall and temperature was found when all sites with various vegetation cover were evaluated together. However, some trends appeared when sites with different types of vegetation cover were evaluated separately. The rate of SOC sequestration was significantly related to the temperature at sites covered with coniferous forests and grasslands (Fig. 3). The rate decreased with increasing temperature under conifers and increased with increasing temperature in grasslands. Deciduous forests showed no significant correlation with temperature. This relationship between temperature, SOC storage and vegetation corresponds with the natural geographical distribution of grasslands, coniferous forests and deciduous forests, with coniferous forest being typical for northernmost region, grassland for south of temperate zone and deciduous forest in between. This indicates that for reclamation of post-mining sites, the planted vegetation should be typical of the particular biome in which the post-mining site occurs. In other words, grasses should be planted at warmer sites, conifers at colder sites and deciduous trees at intermediate sites.

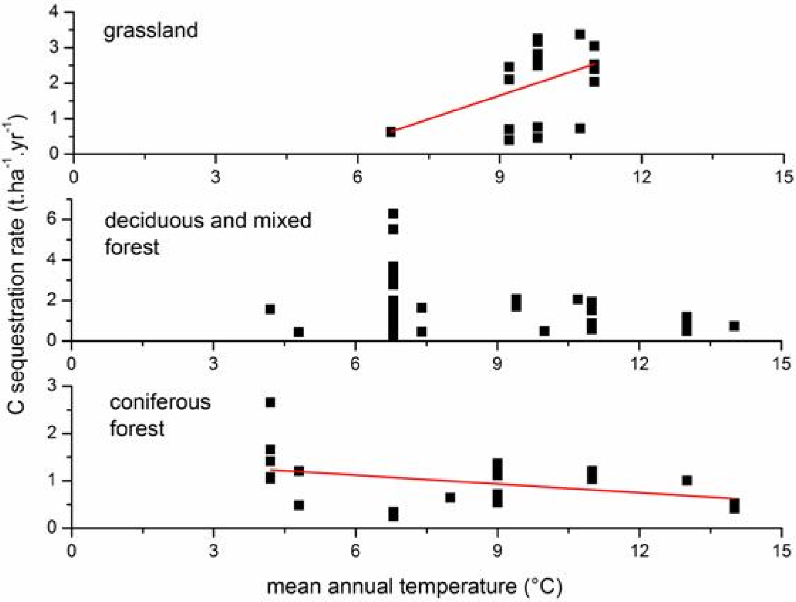

Fig. 3. Effect of temperature on C sequestration rate under different vegetation based on data from Vindušková and Frouz (2013)

4. The effect of soil organic matter accumulation on soil chemistry and other soil properties

Soil organic matter accumulation affects also other elements besides C. Major source of N in ecosystems developing without artificial fertilization are nitrogen-fixing plants, which live in symbiosis with bacteria and actinomycetes. Frouz et al. (2014a) compared differences in N content in various soil layers between plantations of nitrogen-fixing alder (*Alnus glutinosa*) and unreclaimed sites with spontaneous regrowth without N-fixing trees. The difference in N content was the highest in the litter and fermentation (Oe) layer, whereas in the organomineral A horizon, the difference between fixers and non-fixers was low and non-significant.

Phosphorus is another important element crucial for plant growth. The principal source of P is the geological substrate, and the total P content may decrease during ecosystem development. This decrease is caused by a loss of P through leaching but also by growth of plants, which bind P in their tissues. Accumulation of P in plants and, consequently, in decomposing litter may affect the depth distribution of P, resulting in a high P content in organic layers near the soil surface, a P-depleted layer underneath and, again, higher P content in the overburden unaffected by roots (Bartuška and Frouz, 2015). Similarly to P, other nutrients such as potassium come from the geological substrate, and their content in upper soil layers may decrease during ecosystem development. For elements such as K and Na, however, leaching probably contributes more to their loss from the upper soil layer because of their higher mobility (Brady and Weil, 1999).

Soil organic matter has a high buffering potential and can shift soil pH towards neutral or slightly acidic values (Brady and Weil, 1999; Bartuška and Frouz, 2015). Consequently, soil organic matter accumulation in an acidic overburden can increase the pH to slightly acidic (Šourková et al., 2005a), while in alkaline overburden, it can decrease the pH to neutral or slightly acidic (Šourková et al., 2005b). These changes in pH also affect the availability of other nutrients (Brady and Weil, 1999).

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Manuscript 5

Vindušková, O., Pánek, T., Frouz, J., (prepared manuscript):
Soil development during last 13,000 years along a chronosequence of landslides in Central Europe.

Soil development during last 13,000 years along a chronosequence of landslides in Central Europe

Short title: Soil development on landslides in central Europe

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Abstract

For the first time, we investigated long-term (Holocene scale) soil development on sedimentary parent substrate under semi-natural temperate forest. We studied a unique chronosequence of 26 landslides ranging in age from 4 to ~13 000 years located in the Western Carpathians along the border of Czech Republic, Slovakia and Poland. Total soil organic carbon (C), nitrogen (N), and phosphorus (P), pH, and electrical conductivity was measured in landslides as well as in adjacent undisturbed sites.

Both C and N stocks increased rapidly in the first 100 years both in the mineral soil and in the forest floor. C stock in mineral soil then leveled out at a steady state of 51 t ha^{-1} (adj. R^2 0.35) resembling the median of undisturbed sites (57 t ha^{-1}), while mineral N stock decreased significantly in the older landslides. In contrast, the forest floor C and N stocks continued to increase linearly.

Total P in <2mm soil showed a rapid increase in the first 100 years due to redistribution of P from the rock and greater depths followed by a slow decrease significant also for total soil P (including rocks) caused by leaching, erosion and wood harvest. pH and bulk density decreased while electrical conductivity and the C:N, N:P, C:P ratios increased along the chronosequence.

These results suggest that most dynamic soil development occurs in the first 100 years, after which mineral soil becomes saturated by organic matter and further processes are driven by slow loss of phosphorus.

Significance statement

What is the capacity of soils to store carbon and how is this constrained by the nutrient status of soil? How quickly can soils recover after a major disturbance? Answering these questions is crucial for prediction of future feedbacks to climate change. However, most

chronosequence studies addressing these questions have been carried out in rather extreme climate or parent rock environments. Here, we present results from a unique chronosequence on sedimentary bedrock under semi-natural temperate forest. Most of carbon (C) and nitrogen (N) in the mineral soil is accumulated during the first 100 years of development, after which C levels out and N slowly decreases. Total phosphorus decreases along the chronosequence, driving the system towards P limitation and tighter nutrient cycling promoting accumulation of C and N in the more labile forest floor rather than in the mineral soil.

1. Introduction

Soil organic matter (SOM) is an important driver of soil quality and also a crucial pool in the global carbon cycle. Carbon sequestration in soils has been recognized as a possible tool to mitigate the on-going increase of CO_2 in the atmosphere (Lal, 2004). The potential of land use change to increase soil carbon storage has been extensively studied, especially following secondary succession or afforestation of agricultural land (Lugo and Brown, 1993; Post and Kwon, 2000; Poeplau et al., 2011; Yang et al., 2016) and also following primary succession or reclamation of land with no or low biological activity (Crocker and Major, 1955; Sollins et al., 1983; Crews et al., 2001; Vindušková and Frouz, 2013). However, the size and stability of the long-term capacity of soils to store carbon still remains unclear mainly because it is difficult to determine the age of older natural soils (Hassink, 1997) and also due to the complex interplay of soil-forming factors such as climate or parent material. Both the size and stability of the potential soil carbon pool represents a major uncertainty in the models of soil carbon (C) turnover and earth system models as such.

Soil C dynamics are closely linked to the nitrogen (N) and phosphorus (P) cycles since these elements represent the most common nutrients limiting terrestrial primary productivity. Nitrogen is typically limiting to young ecosystems because it is nearly absent from most parent rocks. Gradually, nitrogen is accumulated in the ecosystem via biological N fixation and atmospheric deposition. In contrast, phosphorus undergoes different dynamics during soil development as proposed by the conceptual model of Walker and Syers (1976). The primary source of P is the parent rock from which it is released by weathering, taken up by plants or transformed into secondary iron and aluminum phosphates and can be eventually lost by leaching or erosion. This gradual P transformation and loss may in the absence of other P inputs lead to P limitation in old ecosystems, as typically found in the tropics (Vitousek et al., 2010). This affects the whole ecosystem development in a process called retrogression in which ecosystem production decreases eventually setting a feedback to C and N pools in the soil (Wardle et al., 2004; Peltzer et al., 2010).

Chronosequence studies represent a unique tool to study soil development on millennial time-scales (Stevens and Walker, 1970). Unfortunately, most of the previous chronosequence studies have been carried out in rather extreme climatic and/or parent rock environments such as tropical forest on volcanic islands (e.g. Crews et al., 1995), exposed moraines after retreating glaciers (e.g. Crocker and Major, 1955), sand dunes in Australia (Turner and Laliberté, 2015) and others (Wardle et al., 2004). In contrast, chronosequences studies (>10,000 years) in temperate climate and on sedimentary parent material have been scarce and restricted to sand dunes (Franzmeier et al., 1963; Syers et al., 1970), even though 73% of land surface is covered by sedimentary rocks (Wilkinson et al., 2009) and the relative continental area occupied by temperate climate is expected to increase according to global climate projections (Belda et al., 2016). Moreover, most studies focused on strictly natural ecosystems undisturbed by human use and extrapolating the findings of these studies to temperate zones of North America and Eurasia where land has been severely impacted by human use is questionable.

Landslides are relatively fast movements of rock or soil along slip surfaces. They are important hazardous phenomena but also offer a unique opportunity to study soil using the chronosequence approach. Certain types of catastrophic landslide events (e.g., rapid rockslides, earthflows or rock avalanches; typology after Cruden and Varnes, 1996) create new land surfaces where soil development is completely restarted. Newly exposed rock surfaces are colonized by plants in the process of primary succession which is characterized by little or no biological legacy left by the pre-disturbance ecosystem (Walker and Shiels, 2013).

Here we report the results of a study of long-term soil carbon, nitrogen and phosphorus dynamics along a chronosequence of 26 landslides ranging in age from 4 to 13 000 years located along the border of Czech Republic, Slovakia, and Poland. This chronosequence is unique, because of its large time scale, temperate climate, sedimentary parent substrate and semi-natural forest in older landslides. The aims of this study were:

- to determine the soil carbon storage capacity of the studied soils and the time required to reach this capacity;
- to compare the dynamics of soil phosphorus with the conceptual model of Walker and Syers (1976);
- to estimate the time required for different soil properties to recover to the levels found in soils undisturbed by landslides.

We expected that storage of carbon and nitrogen would be relatively fast and soils would become saturated over decades or centuries. We expected that over the over millenial time-scale, the loss of P from soil would become the key driver of soil carbon and nitrogen dynamics and that different soil properties would recover to pre-disturbance levels at different rates.

2. Methods

2.1. Study area

The Flysch Belt of the Outer Western Carpathians is located along the border of Czech Republic and Slovakia (Fig. S1). The bedrock consists of alternating layers of Cretaceous and Paleogene sandstones, claystones and shales with different water permeability and rock mass strength. These characteristics combined with a specific fold-and-thrust structure formed in Paleogene and Neogene drive the susceptibility of this area to mass movements. Main triggers of landslides are especially heavy rainfalls and/or snowmelt (Pánek et al., 2013a). Some unstable slopes are subject of repeated sliding with the recurrence of activity in the orders of few years to several ka (Pánek et al., 2013a).

For the purpose of this study, 22 landslide areas were chosen of which 4 included landslides of two different ages resulting in total of 26 landslide sites ranging in age from 4 to almost 13 000 years. The age of landslides older than 100 years has been previously determined by radiocarbon dating of organic material buried in the landslide, in a landslide-dammed lake or in an associated peat bog (Pánek et al., 2013a). Radiocarbon ages were calibrated using IntCal 13 calibration curve (Reimer et al., 2013) in OxCal v.4.2.4 software (Bronk Ramsey, 2009) and expressed for the purpose of this study as median central ages in cal BP (Table S1). The age of recent landslides (<100 years) was stated from historical sources, technical reports, eyewitness accounts and personal observations (Pánek et al., 2011a). All the studied landslides (Table S1) contain portions which were significantly disturbed during movement (e.g. headscarps, lateral levees, lobes) and majority of them are classified as catastrophic landslides of the flow type (Hungr et al., 2001).

All the studied landslides (Table S1) are classified as catastrophic flow-like landslides. The specific sites were chosen for the high certainty that the soil development was completely reset by the deep-seated landsliding event. The area and elevation of the studied landslides ranges from 0.6 to 150 ha and from 250 to 745 m a.s.l., respectively. Mean January and July temperatures range from -2 to -5 °C and from 14 to 18 °C, respectively. Mean annual precipitation ranges from 600 to 1200 mm.

The soil classes of the studied soils range from soils with initial soil formation (Leptosols, Regosols) and moderately developed soil profile (Cambisols) to Umbrisols and Podzols in some of the oldest sites. All the soils are generally shallow with high rock content and a soil texture of loam or sandy loam with no visible signs of soil development below 30 cm.

Younger landslides are vegetated by woody spontaneous regrowth or pine plantation (1 site) and older landslides (>80 years) and control sites are covered by mature semi-natural/planted forest dominated by spruce and beech.

2.2. Sampling and sample preparation

Soil samples were collected at 26 landslides including 4 recurrences and at 22 adjacent undisturbed sites as a control. Landslides were sampled either at zone of accumulation (lobe or main accumulation body) or headscarp (zone of depletion) depending on the landslide type/morphology and the dating technique (Table S1). For ^{14}C-dated landslides, soil was sampled near the drilling location of the dated organic material. For younger landslides, headscarp was sampled only if it contained relatively gentle slope that would minimize post-landslide erosion. In the rest of the younger landslides, lower center (body) of landslides were sampled in order to minimize edge effect and erosion risk.

