

Nitrogen, organic carbon and sulphur cycling in terrestrial ecosystems: linking nitrogen saturation to carbon limitation of soil microbial processes

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Abstract Elevated and chronic nitrogen (N) deposition to N-limited terrestrial ecosystems can lead to ‘N saturation’, with resultant ecosystem damage and leaching of nitrate (NO_3^-) to surface waters. Present-day N deposition, however, is often a poor predictor of NO_3^- leaching, and the pathway of the ecosystem transition from N-limited to N-saturated remains incompletely understood. The dynamics of N cycling are intimately linked to the associated carbon (C) and sulphur (S) cycles. We hypothesize that N saturation is associated with shifts in the microbial community, manifest by a decrease in the fungi-to-bacteria ratio and a transition from N to C limitation. Three mechanisms could lead to lower amount of bioavailable dissolved organic C (DOC) for the microbial

community and to C limitation of N-rich systems: (1) Increased abundance of N for plant uptake, causing lower C allocation to plant roots; (2) chemical suppression of DOC solubility by soil acidification; and (3) enhanced mineralisation of DOC due to increased abundance of electron acceptors in the form of SO_4^{2-} and NO_3^- in anoxic soil micro-sites. Here we consider each of these mechanisms, the extent to which their hypothesised impacts are consistent with observations from intensively-monitored sites, and the potential to improve biogeochemical models by incorporating mechanistic links to the C and S cycles.

Keywords Nitrogen · Carbon · Sulphur · Acidification · Forest soil · Modelling

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Introduction

In unmanaged and remote ecosystems, nutrient allocation within plants and soil microbial communities have developed into long-lasting climatically driven equilibria, which have been repeatedly re-established after natural ecosystem disturbances during the pre-industrial period (e.g., Vitousek 2004). In the pre-industrial period, atmospheric deposition of reactive nitrogen (N) ($N_r = \text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) and sulphate (SO_4^{2-}) were low and stable, and it is likely that all available N forms in soils were immobilized by microbial and plant biomass. The soil C:N ratio decreased only slowly because the net ecosystem N gain from N_2 fixation and low N_r deposition was to a large extent balanced by terrestrial exports of recalcitrant dissolved organic N (DON), whereas NO_3^- leaching was probably small, similar to the current situation in N-limited terrestrial ecosystems (Perakis and Hedin 2002; Vitousek 2004). Since the beginning of the industrial period, however, soil biogeochemistry and fertility of ecosystems adapted to these steady state conditions have begun to change due to rapidly increasing SO_2 , NO_x , and NH_3 emissions from energy and food production, and consequent SO_4^{2-} and N_r deposition (Reuss and Johnson 1986). A new steady-state has not yet been established during the industrial period, because S and N emission/deposition rates have not stabilized and the ecosystem response is slow (Smith et al. 2011; Kopáček and Posch 2011).

As N_r is deposited on terrestrial ecosystems, ecosystem requirements for additional N are reduced. An early ecosystem response is a reduction in rates of more energy demanding N_2 fixation (DeLuca et al. 2008). A major subsequent symptom accompanying elevated N_r inputs is the alleviation of the natural N limitation of unmanaged ecosystems, triggering a cascade of changes in both terrestrial and aquatic ecosystems (Galloway et al. 2004). Consequences of long-term N enrichment include changes in ecosystem biodiversity (Emmett 2007; Bobbink et al. 2010), microbial composition (Treseder 2004; Högberg et al. 2007a, b), internal N cycling (Aber et al. 1998), and NO_3^- leaching (Stoddard 1994). These responses are all biologically mediated, and are often assumed to be associated with the general role of N as a limiting nutrient in terrestrial ecosystems.

In this synthesis we suggest that changes in the ability of the terrestrial ecosystem to retain N are due not just to the role of N as a nutrient, but also to mechanisms associated with NO_3^- as a strong acid anion in soil solution, and as an electron acceptor in microbial energy metabolism. Elevated N_r and SO_4^{2-} inputs change the physico-chemical equilibria and redox conditions of soil solutions, and thereby affect C cycling and pools of bioavailable dissolved organic carbon (DOC) for soil microorganisms (Gauci et al. 2004; Alewell et al. 2008). The microbial communities in the ecosystem thus may transit from N limitation (C saturation) to C limitation (N saturation), and the ecosystem may start to leach NO_3^- in runoff. We synthesise information on trends in soil and water chemical composition in natural areas during industrial period, links between NO_3^- leaching and terrestrial C cycling, N saturation hypotheses, and microbial and chemical factors affecting DOC bioavailability in soils. Then, we estimate the potential effect of SO_4^{2-} and NO_3^- as electron acceptors in microbial processes on soil pools of bioavailable DOC. Finally, we link N saturation to C limitation of soil microbial processes in a new conceptual scheme combining the N, C, and S cycles.

Observed trends in N_r and SO_4^{2-} deposition and surface water chemistry

Elevated emissions and deposition of S and N compounds in Europe and eastern North America since the early 1800s caused significant acidification of soils and waters in many acid sensitive areas. Chemical changes included elevated leaching of strong acid anions (mostly SO_4^{2-} and NO_3^-) and the acid cations H^+ and ionic aluminium (Al^{n+}); reduced soil pools of base cations (calcium, magnesium, potassium, and sodium); their partial replacement by H^+ and Al^{n+} ; increased ionic strength of soil solutions; and changes in N cycling (Reuss and Johnson 1986; Aber et al. 1989, 1998). Disentangling the individual effects of N_r and SO_4^{2-} deposition on terrestrial N cycling is difficult, because their deposition fluxes are strongly spatially and temporally correlated in many regions. This situation has changed somewhat in Europe and North America since the 1980s, when the impacted ecosystems started to

recover from acidification due to efficient S emission controls (Smith et al. 2011). The resulting reduction in S deposition has caused a general decline in surface water SO_4^{2-} in these areas (Stoddard et al. 1999; Evans et al. 2001). Many soils have switched from being a sink to a source of S (Driscoll et al. 1998; Prechtel et al. 2001). Fluxes of SO_4^{2-} in runoff from catchments with thin soils have decreased rapidly (Evans et al. 2001) in comparison to catchments with thick soils and high SO_4^{2-} retention capacity (Alewell 2001).

In contrast to S, global Nr emissions continue to increase, and have been effectively reduced only in Europe (Kopáček and Posch 2011). The response of NO_3^- leaching to Nr deposition is less straightforward than in the case of S. The maximum ($\sim 50\%$) decline in Nr emission and deposition occurred in the central European region (Kopáček et al. 2012), where it resulted in a prompt decrease in NO_3^- leaching (Veselý et al. 2002; Kopáček et al. 2005). Other regions of Europe with more modest declines in Nr deposition have resulted in either no change or only small decreases in NO_3^- leaching (e.g. the United Kingdom; Monteith et al. 2012). In parts of northeastern North America, NO_3^- leaching has decreased despite unchanged Nr deposition (e.g., Driscoll et al. 2003). Interestingly, some of the observed decreases in NO_3^- leaching were more pronounced than the decline in Nr deposition (Veselý et al. 2002; Driscoll et al. 2003; Oulehle et al. 2008). These observations are from areas rapidly recovering from acidification due to reduced SO_4^{2-} deposition, and many of the same regions also exhibit increasing DOC leaching (Monteith et al. 2007). Goodale et al. (2005) hypothesized that the decline in NO_3^- leaching could result from increased N immobilization and/or denitrification driven by increased availability of terrestrial DOC. Monteith et al. (2007) showed that increasing DOC concentrations coincide in time and space with decreasing SO_4^{2-} deposition. The apparent co-occurrence of these trends at numerous sites suggests that N, C, and S should be considered together.

Further strong evidence of close links between the N and C cycles come from spatial and seasonal variability of NO_3^- leaching, and its apparent links to pools and concentrations of organic C. (1) The characteristics of NO_3^- losses from natural terrestrial ecosystems (rate of the response, proportion of the Nr

input, and seasonal trends) are not uniform and reflect differences in vegetation, pools and composition of soil, landscape characteristics, hydrology (water residence time in soil), and land use history (e.g., Dise and Wright 1995; Gundersen et al. 1998; Goodale et al. 2000; Kopáček et al. 2005). Among all factors, the most important characteristics determining the capacity of these systems to accumulate N in the long term are related to the pool size of organic C (Fig. 1a; Evans et al. 2006), i.e., the ability of the soil to retain N through a stoichiometric sink (Curtis et al. 2011). Systems with high pools of organic C have usually higher N accumulation capacities and lose less NO_3^- than C-poor soils (Evans et al. 2006). (2) Tight inverse relationships between NO_3^- and DOC concentrations are typically observed in mountain lakes and streams both on spatial and temporal scales (Fig. 1b; Goodale et al. 2005; Helliwell et al. 2007; Camarero et al. 2009). Similar negative nonlinear correlations between NO_3^- and DOC concentrations exist along a hydrologic continuum from soils, through freshwater systems to the open ocean, indicating that resource stoichiometry strongly couples DOC and NO_3^- cycling (Taylor and Townsend 2010). (3) Straightforward effects of DOC availability on NO_3^- immobilization have been demonstrated by experimental additions of bioavailable DOC sources to soils and near-stream environments, which stimulated NO_3^- assimilation and denitrification (Azam et al. 1988; Hedin et al. 1998), as well as to streams, which stimulated NO_3^- assimilation and bacterial growth (Bernhardt and Likens 2002).

Considering organic C and N cycles together seems to be necessary to identify factors governing ecosystem capacity to accumulate N (Gårdenäs et al. 2011), because heterotrophic microbes, relying on bioavailable dissolved organic C, are responsible for most N transformations in soils (e.g., Demoling et al. 2008; Barton and Northup 2011). This implies that environmental changes affecting organic C solubility and bioavailability in soils could also affect N cycling. Several processes have the potential to induce a shortage in bioavailable DOC in soils. Two of them—decreased allocation of plant photosynthates to soils, associated with elevated Nr availability, and chemical suppression of DOC, resulting from soil acidification—have been well established in the literature. In contrast, a role of SO_4^{2-} and NO_3^- as electron

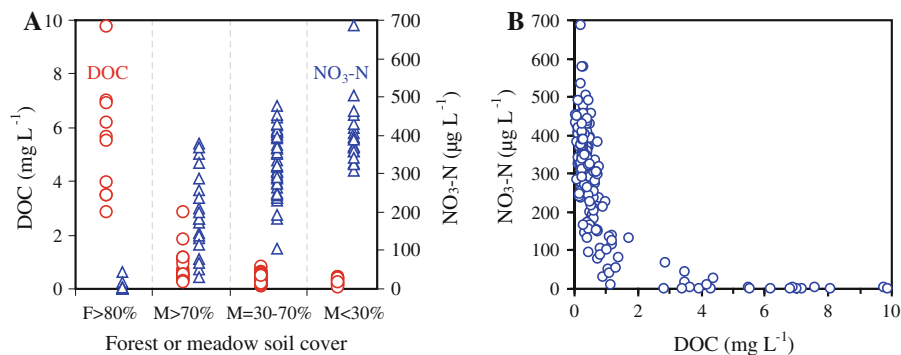


Fig. 1 Concentrations of DOC and NO₃⁻ in the Tatra Mountain lakes: **a** Data are divided according to the soil carbon pools in catchments (F > 80 % is deep forest soil covering >80 % area; M > 70 %, M = 30–70 %, and M < 30 % are

shallow soils of dry alpine meadows covering >70 %, 30–70 %, and <30 % area, respectively). **b** NO₃⁻ versus DOC concentrations. Data are derived from Kopáček et al. (2000)

acceptors in anaerobic respiration has only been considered in a few studies (e.g., Hedin et al. 1998; Alewell et al. 2008) as a factor significantly increasing DOC mineralization and, hence, reducing pools of bioavailable DOC. These studies show that diffusion of SO₄²⁻ and NO₃⁻ to anaerobic soil micro-sites can increase mineralization of bioavailable DOC and further reduce its availability for N immobilizing microorganisms.

