## Nutrient leaching in dry heathland ecosystems: effects of atmospheric deposition and management

Werner Härdtle · Goddert von Oheimb · Marion Niemeyer · Thomas Niemeyer · Thorsten Assmann · Hartmut Meyer

Received: 16 March 2007/Accepted: 22 August 2007/Published online: 7 September 2007 © Springer Science+Business Media B.V. 2007

Abstract Atmospheric nutrient deposition has contributed to widespread changes in sensitive seminatural ecosystems throughout Europe. For an understanding of underlying processes it is important to quantify input-output flows in relation to ongoing atmospheric inputs and current management strategies. In this study we quantified losses of N, P, Ca, Mg, and K via leaching in heathland ecosystems (Lüneburger Heide, NW Germany) as a function of current deposition rates and different management measures (mowing, prescribed burning, choppering, sod-cutting) which aim to prevent shrub and tree encroachment. Leaching was only moderately related to atmospheric input rates, indicating that leaching was mostly affected by internal turnover processes. Leaching significantly increased for most of the nutrients after the application of management measures, particularly in the choppered and sod-cut plots. However, atmospheric nutrient inputs exceeded leaching outputs for most of the nutrients, even in the plots subjected to management. Despite high deposition rates (20-25 kg N ha<sup>-1</sup> year<sup>-1</sup>), retention of atmospheric N input ranged between 74% and 92% in the control plots. In the treated plots, N retention decreased to 59-80%. However, in the study area

W. Härdtle  $(\boxtimes)$  · G. von Oheimb · M. Niemeyer · T. Niemeyer · T. Assmann · H. Meyer Institute of Ecology and Environmental Chemistry, University of Lüneburg, Scharnhorststr. 1, Lüneburg 21335, Germany e-mail: haerdtle@uni-lueneburg.de

mean N leaching in the controls has almost doubled since 1980 and currently amounts to 3.7 kg ha<sup>-1</sup> year<sup>-1</sup>, indicating an early stage of N saturation. Our study provides evidence that leaching did not compensate for atmospheric nutrient deposition, particularly as regards N. Management, thus, will be an indispensable tool for the maintenance of the low-nutrient status as a prerequisite for the long-term preservation of heathland ecosystems.

**Keywords** Calluna vulgaris · Element budget · Element retention · Nitrogen · Nutrient limitation · N saturation

#### Introduction

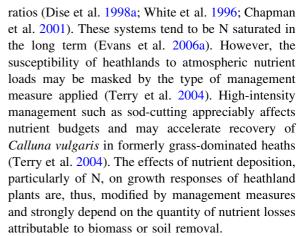
Heathland ecosystems dominated by evergreen dwarf shrubs are characterised by low levels of plant available nutrients and are, thus, typical of NW European landscapes with acid, mostly podzolic soils (Aerts and Chapin 2000). Heathlands have conservative element cycles and high turnover times of nutrients in plants and soil (Nielsen et al. 1999; Schmidt et al. 2004). Increased atmospheric input of nutrients, particularly of N, is therefore a major threat to heathlands, leading to increased production of biomass, the accumulation of soil organic matter and accelerated nutrient cycles, and finally resulting in a progressive replacement of dwarf shrubs by grasses and a loss of biodiversity (Heil and Bobbink 1993;



Rode 1999a, b; Kirkham 2001). As a result, the European lowland heath area has decreased continuously during recent decades (Power et al. 2001), and the conservation of the remaining heathlands has become a major issue in European nature conservation (Webb 1998; Marcos et al. 2003).

In this context, the employment of management measures to remove nutrients has increased in importance (Erismann and de Vries 2000; van Diggelen and Marrs 2003). Heathland management, aimed primarily at the prevention of tree, shrub and grass establishment, is now considered necessary to address the ecosystem impacts caused by atmospheric nutrient loads (Härdtle et al. 2006). For example, the type and frequency of heathland management measures determine the quantities of nutrients removed from plant and humus components (Power et al. 2001). Management practices have, thus, an impact on the nutrient budgets of heathland ecosystems and, by reducing nutrient stores, have the potential to affect ecosystem responses to atmospheric nutrient loads (Terry et al. 2004). In addition to those management measures with a long tradition in heaths (mowing, prescribed burning, sod-cutting, grazing; Werger et al. 1985; Power et al. 2001; Nilsen et al. 2005), new methods such as choppering have been developed in order to compensate for increasing management costs (Niemeyer et al. 2007).