In all cases, gentle slopes were chosen for soil sampling. Litter and fermentation layer was collected from a 30x30cm area. Due to high rock content, soil was sampled from a pit of known volume (30x30x30 cm) in three 10-cm layers. From each layer, larger rocks and soil were weighed separately and a representative soil sample of about 0.5 to 1 kg (depending on the content of smaller rocks) was taken for laboratory analyses. Three pits were sampled at landslide sites and one pit at control sites. Where the pits contained large rocks that could not be easily extracted from the pit, their volume was estimated and recorded. In two pits, the deepest (20-30 cm) layer was not sampled because it contained only parent rock. In one pit, the deepest layer was excluded from further analysis due to visual signs of previous soil development (soil surface buried by the landslide).

In the laboratory, forest floor samples were air-dried and weighed. Fresh coarse woody debris >2 cm diameter that could not be easily cut into smaller pieces was excluded from the samples. About 200 g of each sample was homogenized using a smoothie blender.

Soil samples were air-dried, gently crushed and sieved through a 2-mm sieve. Rock and gravel (>2mm, hereinafter rock) was weighed and a representative sample was kept for rock density and total P measurements. Subsamples of forest floor and <2mm soil (hereinafter fine soil) samples were ball-milled in a Retsch MM400 prior to total C, N, and P analyses. Rock subsamples were ground using an aluminum oxide mortar and pestle.

2.3. Laboratory analyses

pH and electrical conductivity (EC) was measured in a 1:5 fine soil:water suspension. Total CN contents of forest floor and soil were analyzed using an EA 1108 elemental analyser (Carlo Erba Instruments, UK). Soils from two sites that reacted with hydrochloric acid were subsequently treated by 2 drops of 1:1 HCl in silver capsules and analyzed for organic C (OC). Total P content was measured in soil after acid digestion (HNO_3, $HClO_4$) by the molybdenum blue method using spectrophotometry at 889 nm.

2.4. Data analysis

An average of the measured rock densities (2.28 g cm^{-3}) was used for converting field-estimated volume of rock that could not be extracted from the pit to mass, as well as for calculating volumetric rock content from total dry mass of rock in layer. Total volumetric rock content (v/v) was calculated as an average of the three layers.

The following two bulk densities were calculated from the measured data. Firstly, bulk density of fine soil (BD fine) was calculated from dry mass of fine soil divided by volume of layer filled with fine soil; volume filled with fine soil was calculated by subtracting volumetric rock content from total layer volume. Secondly, total bulk density (BD total) was calculated from the sum of dry mass of rock and fine soil, divided by the total layer volume.

In the analysis of rock content and bulk density, two layers were excluded as outliers (where estimate of rock content exceeded 100% or calculated bulk density of fine fraction exceeded specific density of quartz – 2.65).

Carbon, nitrogen and phosphorus stocks (i.e. contents on an area basis, t ha^{-1}) in mineral soil were calculated from the C, N, and P content per unit weight of fine soil based on the dry mass of fine soil in layer. Rock P stocks were calculated from the P content in rock and dry mass of rock in layer. Fine soil P and rock P were summed to obtain total P stock. C and N stocks in forest floor (litter and fermentation layer) were calculated from the C or N content and dry mass per area of the respective layer. Forest floor and mineral soil stocks were summed to obtain the total stock.

Before data analysis, two pits sampled under non-woody vegetation were excluded from the dataset.

Before the analyses of changes along the chronosequence, the age of landslide was log-transformed. The median of control sites was used for statistical comparison between landslides and control sites because in some cases the data did not have normal distribution. Before t-test, landslide data were tested for normality using the Shapiro-Wilk test and alternatively tested by one-sample Wilcoxon signed rank test.

Apart from the traditional linear, logarithmic and polynomial regression, the Hill function was used (Eq. 1):

$$y = V_{\max} \frac{x^n}{k^n + x^n} \qquad \text{(Eq. 1)}$$

where V_{max} is the saturation maximum which y approaches asymptotically. Originally introduced in biochemistry to describe the binding of ligand to enzyme, it has been also used in ecology as a convenient sigmoid saturation function (de Boer, 2004).

Most statistical analyses were performed using OriginPro 2016. The estimates of the age when the landslides reaches the median value of a parameter for the linear and logarithmical models were calculated in R including its 95% confidence intervals using the *calibrate* function from the *investr* package (Greenwell and Schubert Kabban, 2004) with median of control sites as the value for mean response. For the other nonlinear models, only point age estimates were calculated by solving the model equation for y equaling median of control sites.

The effect of layer depth on C:N ratio was tested by fitting a linear mixed effects model (LME) with layer as fixed effect and pit nested in site as random effect using the *nlme* package of R (Pinheiro et al., 2016). Ratios were log transformed to improve normality of residuals and homogeneity of within-group variances.

3. Results

3.1. Rock content, bulk density

Rock content and bulk densities are shown in Figure 1 and reported with sample standard deviations in Table S2.

Rock content of soils was highly variable ranging from 4 to 57 % in landslides and from 2 to 47 % in control sites. Landslides exhibited a mean rock content of 31% which was significantly higher than the median of control sites (18%, one-sample t-test, $p<0.05$). No significant relationship was found between rock content and age of landslide.

Bulk density is presented either as bulk density of fine soil (BD fine, Fig. 1b) which represents the situation in which bulk density rings would be sampled in-between rocks, or as total bulk density (BD total, Fig. 1c) which includes also the mass of rocks and is therefore higher and influenced by rock content. Both bulk densities were also highly variable among landslide sites. In the 0-30 cm layer, BD fine ranged from 0.47 to 1.31 g cm^{-3} with a mean value of 0.87 g cm^{-3} and BD total ranged from 0.73 to 1.78 g cm^{-3} with a mean value of 1.30 g cm^{-3}.

Both BD fine (adj. R^2 0.40) and BD total (adj. R^2 0.26) declined logarithmically along the landslide chronosequence in the first 10 cm of soil and a similar non-significant trend was observed for BD fine in the 10-20 cm layer (Fig. 1bc, for equations see Table S3, adj. R^2 0.26). The fitted models predicted that median bulk density of control sites is reached after 0.3 and 4.3 ky on landslides for BD fine and BD total, respectively (Table S3).

Bulk densities in the two deeper layers did not show any significant change with age of landslides but BD total in the 20-30 cm layer was significantly higher in landslides than the control (one-sample t-test, $p<0.05$) which reflects the higher rock content in landslides.

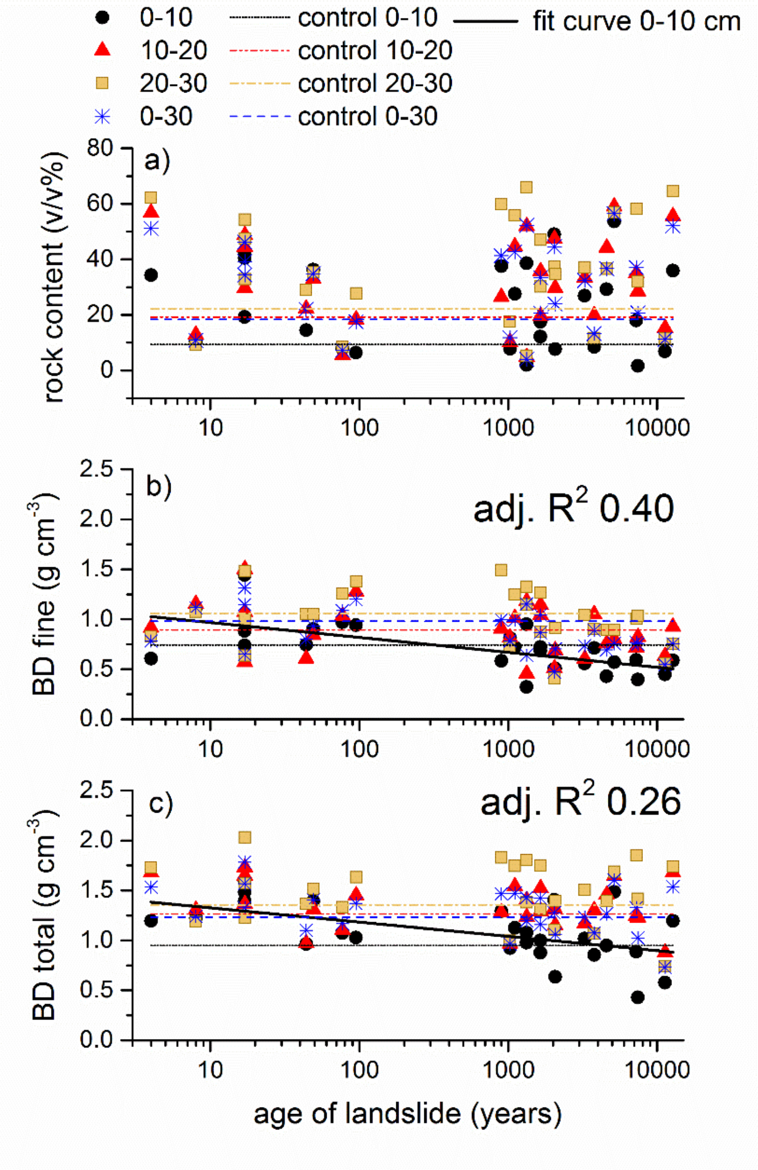

Fig. 1. Volumetric rock content (a), bulk density of fine soil (b), and total bulk density (c) along a chronosequence of landslides in the 0-10, 10-20, and 20-30 cm layers. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Horizontal lines represent median of adjacent undisturbed control sites for each layer. Only fit curves of significant relationships ($p<0.05$) are shown; for respective regression equations see Supplementary material Table S3.

3.2 pH, EC

The pH values on landslides (Fig. 2a, Table S2) in the three different layers ranged from 4.3 to 7.9, in comparison with 3.9 to 6.8 found in the control sites. The pH in landslides decreased linearly with age in all three layers (Fig. 2a, Table S3, adj. R^2 0.61, 0.52, 0.32 for 0-10, 10-20, 20-30 cm, respectively). pH of the control sites was reached at landslides after 3.5, 3.6, 2.4 ky in the 0-10, 10-20, 20-30 cm layers, respectively.

Electrical conductivity (EC) of soil (Fig. 2b) ranged from 23.2 to 237.4 µS cm^{-1} in landslides and from 22.6 to 184.8 µS cm^{-1} in control sites. EC in the first 10 cm increased logarithmically with the age of landslide (adj. R^2 0.14, Table S3). According to the model, median of control sites was reached already after 65 years in landslides. In all three layers of the older landslides (≥900 years), EC was significantly higher than the control (three one-sample t-tests, $p<0.05$).

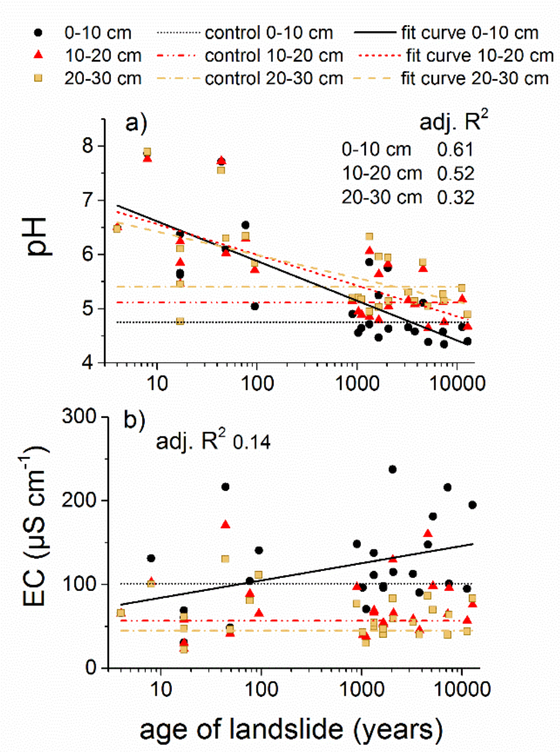

Fig. 2. pH (a) and electrical conductivity (b) of soil along a chronosequence of landslides in the 0-10, 10-20, and 20-30 cm layers. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Horizontal lines represent median of adjacent undisturbed control sites for each layer. Only fit curves of significant relationships ($p<0.05$) are shown; for respective regression equations see Supplementary material Table S3.

3.3. C, N and P stocks in forest floor and mineral soil

3.3.1. Forest floor

Both C and N stocks in both the litter (L) and fermentation (F) layer (Table S2) increased linearly with age of landslide (Fig. 3, Table S3). For carbon, the levels found at control sites were reached after 4.1 and 1.8 ky in the L and F layer, respectively. The N stocks were reached at similar rates (4.1 and 1.6, respectively).

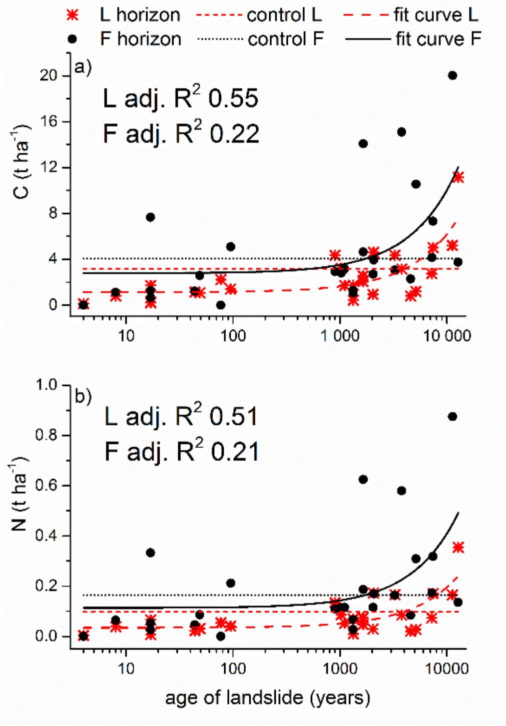

Fig. 3. Carbon (a) and nitrogen (b) stocks (t ha^{-1}) in the litter (L) and fermentation (F) layer of forest floor along a chronosequence of landslides. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Horizontal lines represent median of adjacent undisturbed control sites for each layer. Only fit curves of significant relationships ($p<0.05$) are shown; for respective regression equations see Supplementary material Table S3.

