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1   **Modelling changes in nitrate leaching using the MAGIC model with linked microbial**
2   **and nitrogen processes**
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19

20   **Abstract**
21

22   We apply a new formulation of nitrogen (N) and carbon (C) cycling in the acidification
23   model MAGIC to simulate changes in water chemistry over the past 30 years at three
24   coniferous-forested sites in the Czech Republic where deposition of sulphur (S) and N has
25   decreased by > 80% and 40%, respectively. Sulphate concentrations in waters have declined
26   commensurately, but nitrate concentrations have shown much larger decreases relative to
27   deposition. This behaviour is inconsistent with most conceptual models of N saturation, and
28   with earlier versions of MAGIC which assumed that N retention was functionally
29   proportionate to N deposition or related to the soil C/N ratio; neither can reproduce the
30   observed changes in NO_3. The new formulation effectively simulates observed changes in
31   nitrate, as well as changes in soil C/N. The model suggests that, despite recent apparent
32   recovery, progressive N saturation will lead to increased future nitrate leaching, ecosystem
33   eutrophication and re-acidification.
34

35   **Capsule**
36

37   Process-based modelling of the carbon and nitrogen dynamics in forest ecosystems
38

39   **Key words**
40

41   Nitrogen; saturation; leaching; acidification; Norway spruce
42

43   **1. Introduction**
44

45   Surface waters in acid-sensitive regions of Europe have been severely affected by decades of
46   elevated sulphur (S) and nitrogen (N) deposition. During the past 25 years deposition of S has
47   decreased by >80% (Schöpp et al., 2003) following implementation of international
48   agreements on reduction of emissions of air pollutants under the auspices of the United
49   Nations Economic Commission for Europe (UNECE) Convention on Long-Range
50   Transboundary Air Pollution (LRTAP) (UNECE, 2002). Despite substantial decreases in

emissions of N compounds (NH_3 and NO_x) (Kopáček and Posch, 2011), reductions in N deposition are often proportionally much smaller (Fowler et al., 2005). In response to the decreased S and N deposition, surface waters have begun to recover from acidification (Jenkins et al., 2003; Stoddard et al., 1999; Wright et al., 2005). As sulphate (SO_4) concentrations have decreased, nitrate (NO_3) has become increasingly important as a proportion of the acid anion leaching from many catchments (e.g. Curtis et al., 2005). In acid soils, much of the NO_3 leached from soil is accompanied by the acid cations H^+ and inorganic aluminium (Al_i). Chronic deposition of elevated amounts of N also affects the nutrient status of terrestrial and aquatic ecosystems and can cause changes in biodiversity (De Vries et al., 2010).

Process-oriented catchment-scale biogeochemical models provide tools to simulate changes in surface water and soil chemistry in response to changes in S and N deposition. These models commonly include processes to describe the retention and loss of N in terrestrial ecosystems. MAGIC (Model for Acidification of Groundwater In Catchments) is one such model (Cosby et al., 2001; Cosby et al., 1985a; Cosby et al., 1985b). MAGIC has been widely used in a variety of applications to simulate acidification of soil and surface water (Cosby et al., 2001).

In the early versions of MAGIC (versions 1-5) retention of N was calculated simply as the difference between N deposition and runoff output. The fraction retained was assumed to be unchanged for the historical and future simulated years.   With version 7 (Cosby et al., 2001) the fraction N retained was described as a function of the N richness of the ecosystem. This was largely based on empirical data such as the synoptic data from forested sites in Europe (Dise et al., 1998; Gundersen et al., 1998) and subsequently North America (Aber et al., 2003; Lovett et al., 2002), and from experimental studies such as the NITREX experiments (Emmett et al., 1998). These data showed that N-rich sites leach a larger fraction of incoming N relative to N-poor sites. The soil C/N ratio is often used as a measure of N-richness. The C/N ratio is a measure of the state of the system, and as such is the product of N retention processes such as microbial N immobilisation and N mineralisation.

Because the organic matter pool in soils is often quite large, the C/N ratio changes only slowly in response to retention of N from deposition. Furthermore, as a measure of the bulk properties of the whole soil, the C/N ratio does not necessarily reflect the N-richness of the actively cycling component of the organic matter. Forest floor C/N ratio appears to be a particularly robust indicator of catchment N export across large regional gradients and long time-frames (Dise et al., 1998; Gundersen et al., 1998), and is useful in understanding spatial patterns among the Czech catchments (Oulehle et al., 2008). However, it does not appear to be useful in understanding relatively short-term changes in N dynamics (1–2 decades). Data from the NITREX experiment in Sweden (Moldan et al., 2006) show that the soil C/N ratio is unresponsive to short-term environmental change. The non-linear nature of the relationship between soil C/N and NO_3 export also makes it more difficult to apply in a predictive framework, as small (and difficult to detect) changes in soil C/N can result in large NO_3 increases once the threshold for accelerated NO_3 leaching (C/N of approximately 22–25) has been passed. Thus, large and rapid changes in N leaching cannot be accounted for simply by the C/N ratio of the soil, or the bulk "N-richness" of the ecosystem. It is more likely that the actual strength of the various N sinks and the factors that control them determine the fate of the incoming N within the ecosystem (Lovett and Goodale, 2011).