Established mechanisms for Nr and SO₄²⁻ impacts on biogeochemical processes

Conceptual models of N saturation

The original conceptual model of N saturation (Aber et al. 1989) postulates a series of changes that occur in N-limited terrestrial ecosystems during long-lasting exposure to elevated N inputs. The ecosystem is assumed to progress through a sequence of consecutive changes: N enrichment of plant tissues and litter; elevated soil N pools; stimulated N mineralization and nitrification; and finally NO₃⁻ leaching. A number of fertilization experiments, however, showed high and rapid retention of Nr in soil organic matter (SOM) without first passing through the aboveground plants (Aber et al. 1998). This led to the conclusion that mycorrhizal fungi (and not vegetation directly) are the primary Nr sink (Aber et al. 1998) and that suppression of mycorrhizal functioning at elevated Nr availability (see next section) may be followed by a change in fungi:bacteria ratio (Tietema 1998), increased NH₄⁺

availability for nitrifiers, and NO₃⁻ mobility and leaching.

The hypothesis of Aber et al. (1998) assumes that N is accumulated in the vegetation and soil until retention capacity of these sinks is reached. The ecosystem response to elevated Nr inputs should thus be relatively slow, with a relatively long phase between the beginning of Nr input and onset of NO₃⁻ leaching. However, most experimental studies with either elevated or reduced Nr inputs to terrestrial ecosystems (e.g., Emmett 2007; Moldan and Wright 2011) and stable isotope experiments (for review see Curtis et al. 2011) have shown that NO₃⁻ leaching responds rapidly to Nr inputs. Lovett and Goodale (2011) have assumed in a new conceptual model that the added N can flow simultaneously to all sinks in the system, and that its fate and losses depend on the size of the sinks and the factors that control them. N losses from the system may thus be the results of either capacity or kinetic saturation. Capacity N saturation occurs when the N sinks in the vegetation and soil are filled up, while kinetic N saturation occurs when a sink accumulates N at the rate lower than the rate of N input (Lovett and Goodale 2011). This suggests that NO₃⁻ leaching can occur even if the N retention capacity has not yet been saturated, as is in fact observed at many sites.

This conceptual model is in agreement with a general picture of N cycling in terrestrial ecosystems formulated by Schimel and Bennett (2004). Their scheme incorporates three important assumptions for N cycling in soils: (1) The primary N source for both plants and microbes in N-limited ecosystems is low molecular weight organic monomers which result

from the depolymerization of N-containing polymers by microbial extracellular enzymes. (2) Plants take up first organic N, then NH_4^+ and finally NO_3^- , depending on the relative abundance of these in soil (Nordin et al. 2001). (3) Soil micro-sites with different availability of substrate (electron donors) and energy (electron acceptors), redox conditions, and N mineralization and immobilization rates provide large small-scale heterogeneity and gradients of soil properties (e.g., Schimel and Bennett 2004; Alewell et al. 2006, 2008). This heterogeneity is followed by the heterogeneous distribution of microorganisms, connected with resources by water (diffusion and convection) (e.g., Ekschmitt et al. 2008). Altogether, this means that all microbial processes can occur simultaneously in individual micro-sites within a relatively small distance in the soil, provided they are thermodynamically and physiologically possible under the actual substrate and energy availabilities, and the environmental conditions (e.g., moisture, temperature, pH, ambient toxicity, etc.).

Based on these assumptions, Schimel and Bennett (2004) described four gradual stages of N cycling in terrestrial ecosystems along a gradient of N availability for microbial and plant communities: (1) In extremely N-limited ecosystems, production of inorganic N forms is negligible, with low litter input and slow decomposition rate, and plants and microbes compete primarily for N at the organic-monomer stage. (2) In moderately N-limited ecosystems, microbes begin to mineralize N particularly in N-rich micro-sites. The NH_4^+ produced diffuses away and is mostly used by the N-limited microbes in the N-poor sites, with negligible amounts remaining for nitrifiers and plants. (3) As N availability increases further, mineralization rates and NH_4^+ diffusion from N-rich micro-sites increase, alleviating the competition between plants and microbes for N. NH_4^+ becomes the dominant available soil N pool. Plants can utilize NH_4^+ remaining in the system after microbial demands are met, which can promote net primary production and increase N concentrations in plant tissue. The supply of the surplus NH_4^+ to nitrifiers is still low and NO_3^- is localized only in N-rich micro-sites. (4) Finally, at high N availability, more NH_4^+ remains for nitrifiers, the system becomes progressively more NO_3^- dominated, and plant preferences for NO_3^- increase with soil NO_3^- concentrations.

The N saturation (Lovett and Goodale 2011) and the general N cycling (Schimel and Bennett 2004) concepts assume that all processes of N transformation occur in the soil simultaneously, and can explain the rapidity of ecosystem responses to added Nr. Terrestrial N losses (amounts and forms) depend on the stage of N limitation and the N retention capacity of the ecosystem prior to the elevated Nr input. If the system is extremely N-limited (i.e., in stage 1 of the concept by Schimel and Bennett 2004) both the amount and duration of Nr input necessary to cause NO_3^- leaching should be higher than in systems, which have reached stage 3. Stage 3 is typical for moderately fertile temperate forests (Pastor et al. 1984).

Effects of Nr and SO_4^{2-} on soil microbial processes and C cycling

Fungi dominate decomposition of SOM in the litter layer, where oxygen availability enables enzymatic reactions involved in the utilization of phenolic substrates (including lignin). These reactions exude substantial amounts of soluble low molecular weight organic matter (LMW OM), which serves, together with plant photosynthates exuded by roots, as a C and energy source for other saprotrophic organisms (Ekschmitt et al. 2008; Janssens et al. 2010). Fungal mycelia can transfer the necessary C to nutrient-rich micro-sites or nutrients back to C-rich micro-sites, and only a small fraction of nutrients is released in inorganic form and lost (Lindahl et al. 2002; Boberg et al. 2010). Hyphal fungi are thus more effective in competition for nutrients in nutrient-poor soils than bacteria, which generally rely on solute transport. This causes bacteria to be more dependent on water content and the presence of soluble compounds in soil than fungi (Ekschmitt et al. 2008; Schmidt et al. 2011).

Nr enrichment reduces the fungal contribution to the soil microbial biomass, decreases the fungi:bacteria ratio, and affects the activity of the rhizosphere, particularly of mycorrhizal root symbionts (Treseder 2004; Högberg et al. 2007b; Boyle et al. 2008; Ramirez et al. 2010; Zak et al. 2011). Mycorrhizal immobilization of N is driven by plant photosynthesis. Mycorrhizal fungi use photosynthates from the host plants as the dominant carbon source, strongly remove available N in soils, and in N-limited ecosystems supply plants with most of the necessary N in the form

of organic N monomers (Högberg et al. 2007a). Under conditions of elevated Nr availability, plants can utilize mineral N (unused by or inaccessible to microorganisms) and their dependence on the mycorrhizally-derived organic N monomers decreases (Johnson et al. 1997; Schimel and Bennett 2004). The reduced need for symbiotic nutrient exchange results in the promotion of above-ground biomass production at the expense of below-ground carbon allocation (Treseder 2004; Janssens et al. 2010). The elevated Nr supply to soils thus directly regulates supply of energy-rich plant exudates to mycorrhizal fungal symbionts, and reduces the biomass of mycorrhizal fungi (Högberg et al. 2007b).

In addition to this mechanism, mycorrhizal biomass can also be reduced due to decreases in fine root biomass, which in turn results from two effects of Nr and SO_4^{2-} deposition: (1) As N limitation decreases, plants reduce their fine-root biomass (Clemensson-Lindell and Persson 1995; Nadelhoffer 2000). (2) The toxic Al^{n+} forms produced by soil acidification inhibit plant root growth and branching (Göransson and Eldhuset 1991; Heim et al. 2000). The total area of fine roots (habitats for mycorrhizal colonization), and consequently mycorrhizal biomass, decreases (Demoling et al. 2008).

The changes in functioning of the soil microbial community, resulting from decreasing fungi:bacteria ratio, also affect litter decomposition and mineralization of soil N pools. (1) Decomposition rates of easily-degradable organic C (e.g., leaves of most broadleaf trees and herbs, fine roots) increase, while those of recalcitrant organic C, like conifer needles or woody biomass, decline (Knorr et al. 2005; Janssens et al. 2010) due to low activity of the lignin-degrading enzymes produced mainly by fungi (Waldrop et al. 2004; Frey et al. 2004). (2) Provided that fungi dominate the decomposer community (e.g., in natural forest ecosystems and grasslands), net N mineralization and leaching are usually low due to the active fungal C translocation and lower N demand (Boberg et al. 2010; De Vries et al. 2006). The reduced fungi:bacteria ratios at higher N availability in soils result in higher N mineralization and N losses (De Vries et al. 2006; Högberg et al. 2007a). We can deduce that fungi play a dominant role in N cycling in N-limited ecosystems, i.e., in the first two stages of Schimel and Bennett (2004). In contrast, bacteria are

distributed heterogeneously in small-scale habitats, physically connected by water, and “wait” for DOC and nutrients to be transported to their surfaces by diffusion (Ekschmitt et al. 2008), or along preferential flowpaths, where hotspots of microbial activity have been inferred from high rates of N uptake associated with macropore flows during ^{15}N tracer studies (Hagedorn et al. 1999; Evans et al. 2008). With increasing N availability in soil solutions, more N is transported to bacteria and their role in N cycling increases.