To date, much of the research has addressed the impacts of management measures and nutrient deposition on soil properties and nutrient budgets of heathland ecosystems (e.g. Matzner and Ulrich 1980; Diemont 1996; Power et al. 1998; Mitchell et al. 2000; Barker et al. 2004; Terry et al. 2004). This research provided the theoretical basis for models currently used to predict heathland responses to management and ongoing atmospheric nutrient loads. There is strong evidence that in heathlands exposed to low levels of nutrient deposition (N deposition <20 kg ha<sup>-1</sup> year<sup>-1</sup>) the bulk of nutrients added are accumulated in the soil compartment, particularly with respect to N (Power et al. 2001; Nielsen et al. 2000). At these sites, N addition may cause small decreases in the soil C/N and low rates of inorganic N leaching (Dise et al. 1998a; Evans et al. 2006a). In contrast, moderate to high deposition rates of N (>20 kg ha<sup>-1</sup> year<sup>-1</sup>) mostly entail high N losses with seepage water and distinctly decreasing soil C/N



Nutrient losses via leaching represent a key uncertainty in quantifying long-term trends in ecosystem nutrient budgets (Sverdrup et al. 2006; Chen and Mulder 2007). Whilst nutrient leaching in heaths has been analysed in several studies (Nielsen et al. 2000; Schmidt et al. 2004; Herrmann et al. 2005), there is still scant information on the impact of different management measures on nutrient leaching under current rates of atmospheric nutrient deposition (Pilkington et al. 2005).

The objective of the present study was to quantify nutrient leaching (of N, P, Ca, Mg, K) in relation to management strategies and current atmospheric nutrient loads. Besides grazing, in the Lüneburger Heide mowing, prescribed burning, choppering and sod-cutting are commonly applied management procedures. We analysed the impact of these measures on leaching rates and compared the results with leaching patterns found for unmanaged sites. The following questions were addressed: (i) How are leaching patterns related to atmospheric nutrient inputs? (ii) To what extent will nutrient leaching increase in heaths subjected to mowing, prescribed burning, choppering, and sod-cutting? (iii) What are the retention rates of nutrients in relation to current deposition rates and management measures?

#### Methods

Study area

Our study area is the Lüneburger Heide nature reserve (Lower Saxony, NW Germany; 53°15′ N,



9°58′ E, 105 m a.s.l.), the site of the largest complex of heathlands (about 5,000 ha) in NW Germany. The study area is characterised by Pleistocene sandy deposits. Prevailing soil types are nutrient-poor podzols or podzolic soils (for a detailed description of sites and soil profiles see below). The climate is of a humid suboceanic type (Niemeyer et al. 2005).

#### Management measures

In this study we compared the impact of mowing, prescribed burning, choppering, and sod-cutting on leaching rates. All management measures (i.e. treatments) were carried out during the winter of 2001/2002 (see Table 1).

- Mowing is primarily applied to stands dominated by *Calluna vulgaris* in order to initiate its vegetative regeneration. Above-ground biomass was cut with a mower to a height of 10 cm (lowintensity mow; Webb 1998; Terry et al. 2004). Hence, mowing did not affect the organic layer.
- Prescribed burning procedures in winter are lowintensity measures characterised by "low temperature fires" (Power et al. 2001). They affect the
  above-ground biomass, whilst the organic layers
  remain untouched. Periods of fine weather are
  needed for the burning procedure. Prescribed
  burning is comparable to mowing in that it is
  primarily applied to stands dominated by *Calluna*vulgaris in order to initiate regeneration from
  both seed and root stocks.

**Table 1** Timetable for treatments and species composition of sample plots prior to treatment (vegetation data from Härdtle et al. 2006 and Niemeyer et al. 2007; n of relevés = 4 per

- Choppering is a high-intensity measure that creates bare soil by removing the above-ground biomass and most parts of the organic layer (with only a thin layer of organic material remaining on the soil surface; Niemeyer et al. 2007). A rotary tiller equipped with rotary blades was used in the choppering process.
- Sod-cutting is a high-intensity measure carried out with a rotary hoe. In this procedure, the above-ground biomass and the organic layers were completely removed and the A-horizon was partially removed. Sod-cutting, as well as choppering, is applied to stands where *Deschampsia* flexuosa has partially replaced dwarf shrubs (Werger et al. 1985).