1 Here we describe an alternative formulation of N retention and loss in soil based directly on
2 the microbial processes which determine the balance of N mineralisation and immobilisation,
3 and incorporate this into MAGIC (MAGIC 7ext). This new model formulation is tested using
4 long-term (>15 year) data from three monitoring sites in the Czech Republic. The sites are
5 located within a region that experienced exceptionally high rates of S and N deposition in the
6 1980s-90s, followed by very large and rapid reductions during the last two decades. They
7 include soil, stream and lake catchment data, and thus provide a robust test of model
8 performance for multiple ecosystem components over a period of major change in pollutant
9 loadings.
10
11 **2. Materials and methods**
12
13 *2.1. The model*
14
15 MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the
16 long-term effects of acidic deposition on surface water chemistry (Cosby et al., 2001; Cosby
17 et al., 1985a; Cosby et al., 1985b). The model simulates soil and surface water chemistry in
18 response to changes in drivers such as deposition of S and N, silvicultural practices, and
19 climate. MAGIC calculates for each time step (in this case year) the concentrations of major
20 ions under the assumption of simultaneous reactions involving SO_4 adsorption, cation
21 exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of
22 inorganic and organic C. MAGIC accounts for the mass balance of major ions in the soil by
23 bookkeeping the fluxes from atmospheric inputs, chemical weathering, net uptake in biomass
24 and loss to runoff.
25
26 Data inputs required for calibration of MAGIC comprise lake and catchment characteristics,
27 soil chemical and physical characteristics, input and output fluxes for water and major ions,
28 and net uptake of base cations and N by vegetation. Here, we describe the new formulation of
29 the MAGIC N model for the first time.
30
31 The soil organic matter (SOM) pool is the central feature of the N dynamics in the new
32 version of MAGIC (Figure 1). The dynamics of the SOM pool are driven by decomposer
33 activity and exchanges with the soil solution. Decomposers process the C and N content of
34 SOM, using part of the organic matter for energy and part to generate new biomass (which
35 remains in the SOM). The turnover of SOM results in the release of CO_2, NH_4, dissolved
36 organic carbon (DOC) and dissolved organic nitrogen (DON) to soil solution as the result of
37 decomposition and solubilisation, and the removal of inorganic N from soil solution as the
38 result of decomposer growth.
39
40 The plant litter flux provides inputs of organic C and N to the soil organic matter (SOM)
41 pool. This flux includes below ground components of plant litter as well as inputs from N
42 fixing species. The plant uptake flux removes inorganic N from soil solution. MAGIC does
43 not explicitly model plant dynamics. The plant uptake fluxes, therefore, are provided as
44 inputs to the model. Observed litter data (C flux and C/N ratio) are used to set the organic C
45 and N inputs to SOM. The plant uptake of inorganic N from soil solution are then estimated
46 as the amount necessary to replace the annual plant N losses through litter, with perhaps a
47 small additional increment to represent the annual storage of N in woody tissue.
48
49 Inorganic N enters the model as deposition (wet and dry) of NO_3 and NH_4. Inorganic nitrogen
50 (N_2) is lost to the atmosphere as a result of denitrification in the soil. Carbon dioxide (CO_2)

resulting from respired SOM is lost to the atmosphere through gas exchange. Within the soil solution, NH_4 can be nitrified to NO_3. As water moves through the soil at each time step, the dissolved C and N constituents are transported out of the soil as dissolved NO_3, NH_4, DON and DOC in solution. When a multiple soil layer version of MAGIC is implemented, these C and N fluxes would pass to the next soil layer. After the last layer, these fluxes enter the surface water compartment.

Time series of plant litter and N fixation (FC1 and FN1) (Figure 1) are external inputs to SOM. At each time step, decomposers process some of the C and N content of SOM (FC2 and FN2). A portion of this C and N turnover returns to the SOM as decomposer biomass (FC3 and FN3), while the remainder is lost from SOM to soil solution as CO_2 and NH_4 (decomposition and mineralization; FC4 and FN4), or as DOC and DON (solubilisation; FC5 and FN5).

The fraction of total organic C in SOM turnover that is returned to the SOM as C in new decomposer biomass (i.e., the ratio FC3/FC2) is specified in the model using the parameter Cfrac (which is optimized during calibration as described below). Similarly, the fraction of total organic N in SOM turnover that is incorporated in new decomposer biomass (i.e., the ratio FN6/FN2) is specified by the parameter Nfrac (also optimized as described below).The new decomposer biomass that is produced in this cycle must have the characteristic C/N ratio of the decomposer organism and this ratio must be maintained in the return fluxes FC3 and FN3 entering the SOM. If the N flux from SOM turnover (FN6) is smaller than the N flux needed for the new decomposer biomass (i.e., FN6 < FN3), the additional N required for the new decomposer biomass is obtained from soil solution (immobilization; FN7). This process of immobilization of inorganic N from soil solution will vary in time as the C/N ratio of the SOM changes. As nitrogen accumulates in the SOM, the C/N ratio of the SOM declines and more of the N needed for new decomposer biomass can be derived from the SOM turnover (FN6). In turn, the immobilization flux (FN7) will decline leaving higher concentration of inorganic N in soil solution.

The organic C lost from SOM to soil solution during turnover can appear as CO_2 (decomposition; FC4), or as DOC (solubilisation; FC5). The fraction of organic C lost from SOM as DOC (i.e., FC5/(FC4+FC5)) is specified in the model by the parameter Dfrac. This parameter is optimized to match observed DOC in soil runoff. The C/N ratio of the DOC in runoff is assumed to be the same as the C/N of the SOM, thus allowing calculation of the DON flux (FN5). The amount of N released to the soil solution as NH_4 (mineralization; FN4) is determined at each time step by mass balance (FN4 = FN2 − FN5 − FN6).

2.2. Site descriptions

Three sites in the Czech Republic, representing a stream, a lake and a terrestrial monitoring plot (i.e. soil water) respectively, were selected on the basis of long-term monitoring data that showed dramatic changes in acidic deposition and NO_3^- leaching during the last decades (Hruška et al., 2002; Majer et al., 2003; Oulehle et al., 2007).

The Načetín forest plot (soil water site) is located on the ridge of the Ore Mountains, northwestern Czech Republic, in the centre of the so-called "Black Triangle" – formerly one of the most polluted regions in Europe, with the highest areal SO_2 emissions (Figure 2, Table 1)(Oulehle and Hruska, 2009). The region was not glaciated. Extremely high sulphur emissions from nearby power plants burning high-sulphur lignite (a maximum S deposition

of 800 mmol m^{-2} yr^{-1} in the late 1980s; Berge, 1997) caused widespread forest diebeck in the region (Moldan and Schnoor, 1992). The spruce forest at the site is one of the few remaining mature forest stands in the region. Monthly measurement of bulk precipitation, throughfall and soil water (90 cm depth) started in 1994 (Oulehle et al., 2006).