3.3.2. Mineral soil

C stock in the mineral soil (Table S2) ranged from 8 to 91 t ha^{-1} in landslides and from 22 to 89 t ha^{-1} in the control sites. The mean contribution of each layer to the C stock was 52, 26 and 21 % for the 0-10, 10-20, and 20-30 cm layers. This distribution did not change with the age of landslide and a similar distribution was observed in the control sites (Table S2).

C stock changed significantly with the age of landslide and could be described by a logarithmic (adj. R^2 0.19), polynomial(logx) (adj. R^2 0.34), or by the Hill equation (adj. R^2 0.35) (only the last is shown in Figure 4a, see Table S3 for all three equations). Interestingly, the capacity parameter 51 t ha^{-1} found by fitting the Hill function is quite close to the median stock for control soils (57 t ha^{-1}). According to both the Hill and polynomial models, median of C stock in control sites is never reached. According to the polynomial(logx) model, a maximum of 56.3 t ha^{-1} is reached after 620 years of soil development after which the stock slowly decreases.

N stock in the mineral soil ranged from 1.0 to 8.6 t ha^{-1} in landslides and from 1.6 to 6.3 t ha^{-1} in control sites (Table S2). The mean contribution of each layer to the N stock was 49, 28 and 23 % for the 0-10, 10-20, and 20-30 cm layers. This distribution did not change with the age of landslide except in the 10-20 cm layer, contribution of which decreased logarithmically with the age of landslide (adj. R^2 0.12). The same mean distribution was observed in the control sites (Table S2).

N stock changed significantly with the age of landslide and was best described by a polynomial(logx) model (adj. R^2 0.31), as opposed to the Hill model which explained only 7% of variability in data (only polynomial fit is shown in Figure 4b, see Table S2 for both equations). The control stock of 4.2 t ha^{-1} was reached already after 70 years of soil development on landslides (according to the polynomial model, Fig. 4b). The maximum N stock of 4.7 t ha^{-1} was reached after about 300 years after which it decreased to drop below the median of control sites after 1.3 ky.

The mean total P contents (min–max) in <2mm soil were 479 (177–1027), 376 (159–721), 330 (136–672) mg kg^{-1} in the 0-10, 10-20, and 20-30 cm layers. The respective values for control sites were 418 (220–1006), 306 (93–836), and 277 (101–585) mg kg^{-1}. However, due to variable rock content and bulk densities, stock in weight per area is a better indicator of soil P reserve. The total phosphorus stocks (P_{tot}) in mineral soil divided into fine soil (P_{fine}) and rock and gravel (P_{rock}) are presented in Fig. 4c and Table S2. The P_{fine} in landslides ranged from 0.25 to 1.53 t ha^{-1} with a mean value of 0.65 t ha^{-1} that was very close to the median stock of control sites (0.68 t ha^{-1}). In landslides, P_{fine} represented on average 62 % of P_{tot} which was significantly less than in control sites (74 %, one-sample t-test, $p<0.05$) and corresponded with the higher rock content found in landslides. There was no significant relationship between age and the distribution of total P among fine soil and rock. Similarly to nitrogen, P_{fine} followed a polynomial(logx) trend (adj. R^2 0.22). The median control stock of 0.68 t ha^{-1} was reached already after 14 years of soil development on landslides (according to the model, Fig. 4b). The maximum P_{fine} of 0.93 t ha^{-1} was reached after 177 years after which it decreased to decline below the control stock after 2.3 ky.

No significant relationship was found between rock P content and age of landslide. Mean P_{rock} in landslides was 0.44 t ha^{-1} which was significantly higher than the median value for control sites (0.21 t ha^{-1}, one-sample t-test, $p<0.05$). P_{tot} showed a linear decrease with the age of landslide (adj. R^2 0.15) which predicted that it drops beneath the median control stock of 0.93 t ha^{-1} after 5.4 ky.

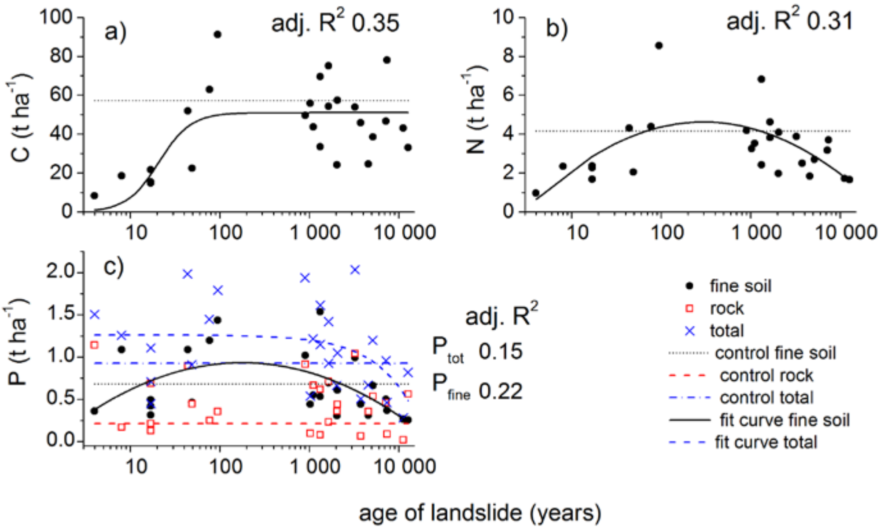

Fig. 4. Carbon (a), nitrogen (b) and phosphorus (c) stocks (t ha^{-1}) in the mineral soil along a chronosequence of landslides. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Phosphorus stocks are presented separately for P_{fine} (<2mm soil), P_{rock} (rock and gravel, >2mm) and as their sum – P_{tot} (total P stock). Horizontal lines represent median of adjacent undisturbed control sites. Only fit curves of significant relationships ($p<0.05$) are shown; for respective regression equations see Supplementary material Table S3.

3.4. Total CN stocks, relative contribution of forest floor to total stocks

Total soil stocks of C and N, obtained as a sum of the mineral and forest floor stocks, followed similar trends as the mineral soil stocks although there were some differences (Fig. 5, see Table S3 for equations). For carbon, polynomial(logx) model was not significant this time, the fit of the logarithmic model was slightly worse (adj. R^2 0.25), but the Hill equation explained even more variability (adj. R^2 0.40). Again, the Hill model predicted that the median C stock of control sites is never reached in landslides. The capacity parameter of the Hill equation (60 t ha^{-1}) to which the C stock approaches was again close to the median of control sites (64 t ha^{-1}).

For nitrogen, the polynomial(logx) fit was slightly worse than for the mineral soil (adj. R^2 0.28), but still better than the fit of the Hill curve (adj. R^2 0.12). The median stock for control soils was 4.4 t ha^{-1} which was reached after 94 years of soil development on landslides (according to the polynomial model, Fig. 5b). The maximum total N stock of 4.8 t ha^{-1} was reached after 345 years. The model also predicted that after 1.2 ky, N stock in landslides begins to decline when compared to median of control sites.

The contribution of forest floor to total C and N stocks was highly variable, ranging from 2 to 37 % for C, and from 0 to 38 % for N. Similarly, the contribution ranged also in control sites – from 4 to 45 % for C, and 2 to 29 % for N. The median of control was 13 and 7 % for C and N, respectively. In landslides, contribution of forest floor to total stock increased linearly along the chronosequence both for C (adj. R^2 0.42) and N (adj. R^2 0.52) (data not shown, equation in Table S3). The median distribution found in control sites was reached in landslides after 2.4 and 1.9 ky for C and N, respectively. Generally, organic horizons contributed relatively more to total C than to total N stock (paired sample t-test, $p<0.05$, mean difference 5%).

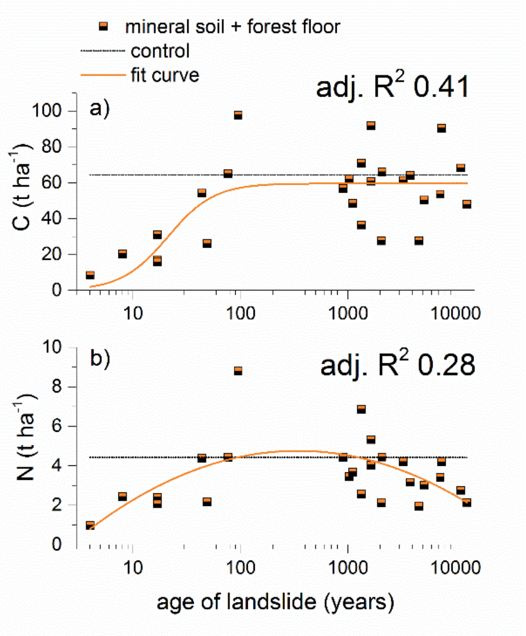

Fig. 5. Carbon (a) and nitrogen (b) stocks (t ha^{-1}) in the whole soil profile, including forest floor along a chronosequence of landslides. Horizontal lines represent median of adjacent undisturbed control sites. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Only fit curves of significant relationships ($p<0.05$) with the highest adj. R^2 are shown; for respective regression equations see Supplementary material Table 2.

3.5. Stoichiometry – C:N, C:P, N:P

The C:N, C:P and N:P ratios in the 0-30 cm mineral soil decreased with depth and increased with the age of landslide (Fig. 6, Table S2, S3). C:N ratio was significantly higher in the first 10 cm layer (median value 13.8) than in the two deeper layers (12.0 and 11.6) which did not differ significantly (LME, Tukey post-hoc test, $p<0.001$). The C:N ratio in the 0-30cm depth ranged from 6 to 25 and the increase with age was linear (Fig. 6a, Table S3, adj. R^2 0.59). However, we did not observe any distinct age trend for the C:N ratio in forest floor (nor in litter and fermentation layers separately).

The increase in C:P and N:P ratios with age followed a logarithmic trend both when calculated using P in <2mm soil (P_{fine}) (adj. R^2 0.52 and 0.40, respectively) and total P stocks which included rock P (P_{tot}) (adj. R^2 0.23 and 0.13, respectively).

4. Discussion

The main trends in soil properties observed along the landslide chronosequence are summarized in Fig. 7. These results provide insight into temporal trends of long-term soil development in the last 13,000 years in Central Europe.

4.1. Carbon

The mineral soil C and N stocks followed a pattern often observed during ecosystem development – a rapid increase during the initial so-called progressive phase followed by a period of lower accumulation rates (Schlesinger, 1990; Peltzer et al., 2010; Vindušková and Frouz, 2013). Interestingly, the initial accumulation of SOM was relatively rapid when compared to other chronosequence studies of primary succession. Out of the capacity of 51 t ha^{-1} found by the Hill function, a mineral C stock of 50 t ha^{-1} was reached already after 107 years (Fig. 4a). Similar dynamics were found on a 270-year-old floodplain chronosequence in Alaska where the soil C storage leveled off after 153 years at over 60 t ha^{-1} (Kaye et al., 2003). Similarly, C and N in the upper 15 cm accumulated to steady state levels within 145 years on the Lake Michigan dune sequence (Lichter, 1998). However, the capacity of soil to store C may be reached much slower. Schlesinger et al. (1990) postulated that the period of rapid increase of soil organic matter is up to 3,000 years. Indeed on Hawaiian lava flows, up to 74 t ha^{-1} of C was accumulated after 3400 years; however, the stocks of 110-136 year old sites ranged only from 3 to 25 t ha^{-1} (Raich et al., 1997). In another Hawaiian chronosequence, soil C increased from 37 t ha^{-1} after 400 years to 106 t ha^{-1} after 5000 years of soil development (Kitayama et al., 1997). On the other hand, 110 years of development on Krakatau volcano lead to comparable or higher C stocks ranging from 49 to 140 t ha^{-1} (Schlesinger et al., 1998). In our chronosequence, soil C stocks were best described by the Hill function indicating a slow increase towards a steady state (Fig. 4a). However, chronosequences vary greatly in the fate of soil C and N stocks during the later stages of ecosystem development after the quasi steady-state is reached (Peltzer et al., 2010). After the progressive phase, C and N stocks may either continue to accumulate slowly, remain constant, or even decrease. For example, in the chronosequence in Hawaii mentioned above, the soil C stock dropped after 9000 years to 61 ta ha^{-1} together with aboveground biomass (Kitayama et al., 1997). Chen et al. (2015) found soil C and N to peak after about

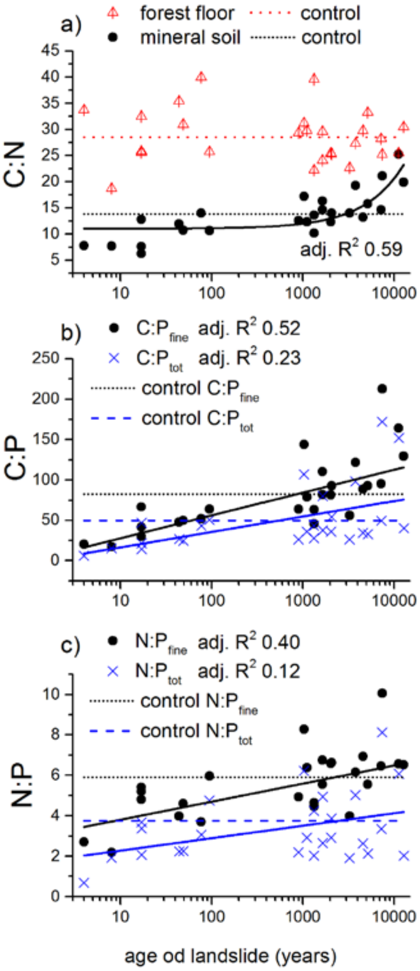

Fig. 6. C:N ratio of forest floor and mineral soil, C:P and N:P ratios of mineral soil, calculated using P in <2mm soil (P_{fine}) or including rock P (P_{tot}) along a chronosequence of landslides. One point represents a mean value of three pits and sample standard deviations are given in Table S2. Horizontal lines represent median of adjacent undisturbed control sites. Only fit curves of significant relationships ($p<0.05$) with the highest adj. R^2 are shown; for respective regression equations see Supplementary material Table S3.