Elevated Nr and SO_4^{2-} deposition thus affects both N and C cycling in soils via changes in composition of soil microbial communities. On the basis of the above separately demonstrated effects of Nr and SO_4^{2-} on the C cycle, we propose the following sequence of possible changes in pools and fluxes of soil organic C: Compared to the preindustrial period (Fig. 2a), the biomass of fine roots and mycorrhizal fungi decreases, their supply with photosynthates decreases, and fungi:bacteria ratio in soils decreases (Fig. 2b), which continuously changes the original soil ecosystem functioning. Decreasing fungal biomass results in reduced litter decomposition (higher litter accumulation), decreased production of LMW OM for other decomposers, and reduced fungal SOM production and CO_2 efflux. These changes in fungal C cycling affect N cycling (N distribution between fungi and bacteria), and consequently, bacterial C cycling. As fungi:bacteria ratio decreases, more N is turned over by bacteria. Originally N-limited free bacteria can utilize available DOC in the C-rich micro-sites (not affected by lower LMW OM production) and transform it to the bacterial SOM. This leads to a more rapidly decreasing soil C:N ratio (because bacterial C:N is lower than fungal C:N) and to elevated CO_2 efflux by bacteria (Fig. 2b).

Effects of Nr and SO_4^{2-} on chemical suppression of DOC solubility and bioavailability

The negative relationship between DOC concentration in soil solutions and soil acidification by acid rain has been indicated by numerous field and laboratory observations (e.g., Kalbitz et al. 2000; Clark et al. 2006; Hruška et al. 2009; Ekström et al. 2011; Evans et al. 2012), as well as modelling (Tipping and Hurley

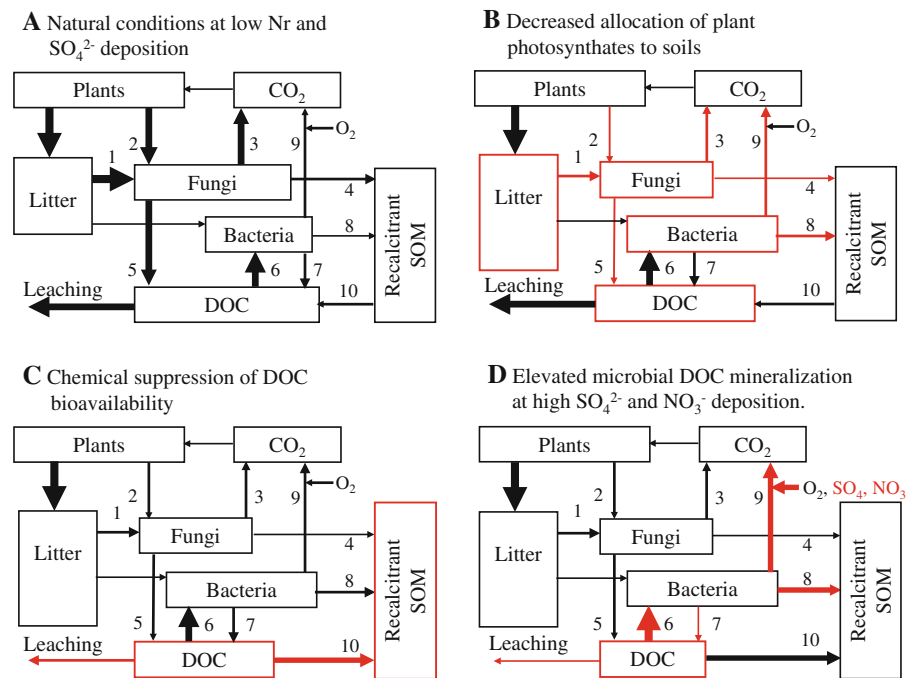


Fig. 2 Conceptual scheme of C cycling in soils **a** under natural conditions, **b** after decreased allocation of plant photosynthates due to elevated Nr deposition and soil acidification, **c** after suppression of DOC solubility and bioavailability as soil acidifies, and **d** after elevated microbial DOC mineralization due to elevated concentrations of electron acceptors (SO_4^{2-} and NO_3^-). Numbers identify specific carbon fluxes changing due to elevated Nr and SO_4^{2-} inputs: 1 Litter decomposition by fungi, 2 plant exudation of photosynthates, 3 fungal respiration, 4 production of soil organic matter (SOM) in fungal biomass, 5 fungal production of DOC, including low molecular weight organic matter available for bacteria, 6 bacterial uptake of DOC, 7 DOC production by fermentation, 8 production of SOM in bacterial biomass, 9 bacterial CO_2 production due to elevated

availability of electron acceptors, and 10 net change in DOC solubility and bioavailability associated with acidification-induced chemical suppression. Red arrows and boxes show fluxes and pools changed compared to the previous stage (a through d), but the processes may occur together. Elevated Nr availability and soil acidity decrease plant exudation, biomass of mycorrhizal fungi, litter decomposition, and fungi:bacteria ratio, affecting fluxes (1–5). Soil acidification decreases DOC solubility (flux 10). Elevated availability of Nr and electron acceptors increases the microbial DOC mineralization and decreases fermentation, affecting fluxes (6–9). All these changes contribute to lower concentrations of bioavailable DOC in soils and lower DOC leaching

1998). The acidity effect on DOC solubility acts as a partial buffer against acidification (Evans et al. 2008). The chemical effect is caused by elevated fluxes of strong acid anions, which reduce soil water concentrations of DOC. As soil water acidifies and ionic strength increases, DOC solubility is reduced by a combined effect of protonation of functional groups and coagulation of individual molecules to insoluble aggregates (Stumm 1992; Nierop et al. 2002). The negative effects of acidity on DOC solubility in organic soils have recently been demonstrated in field manipulation experiments and shown to be associated with pH-dependent changes in the dissociation of weak organic acids (Ekström et al. 2011; Evans et al. 2012).

Progressive acidification also increases soil ability to adsorb anions (including organic acids) because the total positive surface charge of Al and Fe oxyhydroxides increases as pH declines to ~ 3 – 3.5 (Stumm 1992). DOC sorption to mineral surfaces thus further reduces its mobility (Kalbitz et al. 2000, 2005) and possible diffusion to bacteria. Moreover, aggregation and adsorption to the solid phase protects DOC against enzymatic depolymerisation to low molecular weight molecules (Scheel et al. 2007), which can be transported across cell membranes. Additionally, the soil pH itself can affect microbial enzyme activity; phenol oxidase and peroxidase activities generally decrease as soil pH declines (Toberman et al. 2008; Sinsabaugh 2010).

Both laboratory and field experiments have documented the suppressive effect of soil acidification not only on DOC solubility, but also on its bioavailability. Scheel et al. (2007) showed that organic particulates, resulting from precipitation of soil DOC with Al^{n+} , became substantially stabilized against microbial decay, so that its mineralization was an order of magnitude lower than that of the original DOC. Moreover, recalcitrance of these particles increased as the pH at which the precipitate formed decreased. Similarly, Mulder et al. (2001) observed that artificial addition of Al^{n+} (as AlCl_3) to the forest floor caused a pronounced decrease in DOC leaching and a 30–40 % reduction of decomposition rate of SOM. Hence, we can assume that soil acidification caused by atmospheric deposition of SO_4^{2-} and Nr contributes to DOC immobilization in soils, as well as to its lower bioavailability for bacteria (Fig. 2c).

Effects of SO_4^{2-} and NO_3^- as electron acceptors on soil pools of bioavailable DOC

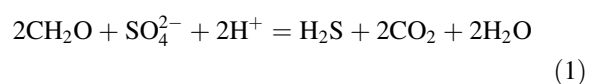
Microbial metabolism depends on the use of electron donors and electron acceptors in redox reactions that generate energy. Generally, bioavailable DOC dominates among electron donors and O_2 dominates among electron acceptors in soils. The role of SO_4^{2-} and NO_3^- as electron acceptors for microbial processes is important in anoxic soils, as well as in microsites with periodic or negligible O_2 in otherwise relatively well aerated soils (e.g., Hedin et al. 1998). Hence, we might expect that more bioavailable DOC has been mineralized in soils after their enrichment with electron acceptors by elevated deposition of SO_4^{2-} and NO_3^- (Fig. 2d), as flows from studies by Hedin et al. (1998) and Alewell et al. (2008). The question, however, is to what extent this process could increase C mineralization and decrease the overall pool of bioavailable DOC in soils, and if this change could play an ecologically significant role? This undoubtedly depends on the SO_4^{2-} and NO_3^- fluxes and their microbial reductions. The efficiency of the latter process generally reflects the physico-chemical properties of soils, pools of bioavailable DOC, water residence time, and hydraulic connectivity, which enables diffusion of electron acceptors and DOC to microbes (Hedin et al. 1998; Alewell et al. 2006,

2008). Nitrate is preferentially used over SO_4^{2-} as an electron acceptor during microbial metabolism in relatively DOC-poor systems, with insignificant SO_4^{2-} reduction unless NO_3^- -N is first reduced to concentrations $<0.2 \text{ mg L}^{-1}$ (Hedin et al. 1998). However, Alewell et al. (2008) showed that these processes (even though attributed to different redox conditions) can occur simultaneously on a soil microscale under DOC-rich conditions.

Microbial sulphate reduction

Stable isotope ($\delta^{34}\text{S}$) studies and budget calculations suggest that biological S turnover in forest soils is an important contributor to SO_4^{2-} leaching (Torssander and Mörth 1998; Novák et al. 2000). Organic cycling of atmospherically-derived S plays an important role in S polluted coniferous forests in central Europe (Novák et al. 2000, 2005) and probably also in Scandinavia (Mörth et al. 2005) and the United Kingdom (Bartlett et al. 2009). Sites near industrial S emission sources have higher S pools in the forest floor than unpolluted sites; 75–95 % of this soil S is present as organically-bound S, and this proportion increases with atmospheric SO_4^{2-} loads (Novák et al. 2005). Sulphur isotope and mass budget studies in highly SO_4^{2-} polluted areas indicated that 30–70 % of soil and stream water SO_4^{2-} was organically cycled (Novák et al. 2000, 2003), i.e., reduced, eventually incorporated in biomass, and oxidized back to SO_4^{2-} . Moreover, Novák et al. (2004) observed that 95 % of the deposited ^{35}S was cycled or retained in a severely polluted spruce forest soils for several months and H_2S volatilization represented ~ 20 % of atmospheric SO_4^{2-} input in summer months. This suggests that the proportion of the organically cycled atmospheric SO_4^{2-} could be even higher than that observed in the surface waters (Novák et al. 2000, 2003).

Dissimilatory SO_4^{2-} reduction, when S serves as the terminal acceptor of electrons released in microbial oxidation of bioavailable DOC, can be described by:



This reaction requires 1 mol of S for oxidation of 2 mols of C in the form of glucose. The reduced S may

be further used by S-oxidizing bacteria (and oxidized back to SO_4^{2-}) as an electron donor (energy source) after aeration of the originally anoxic micro-site, e.g., after its erosion or during dry periods (Clark et al. 2006), or in the presence of NO_3^- (An and Gardner 2002). This means that the deposited SO_4^{2-} can be repeatedly recycled in the reduction–oxidation process.