The Lysina catchment (stream water site) is located in the large spruce forest on the unglaciated plateau of the Slavkov Forest in western Czech Republic (Figure 2, Table 1). The catchment has been monitored since 1989 and 1990 for runoff (stream water) and deposition (bulk and throughfall), respectively. The chronically acidic stream at Lysina experienced marked declines of sulphate (SO_4), nitrate (NO_3), calcium (Ca) and magnesium (Mg) concentrations in the 1990s (Hruška and Krám, 2003).

Čertovo Lake (lake water site) is a small (10 ha) lake of glacial origin located in the Bohemian Forest in the southwestern Czech Republic (Figure 2, Table 1). It has been a nature reserve since the 1930s. The lake has maximum depth of 36 m and water retention time of 1.8 yr. The catchment is a forest of mature spruce trees. The lake has been the object of irregular hydrobiological research since the 1870s (Vrba et al., 2003). Regular chemical monitoring began in 1984 (Veselý et al., 1998), and mass budgets of major element fluxes in the catchment-lake system have been available since 1998 (Kopáček et al., 1998). Bulk deposition and throughfall have been measured since 1991 (Hruška et al., 2000) and were reconstructed back to 1860 (Kopáček et al., 2001).

2.3. Deposition

Deposition (both bulk and throughfall) has been measured at the three sites since the beginning of the 1990s. These data show a dramatic decrease in S deposition and to a lesser extent also N deposition since 1990 (Figure 3). Throughfall data were used here for S and N. At Načetín S deposition declined from 66 kgS ha^{-1} yr^{-1} to 13 kgS ha^{-1} yr^{-1} (81%) and N deposition decreased from 29 kgN ha^{-1} yr^{-1} to 17 kgN ha^{-1} yr^{-1} (41%) compared to the peak in 1980s. At Lysina S deposition decreased from 44 kgS ha^{-1} yr^{-1} to 6.4 kgS ha^{-1} yr^{-1} (85%) and N deposition decreased from 13 kgN ha^{-1} yr^{-1} to 8.7 kgN ha^{-1} yr^{-1} (33%). At Čertovo S deposition declined from 42 kgS ha^{-1} yr^{-1} to 7.2 kgS ha^{-1} yr^{-1} (83%). N deposition declined from 25 kgN ha^{-1} yr^{-1} to 17 kgN ha^{-1} yr^{-1} (32%) (Table 1).

For the period prior to observations we use estimates of S and N deposition derived by Kopáček et al. (2001) and Schöpp et al. (2003) based on historical estimates of European S and N emissions. The trends were scaled to the measured deposition at each of the sites for the period of observations (1991-2009). For the future period to the year 2050 we use the current models (Current Legislation scenarios − CLE) of the 'Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, http://www.ceip.at/emission-data-webdab), which project lower emissions of S and N compounds in Central Europe in 2010 and 2020 than the values originally based on the Gothenburg Protocol (Schöpp et al., 2003).

Deposition in base cations and chloride (Cl) were modelled by a procedure similar to that used by Majer et al. (2003), with the exception for the 1991–2009 period, when the measured data were used. The trends in base cations and Cl deposition were similar (but less steep) to the trend in SO_4 deposition (Figure 3), with maxima in the 1980s, reflecting maximum dust emissions from coal consumption and industrial processes (Hedin et al., 1994) and Cl emissions associated with coal consumption (Evans et al., 2011) and industry (Veselý et al.,

2002) in this period. Future deposition of base cations and Cl were held constant at 2009 levels.

2.4. Calibration procedure

MAGIC was calibrated to the average water chemistry for the period 1994-1995 (Načetín), 1991-1992 (Lysina) and 2000 (Čertovo Lake), respectively, and the soil chemistry for each site. The calibrations at each site proceeded by sequential steps. The first steps involved calibration of the strong-acid anions; Cl and SO_4 were calibrated by adjusting the deposition inputs as described by Wright and Cosby (2003) such that for both ions mass balance for the catchment-lake systems were obtained.

Calibration of the NO_3 concentrations in water came next. For simulation at a given site, the values Cfrac and Nfrac, and the initial C and N content of the SOM pool were specified. These values were jointly selected in an optimization procedure that minimized the differences between simulated and observed values of a number of criteria, given the input time-series of litter, runoff, and inorganic N deposition at each site. The values to be matched included the C content, the C/N ratio of the soil organic matter at the site, and the concentrations of inorganic N, DON and DOC in runoff. The simulated values for the pools of C and N and the C/N ratio in the soil were forced to match the observed values for the year for which soil measurements were available. The C/N ratio (mol/mol) of new microbial biomass was assumed to be 10 (Cleveland and Liptzin, 2007).

This optimisation procedure resulted in the modelled sum of strong acid anions (SAA) in water equal to that observed. The next steps involved calibration of the base cations Ca, Mg, Na, and K. A trial and error process was used to adjust the weathering rates of Ca, Mg, Na, and K and initial soil exchange pools of these four cations until modelled concentrations of base cations in the streamwater and modelled pools of base cations in the soil matched the observed for the calibration period. This step calculated the soil-soil solution selectivity coefficients for base cations and Al exchange. At this point the modelled sum of base cations (SBC) equalled the observed for the calibration period, and thus also the modelled acid neutralising capacity (ANC) equalled the observed ANC (ANC was defined as SBC-SAA).

The final step entailed calibration of the weak acids and bases such that the simulated concentrations of H^+, Al_i and organic anions (A^-) matched observations. This was achieved by adjusting the dissociation constants for organic acids, aluminium hydroxide, fluoride, and sulphate species, and organic aluminium complexes. We used tri-protic model for organic acids with dissociation constants given by Hruška et al. (2003).