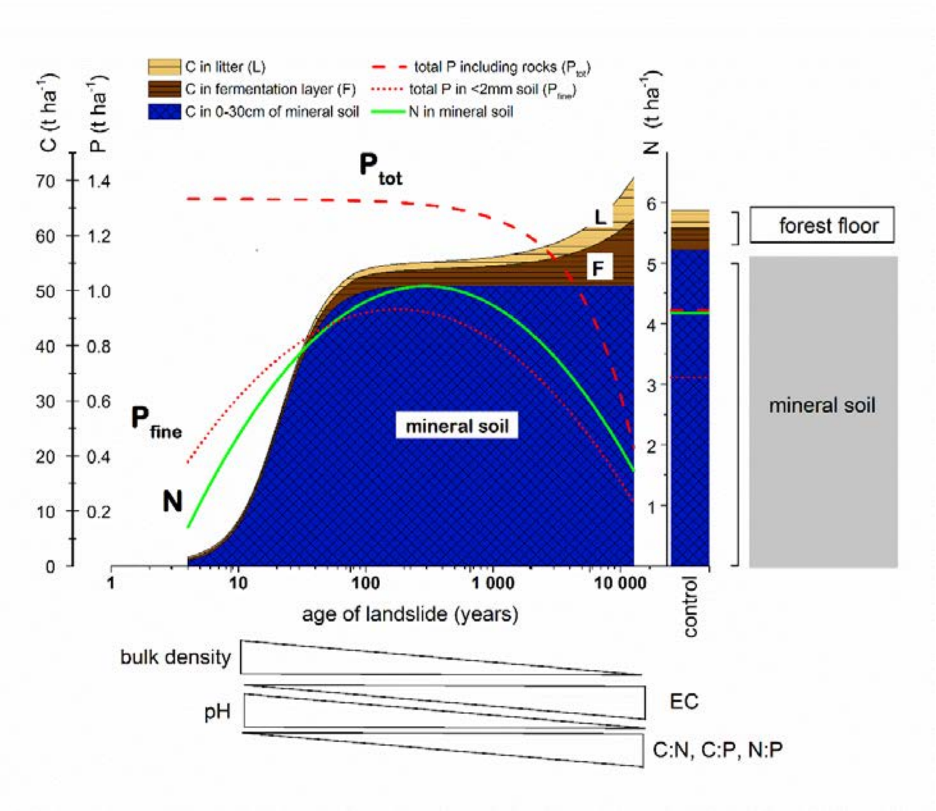

Fig. 7. Soil development along a chronosequence of landslides in Central Europe. Temporal change of carbon (C) stocks is shown for the forest floor (litter – L, and fermentation layer – F) and the mineral soil (0-30 cm), separately. Pattern for nitrogen (N) is shown for simplicity only for the mineral soil. Total phosphorus is shown either as P in fine (<2mm) mineral soil (P_{fine}) or P including rocks (P_{tot}). C, N and P trends are scaled, whereas trends for bulk density, pH, EC and the stoichiometric ratios are only schematic denoting increase or decrease along the chronosequence.

130-170 ky and decline in the oldest sites on the Cooloola chronsequence in Australia. A decline in C and N in the oldest sites has been also observed on a 2 million-year coastal dune sequence at Jurien Bay, Australia (Turner and Laliberté, 2015). Generally in well-drained soils, C accumulation patterns follow aboveground net primary productivity (Crews et al., 1995; Kitayama et al., 1997).

In forest soils, substantial amount of carbon can be stored in the forest floor but this represents a relatively less stable C pool than can be lost rapidly by fire, erosion or decomposition under changed (micro)climate. Out of the total stock on landslides, 2 to 37 % of C and 0.4 to 38 % of N was stored in the forest floor. Generally, the forest floor stocks of both C and N alone increased linearly along the chronosequence (Fig. 3ab) in contrast to mineral stocks (Fig. 4ab). Also, the contribution of forest floor to total stocks increased linearly along the landslide chronosequence both for C and N. In other words in the older landslides, C and N tended to accumulate more in the surface horizons rather than in mineral soil. The possible explanation behind this phenomenon may be that: 1) the soil C-saturation capacity of the mineral soil (determined by available mineral surfaces) may have been reached (Six et al., 2002); 2) decomposition rate and mixing of organic and mineral layers were reduced as a consequence of decreased litter quality inducing a shift in soil microbial and fauna community (Peltzer et al., 2010). We hypothesize that the latter mechanism is more likely and is driven by the increasing P limitation of the ecosystem.

However, when we summed forest floor and the mineral soil, total soil C stocks followed the age pattern of the mineral soil, reached 59 t ha^{-1} after 187 years and approached a steady state of 60 t ha^{-1} thereafter (Fig. 5a). Again the period of rapid increase was rather short when compared to other chronosequences. A logistic increase of C in upper 15 cm soil and O horizon was observed also during 2375 years of primary succession on sand dunes of Lake Michigan and it took 440 years to approach the steady-state levels (Lichter, 1998).

In our study, the total C stock steady state was again comparable to the stock found in adjacent undisturbed sites (64 t ha^{-1}, Fig. 5a). However, both of these values were comparatively lower than the mean C stock of 118±2 t ha^{-1} (±CI) given by Schlesinger (1977) for temperate forests. This may be caused by i) the higher sampling depth in studies reviewed by the author, or ii) relatively cooler montane climate and iii) lower phosphorus content in our chronosequence. Our results confirm that the capacity of soil to store carbon is limited and that the size of this capacity and the rate at which it is reached after major disturbance is highly variable.

4.2. Nitrogen

In our study, total N in the mineral soil first increased dramatically during the first 100 years together with C (C:N ratio does not change), peaked at 4.7 t ha^{-1} after about 300 years of soil development and then slowly decreased (Fig. 4b). Similar pattern was followed by total soil N when summed for mineral soil and the forest floor with a maximum of 4.8 t ha^{-1} (Fig. 5b). The rate and size of N accumulation found in landslides in the first 100 years is in good accordance with previous studies. Generally, soil N is known to increase during primary succession, together with soil C (Walker and Del Moral, 2003). In a review of 20 studies of primary succession, Walker (1993) found that N accumulation rates were greatest in the first 50–200 yrs and N stocks leveled off after 100–1000 years between 2 and 5 t ha^{-1}. Similarly, Kaye et al. (2003) found that nitrogen accumulation rate approaches zero after 200 years on floodplains in Alaska. Syers et al. (1970) observed a rapid increase in the first 1000 years followed by a slower increase on a sand dune chronosequence in New Zealand. Also in other chronosequences, total N in soil was found to attain a steady state after an initial period of increase (Olson, 1958; Richardson et al., 2004). But why did N decrease in mineral soil in the older landslides? Peltzer et al. (2010) reviewed 9 long-term chronosequences and indicated that in some cases, total soil N may decline in the retrogressive stage of the ecosystem development but did not give any explicit explanation for this phenomena. A decrease in total N was found in Glacier Bay after vegetation cover shifted from alder to spruce forest around 100 years of ecosystem development (Crocker and Major, 1955) and also in the subtropical Cooloola dune chronosequence after about 200,000 years (Chen et al., 2015). We propose on of the two following mechanisms or their combination for the observed N decrease in older landslides: 1) decrease in N inputs due to limitation by P, 2) increase in outputs due to forest harvest and leaching. Resulting N deficiency may have in turn promoted utilization of more easily available N sources accumulated during the progressive phase of ecosystem development.

Firstly, it has been postulated by Walker and Adams (1958) that N accumulation in the ecosystem will stop when all the remaining soil P has been converted to organic P or unavailable inorganic P. The on-going transformation of P from primary minerals into forms less available to plants together with loss of P via leaching and erosion may lead to P limitation in older ecosystems (Walker and Syers, 1976). Although we did not investigate the dynamics of the different P fractions, we may expect that the availability of P forms in older landslides decreased. P limitation occurs when the demand exceeds supply and this consequently leads to biological responses in plants enabling tighter recycling of nutrients in the ecosystem, such as high nutrient-use efficiency, lower quality and decomposition rates of plant litter and accumulation of nutrients in plants (Peltzer et al., 2010). Consequently, N can also become less available because it can be bound in plant litter and humus in increasingly unavailable forms such as protein-polyphenol complexes (Northup et al., 1995b; Peltzer et al., 2010).

Secondly, since most of the older landslide sites are semi-natural forests historically harvested for wood production, the long-term N outputs are higher than in other chronosequences of strictly natural ecosystems. Intensive management practices such as clear-cutting can lead to elevated nitrogen losses from ecosystems via leaching (Vitousek et al., 1979). Excessive leaching of N can occur under high levels of precipitation or in acidic soil conditions (Walker and Del Moral, 2003). Removal of tree biomass and subsequent uptake of nitrogen by the young forest likely added to nitrogen losses from soil.

4.3. C:N ratio

We observed a continuous increase in the C:N ratio of mineral soil throughout the chronosequence ranging between 6 and 25 (Fig. 6a). This might have been partly the effect of the overall decrease in N stocks in older landslides. Although, a similar pattern has been observed in many chronosequences differing in climate and parent material even when total nitrogen did not decrease (Dickson and Crocker, 1953; Crocker and Dickson, 1957; Syers et al., 1970; Sollins et al., 1983; Kaye et al., 2003; Chen et al., 2015; Turner and Laliberté, 2015). However, Kaye et al. (2003) synthesized soil C:N data from seven other chronosequences and found that both increase and decrease in C:N ratio can occur in the first 200 years of succession, after which the C:N ratio changes more slowly but tends to increase. Similarly, Bockheim et al. (1980) reviewed 27 chronosequences world-wide and found C:N ratio to both increase or decrease with time. They attributed the C:N decrease to absence of conifers in the sequences and the C:N increase to a gradual decrease in nitrogen-fixing species and a concurrent increase in coniferous litter byproducts in the soils. In contrast, Wen et al. (2016) did not observe any significant C:N ratio change following 59 years of agricultural abandonment in China. With a few exceptions, the increase in C:N ratio during succession seems to be the prevailing pattern. This is little unexpected since C:N ratio is known to decrease during aging of soil organic matter (due to decomposition) and typically decreases down the soil profile (Post et al., 1985). This was also true for our landslides where the top 10 cm layer had higher C:N ratios than the two deeper layers. It is therefore surprising that, the C:N ratio of SOM on older landslides is higher. Also, the C:N ratio of forest floor nor litter alone did not change significantly along the chronosequence (Fig. 6a) excluding litter C:N change as a possible factor behind the C:N increase in mineral soil. It would be worth further investigation which other parameters of litter quality (such as polyphenol content see Northup et al. (1995a) or lignin:N ratio) might be behind the C:N widening during soil development.

4.4. Phosphorus

Young landslide soils were found to be richer in total P than control sites (Fig. 4c) indicating that landslide event rejuvenates parent substrates leading to increased P availability in the initial stage of soil development. However, the total P stocks in the <2mm soil found both in the control and in the landslide soils are at the lower end of the range of values reported for European temperate forests (e.g. Talkner et al., 2009: 0.9–1.4 t ha^{-1}; Prietzel and Stetter, 2010: 0.7–1.8 t ha^{-1}). Similarly, the mean P contents in the <2mm soil in the 0-10 cm in landslides and control sites (479 and 418 mg kg^{-1}) were two times lower than the mean (966 mg kg^{-1}) reported for 79 European beech forests (Talkner et al., 2015). This may be an effect of intrinsic low P contents of the sedimentary parent substrates which are generally poorer in P than igneous rocks (Peltzer et al., 2010).

Total P stocks changed significantly during soil development on landslides. P in the <2mm soil increased rapidly in the first 100 years followed by a slower decrease in the sites older than 100 years (Fig. 4c). Similar trend was observed in the 0-20 cm surface layer on a 2 million-year coastal dune chronosequence in SW Australia (Turner and Laliberté, 2015) as well as in the Franz Josef chronosequence in New Zealand (Walker and Syers, 1976). We may assume that the initial increase is an effect of redistribution of P from greater depths and rocks and the build-up of organic P as was previously observed elsewhere (Crews et al., 1995; Richardson et al., 2004). The subsequent decrease in P_{fine} along the chronosequence corresponds with the overall decrease found in total P (when including rock P, Fig. 4c) and is consistent with the model of Walker and Syers (1976) as well as observations from many long-term chronosequences world-wide (Lajtha and Schlesinger, 1988; Lichter, 1998; Chen et al., 2015; Turner and Laliberté, 2015). Even though in some chronosequences P only undergoes transformation to less available forms but total P does not decrease (Crews et al., 1995), here we observe significant total P loss that may be attributed to leaching, erosion and wood harvest.

Interestingly, no significant decrease was found in rock P along the landslide chronosequence (Fig. 4c) as opposed to the Franz Josef chronosequence in New Zealand where P in stones (>2 mm) decreased sharply after exclusion of one site (Walker and Syers, 1976). The effect of rock P weathering may have been hidden in our chronosequence by the high variability of rock content and rock P concentrations among the chronosequence sites.

As already indicated, the decreasing total P content as well as assumed transformation of P into less available organic and inorganic forms along the chronosequence may have been an important driver of the development of other soil properties such as the mineral N decrease, C:N increase, and accumulation of organic matter in the forest floor. P limitation has been suggested as one of the potential drivers of the retrogressive phase of ecosystem development (Wardle et al., 2004). The rate at which ecosystem approaches the retrogressive phase is highly variable. Based on data from 6 chronosequences, Wardle et al. (2004) concluded that the ecosystem usually enters the decline phase in which P becomes limiting after a few thousand years of development. In contrast, the progressive phase lasted for about 250 000 years in the Cooloola Dune sequence in Australia (Walker et al., 2010) or even about 750 000 years in another semi-arid chronosequence (Selmants and Hart, 2008). Accordingly, Walker and Syers (1976) observed little change in total P in a chronosequence subjected to dry and warm climate as opposed to marked changes in chronosequences with wetter climates which promote weathering and leaching.