Undoubtedly, the extent of dissimilatory SO_4^{2-} reduction may differ between sites, reflecting differences in soil physico-chemical properties. Generally low SO_4^{2-} reduction can be expected in C poor and well aerated systems (such as sandy soils), with a low capacity to reduce SO_4^{2-} . In very C-rich systems (such as peatlands), the effect on DOC concentrations is probably difficult to detect, because the resulting change in DOC leaching may be masked by the quantitatively more important chemical effects on SOM solubility (Evans et al. 2012). The pH increase accompanying SO_4^{2-} reduction (Eq. 1) may increase SOM solubility and mitigate the decrease in DOC concentrations associated with the mineralization of bioavailable DOC. The relatively highest effects, however, can be expected in mountain forest soils, with intermediate-size organic C pools, high richness of anoxic micro-sites, and usually high wet and dry SO_4^{2-} deposition, e.g., in the spruce forest areas where the studies by Novák et al. (2000, 2003) were performed.

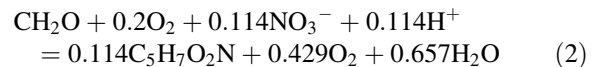
For simplicity of further estimates of the ecological importance of S cycling on soil DOC, we assume that (i) the repeated use of SO_4^{2-} is not quantitatively important, (ii) 50 % of the deposited SO_4^{2-} undergoes a microbial reduction/oxidation cycle (the middle of the range observed in the central European forest soils by Novák et al. (2000, 2003), and (iii) effects of other S transformations (assimilatory reduction and oxidation of the reduced S forms) on the C cycle can be neglected. Under such conditions, we can expect that 1 mol of bioavailable DOC is oxidized per mol of deposited SO_4^{2-} .

Microbial nitrate reduction

Curtis et al. (2011) have evaluated results of numerous isotopic studies employing natural abundances of ^{15}N and ^{18}O in precipitation and surface water NO_3^- , and conclude that the majority of NO_3^- leaching to waters

has been microbially transformed (i.e., reduced to NH_4^+ and then oxidized again via nitrification) even in C-poor systems. We can consider two major pathways:

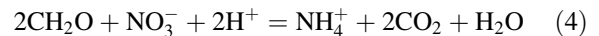
- (1) NO_3^- assimilation by microbes (Eq. 2; Mara and Horan 2003):



followed by mineralization of organically-bound N and nitrification of the liberated NH_4^+ :

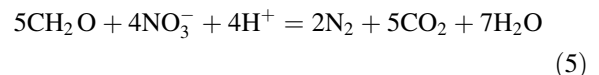


- (2) Dissimilatory nitrate reduction to ammonium (DNRA):



followed by nitrification (Eq. 3).

Another important process involved in NO_3^- cycling is denitrification:



Similarly to SO_4^{2-} , all these microbial NO_3^- reductions require energy gained from oxidation of bioavailable DOC. Both NO_3^- assimilation and DNRA involve the reduction of N from an oxidation state of +V to –III, but they differ in the necessary DOC demand. Reaction (2) includes both DOC needed for assimilative N reduction and the cell growth and maintenance. The net DOC amount for NO_3^- reduction is thus lower than suggested by the stoichiometry of Eq. (2) and can be estimated as the difference between C demand for assimilation of 1 mol N in the form of NO_3^- and NH_4^+ , which is 3.76 and 3.02 mol CH_2O , respectively (Mara and Horan 2003). The difference of 0.74 mol C mol $^{-1}$ N represents the minimum C (and energy) demand for electron transfer during NO_3^- reduction. However, the energy transfers by the organisms are not 100 % efficient. Bacteria promote electron transfer using adenosine triphosphate (ATP) and the efficiency of the energy transfer in ATP formation is assumed at ~55 % (Mara and Horan 2003). Consequently, the amount of bioavailable DOC required for bacterial assimilation of NO_3^- can be estimated at ~1.4 (=0.74/0.55) mol mol $^{-1}$ N. A similar estimate can

be obtained via an alternative calculation of the energy required for the transfer of eight electrons during NO_3^- reduction. Ideally, three ATPs are used per electron pair transferred to the terminal electron acceptor (i.e., $1.5 \text{ ATP electron}^{-1}$; Mara and Horan 2003). The free energy released by ATP hydrolysis is 31.8 kJ mol^{-1} (Barton and Northup 2011). Hence, the minimum amount of energy for NO_3^- reduction during N assimilation is 382 kJ mol^{-1} ($= 8 \times 1.5 \times 31.8$). Again assuming 55 % efficiency of the energy transfer in ATP formation, the total amount of necessary energy is $\sim 694 \text{ kJ mol}^{-1} \text{ N}$ ($= 382/0.55$), which is 1.38 times more energy than is released by aerobic respiration of 1 mol CH_2O in the form of glucose ($501 \text{ kJ mol}^{-1} \text{ C}$; Hedin et al. 1998). We assume that similar DOC demand is associated also with fungal NO_3^- assimilation. However, total amount of bioavailable DOC removed from the system during assimilation of 1 mol NO_3^- is higher in the case of fungi than bacteria due to higher C:N ratios of fungal biomass (Šantrůčková et al. 2009).

The amount of DOC consumed by NO_3^- reduction during DNRA is more straightforward (Eq. 4) than NO_3^- assimilation. Based on stoichiometry, two mols of bioavailable DOC are oxidized per each mol of the NO_3^- reduced in DNRA.

The DOC demand of denitrification depends on the terminal oxidation state of N, i.e., proportion of the produced N_2 , N_2O , and NO , which is pH dependent. For simplicity we assume that most of NO_3^- is denitrified to N_2 . Then, 1 mol of NO_3^- enables oxidation of 1.25 mol of DOC (Eq. 5).

Consumption of bioavailable DOC due to microbial NO_3^- and SO_4^{2-} reduction

The total amount of DOC removed from soil solutions by microbial NO_3^- reduction depends on the relative proportion of denitrification, assimilation, and DNRA in the NO_3^- cycling in soils. Gundersen et al. (1998) reported denitrification losses of 3–4 kg N ha^{-1} year $^{-1}$ at NO_3^- doses of 8–17 kg N ha^{-1} year $^{-1}$ to coniferous forest stands (i.e., 20–50 % of the input). This is similar to global estimates of 10–40 % (average 25 %) of the N input to terrestrial systems, which is assumed to be denitrified (Galloway et al. 2004). Consequently, we may assume that ~ 25 % of

the deposited NO_3^- is denitrified and the remaining 75 % is reduced either via NO_3^- assimilation or DNRA, and then further microbially processed. The potential for significant DNRA exists in most soils, but is more important under anoxic conditions in microsites rich in low molecular weight C sources, and at soil bioavailable DOC to NO_3^- ratios >12 (Yin et al. 1998; Rütting et al. 2011). The relative proportion of DNRA in total gross NO_3^- consumption ranges from negligible (<1 %) to dominant (~ 99 %) values in temperate forests and grasslands, depending on annual temperature and soil moisture (Rütting et al. 2011). For an approximate estimate of the effect of the microbial NO_3^- reduction on DOC cycling, we assume that the proportion of NO_3^- assimilation and DNRA is equal. The average DOC removal associated with microbial reduction of deposited NO_3^- can thus be roughly estimated at $\sim 1.6 \text{ mol C mol}^{-1} \text{ N}$ ($= 0.25 \times 1.25 + 0.75/2 \times 1.4 + 0.75/2 \times 2$). The individual components of this equation represent the proportions of denitrification (0.25), assimilation (0.75/2), and DNRA (0.75/2) in the total microbial NO_3^- reduction; the values 1.25, 1.4, and 2 mol C $\text{mol}^{-1} \text{ N}$ represent the carbon demands of these processes, respectively. Other processes involved in NO_3^- cycling in soils are neglected. The selected proportions of individual processes in NO_3^- reduction in this trial have only limited effects on the final coefficient, which varies between 1.25 and 2 mol C $\text{mol}^{-1} \text{ N}$, with minimum and maximum for 100 % proportion of denitrification and DNRA, respectively. This estimate does not include NO_3^- produced in soils by nitrification of the deposited NH_4^+ , which partly underestimates the effect of the elevated Nr deposition on the consumption of bioavailable DOC.

The approximate estimates of bioavailable DOC mineralized to CO_2 by microbial reduction of deposited SO_4^{2-} (50 %) and NO_3^- (100 %) in soils at the average consumption of 2 and 1.6 mol C mol^{-1} of the reduced S and N, respectively, can be calculated on a molar basis as $\Delta\text{DOC} = \Delta\text{CO}_2 = 0.5 \times 2 \times (\text{SO}_4^{2-} \text{ deposition}) + 1.6 \times (\text{NO}_3^- \text{ deposition})$. Applying this estimate to Čertovo Lake catchment, a site in the Bohemian Forest, Czech Republic, indicates that elevated atmospheric deposition of electron acceptors could play an important role in the overall concentrations of bioavailable DOC in soil water (Fig. 3). The Bohemian Forest is similar to the sites at which Novák

et al. (2000, 2003) conducted the soil–water $\delta^{34}\text{S}$ studies. During the peak of acidic emissions (Fig. 3a) and deposition (Fig. 3b) in the 1980s, the fluxes of atmospherically deposited SO_4^{2-} and NO_3^- in this area averaged 126 and 100 $\text{mmol m}^{-2} \text{ year}^{-1}$, respectively (Majer et al. 2003). The associated hypothetical DOC oxidation to CO_2 amounts to 286 $\text{mmol m}^{-2} \text{ year}^{-1}$ (Fig. 3c), with almost equal contributions from microbial SO_4^{2-} and NO_3^- reduction. This CO_2 flux would be equivalent to a decrease of $\sim 2.5 \text{ mg L}^{-1}$ in DOC concentrations at an average runoff of 1.35 m year^{-1} ($286 \text{ mmol m}^{-2} \text{ year}^{-1} \times$

$12 \text{ mg mmol}^{-1}/1350 \text{ L m}^{-2} \text{ year}^{-1} = 2.5 \text{ mg L}^{-1}$). In other words, microbial reduction of deposited SO_4^{2-} and NO_3^- would be able to reduce DOC leaching by $\sim 2.5 \text{ mg L}^{-1}$, compared to the pre-industrial period of negligible deposition of electron acceptors. Similarly calculated, the current (2008–2011) DOC leaching is still by 0.9 mg L^{-1} lower than its hypothetical value at zero deposition of electron acceptors (Fig. 3d). A comparison of the modelled change in DOC concentrations with the observed (and adjusted) DOC concentrations in the Bohemian Forest lakes shows that the proposed