#### Sample plots

Within a 100 ha heathland area, 16 sample plots were randomly selected, each  $20 \times 40 \text{ m}^2$  in size (4 replicates per management measure). Each sample plot was divided into two subplots ( $20 \times 20 \text{ m}^2$ ). Each respective management measure was carried out in one subplot (treatment), and the second subplot served as a control (untreated subplot). The management measure applied to a sample plot was appropriate to its species composition. Thus, the sample plots selected for mowing and prescribed burning were dominated by *Calluna vulgaris*, while in the sample plots selected for choppering and sod-cutting Poaceae were dominant (see Table 1).

management measure; mean cover of species in %; species covering >1% of the sample plots are listed)

Time when treatment took place Prevailing species in sample plots	Mowing (February 2002) Mean cover (%)	Prescribed burning (October 2001) Mean cover (%)	Choppering (December 2001) Mean cover (%)	Sod-cutting (January 2002) Mean cover (%)
Calluna vulgaris	80	56	40	38
Deschampsia flexuosa	10	19	66	26
Molinia caerulea			<1	36
Hypnum cupressiforme	40	22	30	49
Dicranum scoparium	23	20	23	6
Other species	<1	<1	<1	<1



The age of *Calluna vulgaris* in all sample plots ranged between 10 years and 15 years. All sample plots had been unmanaged during the decade prior to our study.

In complementary studies carried out by Härdtle et al. (2006) and Niemeyer et al. (2007) the profile of soils in all sample plots was examined. Soils were characterised by the following sequence of horizons (the mean thickness of a particular horizon is given in brackets  $\pm$  1SD, n = 16): organic layer (3.9 cm  $\pm$  0.5)—albic horizon (ab: 10.2 cm  $\pm$  2.4)—spodic horizon (sd: 8.3 cm  $\pm$  1.9)—sandy bedrock (below 22.4 cm). In addition, in the complementary studies mentioned above nutrient stores (for N, P, Ca, Mg, K) and C/N ratios were determined prior to treatments in all sample plots in the above-ground biomass, the organic layer, and the albic horizon. In order to support the

interpretation of our findings, these results were taken into consideration in our study and are shown in Table 2.

#### Determination of atmospheric nutrient deposition

Atmospheric nutrient deposition was analysed by means of 12 bulk deposition samplers installed 100 cm above ground in the area where sample plots were situated (i.e. 3 samplers per treatment; Münden 200, Inst. of Forest Hydrology, Han. Münden, Germany). Samples were collected fortnightly for a period of 1 year (from autumn/winter 2001 to autumn/winter 2002; starting immediately after the management measures had taken place). For the determination of total N, samples were dissolved in a  $K_2SO_4$ -NaOH solution according to the Koroleff

**Table 2** Nutrient stores (kg ha<sup>-1</sup>) and C/N ratios in the above-ground biomass, organic layer and A-horizon of sample plots prior to treatment, including percentage of removal of above-ground biomass and humus layers due to treatments; mean

values (n = 4 for nutrient stores, n = 8 for C/N values per treatment) and SD (in brackets); all data from Härdtle et al. (2006) and Niemeyer at al. (2007)