Another factor affecting the rate at which ecosystem reaches P limitation is presumably the intrinsic P content of parent substrate. This may be the reason behind much longer intervals during which C and N is accumulated on volcanic lava flows as discussed above. We may conclude, that the rate at which retrogressive soil features developed in the studied chronosequence was relatively high and may be explained by the humid climate and intrinsically low P contents of the sedimentary parent substrate.

4.5. N:P, C:P

The N:P and C:P ratios increased along the landslide chronosequence supporting the patterns reported in other studies of primary succession (Wardle et al., 2004; Turner and Laliberté, 2015) and indicating increase in P limitation relative to N. The soil N:P ratio has been shown to negatively correlate with foliar P concentrations in European beech forests (Talkner et al., 2015). P limitation has been repeatedly inferred from soil P status and the N:P ratio (Menge et al., 2012). Wardle et al. (2004) proposed to use the Redfield ratio (N:P = 16) as a value above which phosphorus becomes limiting for biological processes relative to N. However, Redfield observed this ratio in marine planktonic biomass and ocean water. Cleveland and Liptzin (2007) searched for similar general pattern in soil and found an average C:N:P ratio of 212:15:1 (C:N =14) for forest soils based on data typically from the 0-10 cm layer. In contrast, Talkner et al. (2015) compiled data from 79 European beech forests and found the most N:P ratios in the range from 2 to 15 suggesting that these soils are relatively richer in P or poorer in N relative to average forest soil. In the 0-10 cm layer, our control sites had an average C:N:P ratio of 157:10:1 (C:N = 16) indicating that undisturbed soils in our study area are relatively depleted in P when compared to other European beech forests which may be given by the intrinsically low P content of the sedimentary bedrock. However in landslides, the N:P ratio in the first 10 cm ranged between 3 and 15 and exceeded 10 only in the three oldest sites suggesting that landslides soils are relatively richer in P than the undisturbed soils in the area.

However, in some very old ecosystems, much wider N:P ratios may occur indicating more pronounced P limitation. For example, in a 2 million-year chronosequence in Australia, the N:P ratio increased from 4 to 42 in the oldest sites (Turner and Laliberté, 2015). Similarly, N:P increased from 1-4 to 27-30 in the 500,000-year-old Cooloola chronosequence (Chen et al., 2015).

It should be noted that although the N:P ratio and soil P status suggest that landslides develop toward P limitation, only a fertilization experiment similar to those from Hawaii (Vitousek and Farrington, 1997) and Cooloola sequence (Laliberté et al., 2012) could confirm this hypothesis.

4.6. Rock content, bulk density, pH, EC

In our study, soils on landslides had higher rock content than in the control sites. Higher content of rock fragments compared to adjacent soils were reported also in other studies on landslides (Cheng et al., 2016) and is typical also for chronosequences on glacial tills (Stevens and Walker, 1970).

As a consequence of organic matter accumulation, bulk density decreased in the top 0-10 cm layer in accordance with observations of other chronosequence studies (e.g., Dickson and Crocker, 1953; Crocker and Dickson, 1957; Stevens and Walker, 1970).

pH of soil decreased during succession on landslides, with the highest decrease observed in the top 10 cm layer. This is in accordance with previous studies on volcanic islands, glacial moraines, floodplains and dunes that show that soil pH generally declines in primary succession as organic acids accumulate (e.g. Salisbury, 1925; Burges and Drover, 1953; Wilson, 1960; Bockheim, 1980; Crews et al., 1995; Walker and Del Moral, 2003; Turner and Laliberté, 2015). The dynamics of the pH change on landslides were also similar to other sequences – most change occurred in the first 1000 years or even earlier. For example, Lichter et al. (1998) observed pH to decrease in the upper 15 cm mineral horizon from 8.5 to 4.3 after 440 years of primary succession on sand dunes.

Electrical conductivity increased along the chronosequence in the top 0-10 layer and was generally higher in the older landslides than in control sites in all three layers. This may be due to the change in pH in combination with continuous weathering of the relatively less weathered landslide soil containing higher amount of rocks.

4.7. Recovery rate of different soil properties

Different soil properties recovered from the major disturbance at different rate. The properties that reached the level of undisturbed soils most rapidly (during first 100 years of soil development) were P in <2mm soil, EC in 0-10 cm layer, and the mineral and total N stock confirming that landslide event represents a disturbance that rejuvenates parent substrate in terms of nutrients. Contents of major nutrients (N and P) were recovered within the first 100 years together with intensive soil organic matter accumulation after which C storage in mineral soil reached levels near saturation capacity. However after 2 to 3 hundred years, N and P stocks in <2mm soil reached a maximum and decreased back below the level of undisturbed sites after 1–2 thousand years. In contrast, it took more than 5 thousand years to exhaust the total P stocks including P in rocks to the level found in undisturbed soils suggesting that rocks which are abundant in the landslide soils represent an important P source from which P is slowly released by weathering. Interestingly, when the capacity of mineral soil to store C and N was reached, forest floor stocks continued to accumulate and recovered to levels of undisturbed sites much later (after 1.5 and 4 ka for the F and L layers, respectively).

4.8. Limitations

It has been previously recommended that chronosequences should be preferentially established in areas undisturbed by human use (Stevens and Walker, 1970). However, we believe that our chronosequence under semi-natural temperate forest also brings valuable information as 99 % of temperate forests has been impacted by human use (Tyrrell et al., 2012).

The chronosequence approach requires that soil-forming factors other than time should be constant or vary only limitedly. In our chronosequence, the bedrock consisted of a varying mixture of sandstones, claystones and shales. However, certain variability in rockiness or particle size of the parent substrate has been previously admitted and accepted also in other chronosequence studies (Sollins et al., 1983; Crews et al., 1995) and we believe that we have compensated for this variability by the exceptionally large number of sites included in our study. Moreover, it should be noted that as in other similar chronosequences of millennial time-scale, the constancy of the climate factor could not be fully secured. However, the development of all sites falls into the Holocene period during which climate has been fairly stable in Central Europe, especially in the last 8,000 years. Only the two oldest sites (>11,000 yr) may have experienced distinctly cooler climate in the first 2 or 3 thousand years (Davis et al., 2003).

Another limitation of our study is that there were no suitable landslides available aged between 100 and 900 years. Further, lower number of landslides available from the earlier stages of Holocene is attributed to erosion of older landslides and/or burial of these sites by younger reactivations (Pánek et al., 2013a).

5. Conclusions

The soil carbon storage capacity of about 50 t ha^{-1} was reached during the first 100 years of soil development on landslides. After this initial phase of rapid soil organic matter accumulation, the C stock in mineral soil did not change while nitrogen decreased leading to a widening C:N ratio. In contrast, forest floor C and N stocks continued to accumulate with no change in the C:N ratio. The dynamics of C and N were likely driven by the gradual loss of P from soil through leaching and erosion as well as transformation of P to forms less available to plants as predicted by the conceptual model of Walker and Syers (1976). The relatively humid climate and low initial contents of P in parent substrate of the chronosequence may have supported relatively rapid development of P limitation which likely lead to tightening of nutrient cycling and decreased N availability. Historical wood harvest in the studied area probably added to the N and P losses from soil. However, only fertilization experiments could confirm P limitation in older landslides.

Many soil features were observed to change with the age of landslide, often approaching the status of the control undisturbed soils. The rate of this recovery differed strongly among parameters and ranged from decades to millennia.

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Supplementary data

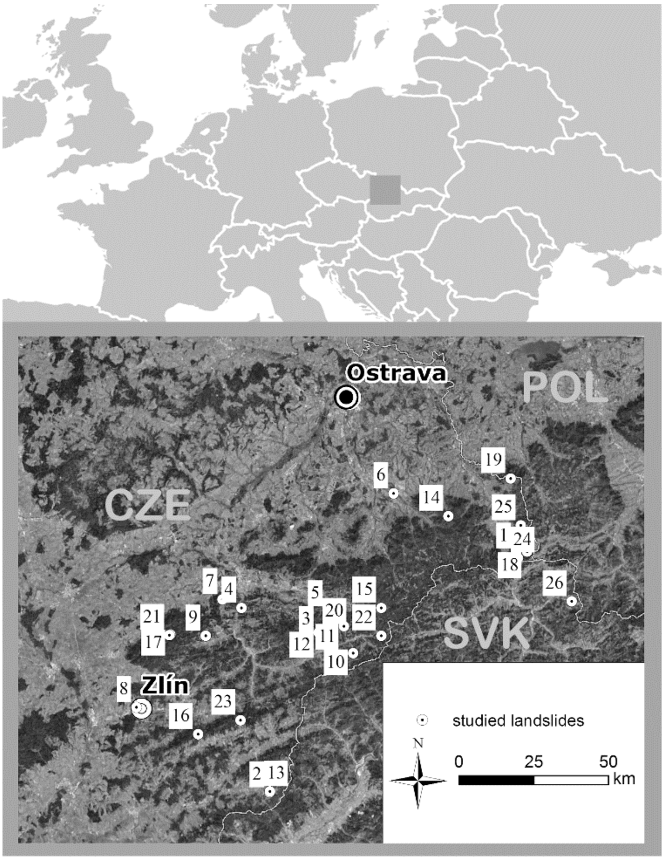

Fig. S1. Map of 26 studied landslides along the border of Czech Republic (CZE), Slovakia (SVK) and Poland (POL). Different numbers denote different landslide sites listed in the same order in Table S1.

Table S1 List of studied landslides. MAP - mean annual precipitation

Site		Age	Longitude	Latitude	Mean temp. (°C)			Altitude (m asl)	Area (ha)^2	Length (m)^2	Width (m)^2	Height (m)	Landslide event date	Closest		Age published	Predominant	
ID	Name	(cal)^1	°N	°E	Jan	Jul	MAP (mm)							town	Sampling area	first in	parent rock	Landslide type^3
1	Girová young	4	49.531	18.792	-3 to -4	15 to 16	850–1000	697	20	1530	650	275	May 2010	Mosty u Jablunkova	headscarp	Pánek et al. 2011a	claystone/ shale	rotational–translational landslide/earthflow
2	Hluboče young	8	49.062	18.051	-2 to -3	16 to 17	600–750	505	6	770	110	186	Apr 2006	Brumov-Bylnice	accumulation	Klimeš et al. 2009	claystone/ shale	rotational–translational landslide/earthflow
3	Brodská young	17	49.376	18.199	-4 to -5	14 to 15	1000–1200	685	3	685	90	175	Jul 1997	Nový Hrozenkov	accumulation	Pánek et al. 2013b	claystone/ shale	rotational–translational landslide/earthflow
4	Bystřička	17	49.425	17.967	-3 to -4	16 to 17	700–800	405	2.5	470	70	125	Jul 1997	Bystřička	accumulation	Rybář and Stemberk, 2000	claystone/ shale	rotational–translational landslide/earthflow
5	Hutisko	17	49.418	18.226	-3 to -4	15 to 16	850–1000	520	2.5	315	50	80	Jul 1997	Hutisko-Solanec	accumulation	Krejčí and Kirchner, 1997	claystone/ shale	rotational–translational landslide/earthflow
6	Skalice	44	49.649	18.424	-3 to -4	17 to 18	650–750	376	na	na	na	na	Aug 1972	Skalice	accumulation/ lobe	Pánek et al. 2011b	claystone/ shale	debris flow
7	Oznice	49	49.442	17.910	-3 to -4	16 to 17	700–800	545	5	430	136	85	Apr 1967	Oznice	headscarp	Burkhardt et al. 1972	claystone/ shale	rotational–translational landslide
8	Zlín	77	49.230	17.651	-2 to -3	17 to 18	600–700	250	0.6	170	35	40	1939–1941	Zlín	accumulation	Klimeš et al. 2015	claystone/ shale	earthflow
9	Hošťálková	95	49.370	17.859	-3 to -4	16 to 17	700–800	455	22	750	300	130	Jan 1919	Hošťálková	accumulation/ lobe	Pánek et al. 2013b	claystone/ shale	rotational landslide/earthflow
10	Pluskovec	900	49.336	18.302	-4 to -5	14 to 15	1000–1200	655	11	745	260	170	na	Pluskovec	accumulation/ lobe	Pánek et al. 2013b	claystone/ shale	rotational-translational landslide
11	Jezerné	1 030	49.389	18.275	-4 to -5	14 to 15	1000–1200	620	6	690	100	185	na	Velké Karlovice	accumulation/ lobe	Pánek et al. 2013b	sandstone	rock avalanche
12	Brodská old	1 110	49.377	18.199	-4 to -5	14 to 15	1000–1200	670	na	na	na	na	na	Nový Hrozenkov	accumulation	Pánek et al. 2013b	claystone	rotational–translational landslide/earthflow
13	Hluboče old	1 330	49.064	18.052	-2 to -3	16 to 17	600–750	560	na	na	na	na	na	Brumov-Bylnice	accumulation	Klimeš et al. 2009	claystone/ shale	rotational–translational landslide/earthflow
14	Ropice	1 330	49.604	18.589	-4 to -5	14 to 15	1000–1200	705	38	1020	150	250	na	Řeka	accumulation/ lobe	Pánek et al. 2009a	sandstone	rock avalanche
15	Lučovec	1 650	49.425	18.387	-4 to -5	14 to 15	1000–1200	700	13	600	250	125	na	Mezivodí	accumulation/ lobe	Pánek et al. 2009b	claystone/ shale	rotational–translational landslide/earthflow
16	Slopné	1 650	49.177	17.837	-2 to -3	16 to 17	650–750	475	5	470	130	95	na	Slopné	accumulation/ lobe	Pánek et al. 2013b	claystone/ shale	rotational–translational landslide/earthflow
17	Smrdutá young	2 040	49.373	17.753	-3 to -4	15 to 16	850–1000	600	6	670	115	225	na	Chvalčov	accumulation/ lobe	Pánek et al. 2013a	sandstone/ conglomerate	rock avalanche