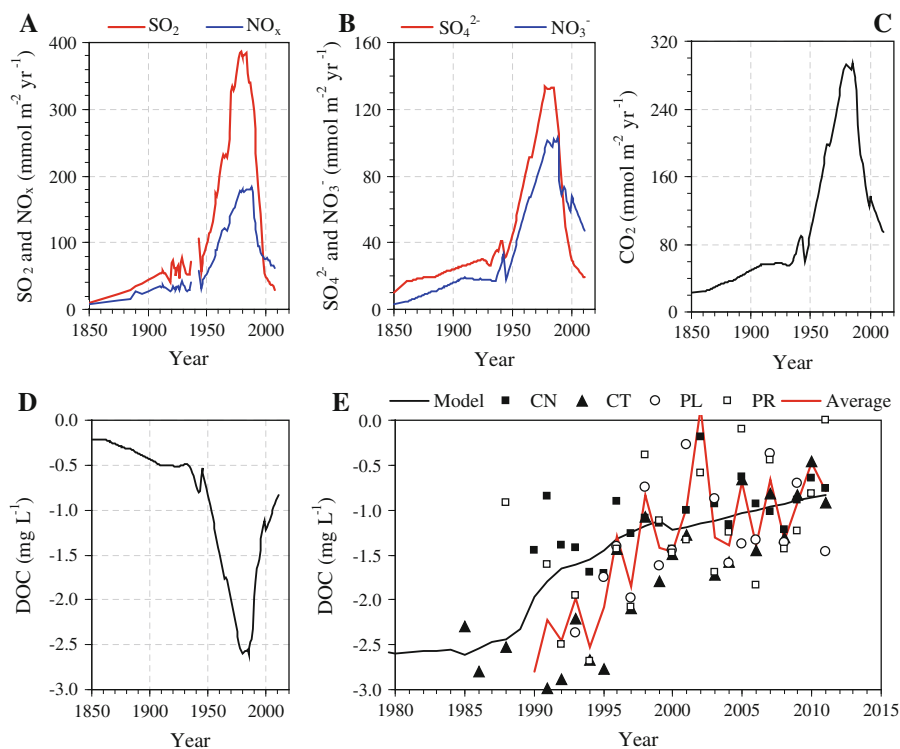


Fig. 3 Historical trend in **a** anthropogenic SO_2 and NO_x emissions in the area of the Czech Republic and Slovakia and **b** SO_4^{2-} and NO_3^- deposition in the Bohemian Forest (Czech–German–Austrian border) (Majer et al. 2003). **c** CO_2 emission from microbial reduction of atmospherically-deposited $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$, calculated on a molar basis as $\text{CO}_2 = \text{S} + 1.6 \times \text{N}$, assuming 50 % reduction of deposited SO_4^{2-} at the DOC consumption of $2 \text{ mol mol}^{-1} \text{ S}$ (Eq. 1), and 100 % reduction of deposited NO_3^- by denitrification (25 %), DNRA (37.5 %), and during N assimilation (37.5 %) at the DOC consumption of 1.25, 2.0, and $1.4 \text{ mol mol}^{-1} \text{ N}$, respectively. **d** Modelled decrease in DOC concentrations resulting from reduction of deposited SO_4^{2-} and NO_3^- compared to preindustrial period with natural S and N emissions (zero value). In this calculation, one mol of CO_2 production

equals one mol of DOC removed. Concentrations were calculated using an average runoff in the area of 1.35 m year^{-1} (Majer et al. 2003). **e** Detail of recovering trend in DOC concentration after reduced SO_4^{2-} and NO_3^- deposition. Modelled values from panel (d) are compared to observed changes in the autumn DOC concentrations in the Bohemian Forest lakes (CN Černé, CT Čertovo, PL Plešné, and PR Prášílské) and their average value (red line). The observed concentrations were adjusted to their 2008–2011 averages of 1.6, 3.4, 3.9 and 5.0 mg L^{-1} in CN, CT, PL, and PR, respectively. Adjusted values (C_i^*) were calculated for each year (i) using the 2008–2011 average observed (C_{avg}) and modelled (C_{avg}^M) concentrations as $C_i^* = C_i - (C_{\text{avg}} - C_{\text{avg}}^M)$.

mechanism could be responsible for ~55 % of the observed change since 1991. The modelled increase in DOC concentrations was 0.7 mg L^{-1} , whereas actual lake DOC concentrations increased by $0.5\text{--}1.8 \text{ mg L}^{-1}$ (1.3 on average) in four monitored lakes during this period (Fig. 3e).

Despite the considerable uncertainty of the real proportions of SO_4^{2-} and NO_3^- reduced in soils by individual microbial processes, this assessment suggests that elevated fluxes of mobile electron acceptors can have ecologically important effects on DOC cycling, and that they could significantly consume DOC in soils. The supported anaerobic respiration probably further accelerates the shift from a fungal- to bacterial-dominated microbial community in soils. The increased opportunity to use SO_4^{2-} and NO_3^- as electron acceptors also brings a competitive advantage to mineralising over fermenting bacteria (Madigan et al. 2010). This may further increase the total bacterial CO_2 efflux, reduce pool of bioavailable DOC in soil solution for the outcompeted fermentation bacteria, and reduce their DOC transformation and contributions to DOC leaching (Fig. 2d).

Linking N saturation to carbon limitation of soil microbial processes in acidified soils: a new conceptual hypothesis

The ecological importance of individual processes lowering soil pools of bioavailable DOC (decreased allocation of plant photosynthates, chemical suppression, and elevated mineralization at increased availability of electron acceptors; Fig. 2) varies with the physico-chemical and biological properties of the plant-soil system, and the levels of Nr and SO_4^{2-} deposition. The combined effects of these processes could be sufficiently strong to continuously reduce bioavailable DOC to such an extent that bacterial processes switch from N limitation to C limitation. The declining pool of bioavailable DOC is accompanied by progressively-increasing N availability in soils (Taylor and Townsend 2010), which can result in ecosystem transition from stage 3–4 in the conceptual model of Schimel and Bennett (2004), and to a breakpoint between Nr immobilization and NO_3^- leaching. Some ecosystem responses to changing Nr and SO_4^{2-} deposition affect the soil C and N cycles

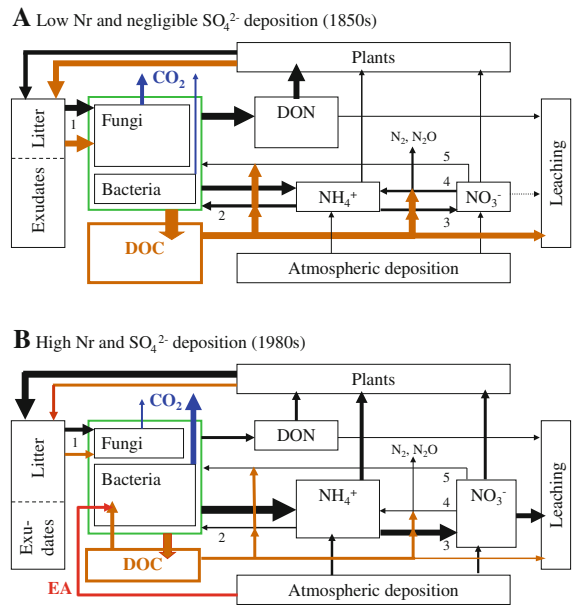


Fig. 4 Conceptual scheme of the coupled C and N cycling in soils **a** at the beginning of industrial period (1850s) and **b** during high Nr and SO_4^{2-} deposition (1980s). *Black arrows* indicate N fluxes, *brown arrows* are DOC fluxes, *blue arrows* are CO_2 fluxes, and *red arrows* are fluxes of electron acceptors (EA = $\text{SO}_4\text{-S} + \text{NO}_3\text{-N}$). *Numbers* identify specific changes caused by elevated availability of Nr and EA: 1 Decreasing fungi:bacteria ratio, lower litter decomposition, lower exudation of plants' photosynthates, higher N input via N-richer litterfall, and higher mineralization at elevated availability of Nr, 2 lower bacterial NH_4^+ immobilization in microbial biomass at lower DOC, 3 higher NO_3^- production due to promoted nitrification at lower DOC, 4 lower denitrification and dissimilatory nitrate reduction to ammonium at lower DOC, and 5 bacterial NO_3^- immobilization in microbial biomass, which may be potentially lower due to lower concentrations of bioavailable DOC, or higher due to higher NO_3^- concentrations in the system. Changes in NH_4^+ leaching are expected to be small and are not shown. (Color figure online)

independently, while others influence both cycles, and moreover, the cycles influence each other. To explain a possible interconnectedness of the associated processes, we put forward the following conceptual hypothesis, linking the N and C cycles with S cycling in terrestrial ecosystems exposed to elevated Nr and SO_4^{2-} deposition.

Compared to the preindustrial period, when the system was N-limited and terrestrial N export was dominated by DON (Fig. 4a), elevated input of Nr alleviates N limitation, and together with SO_4^{2-} deposition causes soil acidification and increases availability of electron acceptors for soil microbial

processes. The chemical and microbial responses to these changes can affect C and N cycling through a chain of both sequential and parallel effects, as follows:

- (1) Elevated Nr availability diminishes plant dependence on mycorrhizal supply of organic N monomers, which leads to reduced exudation of photosynthates (Fig. 3b) and to increased N concentrations in the plant tissue, and therefore to increased N fluxes in litterfall back to the soils (Fig. 4b).
- (2) The reduced supply of photosynthates and elevated availability of N change soil microbial community and both the fine root biomass and fungi:bacteria ratio decrease. Fine root biomass also decreases due to Al^{3+} toxicity in strongly acidified soil.
- (3) Due to decreasing fungal biomass, litter decomposition and fungal production of LMW OM slow down, but bacterial DOC mineralization increases because of elevated availability of N (the limiting nutrient) and electron acceptors for anaerobic respiration (Fig. 3b, d).
- (4) As Nr and SO_4^{2-} deposition increase, bacteria become less and less N and energy (electron acceptor) limited, and can mineralize progressively more bioavailable DOC, while less remains for the outcompeted fermenting bacteria and the leaching of DOC decreases (Figs. 3d, 4b).
- (5) Elevated N mineralisation occurs at higher Nr availability in soils, producing more NH_4^+ . In parallel, the pool of bioavailable DOC decreases due to the elevated mineralization. Consequently, relatively less bioavailable DOC remains for NH_4^+ assimilation and immobilization in microbial biomass, leaving more NH_4^+ for nitrifiers. As a result, internal NO_3^- production increases.
- (6) The higher bacterial demand for DOC under elevated availability of Nr and electron acceptors comes into conflict with increasing chemical suppression of DOC solubility and bioavailability in the progressively acidifying soils (Fig. 3c), and finally results in the C limitation of microbial metabolism.
- (7) Due to reduced pools of bioavailable DOC, NO_3^- removal by denitrification and DNRA decrease (Fig. 4b).
- (8) Bacterial assimilation of NO_3^- , which depends on the stoichiometric NO_3^- to DOC ratio in the substrate, may initially increase with increasing NO_3^- concentrations, but then decrease due to lower pool of bioavailable DOC.