3. Results

3.1. Model outputs

The model with the new N dynamics was successfully calibrated to the observed water NO_3 data at all three sites. The model simulated the observed large decreases in NO_3 concentrations over the period 1990-2010 at Načetín and Lysina, as well as the observed rise and fall in NO_3 concentrations over the 50-year period at Čertovo Lake (Figure 4).

The calibrated C and N parameters were quite similar among the three sites (Table 2). The parameter Cfrac was 21-25% and Nfrac 45-80%. The C fluxes used to calibrate the model at

1   the three sites were held constant throughout the 200-year simulation period, with the
2   exception of the annual amount of organic C processed in soil organic matter (SOM) turnover
3   (flux FC2 in Figure 1), which was reduced during the period of severe soil acidification
4   (1970-1990). The resulting C fluxes for three key years at Načetín are shown in Table 3.
5
6   The N fluxes into and out of the ecosystem were either measured or estimated, and linked to
7   the C fluxes by means of C/N ratios of organic matter in the various pools. The resulting N
8   fluxes within the soil compartment show large changes during the 145-year period 1860 to
9   2005, here shown for Načetín (Table 3). Under the assumptions that plant uptake of N and
10   litterfall of organic N are constant over the entire period, the changes in N deposition give
11   rise to large changes in inorganic N leaching. The other two sites behaved similarly (Suppl.
12   Tab. S1, S2).
13
14   During the simulation N mineralization (FN4) increased as N accumulated in the SOM.
15   Consequently inorganic N immobilization decreased as more N needed by microbes was
16   directly derived from the mineralization of SOM. As the organic C processed in SOM
17   turnover was assumed to decrease during the 1980s, however, more inorganic N was left in
18   the soil solution as a result of lower inorganic N immobilization (FN7) and was thus directly
19   available for leaching (fN1).
20
21   The simulations suggest that the inorganic N inputs in deposition over the 150-year period
22   1860-2009 have gone to a small amount of denitrification (7-14%), and increases in N stored
23   in the soil organic matter pool (26-72%), leached as organic N (4-25%), and leached as
24   inorganic N (2-42%) (Table 4). At Načetín and Lysina the largest fraction of the input N has
25   gone to the soil, while at Čertovo Lake, the largest fraction has been lost by leaching. This
26   indicates that Čertovo Lake is the most "N saturated" of the three sites, in that for the past
27   several decades, N outputs by leaching approximately balance N inputs by deposition.
28
29   The acid-base calibration was also successful. The simulated concentrations of major ions,
30   pH and Al_i in runoff (or soilwater in the case of Načetín) matched observed values for the
31   calibration year (Figure 6).
32
33   *3.2. Long-term trends*
34
35   At the three sites the large observed changes in NO_3 in surface and soil water were well
36   simulated by the model (Figure 6). At Čertovo Lake the measured and simulated
37   concentrations of nitrate (NO_3) went from very low levels prior to 1950, peaked in the 1980s
38   at 100-120 µeq L^{-1} and then showed a sharp decline back to about 40 µeq L^{-1} by the year
39   2000 (Figure 6). At all three sites the observed and modelled concentrations of NO_3 have
40   declined sharply during the last 25 years, much more steeply than the N deposition during
41   this same period.
42
43   The new microbial formulation of C and N processes in MAGIC 7ext captured the observed
44   changes in NO_3 leaching at the three sites. Neither the MAGIC version 5 (constant fraction of
45   N deposition retained) nor version 7 (N retention linked to C/N of soil organic matter) gave a
46   satisfactory simulation of the observed large declines in NO_3 flux in leachate at the three
47   sites. The simulations were improved further by including the negative effect of acidification
48   on turnover of SOM during the period of peak S deposition (Figure 4). The descriptions of N
49   retention in the earlier versions of MAGIC were unable to simulate declines in N leaching

greater that the decline in N deposition, without invoking some other major change in ecosystem N cycling, such as N uptake by vegetation.

Over the 200-year simulation period the soil C pool was assumed not to change at the three modelled sites. In contrast the soil N pools increased over the entire 200-year period, due to the partial retention and storage of N deposition from the atmosphere. The simulated C/N ratio in the SOM thus decreased at all three sites over the 200-year simulation period (Figure 5).

The long-term trends in SO_4 are also well described by the model (Figure 6). SO_4 has declined sharply since the mid-1980s, in response to the large declines in S deposition (Figure 3). Because of the large decreases in concentrations of strong acid anions (SO_4+NO_3), the acid neutralising capacity (ANC) has increased dramatically since the 1980s (Figure 6). The increased ANC is reflected in increased pH and decreased Al_i.

The long-term simulated changes in soil base saturation at the three sites followed the typical pattern of decrease during the period of increasing acid deposition, and then a reduction in the rate of decrease since about 1990 as the S and N deposition declined, with a projected slight increase (recovery) over the next 40 years given implementation of the CLE scenario for future S and N deposition (Figure 5).

4. Discussion

4.1. Processes controlling N saturation

Observations of sharply decreasing N leaching in the Czech forests do not follow the assumption that, under ambient N deposition, ecosystems will continuously move towards progressive N saturation, demonstrated by increasing trends in NO_3 leaching. All sites have undergone substantial recovery from acidification in last two decades as a result of large reduction in S deposition. Therefore, the strength of possible sinks for incoming N could have been impaired in the past via negative feedbacks on the ecosystem capacity to retain N. It has been previously shown that forest productivity is negatively affected by atmospheric pollution as mirrored in $\Delta^{13}C$ in tree rings at Čertovo Lake (Šantrůčková et al., 2007) and in tree ring widths in respect of Načetín (Oulehle et al., 2006). However, changes in biomass increment were insufficient to explain large decrease in NO_3 leaching in soil water at Načetín (Oulehle et al., 2011) as the net sink in woody biomass is limited by high C/N ratio. Detection of changes in soil N retention is complicated by the fact that expected changes in the soil pools are usually smaller than the precision with which they can be measured (Moldan et al., 2006). As NO_3 in the soil/stream leachate appears to be predominantly cycled through the microbial pool (Curtis et al., 2011), controls over the soil N retention rate could be attributable to the "efficiency" of microbial community within the soil environment. Hart et al. (1994) showed a strong relationship between microbial respiration and gross rates of N mineralization and immobilization, suggesting that labile C availability is an important control on internal N cycling. Higher C availability (e.g. caused by declining soil acidity, or higher belowground C allocation by trees) might stimulate faster turnover rates of microbial biomass with tightly coupled NH_4 production and NH_4 immobilization leading to efficient retention of mineral N through microorganisms, corroborated by very low N losses as proposed by Corre and Lamersdorf (2004). The stage of N saturation under elevated N deposition is therefore the consequence of dynamic factors that control the strength of the ecosystem N sinks (Lovett and Goodale, 2011) rather than continual progress through series