Table S1 Continued

Site ID	Name	age (cal)[1]	Longitude	Latitude	Mean temp. (°C)		MAP (mm)	Altitude (m asl)	Area (ha)[2]	Length (m)[2]	Width (m)[2]	Height (m)	Landslide event date	Closest town	Sampling area	Age published first in	Predominant parent rock	Landslide type[3]
			°N	°E	Jan	Jul												
18	Girová North	2 070	49.535	18.825	-3 to -4	15 to 16	850–1000	638	5	425	260	115	na	Bukovec	accumulation	Pánek et al. 2014	sandstone	rotational landslide/earthflow
19	Čantoryje	3 260	49.678	18.775	-3 to -4	15 to 16	850–1000	544	na	na	na	na	na	Nýdek	accumulation	Hradecký and Pánek 2004	sandstone/ shale	rotational–translational landslide/earthflow
20	Kobylská	3 780	49.383	18.212	-4 to -5	14 to 15	1000–1200	665	30	800	500	180	na	Karolinka	accumulation/ lobe	unpublished yet	sandstone/ shale	rotational landslide
21	Smrdutá old	4 580	49.371	17.751	-3 to -4	15 to 16	850–1000	535	6	670	115	225	na	Chvalčov	accumulation/ lobe	Pánek et al. 2013a	sandstone/ conglomerate	rock avalanche
22	Homůlka	5 150	49.370	18.387	-4 to -5	14 to 15	1000–1200	745	7	500	180	135	na	Velké Karlovice	accumulation	Pánek et al. 2014	sandstone/ shale	rotational landslide/earthflow
23	Peklo	7 240	49.204	17.964	-3 to -4	15 to 16	850–1000	535	16	970	210	195	na	Drnovice	accumulation/ lobe	Pánek et al. 2013b	sandstone	rotational–translational landslide/earthflow
24	Girová old	7 430	49.523	18.797	-3 to -4	15 to 16	850–1000	578	51	1150	300	170	na	Mosty u Jablunkova	accumulation/ lobe	Pánek et al. 2011a	claystone/ shale	rotational–translational landslide/earthflow
25	Kotelnice	11 280	49.586	18.806	-3 to -4	15 to 16	850–1000	610	58	1100	620	255	na	Písečná	accumulation/ lobe	Hradecký and Pánek 2004	sandstone/ conglomerate	translational landslide
26	Kykula	12 770	49.437	18.959	-4 to -5	14 to 15	1000–1200	699	150	2950	780	420	na	Oščadnica, SR	accumulation/ lobe	Pánek et al. 2010	sandstone	translational landslide/earthflow

[1] recent landslides in years before 2017, ^{14}C dated landslides are expressed in cal. years before 1950

[2] landslide area, length and width cannot be estimated for some ancient landslides

[3] according to classification of Cruden and Varnes (1996)

Table S2 Soil properties (±standard deviation) measured in 26 landslides and 22 control sites. BD - bulk density, BD fine - BD in between rocks, BD total - BD including the mass of rocks, EC - electrical conductivity, C_{ff}, N_{ff} - carbon and nitrogen stocks in forest floor, C_{min}, N_{min} - C and N stocks in the mineral soil, P_{min} - total phosphorus in <2mm soil, P_{rock} - total P in rocks, P_{tot} - total P in soil (P_{min} + P_{rock}). n=3 for each landslide except KY.

landslides		rock content (v/v)				BD fine (g cm^{-3})			
Site ID	Age	0-10 cm	10-20 cm	20-30 cm	total (0-30 cm)	0-10 cm	10-20 cm	20-30 cm	total (0-30 cm)
1	4	0.34 ± 0.18	0.57 ± 0.21	0.62 ± 0.20	0.51 ± 0.22	0.61 ± 0.24	0.92 ± 0.56	0.83 ± 0.19	0.78 ± 0.36
2	8	0.10 ± 0.11	0.13 ± 0.08	0.09 ± 0.04	0.11 ± 0.07	1.11 ± 0.18	1.16 ± 0.07	1.08 ± 0.11	1.11 ± 0.12
3	17	0.40 ± 0.11	0.44 ± 0.10	0.33 ± 0.28	0.39 ± 0.17	0.74 ± 0.44	0.57 ± 0.63	0.64 ± 0.35	0.65 ± 0.43
4	17	0.19 ± 0.07	0.30 ± 0.07	0.54 ± 0.40	0.34 ± 0.26	1.44 ± 0.25	1.50 ± 0.25	1.00 ± 0.86	1.31 ± 0.52
5	17	0.42 ± 0.07	0.49 ± 0.17	0.47 ± 0.32	0.46 ± 0.16	0.88 ± 0.22	1.07 ± 0.17	1.48 ± 1.79	1.10 ± 0.74
6	44	0.14 ± 0.01	0.22 ± 0.13	0.29 ± 0.17	0.22 ± 0.12	0.74 ± 0.04	0.61 ± 0.11	1.05 ± 0.38	0.80 ± 0.28
7	49	0.36 ± 0.08	0.33 ± 0.07	0.35 ± 0.09	0.35 ± 0.07	0.90 ± 0.38	0.84 ± 0.09	1.05 ± 0.49	0.93 ± 0.33
8	77	0.08 ± 0.06	0.05 ± 0.04	0.09 ± 0.09	0.07 ± 0.06	0.97 ± 0.18	1.03 ± 0.22	1.26 ± 0.25	1.09 ± 0.23
9	95	0.06 ± 0.04	0.18 ± 0.09	0.28 ± 0.07	0.18 ± 0.11	0.94 ± 0.03	1.28 ± 0.18	1.38 ± 0.21	1.20 ± 0.24
10	900	0.38 ± 0.40	0.27 ± 0.14	0.60 ± 0.30	0.43 ± 0.31	0.58 ± 0.28	0.91 ± 0.11	1.49 ± 0.72	1.01 ± 0.59
11	1030	0.08 ± 0.05	0.10 ± 0.08	0.18 ± 0.04	0.12 ± 0.07	0.81 ± 0.24	0.82 ± 0.07	0.72 ± 0.24	0.78 ± 0.18
12	1110	0.28 ± 0.14	0.45 ± 0.13	0.56 ± 0.20	0.43 ± 0.19	0.72 ± 0.25	1.01 ± 0.45	1.25 ± 0.60	0.99 ± 0.46
13	1330	0.02 ± 0.01	0.05 ± 0.05	0.05 ± 0.03	0.04 ± 0.04	0.95 ± 0.18	1.18 ± 0.20	1.33 ± 0.16	1.15 ± 0.23
14	1330	0.39 ± 0.26	0.52 ± 0.04	0.66 ± 0.18	0.52 ± 0.20	0.32 ± 0.01	0.46 ± 0.23	1.15 ± 0.93	0.64 ± 0.61
15	1650	0.12 ± 0.13	0.20 ± 0.14	0.30 ± 0.14	0.21 ± 0.14	0.69 ± 0.07	1.04 ± 0.18	0.87 ± 0.24	0.87 ± 0.22
16	1650	0.17 ± 0.11	0.36 ± 0.32	0.47 ± 0.09	0.33 ± 0.22	0.72 ± 0.13	1.14 ± 0.21	1.26 ± 0.15	1.04 ± 0.29
17	2040	0.49 ± 0.19	0.47 ± 0.20	0.37 ± 0.07	0.45 ± 0.15	0.50 ± 0.26	0.51 ± 0.32	0.41 ± 0.08	0.47 ± 0.22
18	2070	0.08 ± 0.10	0.30 ± 0.14	0.35 ± 0.05	0.24 ± 0.15	0.51 ± 0.10	0.69 ± 0.21	0.91 ± 0.21	0.70 ± 0.24
19	3260	0.27 ± 0.04	0.33 ± 0.06	0.37 ± 0.06	0.32 ± 0.07	0.56 ± 0.14	0.61 ± 0.12	1.04 ± 0.12	0.73 ± 0.26
20	3780	0.08 ± 0.07	0.20 ± 0.17	0.12 ± 0.08	0.13 ± 0.11	0.71 ± 0.36	1.05 ± 0.61	0.90 ± 0.14	0.89 ± 0.39
21	4580	0.29 ± 0.17	0.44 ± 0.09	0.37 ± 0.12	0.37 ± 0.13	0.43 ± 0.36	0.76 ± 0.75	0.89 ± 0.56	0.69 ± 0.54
22	5150	0.54 ± 0.29	0.59 ± 0.30	0.57 ± 0.08	0.57 ± 0.23	0.57 ± 0.42	0.80 ± 0.48	0.90 ± 0.04	0.74 ± 0.37
23	7240	0.18 ± 0.13	0.35 ± 0.09	0.58 ± 0.37	0.37 ± 0.27	0.59 ± 0.26	0.71 ± 0.25	1.00 ± 0.05	0.74 ± 0.26
24	7430	0.02 ± 0.02	0.28 ± 0.21	0.32 ± 0.17	0.21 ± 0.20	0.40 ± 0.17	0.82 ± 0.07	1.04 ± 0.16	0.75 ± 0.31
25	11280	0.07 ± 0.06	0.15 ± 0.06	0.11 ± 0.11	0.11 ± 0.08	0.45 ± 0.07	0.63 ± 0.13	0.55 ± 0.16	0.55 ± 0.14
26	12770	0.36 ± NA	0.56 ± NA	0.65 ± NA	0.52 ± 0.15	0.59 ± NA	0.93 ± NA	0.75 ± NA	0.76 ± 0.17
landslides	mean	0.23 ± 0.16	0.32 ± 0.16	0.37 ± 0.19	0.31 ± 0.16	0.71 ± 0.25	0.89 ± 0.26	1.01 ± 0.27	0.87 ± 0.21
	median	0.19	0.31	0.36	0.34	0.70	0.88	1.02	0.79
	min	0.02	0.05	0.05	0.04	0.32	0.46	0.41	0.47
	max	0.54	0.59	0.66	0.57	1.44	1.50	1.49	1.31
control sites	mean	0.18 ± 0.18	0.21 ± 0.12	0.22 ± 0.15	0.20 ± 0.13	0.73 ± 0.30	0.97 ± 0.28	1.08 ± 0.30	0.93 ± 0.24
	median	0.09	0.19	0.22	0.18	0.74	0.90	1.06	0.98
	min	0.01	0.02	0.03	0.02	0.15	0.54	0.45	0.53
	max	0.66	0.42	0.47	0.47	1.25	1.54	1.63	1.35