Altogether, the system moves from stage 3 to stage 4 of the conceptual model of Schimel and Bennett (2004), leading to increased concentrations of NO_3^- in soil and leaching of unused NO_3^- . Even though no study has confirmed the proposed sequence of effects so far, the individual key processes and their sequences have been demonstrated in numerous studies (Table 1).

Hypothesis versus observations

Our hypothesis is not in conflict with previous schemes explaining the development of N-cycling in and NO_3^- leaching from terrestrial ecosystems (Aber et al. 1989, 1998; Schimel and Bennett 2004; Lovett and Goodale 2011), but combines and develops them, and suggests additional mechanisms for several observed responses of upland and forest ecosystems to changing Nr and SO_4^{2-} deposition:

- (1) The higher N availability in soils and lowered supply of plant photosynthates reduce fungi:bacteria ratios, which results in decreased decomposition rates of recalcitrant SOM (Waldrop et al. 2004; Frey et al. 2004; Janssens et al. 2010). This process provides an alternative (or additional) explanation for the observed litter accumulation that occurred in central European spruce forests during the acid rain period, as well as to its rapid mineralisation during the recovery phase, which were ascribed primarily to changes in soil acidification by SO_4^{2-} deposition (e.g., Meiwes et al. 2009; Oulehle et al. 2011).
- (2) The hypothesis causally links elevated NO_3^- , as well as SO_4^{2-} concentrations to reduced DOC leaching during the acidification stage (Gjessing et al. 1998), and their reversed trends during the recovery phase (Monteith et al. 2007).
- (3) It also reasonably explains the maximum NO_3^- leaching from C-poor ecosystems exposed to elevated atmospheric inputs of Nr and SO_4^{2-} (Evans et al. 2006; Curtis et al. 2011). Even

Table 1 Key processes and observed changes in C and N cycling in natural terrestrial ecosystems due to elevated Nr and SO_4^{2-} deposition

Observed processes	References
1 At elevated Nr availability, exudation of plant photosynthates and fungi:bacteria ratio decrease and N concentrations in the plant tissue increase	Treseder (2004), Högberg et al. (2007a, b, 2010), Boyle et al. (2008), Ramirez et al. (2010), Zak et al. (2011), Aber et al. (1989, 1998)
2 Fine root and mycorrhizal biomass decreases at higher Nr availability and Al-toxicity of soil solutions	Göransson and Eldhuset (1991), Clemensson-Lindell and Persson (1995), Heim et al. (2000)
3a High Nr and SO_4^{2-} deposition and lower fungal biomass suppress organic matter turnover and litter decomposition	Waldrop et al. (2004), Frey et al. (2004), Meiwes et al. (2009), Janssens et al. (2010), Oulehle et al. (2011)
3b Reduced fungi:bacteria ratios at higher N availability in soils result in higher mineralization and N losses	De Vries et al. (2006), Högberg et al. (2007a), Boberg et al. (2010)
4a NO_3^- reduction occurs in anoxic soil micro-sites and is related to pools of available DOC	Azam et al. (1988), Hedin et al. (1998), Alewell et al. (2006, 2008)
4b SO_4^{2-} is microbially reduced in forest soils and peatlands	Novák et al. (2000, 2003), Mörth et al. (2005), Alewell et al. (2008), Bartlett et al. (2009)
5 Elevated N mineralization and nitrification occur at higher Nr availability in soils	Aber et al. (1989, 1998), Gundersen et al. (1998), Schimel and Bennet (2004)
6a DOC mobility and availability are suppressed in low pH and Al rich soils	Gjessing et al. (1998), Kalbitz et al. (2000, 2005), Mulder et al. (2001), Monteith et al. (2007), Scheel et al. (2007), Evans et al. (2012)
6b Soil microbial processes may become C limited	Demoling et al. (2008), Boberg et al. (2010)
7 NO_3^- removal by denitrification and DNRA decrease at reduced pool of bioavailable DOC	Hedin et al. (1998), Alewell et al. (2006, 2008), Yin et al. 1998; Rütting et al. 2011
8 Microbial turnover and assimilation of NO_3^- depend on stoichiometric NO_3^- to DOC ratio	Curtis et al. (2011), Taylor and Townsend (2010)

though microbial activity remains high in these soils (Curtis et al. 2011), there is small capacity (i.e., pools of bioavailable DOC) to further accumulate N, and more NH_4^+ remains for nitrifiers. Experiments on highly organic soils show far slower responses to additional Nr application than similar rates of application at mineral soil sites, despite similarly high ambient Nr deposition (e.g. Pilkington et al. 2005), consistent with the suggestion above that the former sites are less susceptible to C limitation and therefore to NO_3^- leaching.

- (4) The hypothesis assumes increased CO_2 efflux from bacterial mineralization at the expense of DOC leaching (Fig. 2D), which is seemingly in contrast to negligible changes in total microbial CO_2 production observed in N addition experiments (Aber et al. 1998). The hypothesis, however, assumes a parallel decrease in the fungal CO_2 efflux due to lower SOM mineralization (Fig. 2b). The decreasing fungi:bacteria ratio thus may result in a negligible net change in the total microbial CO_2 efflux (Šantrůčková et al.

2009), and the net change in the total soil C pool may be that SOM accumulates while DOC leaching decreases. In addition, the estimated increase in CO_2 production due to higher anaerobic respiration in the Bohemian Forest ($0.29 \text{ mol m}^{-2} \text{ year}^{-1}$) was <1 % of total soil respiration of spruce forest ecosystems ($25\text{--}68 \text{ mol m}^{-2} \text{ year}^{-1}$; Borken et al. 1999; Davidson et al. 2006), i.e., probably lower than variability of field measurements.

- (5) Our hypothesis suggests that elevated atmospheric input of electron acceptors to soils and their acidifying effects could cause the abrupt depletion of available DOC and rapidly decrease the N retention capacity of soil. The biogeochemical implication of this process is that NO_3^- leaching could be caused not only by the elevated Nr inputs, but also by SO_4^{2-} deposition high enough to decrease pools of bioavailable DOC to the extent that nitrification is promoted (Fig. 4b). The reverse situation has probably occurred during the recovery phase; decreased SO_4^{2-} deposition (i.e., lower availability of electron

acceptors in soils) led to lower removal of DOC from the system, alleviating C limitation of bacteria, and increasing N immobilisation in bacterial SOM, as well as NO_3^- reduction via denitrification and DNRA. This mechanism could perhaps explain why decreasing SO_4^{2-} deposition was accompanied by decreasing NO_3^- leaching in some regions, despite no change in Nr deposition (Driscoll et al. 2003; Goodale et al. 2005; Oulehle et al. 2008). In contrast, other sites (e.g., in the UK; Monteith et al. 2012) exhibit no clear changes in NO_3^- export despite reduced SO_4^{2-} deposition. Explanatory factors here could include local land-management factors (e.g., forest management or moorland burning), or the excess of bioavailable DOC from the highly organic soils of many UK acid-sensitive catchments. In such soils, it is less likely that C limitation would have led to reduced N assimilation and greater nitrification in the past, and thus less likely that NO_3^- leaching would be decreasing now in response to reducing SO_4^{2-} deposition.

- (6) Most experiments with Nr addition to terrestrial ecosystems, including those with the described kinetic saturation, were done at sites already affected by acidic deposition (Lovett and Goodale 2011). Their kinetic saturation can be, undoubtedly, explained to some extent by natural ecosystem properties and limits of existing microbial population to take up a pulse of N input. There may be partial physical bypass, or the microbial population may not be able to grow fast enough to assimilate all the extra N. According to our hypothesis, it seems also plausible that these sites were close to C limitation already prior to the artificial Nr additions, and consequently, responded to the Nr dose with a rapid transition from stage 3 to stage 4 of the conceptual model of Schimel and Bennett (2004). In such cases kinetic saturation could reflect a shortage of bioavailable DOC (relative to the available N) for microbial N immobilization. This could occur not only due to excess Nr inputs, but also due to reduced amounts of bioavailable DOC (e.g., during the winter decline in below-ground allocation of plant photosynthates; Högberg et al. 2010).

Temporal trends in NO_3^- leaching thus could be partially associated with seasonal changes in bioavailable DOC concentrations in soil solutions.

- (7) Finally, some of the assumed causalities in our hypothesis have been supported by observed biogeochemical changes during recovery from acidification. Increasing pH, lower ionic strength and Al^{n+} toxicity, lower Nr concentrations, and lower availability of electron acceptors in soil solutions after reductions in acidic deposition have increased soil pools of bioavailable DOC and established conditions for recovery of fine roots of plants (Navrátil et al. 2007) and their recolonization with mycorrhizal fungi (Boxman et al. 1998). Observed increases in DOC leaching (Monteith et al. 2007), more rapid litter mineralisation (Meiwes et al. 2009; Oulehle et al. 2011), and reduced NO_3^- leaching (Vesely et al. 2002; Oulehle et al. 2008; Driscoll et al. 2003; Goodale et al. 2005) during the recovery phase probably reflect a partial ecosystem transition back towards preindustrial conditions.

Further research to test the hypotheses

Studies to improve or refute our hypothesis might include: (1) More detailed description of changes and differences in microbial communities and their activities in manipulated versus control plots and understanding of their effects on bioavailability and recalcitrance of soil DOC, (2) more detailed assessment of the fate of NO_3^- and SO_4^{2-} in soils, especially the proportion of individual microbial process involved in their transformations, and (3) laboratory and in situ manipulation experiments with additions of bioavailable DOC, NO_3^- , and SO_4^{2-} , which should indicate how important this is as a constraint on the processes. These experiments should be as comprehensive as possible, including studies on element mass budgets, as well as changes in microbial communities.