of stages of N saturation as originally proposed by Aber et al. (1998, 1989) and Stoddard (1994). According to this alternative conceptual understanding of N saturation, modelling the internal dynamics of the SOM combined with a long-term mass balance approach appears necessary to simulate changes in ecosystem N status.

4.2. Assessment of model performance

The new formulation of C and N processes in the soil applied here clearly gives a more satisfactory simulation of the observed trends in NO_3 in water compared to previous versions of MAGIC model. This new formulation uses the rates of two key microbial processes that govern the amount of C and N fixed in the soil by microbial growth, and the amounts released from the soil by microbial decomposition of SOM. The new microbial formulation simulates both the rapid (and amplified) ecosystem responses to changes in deposition of N, as well as the long-term changes in soil C/N resulting from chronic N deposition and accumulation in SOM.

The earlier formulation in MAGIC 7 was based on the soil C/N ratio and on the empirical observation that N-rich sites generally leach a larger fraction of incoming N as compared to N-poor sites (Gundersen et al., 1998). This formulation has two shortcomings: first, since the C/N ratio of soil organic matter changes only slowly, over the short term large changes in N leaching cannot be accounted for by changes in the C/N ratio; and secondly, the C/N ratio of bulk soil organic matter is in reality a consequence rather than the driver of the long-term retention and loss of N from the soil pool. The new microbially-based formulation thus gives a more realistic simulation of observed changes in N leaching. The observed NO_3 leaching at the three Czech sites has decreased much more than can be accounted for simply by decreased N deposition. Whereas NO_3 concentrations in leachate decreased by 65-95% from peak levels in the late 1980s, N deposition at the sites decreased by only 30-45% (Figure 3). The previous C/N-based approach predicted that over short time periods (< 20 years), the C/N ratio of soil organic matter would not change significantly, the fraction of N retained would not change, and thus the leaching of N would closely match the reduction in N deposition (Figure 4).

The C/N-based approach still remains useful, especially for ecosystems that have experienced long-term slower changes in N deposition. The C/N approach reflects empirical synoptic data on soil C/N ratio and N retention. Both the C/N approach and the new microbial formulation presented here simulate observed long-term changes in N leaching, but the rapid changes observed during the 1950-2010 at the three sites in the Czech Republic are better simulated by the new microbial formulation in MAGIC.

The new formulation also provides a reasonable simulation of the long-term changes in C and N pools (and C/N ratio) in SOM. The simulation is compatible with expectations that the C/N ratio was higher in the past before the onset of chronically-elevated N deposition, and has gradually decreased as a result of retention of incoming N in soil organic matter (Figure 5).

4.3. Limitations of the current model

The model applications assume a balanced C cycle through the simulation, i.e. a constant soil C pool. A number of factors might invalidate this assumption. First, forest management (thinning, harvesting) and climate could significantly alter soil C accumulation in the long-term. Second, there is considerable evidence that ecosystem productivity increases in

response to N deposition in forests (e.g. de Vries et al., 2009; Högberg et al., 2006; Hyvonen et al., 2008; Magnani et al., 2007) and heathlands (Evans et al., 2006a). N enrichment can also suppress decomposition rates (e.g. Berg and Matzner, 1997; Waldrop et al., 2004). Although the magnitude of the effect of N deposition on C accumulation has been debated (e.g. De Schrijver et al., 2008; de Vries et al., 2008; de Vries et al., 2009), it is generally accepted that moderately elevated N deposition does lead to some C accumulation in forest soils. However, this positive effect of N on soil C probably declines, or ceases, at higher N loadings, as ecosystems become N-saturated and productivity is therefore no longer N limited. Given the high rates of NO_3 leaching at the study sites, it is therefore likely that C responses to change in N deposition, at least during recent decades, have been minor. On the other hand, Oulehle et al. (2011) have shown evidence of C accumulation, and subsequent release from the organic horizon of the Načetín plot during the last 15 years due to changes that appear to be driven by soil acidification and recovery during the peak of S deposition. Although this process was not fully modelled here, changes in the turnover of organic matter have been approximated by varying the C fraction term as a function of S deposition. As shown in Figure 4, only a small change in C fraction leads to an improved simulation of NO_3 leaching, which is consistent with the concept of microbial N production and immobilization as described above.

One other recognised limitation of the model is that the projections for future N leaching and acidification to the year 2050 at the three sites assume that current climate and forest management will continue with no change. Both can significantly affect water chemistry. The two microbial processes included in the new formulation of MAGIC are both influenced by climate variables such as soil temperature and moisture, and rates of these processes can be set dependent on these climate variables. This should provide greater potential to simulate climate impacts on N cycling and water chemistry than previous versions of the model. Climate-dependencies remains to be fully parameterised, and will be tested with data from large-scale climate experiments such as CLIMEX (van Breemen et al., 1998), VULCAN (Beier et al., 2009) and CLIMAITE (Andresen et al., 2010), as well as long-term monitoring records at sites with year-to-year variations in weather. The overall objective for future model development and application will be to include the dynamic simulation of C and N turnover as a function of N and S deposition, climate and forest management, in order to evaluate the combined effects of multiple drivers on ecosystem eutrophication and acidification.