Table S2 Continued

landslides		BD total (g cm^{-3})				pH			EC (µS cm^{-1})		
Site ID	Age	0-10 cm	10-20 cm	20-30 cm	total (0-30 cm)	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm
1	4	1.20 ± 0.27	1.68 ± 0.43	1.73 ± 0.29	1.53 ± 0.40	6.5 ± 1.0	6.5 ± 0.9	6.5 ± 0.8	66.1 ± 32.9	65.5 ± 28.9	65.9 ± 32.4
2	8	1.22 ± 0.27	1.30 ± 0.04	1.19 ± 0.05	1.24 ± 0.15	7.9 ± 0.1	7.8 ± 0.2	7.9 ± 0.0	131.1 ± 20.7	102.8 ± 4.1	100.3 ± 4.5
3	17	1.39 ± 0.13	1.36 ± 0.29	1.23 ± 0.36	1.33 ± 0.25	6.4 ± 0.7	6.2 ± 0.6	4.8 ± 1.6	60.6 ± 42.4	58.1 ± 43.0	61.3 ± 45.8
4	17	1.59 ± 0.27	1.73 ± 0.19	2.03 ± 0.49	1.78 ± 0.36	5.7 ± 0.2	5.8 ± 0.2	6.1 ± 0.2	30.9 ± 9.4	23.2 ± 5.2	22.1 ± 1.6
5	17	1.48 ± 0.11	1.65 ± 0.26	1.57 ± 1.20	1.57 ± 0.48	5.6 ± 0.1	5.5 ± 0.4	5.4 ± 0.6	69.3 ± 47.1	29.9 ± 5.5	47.5 ± 22.9
6	44	0.96 ± 0.06	0.97 ± 0.29	1.36 ± 0.44	1.10 ± 0.33	7.7 ± 0.4	7.7 ± 0.4	7.5 ± 0.2	216.8 ± 56.6	170.8 ± 25.3	130.3 ± 17.4
7	49	1.39 ± 0.32	1.31 ± 0.15	1.51 ± 0.21	1.41 ± 0.22	6.1 ± 0.2	6.0 ± 0.2	6.3 ± 0.2	48.7 ± 9.0	41.5 ± 5.2	46.2 ± 7.9
8	77	1.07 ± 0.16	1.10 ± 0.18	1.33 ± 0.31	1.17 ± 0.23	6.5 ± 0.7	6.3 ± 0.7	6.3 ± 0.9	103.8 ± 82.9	89.0 ± 67.5	80.7 ± 45.3
9	95	1.03 ± 0.06	1.45 ± 0.23	1.63 ± 0.15	1.37 ± 0.30	5.0 ± 0.1	5.7 ± 0.3	5.8 ± 0.0	140.8 ± 83.9	65.4 ± 8.5	111.4 ± 88.2
10	900	1.29 ± 0.58	1.28 ± 0.11	1.83 ± 0.53	1.49 ± 0.51	4.9 ± 0.5	5.1 ± 0.3	5.2 ± 0.1	148.6 ± 77.6	96.8 ± 53.9	77.0 ± 29.7
11	1030	0.92 ± 0.24	0.97 ± 0.13	1.00 ± 0.17	0.96 ± 0.16	4.6 ± 0.6	4.9 ± 0.4	5.2 ± 0.3	96.5 ± 37.3	39.5 ± 32.3	43.2 ± 4.4
12	1110	1.13 ± 0.40	1.54 ± 0.39	1.75 ± 0.41	1.47 ± 0.44	4.6 ± 0.2	4.9 ± 0.1	5.2 ± 0.3	70.8 ± 18.9	37.6 ± 11.8	29.9 ± 7.9
13	1330	0.98 ± 0.20	1.23 ± 0.20	1.38 ± 0.12	1.20 ± 0.23	5.9 ± 0.4	6.1 ± 0.4	6.3 ± 0.1	137.8 ± 93.3	66.5 ± 30.9	50.1 ± 17.1
14	1330	1.08 ± 0.52	1.40 ± 0.15	1.80 ± 0.42	1.43 ± 0.47	4.7 ± 0.3	4.9 ± 0.4	4.9 ± 0.3	111.2 ± 78.5	69.1 ± 7.7	54.7 ± 8.3
15	1650	0.88 ± 0.26	1.29 ± 0.19	1.31 ± 0.15	1.16 ± 0.28	4.5 ± 0.1	4.8 ± 0.2	5.0 ± 0.2	95.9 ± 8.5	54.3 ± 3.9	47.0 ± 7.2
16	1650	1.00 ± 0.17	1.52 ± 0.42	1.75 ± 0.03	1.42 ± 0.40	5.2 ± 0.5	5.6 ± 0.5	6.0 ± 0.4	98.2 ± 26.3	52.6 ± 19.3	41.0 ± 6.1
17	2040	1.40 ± 0.18	1.32 ± 0.52	1.11 ± 0.14	1.28 ± 0.31	5.8 ± 0.5	5.8 ± 0.4	5.9 ± 0.3	237.4 ± 92.6	129.6 ± 68.6	83.3 ± 42.5
18	2070	0.63 ± 0.26	1.15 ± 0.33	1.39 ± 0.06	1.06 ± 0.40	4.6 ± 0.6	5.0 ± 0.2	5.1 ± 0.1	115.0 ± 65.0	65.9 ± 18.5	59.0 ± 11.7
19	3260	1.02 ± 0.13	1.17 ± 0.06	1.51 ± 0.05	1.23 ± 0.23	4.7 ± 0.2	5.2 ± 0.2	5.3 ± 0.2	112.6 ± 21.9	58.7 ± 12.1	55.0 ± 9.5
20	3780	0.86 ± 0.29	1.30 ± 0.49	1.07 ± 0.03	1.08 ± 0.34	4.6 ± 0.3	5.1 ± 0.2	5.1 ± 0.3	90.5 ± 19.6	45.5 ± 6.2	40.2 ± 7.9
21	4580	0.95 ± 0.53	1.46 ± 0.37	1.40 ± 0.41	1.27 ± 0.45	5.1 ± 0.8	5.7 ± 0.3	5.9 ± 0.5	147.8 ± 32.9	160.1 ± 169.8	86.3 ± 80.7
22	5150	1.48 ± 0.49	1.64 ± 0.47	1.69 ± 0.09	1.59 ± 0.38	4.4 ± 0.3	4.6 ± 0.3	5.0 ± 0.1	181.3 ± 82.4	98.3 ± 48.2	69.6 ± 17.8
23	7240	0.89 ± 0.39	1.25 ± 0.30	1.85 ± 0.66	1.33 ± 0.59	4.6 ± 0.3	5.1 ± 0.2	5.3 ± 0.1	216.0 ± 70.0	64.9 ± 19.7	39.6 ± 5.5
24	7430	0.43 ± 0.16	1.23 ± 0.36	1.42 ± 0.32	1.02 ± 0.52	4.3 ± 0.6	4.7 ± 0.4	5.1 ± 0.1	101.0 ± 49.2	96.2 ± 40.6	64.1 ± 15.5
25	11280	0.58 ± 0.07	0.88 ± 0.19	0.74 ± 0.33	0.73 ± 0.23	4.7 ± 0.4	5.2 ± 0.1	5.4 ± 0.1	94.9 ± 9.9	56.8 ± 5.3	43.9 ± 5.5
26	12770	1.20 ± NA	1.68 ± NA	1.74 ± NA	1.54 ± NA	4.5 ± NA	4.9 ± NA	5.2 ± NA	117.6 ± NA	57.7 ± NA	52.3 ± NA
landslides	mean	1.08 ± 0.29	1.34 ± 0.23	1.47 ± 0.31	1.30 ± 0.23	5.3 ± 1.0	5.6 ± 0.8	5.7 ± 0.8	117.0 ± 51.7	72.9 ± 36.7	61.6 ± 25.3
	median	1.05	1.31	1.46	1.30	5.0	5.3	5.3	107.5	65.2	54.8
	min	0.43	0.88	0.74	0.73	4.3	4.6	4.8	30.9	23.2	22.1
	max	1.59	1.73	2.03	1.78	7.9	7.8	7.9	237.4	170.8	130.3
control sites	mean	1.01 ± 0.33	1.26 ± 0.22	1.35 ± 0.24	1.21 ± 0.20	4.5 ± 0.7	5.0 ± 0.5	5.3 ± 0.5	105.3 ± 38.1	57.8 ± 16.5	48.1 ± 14.9
	median	0.95	1.27	1.35	1.23	4.7	5.1	5.4	101.0	56.7	45.2
	min	0.42	0.94	0.84	0.82	6.8	6.5	6.6	41.2	31.3	22.6
	max	1.81	1.64	1.87	1.70	3.9	4.4	4.7	184.8	91.1	85.0

Table S2 Continued

landslides		C (t ha^{-1})	N (t ha^{-1})	C (t ha^{-1})	N (t ha^{-1})	C$_{min}$ (t ha^{-1})	C$_{rel}$ (%)			N$_{min}$ (t ha^{-1})	N$_{rel}$ (%)		
ID	Age	Litter (L)	Litter (L)	Ferm. layer (F)	Ferm. layer (F)	0-30 cm	0-10 cm	10-20 cm	20-30 cm	0-30 cm	0-10 cm	10-20 cm	20-30 cm
1	4	0.14 ± 0.28	0.28 ± 0.01	0.00 ± 0.00	0.00 ± 0.00	8.20 ± 6.54	43 ± 12	34 ± 9	23 ± 5	0.98 ± 0.67	41 ± 6	25 ± 15	34 ± 10
2	8	0.80 ± 0.70	0.70 ± 0.03	1.11 ± 1.11	1.11 ± 0.07	18.47 ± 7.19	49 ± 9	24 ± 4	27 ± 5	2.33 ± 0.40	55 ± 4	27 ± 3	18 ± 1
3	17	0.21 ± 0.20	0.20 ± 0.01	1.26 ± 0.80	0.80 ± 0.03	15.32 ± 8.44	55 ± 6	19 ± 10	26 ± 8	2.26 ± 1.56	45 ± 6	34 ± 13	20 ± 18
4	17	0.26 ± 0.30	0.30 ± 0.01	0.64 ± 0.90	0.90 ± 0.04	14.80 ± 5.57	57 ± 3	29 ± 13	14 ± 13	2.37 ± 0.10	56 ± 11	18 ± 4	27 ± 9
5	17	1.71 ± 0.28	0.28 ± 0.03	7.66 ± 6.26	6.26 ± 0.29	21.65 ± 8.92	57 ± 14	32 ± 19	11 ± 14	1.67 ± 0.51	43 ± 16	36 ± 11	21 ± 8
6	44	1.14 ± 0.19	0.19 ± 0.01	1.23 ± 0.66	0.66 ± 0.03	51.86 ± 12.77	53 ± 7	24 ± 6	23 ± 5	4.31 ± 0.91	50 ± 5	27 ± 2	23 ± 4
7	49	1.07 ± 0.20	0.20 ± 0.01	2.58 ± 0.71	0.71 ± 0.02	22.38 ± 7.75	51 ± 7	24 ± 4	25 ± 8	2.05 ± 0.51	57 ± 4	20 ± 4	24 ± 1
8	77	2.23 ± 0.99	0.99 ± 0.01	0.00 ± 0.00	0.00 ± 0.00	62.84 ± 31.26	47 ± 9	30 ± 6	23 ± 6	4.38 ± 1.83	56 ± 10	25 ± 8	19 ± 16
9	95	1.39 ± 0.11	0.11 ± 0.00	5.08 ± 0.49	0.49 ± 0.03	91.25 ± 16.91	52 ± 5	27 ± 2	21 ± 4	8.55 ± 1.56	43 ± 2	29 ± 1	28 ± 1
10	900	4.34 ± 1.14	1.14 ± 0.02	2.93 ± 1.79	1.79 ± 0.06	49.61 ± 23.36	42 ± 15	31 ± 7	28 ± 9	4.19 ± 2.30	47 ± 2	29 ± 2	24 ± 5
11	1030	3.22 ± 0.96	0.96 ± 0.03	2.82 ± 2.53	2.53 ± 0.11	55.93 ± 14.52	48 ± 27	39 ± 29	14 ± 6	3.24 ± 0.45	49 ± 14	37 ± 16	14 ± 18
12	1110	1.71 ± 0.59	0.59 ± 0.03	3.16 ± 1.84	1.84 ± 0.07	43.66 ± 8.32	61 ± 2	25 ± 3	14 ± 2	3.52 ± 0.24	48 ± 24	36 ± 29	16 ± 5
13	1330	0.44 ± 0.21	0.21 ± 0.00	1.05 ± 0.78	0.78 ± 0.01	69.58 ± 13.95	44 ± 3	29 ± 2	27 ± 2	6.82 ± 0.76	59 ± 3	23 ± 5	18 ± 8
14	1330	1.73 ± 1.52	1.52 ± 0.06	1.28 ± 1.13	1.13 ± 0.06	33.48 ± 16.07	51 ± 16	26 ± 5	24 ± 13	2.43 ± 1.08	65 ± 17	24 ± 7	10 ± 10
15	1650	2.55 ± 0.99	0.99 ± 0.03	14.07 ± 1.90	1.90 ± 0.14	75.06 ± 14.86	60 ± 7	27 ± 7	13 ± 5	4.63 ± 1.09	52 ± na	35 ± na	13 ± na
16	1650	2.06 ± 0.93	0.93 ± 0.03	4.63 ± 2.07	2.07 ± 0.10	54.22 ± 21.10	59 ± 7	26 ± 9	15 ± 4	3.81 ± 1.83	41 ± 14	30 ± 6	29 ± 10
17	2040	0.94 ± 0.49	0.49 ± 0.02	2.70 ± 0.97	0.97 ± 0.05	24.12 ± 6.44	49 ± 16	26 ± 9	25 ± 7	1.97 ± 0.61	53 ± 8	32 ± 6	15 ± 4
18	2070	4.60 ± 1.66	1.66 ± 0.06	3.94 ± 3.05	3.05 ± 0.13	57.40 ± 23.84	58 ± 4	22 ± 3	20 ± 1	4.10 ± 1.66	40 ± 7	27 ± 9	33 ± 7
19	3260	4.36 ± 0.76	0.76 ± 0.04	3.05 ± 0.56	0.56 ± 0.04	53.98 ± 10.06	61 ± 9	18 ± 3	21 ± 5	3.88 ± 0.85	62 ± 12	24 ± 4	14 ± 13
20	3780	3.15 ± 0.30	0.30 ± 0.01	15.09 ± 14.85	14.85 ± 0.53	45.77 ± 6.07	56 ± 4	24 ± 8	20 ± 11	2.50 ± 0.79	39 ± 14	33 ± 7	28 ± 11
21	4580	0.81 ± 0.35	0.35 ± 0.01	2.28 ± 1.29	1.29 ± 0.04	24.61 ± 12.95	33 ± 13	17 ± 15	50 ± 28	1.84 ± 0.91	49 ± 15	25 ± 5	26 ± 12
22	5150	1.20 ± 0.47	0.47 ± 0.01	10.55 ± 11.41	11.41 ± 0.30	38.50 ± 15.40	44 ± 11	29 ± 4	26 ± 8	2.69 ± 1.72	54 ± 3	25 ± 4	21 ± 4
23	7240	2.75 ± 1.20	1.20 ± 0.03	4.15 ± 1.67	1.67 ± 0.07	46.71 ± 16.67	68 ± 11	21 ± 4	11 ± 10	3.18 ± 1.02	55 ± 8	29 ± 9	16 ± 5
24	7430	5.01 ± 0.85	0.85 ± 0.05	7.33 ± 1.98	1.98 ± 0.05	78.05 ± 11.44	57 ± 0	23 ± 1	21 ± 1	3.70 ± 0.48	46 ± 12	29 ± 4	25 ± 8
25	11280	5.20 ± 1.30	1.30 ± 0.04	20.03 ± 10.46	10.46 ± 0.58	43.01 ± 7.53	57 ± 8	27 ± 3	16 ± 5	1.72 ± 0.38	34 ± 18	17 ± 14	49 ± 31
26	12770	11.16 ± na	0.00 ± na	3.74 ± na	0.00 ± na	32.97 ± na	57 ± 0	26 ± 0	17 ± 0	1.66 ± na	47 ± 11	31 ± 7	22 ± 14
landslides													
	mean	2.47 ± 2.349	0.65 ± 0.5	4.71 ± 5.02	2.66 ± 3.8	43.59 ± 21.54	53 ± 7	26 ± 5	21 ± 8	3.26 ± 1.67	49 ± 8	28 ± 6	23 ± 8
	median	1.72	0.54	2.99	1.21	44.71	54	26	21	2.93	49	28	22
	min	0.14	0.00	0.00	0.00	8.20	33	17	11	0.98	34	17	10
	max	11.16	1.66	20.03	14.85	91.25	68	39	50	8.55	65	37	49
control sites													
	mean	3.535 ± 2.466	0.107 ± 0.1	5.83 ± 5.00	0.23 ± 0.19	57.45 ± 16.77	52 ± 13	27 ± 9	21 ± 6	4.08 ± 1.42	49 ± 13	28 ± 10	23 ± 7
	median	3.179	0.097	4.06	0.16	57.36	53	26	20	4.17	48	28	22
	min	0.63	0.017	1.56	0.06	22.24	28	12	12	1.60	25	8	13
	max	10.89	0.381	17.1	0.71	88.93	74	47	38	6.27	79	47	44