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References

- Aber JD, Nadelhoffer KJ, Steudler P, Melillo JM (1989) Nitrogen saturation in northern forest ecosystems. *Bioscience* 39:378–386
- Aber JD, McDowell WH, Nadelhoffer KJ, Magill A, Berntson G, Kamakea M, McNulty SG, Currie W, Rustad L, Fernandez I (1998) Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. *Bioscience* 48:921–934
- Alewell C (2001) Predicting reversibility of acidification: the European sulfur story. *Water Air Soil Pollut* 130:1271–1276
- Alewell C, Paul S, Lischeid G, Küsel K, Gehre M (2006) Characterizing the redox status in three different forested wetlands with geochemical data. *Environ Sci Technol* 40:7609–7615
- Alewell C, Paul S, Lischeid G, Storck FR (2008) Co-regulation of redox processes in freshwater wetlands as a function of organic matter availability? *Sci Total Environ* 404:335–342
- An S, Gardner WS (2002) Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Mar Ecol Prog Ser* 237:41–50
- Azam F, Mahmood T, Malik KA (1988) Immobilization-remobilization of $\text{NO}_3\text{-N}$ and total N balance during decomposition of glucose, sucrose and cellulose in soil incubated at different moisture regimes. *Plant Soil* 107:159–163
- Barton LL, Northup DE (2011) *Microbial ecology*. Wiley-Blackwell, Hoboken
- Bartlett R, Bottrell SH, Coulson JP, Lee J, Forbes L (2009) 34 Stracer study of pollutant sulfate behaviour in a lowland peatland. *Biogeochemistry* 95:261–275
- Bernhardt ES, Likens GE (2002) DOC enrichment alters nitrogen dynamics in a forest stream. *Ecology* 83(6):1689–1700
- Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, Bustamante M, Cinderby S, Davidson E, Dentener F, Emmett B, Erisman J-W, Fenn M, Gilliam F, Nordin A, Pardo L, De Vries W (2010) Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol Appl* 20(1):30–59
- Boberg JB, Finlay RD, Stenlid J, Lindahl BD (2010) Fungal C translocation restricts N-mineralization in heterogeneous environments. *Funct Ecol* 24:454–459
- Borken W, Xu Y-J, Brumme R, Lamersdorf N (1999) A climate change scenario for carbon dioxide and dissolved organic carbon fluxes from a temperate forest soil: drought and rewetting effects. *Soil Sci Soc Am J* 63:1848–1855
- Boxman AW, van der Ven PJM, Roelofs JGM (1998) Ecosystem recovery after a decrease in nitrogen input to a Scots pine stand at Ysselsteyn, the Netherlands. *For Ecol Manag* 101(1–3):155–163
- Boyle SA, Yarwood RR, Bottomley PJ, Myrold DD (2008) Bacterial and fungal contributions to soil nitrogen cycling under Douglas fir and red alder at two sites in Oregon. *Soil Biol Biochem* 40:443–451
- Camarero L, Rogora M, Mosello R, Anderson NJ, Barbieri A, Botev I, Kernan M, Kopáček J, Korhola A, Lotter AF, Muri G, Postolache C, Stuchlík E, Thies H, Wright RF (2009) Regionalisation of chemical variability in European mountain lakes. *Freshw Biol* 54:2452–2469
- Clark JM, Chapman PJ, Heathwaite AL, Adamson JK (2006) Suppression of dissolved organic carbon by sulphate induced acidification during simulated droughts. *Environ Sci Technol* 40:1776–1783
- Clemensson-Lindell A, Persson H (1995) Fine-root vitality in a Norway spruce stand subjected to various nutrient supplies. *Plant Soil* 168–169:167–172
- Curtis CJ, Evans CD, Goodale CL, Heaton THE (2011) What have stable isotope studies revealed about the nature and mechanisms of N saturation and nitrate leaching from semi-natural catchments? *Ecosystems* 14(6):1021–1037
- Davidson EA, Richardson AD, Savage KE, Hollinger DY (2006) A distinct seasonal pattern of the ratio of soil respiration to total ecosystem respiration in a spruce-dominated forest. *Glob Chang Biol* 12:230–239
- De Vries FT, Hoffland E, van Eekeren N, Brussaard L, Bloem J (2006) Fungal/bacterial ratios in grasslands with contrasting nitrogen management. *Soil Biol Biochem* 38:2092–2103
- DeLuca TH, Zackrisson O, Gundale MJ, Nilsson M-C (2008) Ecosystem feedbacks and nitrogen fixation in boreal forests. *Science* 30:1181. doi:10.1126/science.1154836
- Demoling F, Nilsson LO, Bååth E (2008) Bacterial and fungal response to nitrogen fertilization in three coniferous forest soils. *Soil Biol Biochem* 40:370–379
- Dise NB, Wright RF (1995) Nitrogen leaching from European forests in relation to nitrogen deposition. *For Ecol Manag* 71:153–161
- Driscoll CT, Likens GE, Church MR (1998) Recovery of surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. *Water Air Soil Pollut* 105:319–329
- Driscoll CT, Driscoll KM, Roy KM, Mitchell MJ (2003) Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environ Sci Technol* 37:2036–2042
- Ekschmitt K, Kandeler E, Poll C, Brune A, Buscot F, Friedrich M, Gleixner G, Hartmann A, Kästner M, Marhan S, Miltner A, Scheu S, Wolters V (2008) Soil-carbon preservation through habitat constraints and biological limitations on decomposer activity. *J Plant Nutr Soil Sci* 171:27–35
- Ekström SM, Kritzbeg ES, Kleja DB, Larsson N, Nilsson PA, Graneli W, Bergkvist B (2011) Effect of acid deposition on quantity and quality of dissolved organic matter in soil-water. *Environ Sci Technol* 45:4733–4739
- Emmett BA (2007) Nitrogen saturation of terrestrial ecosystems: some recent findings and their implications for our conceptual framework. *Water Air Soil Pollut Focus* 7:99–109
- Evans CD, Cullen JM, Alewell C, Marchetto A, Moldan F, Kopáček J, Prechtel A, Rogora M, Veselý J, Wright RF (2001) Recovery from acidification in European surface waters. *Hydrol Earth Syst Sci* 5:283–297
- Evans CD, Reynolds B, Jenkins A, Helliwell RC, Curtis CJ, Goodale CL, Ferrier RC, Emmett BA, Pilkington MG, Caporn SJM, Carroll JA, Norris D, Davies J, Coull MC (2006) Evidence that soil carbon pool determines susceptibility of semi-natural ecosystems to elevated nitrogen leaching. *Ecosystems* 9:453–462
- Evans CD, Norris D, Ostle N, Grant H, Rowe EC, Curtis CJ, Reynolds B (2008) Rapid immobilisation and leaching of

- wet-deposited nitrate in upland organic soils. *Environ Pollut* 156:636–643
- Evans CD, Jones TG, Burden A, Ostle N, Zieliński P, Cooper MDA, Peacock M, Clark JM, Oulehle F, Cooper D, Freeman C (2012) Acidity controls on dissolved organic carbon mobility in organic soils. *Glob Chang Biol* 18(11):3317–3331
- Frey SD, Knorr M, Parrent JL, Simpson RT (2004) Chronic nitrogen enrichment affects the community structure and function of the soil microbial community in temperate hardwood and pine forests. *For Ecol Manag* 196:159–171
- Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA, Karl DM, Michaels AF, Porter JH, Townsend AR, Vörösmarty CJ (2004) Nitrogen cycles: past, present, and future. *Biogeochemistry* 70:153–226
- Gårdenäs AI, Ågren GI, Bird JA, Clarholm M, Hallin S, Ineson P, Kätterer T, Knicker H, Nilsson SI, Näsholm T, Ogle S, Paustian K, Persson T, Stendahl J (2011) Knowledge gaps in soil carbon and nitrogen interactions—from molecular to global scale. *Soil Bio Biochem* 43:702–717
- Gauci V, Matthews E, Dise N, Walter B, Koch D, Granberg G, Vile M (2004) Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. *Proc Natl Acad Sci USA* 101:12583–12587
- Gjessing ET, Riise G, Lydersen E (1998) Acid rain and natural organic matter (NOM). *Acta Hydrochim Hydrobiol* 26:131–136
- Goodale CL, Aber JD, McDowell WH (2000) Long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. *Ecosystems* 3:433–450
- Goodale CL, Aber JD, Vitousek PM, McDowell WH (2005) Long-term decreases in stream nitrate: successional causes unlikely; possible links to DOC? *Ecosystems* 8:334–337
- Göransson A, Eldhuset TD (1991) Effects of aluminium on growth and nutrient uptake of small *Picea abies* and *Pinus sylvestris* plants. *Trees* 5:136–142
- Gundersen P, Emmett BA, Kjonaas OJ, Koopmans CJ, Tietema A (1998) Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *For Ecol Manag* 101:37–55
- Hagedorn F, Mohn J, Schleppl P, Flühler H (1999) The role of rapid flow paths for nitrogen transformation in a forest soil: a field study with micro suction cups. *Soil Sci Soc Am J* 63:1915–1923
- Hedin LO, von Fischer JC, Ostrom NE, Kennedy BP, Brown MG, Robertson GP (1998) Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79:684–703
- Heim A, Luster J, Brunner I, Frey B, Frossard E (2000) Effects of aluminium treatment on Norway spruce roots: aluminium binding forms, element distribution, and release of organic substances. *Plant Soil* 216:103–116
- Helliwell RC, Coull MC, Davies JLL, Evans CD, Norris D, Ferrier RC, Jenkins A, Reynolds B (2007) The role of catchment characteristics in determining surface water nitrogen in four upland regions in the UK. *Hydrol Earth Syst Sci* 11:356–371
- Högberg MN, Chen Y, Högberg P (2007a) Gross nitrogen mineralisation and fungi-to-bacteria ratios are negatively correlated in boreal forests. *Biol Fertil Soils* 44:363–366
- Högberg MN, Högberg P, Myrold DD (2007b) Is microbial community composition in boreal forest soils determined by pH, C-to-N ratio, the trees, or all three? *Oecologia* 150:590–601
- Högberg MN, Briones MJI, Keel SG, Metcalfe DB, Campbell C, Midwood AJ, Thornton B, Hurry V, Linder S, Näsholm T, Högberg P (2010) Quantification of effects of season and nitrogen supply on tree below-ground carbon transfer to ectomycorrhizal fungi and other soil organisms in a boreal pine forest. *New Phytol* 187:485–493
- Hruška J, Krám P, McDowell WH, Oulehle F (2009) Increased dissolved organic carbon (DOC) in central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environ Sci Technol* 43:4320–4326
- Janssens IA, Dieleman W, Luysaert S, Subke J-A, Reichstein M, Ceulemans R, Ciais P, Dolman AJ, Grace J, Matteucci G, Papale D, Piao SL, Schulze E-D, Tang J, Law BE (2010) Reduction of forest soil respiration in response to nitrogen deposition. *Nat Geosci* 3:315–322
- Johnson NC, Graham J-H, Smith FA (1997) Functioning of mycorrhizal associations along the mutualism–parasitism continuum. *New Phytol* 135:575–585
- Kalbitz K, Solinger S, Park J-H, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci* 165(4):277–304
- Kalbitz K, Schwesig D, Rethemeyer J, Matzner E (2005) Stabilization of dissolved organic matter by sorption to the mineral soil. *Soil Biol Biochem* 37:1319–1331
- Knorr M, Frey SD, Curtis PS (2005) Nitrogen additions and litter decomposition: a meta-analysis. *Ecology* 86(12):3252–3257
- Kopáček J, Posch M (2011) Anthropogenic nitrogen emissions during the Holocene and their possible effects on remote ecosystems. *Glob Biogeochem Cycl* 25:GB2017. doi:10.1029/2010GB003779
- Kopáček J, Stuchlík E, Straškrabová V, Pšenáková P (2000) Factors governing nutrient status of mountain lakes in the Tatra Mountains. *Freshw Biol* 43:369–383
- Kopáček J, Stuchlík E, Wright RF (2005) Long-term trends and spatial variability in nitrate leaching from alpine catchment-lake ecosystems in the Tatra Mountains (Slovakia-Poland). *Environ Pollut* 136:89–101
- Kopáček J, Posch M, Hejzlar J, Oulehle F, Volková A (2012) An elevation-based regional model for interpolating sulphur and nitrogen deposition. *Atmos Environ* 50:287–296
- Lindahl BO, Taylor AFS, Finlay RD (2002) Defining nutritional constraints on carbon cycling in boreal forests—towards a less “phytocentric” perspective. *Plant Soil* 242:123–135
- Lovett GM, Goodale CL (2011) A new conceptual model of nitrogen saturation based on experimental nitrogen addition to an oak forest. *Ecosystems* 14:615–631
- Madigan MT, Martinko JM, Stahl DA, Clark DP (2010) Brock biology of microorganisms, 13th edn. Benjamin Cummings, Boston
- Majer V, Cosby BJ, Kopáček J, Veselý J (2003) Modelling reversibility of Central European Mountain Lakes from acidification: part I—the Bohemian forest. *Hydrol Earth Syst Sci* 7:494–509
- Mara D, Horan NJ (2003) Handbook of water and wastewater microbiology. Academic Press, London