4.4. Implications for future nitrogen status

The model suggests that over the next few decades the NO_3 concentrations in water will again increase at Načetín and Lysina, despite assumed constant rates of N deposition. The model simulations indicate that Načetín and Lysina will move towards the situation already reached at Čertovo Lake, whereby N availability from mineralization and deposition exceeds the rate of microbial immobilization. However, susceptibility to inorganic N leaching is generally higher at exposed catchments with shallow soil profiles (in our case Čertovo Lake) (Kopáček et al., 2005) and with lower total soil C pool (Curtis et al., 2011; Evans et al., 2006b). As a consequence, at all three sites NO_3 leaching is expected to gradually become a dominant process causing soil and water acidification, as well as a cause of terrestrial and aquatic eutrophication.

The projections for soil and water acidification in the future at these three sites point to the need for further reductions in S and N deposition in order to reach the environmental target of no undesirable ecological damage to the terrestrial or aquatic ecosystems. Even with the

substantial reduction in acid deposition that has occurred since the late 1980s, the ANC and pH of water are still below, and the concentrations of Al_i still above, acceptable limits for sensitive organism groups such as salmonid fish and benthic macroinvertebrates (Gensemer and Playle, 1999; Herrmann, 2001).

N plays an increasingly important role in the acidification of soil and water at these sites, and elsewhere in Europe (Curtis et al., 2005), as S deposition and leaching of SO_4 has decreased. There is thus a growing need for realistic process-based simulation models for N leaching. The new microbial formulation presented here, based on a relatively simple representation of known processes, and a small number of additional parameters, has the potential to fill this role.

Acknowledgements

Figure captions

Figure 1. Schematic diagram of compartments, fluxes and processes for C and N used to simulate N retention and leaching from terrestrial ecosystems.

Figure 2. Map of the Czech Republic showing the locations of the three sites.

Figure 3. Deposition of S and N at the three sites over the period 1850-2050. The estimated historical trends are from (Schöpp et al., 2003), and the future trends assume full implementation of the CLE scenario (solid line). Circles show the measured annual deposition. Observed data from Lysina (Hruška and Krám, 2003), Načetín (Oulehle et al., 2006) and Čertovo Lake (Kopáček et al., 2009; Kopáček et al., 2001) and unpublished newer data from all sites.

Figure 4. NO_3 concentrations in water observed and simulated by MAGIC at the three sites in the Czech Republic. Top panels show the MAGIC simulations using the current version 7ext (microbial processes) compared with simulations from version 7 (retention of N deposition related to C/N of soil organic matter) and version 5 (constant fraction of N deposition retained in soil). Bottom panels show the results when the parameter Cfrac is held constant compared with the current version (7ext) in which the Cfrac is assumed to be influenced by soil acidity.

Figure 5. Simulated and observed sizes of the N pools (mol m^{-2}) and C/N ratio (mol mol^{-1}) in soil organic matter and % of the soil base saturation at the three sites.

Figure 6. Volume-weighted annual mean concentrations of SO_4, NO_3, ANC, pH, and Al$_i$ simulated (solid lines) and observed (circles) at the three sites.

Table captions

Table 1. Characteristics of the three sites. Estimated (1984-86) and measured (2007-09) S and N deposition are based on throughfall data (Hruška and Krám, 2003; Kopáček et al., 2009; Kopáček et al., 2001; Oulehle et al., 2006) and unpublished newer data from all sites.

Table 2. Values of key C and N pools and fluxes used in calibration and resulting calibrated parameters for the calibration year at the three sites.

Table 3. Annual C and N fluxes at Načetín for three years (1860 early acid deposition, 1985 peak acid deposition, and 2005 present-day). For the C fluxes only the annual amount of organic C processed in soil organic matter (SOM) turnover (FC2) and hence the rate of C entering the soil as new microbial biomass (FC3) were assumed to change during the simulation period. Codes refer to the fluxes shown in Figure 1. Units: mmol m^{-2} yr^{-1}.

Table 4. Long-term (1850-2009) integrated N budgets at the three sites as simulated by MAGIC with the microbial formulation for N dynamics.

Table 5. Values of soil fixed parameters and resulting calibrated parameters for the calibration year at the three sites.

1   Table 1
2

	Načetín	Lysina	Čertovo Lake
Location	50°35'N 13°15'E	50°03'N 12°40'E	49°10'N 13°12'E
Altitude (m)	784	829-949	1028-1343
Drainage area (ha)	-	27	86
Precipitation (mm)	842	950	1554
Runoff (mm)	410*	430	1380
Mean annual temperature (°C)	6.3	5.0	4.2
Forest cover	Norway spruce	Norway spruce	Norway spruce
Average age (yr)	75	50	>120
Soil type	Spodo-dystric Cambisol	Spodo-dystric Cambisol	Spodo-dystric Cambisol
Bedrock	Gneiss	Leucogranite	Mica-schist and quarzite
S deposition (meq m^{-2} yr^{-1}) 1984-86/2007-09	413/80	274/40	264/45
N deposition (mmol m^{-2} yr^{-1}) 1984-86/2007-09	204/120	93/62	180/121

*estimated (Oulehle et al., 2007)

3
4

2

Input parameters	Units	Načetín Soil	Lysina Stream	Čertovo Lake
Initial C pool in soil	mol m^{-2}	1110	935	1351
Initial N pool in soil	mol m^{-2}	29	26	54
Initial C/N in soil	mol mol^{-1}	38	36	25
Plant uptake NH$_4$	mmol m^{-2} yr^{-1}	210	218	357
Plant uptake NO$_3$	mmol m^{-2} yr^{-1}	30	18	178
Nitrification	% of inputs	15	15	50
Denitrification	mmol m^{-2} yr^{-1}	7	7	7
Litter C flux	mmol m^{-2} yr^{-1}	13212	13000	22600
Litter C/N	mol mol^{-1}	55	55	42
Calibrated parameters				
C frac	%	24.5	21.5	23
N frac	%	45	55	80
Decomp frac	%	1	3	2.5