Table S2 Continued

landslides		C_{tot} (t ha^{-1})	N_{tot} (t ha^{-1})	P_{fine} (t ha^{-1})	P_{rock} (t ha^{-1})	P_{tot} (t ha^{-1})	C:N	C:N	C:P_{fine}	C:P_{tot}	N:P_{fine}	N:P_{tot}
ID	Age	LF + 0-30 cm	LF + 0-30 cm	0-30 cm	0-30 cm	0-30 cm	forest floor	0-30 cm	0-30 cm	0-30 cm	0-30 cm	0-30 cm
1	4	9.18 ± 7.12	0.98 ± 0.67	0.36 ± 0.23	1.14 ± 0.44	1.51 ± 0.26	34 ± na	8 ± 4	20 ± 6	6 ± 5	3 ± 1	1 ± 0
2	8	20.80 ± 7.53	2.44 ± 0.50	1.09 ± 0.12	0.17 ± 0.11	1.26 ± 0.20	19 ± 1	8 ± 2	17 ± 7	15 ± 7	2 ± 1	2 ± 1
3	17	17.58 ± 9.94	2.32 ± 1.58	0.42 ± 0.32	0.69 ± 0.28	1.11 ± 0.22	26 ± 3	8 ± 2	41 ± 14	14 ± 9	5 ± 1	2 ± 1
4	17	17.18 ± 5.52	2.41 ± 0.11	0.49 ± 0.04	0.21 ± 0.09	0.71 ± 0.08	32 ± 12	6 ± 2	30 ± 12	22 ± 11	5 ± 0	3 ± 0
5	17	23.31 ± 9.39	2.06 ± 0.78	0.32 ± 0.05	0.13 ± 0.04	0.45 ± 0.08	26 ± 10	13 ± 2	67 ± 18	47 ± 11	5 ± 1	4 ± 1
6	44	56.17 ± 13.67	4.38 ± 0.92	1.09 ± 0.15	0.90 ± 0.39	1.98 ± 0.55	35 ± 4	12 ± 1	48 ± 11	27 ± 8	4 ± 1	2 ± 1
7	49	24.43 ± 8.26	2.16 ± 0.51	0.46 ± 0.12	0.45 ± 0.04	0.91 ± 0.09	31 ± 1	11 ± 1	50 ± 17	25 ± 8	5 ± 1	2 ± 0
8	77	67.23 ± 33.08	4.44 ± 1.84	1.20 ± 0.54	0.25 ± 0.20	1.45 ± 0.58	40 ± 11	14 ± 1	52 ± 5	43 ± 11	4 ± 0	3 ± 1
9	95	99.79 ± 18.46	8.80 ± 1.59	1.43 ± 0.26	0.36 ± 0.09	1.79 ± 0.18	26 ± 1	11 ± 0	64 ± 2	51 ± 5	6 ± 0	5 ± 0
10	900	53.80 ± 25.66	4.44 ± 2.34	1.02 ± 0.78	0.92 ± 0.66	1.94 ± 0.27	29 ± 3	13 ± 2	64 ± 29	26 ± 13	5 ± 2	2 ± 1
11	1030	59.17 ± 14.83	3.44 ± 0.32	0.44 ± 0.18	0.10 ± 0.04	0.54 ± 0.16	31 ± 3	17 ± 3	144 ± 66	107 ± 28	8 ± 3	6 ± 1
12	1110	47.17 ± 8.52	3.68 ± 0.33	0.55 ± 0.04	0.67 ± 0.17	1.22 ± 0.21	30 ± 2	12 ± 2	79 ± 13	36 ± 5	6 ± 0	3 ± 0
13	1330	76.39 ± 14.56	6.86 ± 0.76	1.53 ± 0.10	0.08 ± 0.06	1.61 ± 0.07	40 ± 13	10 ± 1	46 ± 10	43 ± 10	4 ± 0	4 ± 1
14	1330	35.90 ± 17.15	2.56 ± 1.20	0.53 ± 0.26	0.62 ± 0.05	1.15 ± 0.22	22 ± 1	14 ± 1	63 ± 9	28 ± 10	5 ± 1	2 ± 1
15	1650	79.69 ± 15.94	5.33 ± 0.98	0.70 ± 0.22	0.23 ± 0.13	0.93 ± 0.09	24 ± 3	16 ± 1	110 ± 13	80 ± 9	7 ± 0	5 ± 1
16	1650	58.03 ± 22.91	4.04 ± 1.78	0.71 ± 0.40	0.71 ± 0.36	1.42 ± 0.16	30 ± 3	15 ± 2	82 ± 20	38 ± 12	6 ± 1	3 ± 1
17	2040	26.09 ± 7.04	2.12 ± 0.64	0.31 ± 0.12	0.36 ± 0.08	0.67 ± 0.14	25 ± 3	12 ± 1	82 ± 12	36 ± 4	7 ± 1	3 ± 0
18	2070	61.49 ± 25.43	4.44 ± 1.57	0.61 ± 0.18	0.44 ± 0.13	1.05 ± 0.05	25 ± 3	14 ± 2	93 ± 16	54 ± 20	7 ± 1	4 ± 1
19	3260	57.85 ± 10.77	4.21 ± 0.90	0.99 ± 0.30	1.04 ± 0.13	2.03 ± 0.35	23 ± 2	14 ± 2	56 ± 10	27 ± 1	4 ± 0	2 ± 0
20	3780	48.27 ± 6.78	3.17 ± 0.26	0.44 ± 0.23	0.07 ± 0.05	0.51 ± 0.19	27 ± 1	19 ± 5	122 ± 52	98 ± 31	6 ± 1	5 ± 1
21	4580	26.44 ± 13.83	1.94 ± 0.89	0.31 ± 0.22	0.36 ± 0.11	0.67 ± 0.23	30 ± 3	13 ± 2	89 ± 23	35 ± 9	7 ± 2	3 ± 1
22	5150	41.19 ± 17.07	3.02 ± 1.61	0.66 ± 0.71	0.54 ± 0.20	1.20 ± 0.51	33 ± 4	16 ± 4	93 ± 57	33 ± 7	6 ± 2	2 ± 0
23	7240	49.88 ± 17.66	3.42 ± 1.04	0.50 ± 0.03	0.46 ± 0.13	0.96 ± 0.13	28 ± 3	15 ± 1	95 ± 41	50 ± 21	6 ± 2	3 ± 1
24	7430	81.75 ± 11.90	4.19 ± 0.49	0.37 ± 0.06	0.09 ± 0.06	0.46 ± 0.05	25 ± 2	21 ± 1	213 ± 35	172 ± 42	10 ± 1	8 ± 2
25	11280	44.73 ± 7.92	2.76 ± 0.90	0.26 ± 0.01	0.02 ± 0.01	0.28 ± 0.01	26 ± 4	25 ± 1	164 ± 35	152 ± 26	7 ± 2	6 ± 1
26	12770	34.62 ± na	2.15 ± na	0.25 ± na	0.57 ± na	0.82 ± na	30 ± na	20 ± na	130 ± na	40 ± na	7 ± na	2 ± na
landslides												
	mean	46.85 ± 22.97	3.53 ± 1.66	0.66 ± 0.37	0.44 ± 0.32	1.10 ± 0.51	29 ± 5	14 ± 4	81 ± 45	50 ± 41	6 ± 2	3 ± 2
	median	47.72	3.29	0.52	0.40	1.08	29	13	73	37	6	3
	min	9.18	0.98	0.25	0.02	0.28	19	6	17	6	2	1
	max	99.79	8.80	1.53	1.14	2.03	40	25	213	172	10	8
control sites												
	mean	66.81 ± 19.42	4.42 ± 1.45	0.71 ± 0.37	0.34 ± 0.32	1.05 ± 0.48	28 ± 5	15 ± 4	101 ± 54	65 ± 37	7 ± 2	4 ± 2
	median	64.44	4.43	0.68	0.21	0.93	29	14	83	50	6	4
	min	30.85	1.78	0.17	0.05	0.46	19	10	45	29	4	2
	max	108.88	6.55	1.28	1.40	2.14	36	22	262	168	12	7

Table S3 Models describing age trends of different soil properties on landslides. BD - bulk density, EC - electrical conductivity, C_{ff}, N_{ff} - C or N in forest floor, C_{min}, N_{min} - C or N in mineral soil, C_{tot}, N_{tot} - mineral soil + forest floor, m/m - mass fraction.

soil			**landslide**						**control**			
property	unit	layer (cm)	regression type	equation	adj. R^2	p	n	Figure	median	reached in landslides (yr)	LCL	UCL
BD fine	g cm^{-3}	0-10	logarithmic	y= -0.15*logx + 1.12	0.40	0.00032	26	1b	0.74	336	70	1 182
BD fine	g cm^{-3}	10-20	logarithmic	y= -0.08*logx + 1.11	0.08	0.08947	26	not shown	-			
BD total	g cm^{-3}	0-10	logarithmic	y= -0.14*logx + 1.47	0.26	0.00468	26	1c	0.95	4 290	832	557 915
pH		0-10	logarithmic	y= -0.73*logx + 7.35	0.61	1.41E-06	26	2a	4.75	3 475	1 476	12 665
pH		10-20	logarithmic	y= -0.57*logx + 7.13	0.52	2.07E-05	26	2a	5.11	3 632	1 315	19 959
pH		20-30	logarithmic	y= -0.57*logx + 6.85	0.32	0.00155	26	2a	5.40	2 418	589	44 549
EC	µS cm^{-1}	0-10	logarithmic	y= 20.61*logx + 63.60	0.14	0.03566	26	2b	101	65	0	631
C	t ha^{-1}	L	linear	y= 5.05E-04*x + 1.130	0.55	8.36E-06	26	3a	3.18	4 060	2 798	5 757
N	t ha^{-1}	L	linear	y= 1.61E-05*x + 0.035	0.51	2.78E-05	26	3b	0.10	4 066	2 689	5 981
C	t ha^{-1}	F	linear	y= 7.24E-04*x + 2.787	0.22	8.38E-03	26	3a	4.06	1 759	-2 988	4 602
N	t ha^{-1}	F	linear	y= 2.96E-05*x + 0.113	0.21	1.03E-02	26	3b	0.16	1 574	-3 945	4 457
C_{ff}	t ha^{-1}	L+F	linear	y=1.23E-03*x + 3.916	0.47	6.61E-05	26	not shown	6.54	2 135	364	3 674
N_{ff}	t ha^{-1}	L+F	linear	y=4.57E-05*x + 0.148	0.41	2.85E-04	26	not shown	0.27	2 670	759	4 593
C_{min}	t ha^{-1}	0-30	Hill	y= (50.95*x$^{2.424}$)/ (20.79$^{2.424}$ + x$^{2.424}$)	0.35	7.41E-10	26	4a	57.36	not reached (max(lim) = 50.95 t ha^{-1}; 50 t ha^{-1} reached after 107 years)		
C_{min}	t ha^{-1}	0-30	polynomial(logx)	y= -11.31*(logx)^2+ 63.16*logx -31.86	0.34	0.00348	26	4a	57.36	not reached (max = 56.32 t ha^{-1} reached after 620 years)		
C_{min}	t ha^{-1}	0-30	logarithmic	y= 8.34*logx + 20.79	0.14	0.03323	26	not shown	-			
N_{min}	t ha^{-1}	0-30	polynomial(logx)	y= -1.14*(logx)^2+ 5.63*logx -2.33	0.31	0.0053	26	4b	4.17	70/ 1 254 (max = 4.72 t ha^{-1} reached after 295 years)		
N_{min}	t ha^{-1}	0-30	Hill	y= (3.56*x$^{1.663}$/ (8.81$^{1.663}$ + x$^{1.663}$)	0.07	6.60E-08	26	not shown	-			
P_{fine}	t ha^{-1}	0-30	polynomial(logx)	y= -0.204*(logx)^2+ 0.917*logx -0.100	0.22	0.02281	26	4c	0.68	14/ 2 262 (max = 0.93 t ha^{-1} reached after 177 years)		
P_{tot}	t ha^{-1}	0-30	linear	y= -6.11E-05*x + 1.262	0.15	0.03085	26	4c	0.93	5 434	2 322	32 203
C_{tot}	t ha^{-1}	0-30 + LF	Hill	y= (59.73*x$^{2.019}$/ (21.10$^{2.019}$ + x$^{2.019}$)	0.41	1.47E-10	26	5a	64.44	not reached (max(lim) = 59.73 t ha^{-1}; 59 t ha^{-1} reached after 187 years)		
C_{tot}	t ha^{-1}	0-30 + LF	logarithmic	y= 11.81*logx + 18.48	0.25	0.00544	26	not shown	-			
N_{tot}	t ha^{-1}	0-30 + LF	polynomial(logx)	y= -1.06*(logx)^2+ 5.38*logx -2.05	0.28	8.80E-03	26	5b	4.43	94/ 1 244 (max = 4.78 t ha^{-1} reached after 345 years)		
N_{tot}	t ha^{-1}	0-30 + LF	Hill	y= (3.88*x$^{1.623}$/ (9.45$^{1.623}$ + x$^{1.623}$)	0.12	9.33E-09	26	not shown	-			
C_{ff}/C_{tot}	m/m		linear	y= 1.77E-05*x + 0.089	0.42	1.88E-04	26	not shown	0.13	2 346	427	4 095
N_{ff}/N_{tot}	m/m		linear	y= 1.78E-05*x + 0.037	0.52	1.97E-05	26	not shown	0.07	1 851	206	3 211
C:N		0-30	linear	y= 9.77E-04*x + 11.1052	0.59	2.61E-06	26	6a	14	2 794	1 575	4 049
$C:P_{fine}$		0-30	logarithmic	y= 30.85057*logx - 3.04441	0.52	1.96E-05	26	6b	83	600	217	1 718
$C:P_{tot}$		0-30	logarithmic	y= 19.28376*logx - 2.52487	0.23	0.0072	26	6b	50	516	44	5 493
$N:P_{fine}$		0-30	logarithmic	y= 1.00265*logx + 2.83451	0.40	3.09E-04	26	6c	6	1 148	339	6 247
$N:P_{tot}$		0-30	logarithmic	y= 0.60198*logx + 1.71086	0.12	0.04969	26	6c	4	2 501	167	10E+455