- Meiwes KJ, Meessenburg H, Eichhorn J, Jacobsen C, Khanna PK (2009) Changes in C and N contents of soils under beech forests over a period of 35 years. In: Brumme R, Khanna PK (eds) *Functioning and management of European Beech ecosystems*. Springer, Berlin, pp 49–63
- Moldan F, Wright RF (2011) Nitrogen leaching and acidification during 19 years of NH_4NO_3 additions to a coniferous-forested catchment at Gårdsjön, Sweden (NITREX). *Environ Pollut* 159:431–440
- Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Högåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, Keller B, Kopáček J, Veselý J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450:537–540
- Monteith DT, Evans CD, Henrys P, Simpson GL, Malcolm IA (2012) Trends in the hydro-chemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecol Indic*. doi:10.1016/j.ecolind.2012.08.013
- Mörth C-M, Torssander P, Kjønnaas JO, Stuanas AO, Moldan F, Giesler R (2005) Mineralization of organic sulfur delays recovery from anthropogenic acidification. *Environ Sci Technol* 39:5234–5240
- Mulder J, De Wit HA, Boonen HWJ, Bakken LR (2001) Increased levels of aluminium in forest soils: effects on the stores of soil organic carbon. *Water Air Soil Pollut* 130:989–994
- Nadelhoffer KJ (2000) The potential effects of nitrogen deposition on fine-root production in forest ecosystems. *New Phytol* 147:131–139
- Navrátil T, Kurz D, Krám P, Hofmeister J, Hruška J (2007) Acidification and recovery of soil at a heavily impacted forest catchment (Lysina, Czech Republic)—SAFE modeling and field results. *Ecol Model* 205:464–474
- Nierop KGJ, Jansen B, Verstraten JM (2002) Dissolved organic matter, aluminium and iron interactions: precipitation induced by metal/carbon ratio, pH and competition. *Sci Total Environ* 300:201–211
- Nordin A, Högberg P, Näsholm T (2001) Soil nitrogen form and plant nitrogen uptake along a boreal forest productivity gradient. *Oecologia* 129:125–132
- Novák M, Kirchner JW, Groscheová H, Havel M, Černý J, Krejčí R, Buzek F (2000) Sulfur isotope dynamics in two central European watersheds affected by high atmospheric deposition of SO_x . *Geochim Cosmochim Acta* 64(3):367–383
- Novák M, Buzek F, Harrison AF, Přečková E, Jačková I, Fottová D (2003) Similarity between C, N and S stable isotope profiles in European spruce forest soils: implications for the use of $\delta^{34}\text{S}$ as a tracer. *Appl Geochem* 18:765–779
- Novák M, Michel RL, Přečková E, Štěpánová M (2004) The missing flux in a ^{35}S budget for the soils of a small polluted catchment. *Water Air Soil Pollut* 4:517–529
- Novák M, Kirchner JW, Fottová D, Přečková E, Jačková I, Krám P, Hruška J (2005) Isotopic evidence for processes of sulfur retention/release in 13 forested catchments spanning a strong pollution gradient (Czech Republic, Central Europe). *Glob Biogeochem Cycl* 19:GB4012. doi:10.1029/2004GB002396
- Oulehle F, McDowell WH, Aitkenhead-Peterson JA, Krám P, Hruška J, Navrátil T, Buzek F, Fottová D (2008) Long-term trends in stream nitrate concentrations and losses across watersheds undergoing recovery from acidification in the Czech Republic. *Ecosystems* 11:410–425
- Oulehle F, Evans CD, Hofmeister J, Krejčí R, Tahovská K, Persson T, Cudlín P, Hruška J (2011) Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition. *Glob Chang Biol* 17(10):3115–3129
- Pastor J, Aber JD, McLaugherty CA, Melillo JM (1984) Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. *Ecology* 65:256–268
- Perakis SS, Hedin LO (2002) Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. *Nature* 415:416–419
- Pilkington MG, Caporn SJM, Carroll JA, Cresswell N, Lee JA, Ashenden TW, Brittain SA, Reynolds B, Emmett BA (2005) Effects of increased deposition of atmospheric nitrogen on an upland moor: leaching of N species and soil solution. *Environ Pollut* 135:29–40
- Prechtel A, Alewell C, Armbruster M, Bittersohl J, Cullen JM, Evans CD, Helliwell RC, Kopáček J, Marchetto A, Matzner E, Messenburg H, Moldan F, Moritz K, Veselý J, Wright RF (2001) Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrol Earth Syst Sci* 5:311–325
- Ramirez KS, Lauber CL, Knight R, Bradford MA, Fierer N (2010) Consistent effects of nitrogen fertilization on soil bacterial communities in contrasting systems. *Ecology* 91(12):3463–3470
- Reuss JO, Johnson DW (1986) acid deposition, soil and waters. *Ecological studies*, vol 50. Springer, New York
- Rütting T, Boeckx P, Müller C, Klemmedtsson L (2011) Assessment of the importance of dissimilatory nitrate reduction to ammonium for the terrestrial nitrogen cycle. *Biogeosciences* 8:1779–1791
- Šantrůčková H, Tahovská K, Kopáček J (2009) Nitrogen transformations and pools in N-saturated mountain spruce forest soils. *Biol Fertil Soil* 45:395–404
- Scheel T, Dörfler C, Kalbitz K (2007) Precipitation of dissolved organic matter by aluminum stabilizes carbon in acidic forest soils. *Soil Sci Soc Am J* 71:64–74
- Schimel JP, Bennett J (2004) Nitrogen mineralization: challenges of a changing paradigm. *Ecology* 85(3):591–602
- Schmidt MW, Torn MS, Abiven S, Dittmar T, Guggenberger G, Janssens IA, Kleber M, Kögel-Knabner I, Lehmann J, Manning DA, Nannipieri P, Rasse DP, Weiner S, Trumbore SE (2011) Persistence of soil organic matter as an ecosystem property. *Nature* 478:49–56
- Sinsabaugh RL (2010) Phenol oxidase, peroxidase and organic matter dynamics of soil. *Soil Biol Biochem* 42:391–404
- Smith SJ, van Aardenne J, Klimont Z, Andres RJ, Volke A, Delgado Arias S (2011) Anthropogenic sulfur dioxide emissions: 1850–2005. *Atmos Chem Phys* 11:1101–1116
- Stoddard JL (1994) Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In: Baker LA (ed) *Environmental chemistry of lakes and reservoirs*. ACS advances in chemistry series 237. American Chemical Society, Washington, DC, pp 223–284
- Stoddard JL, Jeffries DS, Lükewille A, Clair TA, Dillon PJ, Driscoll CT, Forsius M, Johannessen M, Kahl JS, Kellogg JH, Kemp A, Mannio J, Monteith D, Murdoch PS, Patrick S, Rebsdorf A, Skjelkvåle BL, Stainton MP, Traaen T, van

- Dam H, Webster KE, Wieting J, Wilander A (1999) Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* 401:575–578
- Stumm W (1992) *Chemistry of the solid-water interface. Processes at the mineral-water and particle-water interface in natural systems*. Wiley, New York
- Taylor PG, Townsend AR (2010) Stoichiometric control of organic carbon–nitrate relationships from soils to the sea. *Nature* 464:1178–1181
- Tietema A (1998) Microbial carbon and nitrogen dynamics in coniferous forest floor material collected along a European nitrogen deposition gradient. *For Ecol Manag* 101:29–36
- Tipping E, Hurley MA (1998) A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. *Eur J Soil Sci* 39:505–519
- Toberman H, Freeman C, Artz RE, Evans CD, Fenner N (2008) Impeded drainage stimulates extracellular phenol oxidase activity in riparian peat cores. *Soil Use Manag* 24:357–365
- Torssander P, Mörth C-M (1998) Sulphur dynamics in the roof experiment at Lake Gardsjön deduced from sulphur and oxygen isotope ratios in sulphate. In: Hultberg H, Skeffington R (eds) *Experimental reversal of acid rain effects. The Gardsjön Roof Project*. Wiley, Chichester, pp 185–206
- Treseder KK (2004) A meta-analysis of mycorrhizal responses to nitrogen, phosphorus, and atmospheric CO₂ in field studies. *New Phytol* 164:347–355
- Veselý J, Majer V, Norton SA (2002) Heterogeneous response of central European streams to decreased acidic atmospheric deposition. *Environ Pollut* 120:275–281
- Vitousek PM (2004) *Nutrient cycling and limitation. Hawai'i as a model system*. Princeton University Press, Princeton
- Waldrop MP, Zak DR, Sinsabaugh RL, Gallo M, Lauber C (2004) Nitrogen deposition modifies soil carbon storage through changes in microbial enzymatic activity. *Ecol Appl* 14:1172–1177
- Yin S, Shen Q, Tang Y, Cheng L (1998) Reduction of nitrate to ammonium in selected paddy soils in China. *Pedosphere* 8:221–228
- Zak DR, Pregitzer KS, Burton AJ, Edwards IP, Kellner H (2011) Microbial responses to a changing environment: implications for the future functioning of terrestrial ecosystems. *Fungal Ecol* 4:386–395