Treatment	Nutrient N	Nutrient stores (kg ha <sup>-1</sup> ) in the					
Mowing		Above-ground biomass		Organic layer		A-horizon	
		43% removed	221.5 (7.5)	Not affected	839.8 (122.8)	Not affected	932.0 (260.5)
	P		14.4 (3.2)		29.6 (4.1)		82.7 (5.8)
	Ca		61.7 (0.9)		80.9 (13.6)		168.9 (48.0)
	Mg		17.0 (1.6)		20.1 (1.1)		130.3 (49.4)
	K		61.8 (19.7)		41.6 (4.6)		312.5 (104.9)
Prescribed burning	N	55% removed	196.9 (28.3)	Not affected	736.1 (95.4)	Not affected	1782.3 (196.0)
	P		12.9 (1.4)		23.5 (5.1)		114 (12.0)
	Ca		67.4 (7.5)		56.1 (11.1)		156.8 (22.6)
	Mg		18.2 (1.2)		16.9 (3.4)		70.6 (14.0)
	K		56.3 (10.3)		31.2 (5.1)		298.2 (18.2)
Choppering	N	100% removed	155.0 (37.2)	87% removed	941.4 (181.9)	Not affected	1950.5 (460.8)
	P		10.0 (2.6)		35.8 (7.6)		113.6 (22.3)
	Ca		36.7 (12.5)		100.6 (42.4)		174 (32.2)
	Mg		11.9 (3.8)		25.1 (7.1)		57.9 (10.3)
	K		34.4 (7.8)		32.5 (8.2)		277.6 (48.5)
Sod-cutting	N	100% removed	121.6 (24.4)	100% removed	934.5 (93.3)	32% removed	1728.8 (197.0)
	P		7.4 (1.6)		38.1 (3.0)		100.4 (8.0)
	Ca		34.8 (8.2)		104.7 (40.3)		198.5 (34.7)
	Mg		10.8 (2.4)		27.1 (6.9)		71.9 (15.9)
	K		35.8 (6.6)		51.2 (2.2)		380.6 (50.1)
C/N ratio (prior to management)		38.4 (2.0)		22.1 (3.4)		31.2 (4.1)	



method (Grasshoff et al. 1983), and afterwards subjected to microwave digestion (MLS-ETHOS; MLS-GmbH, Leutkirch, Germany). Total N was measured with an ion chromatograph (IC-DX 120 Dionex; Idstein, Germany). Ca-, K-, Mg- and P-concentrations of samples were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Optima 3300 RL; Perkin Elmer, Burladingen, Germany).

In experiments of 6 years duration, Gauger et al. (2000) compared bulk and total (i.e. wet and dry) deposition data. The authors found that bulk deposition samplers underestimate total N-, Ca-, K-, and Mg-deposition by about 23.2%, 35.3%, 25.0%, and 35.7%, respectively. In order to calculate the total deposition, bulk deposition of N, Ca, K, and Mg was corrected by the factors 1.30, 1.54, 1.33, and 1.55 (following Gauger et al. 2000). However, depending on the roughness of a *Calluna vulgaris*-canopy total N deposition may reach about 200% of bulk deposition (Bobbink et al. 1992).

### Quantification of seepage water and nutrient loss by leaching

Nutrient loss by leaching was determined by means of lysimeters consisting of intact soil cores (100 cm in length and 10 cm in diameter) and tensioncontrolled porous cup soil water samplers (PEsinter/0.45 µm nylon-membrane; Umwelt-Geräte-Technik, Müncheberg, Germany) installed at depths of 100 cm (one lysimeter and one water sampler per subplot; total n = 32). Lysimeters were used for the quantification of seepage water, and water samplers for the determination of nutrient concentrations in the leachate. Nutrient loss by leaching was calculated by multiplying water fluxes with leachate nutrient concentrations. The soil core was obtained by means of a custom-built steel auger that was rammed into the soil using a Pürckhauer-hammer (Grube, Hützel, Germany). After the soil core had been collected, the head of the auger was unscrewed in order to transfer the soil core into a plastic tube which served as lysimeter. The lysimeter was then placed in the borehole. The seepage water was collected at the lower end of the lysimeter and was transferred into samplers using a battery-powered pump. The quantities of seepage water and nutrient concentrations in the leachate were determined every two weeks (simultaneously with deposition samples). In order to avoid effects of soil disturbance on nutrient measurements, lysimeters and water samplers were installed 4 months prior to treatments. The analytical procedure was the same for leachate and deposition samples. We calculated the mean annual rate of water fluxes, leachate nutrient concentrations and nutrient output for each treatment and the corresponding controls.

#### Determination of soil pH

In each subplot the O-horizon was sampled before, immediately after, and 1 year after management measures were carried out (with the exception of the sod-cut subplots, where the O-horizon was completely removed). Each sample consisted of four randomly collected subsamples that were thoroughly mixed, air-dried and sieved (<2 mm). In all samples (4 replicates per management measure) pH $_{\rm H_2O}$  values were measured according to Steubing and Fangmeier (1992). Values were determined using a glass electrode and a pH-meter (SenTix 97 T; WTW, Weilheim, Germany).