3
4
5

1   Table 3
2

		1860	1985	2005
Carbon fluxes				
organic C from plant litter	FC1	13212	13212	13212
organic C processed in SOM turnover	FC2	17499	16433	17499
C in new microbial biomass (new SOM)	FC3	4287	3221	4287
SOM C respired (CO_2 in soil solution)	FC4	13080	13080	13080
SOM C solubilised (DOC in soil solution)	FC5	132	132	132
Nitrogen fluxes				
organic N from plant litter	FN1	240	240	240
organic N processed in SOM turnover	FN2	464	571	634
N in new microbial biomass (new SOM)	FN3	429	322	429
SOM N mineralised (NH_4 in soil solution)	FN4	346	457	473
SOM N solubilised (DON in soil solution)	FN5	4	5	5
organic N from SOM used by microbes	FN6	207	255	283
inorganic N immobilisation by microbes	FN7	222	67	146
organic and inorganic N in runoff	fN1	4	148	5
inorganic N uptake by plants	fN2	240	240	240
denitrification of inorganic N	fN3	7	7	7
atmospheric deposition of inorganic N	fN4	53	206	118

3
4

16

1   Table 4
2

N Budget 1850-2009	Načetín Soil		Lysina Stream		Čertovo Lake	
Inputs	mol m^{-2}		mol m^{-2}		mol m^{-2}	
Total N deposition	16016		7993		14567	
Outputs	mol m^{-2}	*%*	mol m^{-2}	*%*	mol m^{-2}	*%*
Denitrification	1120	7	1120	14	1120	8
Soil N pool change	11593	72	4716	59	3828	26
Organic N leaching	641	4	2028	25	3741	24
Inorganic N leaching	2654	17	172	2	6141	42

3
4

1   Table 5

Fixed parameters	Units	Načetín	Lysina	Čertovo Lake
Discharge, annual	m	0.41	0.43	1.38
Precipitation, annual	m	0.84	0.95	1.44
Soil depth	m	0.9	0.9	0.65
Bulk density of fine soil	$kg.m^{-3}$	706	530	345
CEC	$meq.kg^{-1}$	37.9	59	106
$Al(OH)_3$ solubility constant	log 10	9.1	7.7	8.2
SO_4 adsorption half saturation	$meq.m^{-3}$	500	500	100
SO_4 maximum adsorption capacity	$meq.kg^{-1}$	15	3	20
pCO_2	atm	0.65	0.65	0.45
Temperature	°C	6.3	5	4.5
pK1 of organic acids	-log 10	2.5	2.5	2.6
pK2 of organic acids	-log 10	4.1	4.1	5.7
pK3 of organic acids	-log 10	6.7	6.7	5.9
Dissolved organic acid	$meq.m^{-3}$	30	110	85
Optimised parameters				
Weathering Ca	$meq.m^{-2}$	5.0	29.6	1.8
Weathering Mg	$meq.m^{-2}$	15	11.5	32.4
Weathering Na	$meq.m^{-2}$	0.8	21.1	2.1
Weathering K	$meq.m^{-2}$	0.5	4.3	0.0
Weathering of Σ(Ca+Mg+K+Na)	$meq.m^{-2}$	21.3	66.5	36.3
Weathering F	$meq.m^{-2}$	3	5	0.6
Selectivity coeff. Al-Ca	log	-1.57	1.09	-1.92
Selectivity coef. Al-Mg	log	-0.33	1.5	-0.28
Selectivity coeff. Al-Na	log	-2.17	-0.58	-3.29
Selectivity coeff. Al-K	log	-5.27	-4.24	-5.86
Ca initial condition	% of CEC	6.4	17.5	6.0
Mg initial condition	% of CEC	5.8	5.5	4.1
Na initial condition	% of CEC	1.0	1.2	1.2
K initial condition	% of CEC	1.2	3.3	2.2
Initial base saturation Σ(Ca+Mg+K+Na)	% of CEC	14.4	27.5	13.5

2

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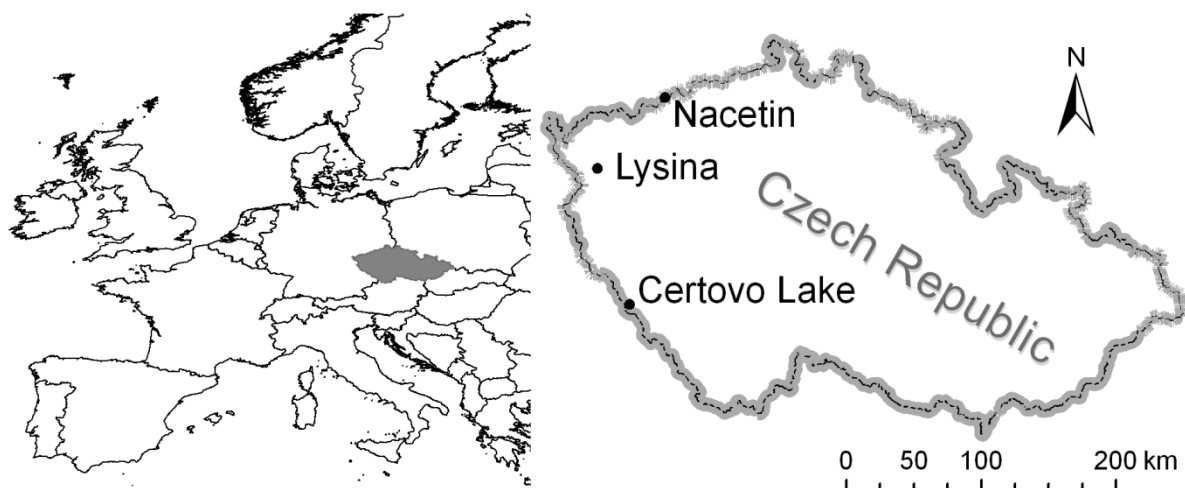
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Figure 1

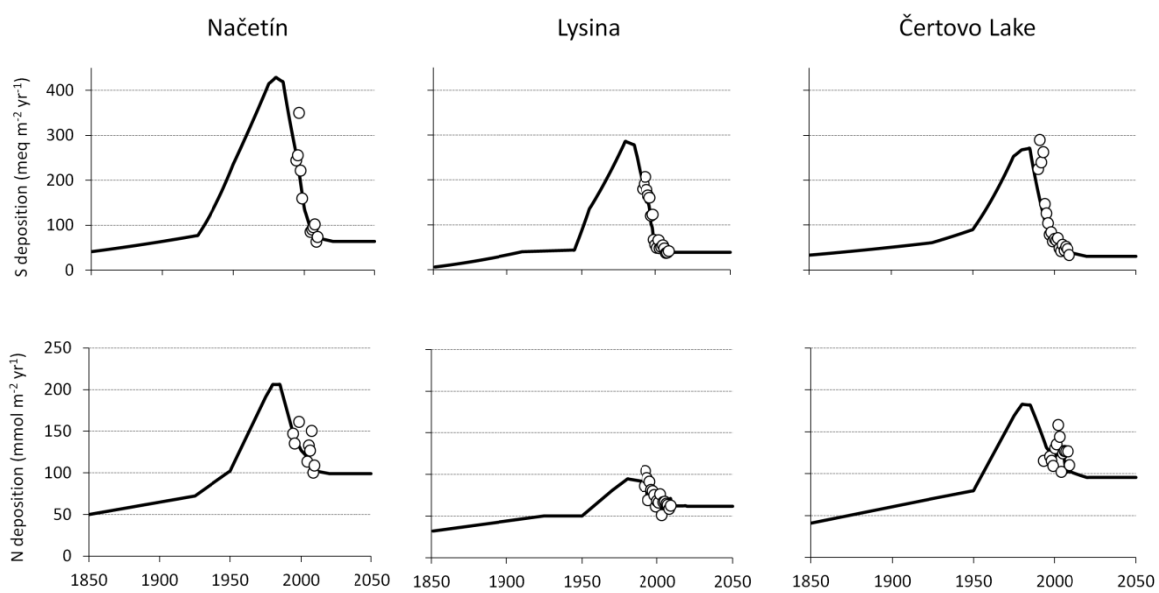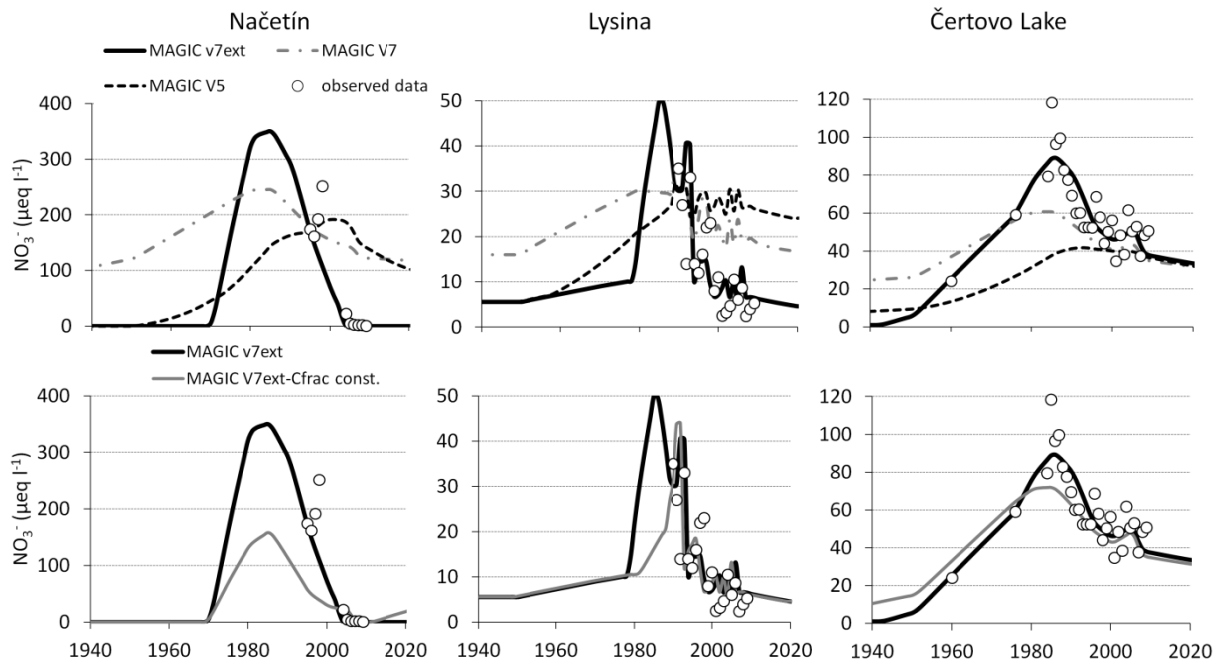**Soil Solution Carbon & Nitrogen Fluxes**

fC1 = organic and inorganic C in runoff
fC2 = inorganic C exchange with the atmosphere

fN1 = organic and inorganic N in runoff
fN2 = inorganic N uptake by plants
fN3 = denitrification of inorganic N
fN4 = atmospheric deposition of inorganic N

Soil Organic Matter Carbon fluxes

FC0 = organic C from N-fixers
FC1 = organic C from plant litter
FC2 = organic C processed in SOM turnover
FC3 = C in new microbial biomass (new SOM)
FC4 = SOM C respired (CO2 in soil solution)
FC5 = SOM C solubilized (DOC in soil solution)

Soil Organic Matter Nitrogen fluxes

FN0 = organic N from N-fixers
FN1 = organic N from plant litter
FN2 = organic N processed in SOM turnover
FN3 = N in new microbial biomass (new SOM)
FN4 = SOM N mineralized (NH4 in soil solution)
FN5 = SOM N solubilized (DON in soil solution)
FN6 = organic N from SOM used by microbes
FN7 = inorganic N immobilization by microbes

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Načetín   Lysina   Čertovo Lake