#### Data evaluation and statistics

Measurement results from atmospheric deposition, leaching and soil pH were subjected to one-way ANOVA with post-hoc Tukey's test. Deposition data were arcsin-transformed and leaching data were logtransformed prior to ANOVA and the calculation of means and SE. In order to compare leaching patterns of treatments and controls and to relate them to atmospheric nutrient inputs, correlation coefficients (Spearman) were calculated for the 26 measured values describing the one-year post-management course of nutrient deposition and leaching. The retention of nutrients added by atmospheric deposition was calculated for the controls and treatments (retention = atmospheric input - leaching loss) and expressed in % values (according to Schmidt et al. 2004):



#### % Retention

$$= \left(\text{Input}_{\text{deposition}} - \text{Output}_{\text{leaching}}\right) / \text{Input}_{\text{deposition}} \times 100$$

All statistical analyses were carried out using the SPSS 14.0 package (SPSS Inc., Chicago, IL).

# **Table 3** Annual amounts of atmospheric nutrient deposition, nutrient leaching, nutrient retention and % of nutrient retention (treatments and corresponding controls) within the first year after the treatments were carried out. With the exception of % retention, all values are in kg ha<sup>-1</sup> year<sup>-1</sup>; values for deposition

#### Results

Atmospheric deposition

A comparison of the atmospheric nutrient deposition data revealed no significant differences (P>0.05) between the 12 bulk deposition samplers. Atmospheric nutrient deposition was therefore considered

are means of n=12, for all the other parameters means of n=4 are given; SD in brackets; asterisks mark significant differences between % retention of the treatments and the corresponding controls

Treatment	Nutrient	N	P	Ca	Mg	K
Mowing	Deposition	20.5 (0.01)	0.3 (0.01)	4.1 (0.03)	1.9 (0.01)	3.3 (0.02)
	Leaching-treatment	4.0 (0.04)	0.3 (0.02)	2.1 (0.39)	2.2 (0.06)	3.5 (0.36)
	Leaching-control	3.0 (0.10)	0.2 (<0.01)	1.1 (0.17)	1.1 (0.04)	2.5 (0.16)
	Retention-treatment	16.5 (0.04)	0.1 (0.02)	2.0 (0.39)	-0.3 (0.06)	-0.3 (0.36)
	Retention-control	17.5 (0.10)	0.2 (<0.01)	3.1 (0.17)	0.8 (0.04)	0.8 (0.16)
	% Retention-treatment	**80 (2.2)	***26 (5.6)	**48 (9.5)	***-17 (3.0)	**-8 (10.9)
	% Retention-control	85 (0.5)	56 (0.2)	74 (4.0)	42 (2.1)	23 (4.9)
Prescribed burning	Deposition	25.0 (0.01)	0.3 (0.01)	4.8 (0.03)	2.8 (0.01)	3.5 (0.02)
	Leaching-treatment	3.9 (1.19)	0.3 (0.02)	5.6 (2.79)	1.7 (0.59)	2.5 (0.60)
	Leaching-control	2.0 (0.54)	0.2 (0.01)	2.0 (1.22)	0.6 (0.18)	1.7 (0.21)
	Retention-treatment	21.1 (1.19)	0.0 (0.02)	-0.8 (2.79)	1.1 (0.59)	1.0 (0.60)
	Retention-control	23.0 (0.54)	0.1 (0.01)	2.8 (1.22)	2.2 (0.18)	1.8 (0.21)
	% Retention-treatment	*84 (24.9)	***11 (4.8)	**-17 (5.1)	*40 (13.7)	*30 (15.5)
	% Retention-control	92 (12.6)	34 (2.6)	59 (3.1)	78 (4.6)	50 (4.8)
Choppering	Deposition	23.6 (0.01)	0.4 (0.01)	4.8 (0.03)	2.6 (0.01)	3.6 (0.02)
	Leaching-treatment	9.7 (3.85)	0.3 (0.05)	6.7 (3.39)	1.0 (0.30)	2.8 (1.59)
	Leaching-control	6.1 (2.16)	0.2 (0.02)	4.9 (1.54)	0.7 (0.26)	1.5 (0.63)
	Retention-treatment	13.9 (3.85)	0.0 (0.05)	-1.9 (3.39)	1.5 (0.30)	0.7 (1.59)
	Retention-control	17.6 (2.16)	0.1 (0.02)	-0.1 (1.54)	1.8 (0.26)	2.1 (0.63)
	% Retention-treatment	59 (17.8)	**9 (1.4)	**-40 (7.1)	60 (11.4)	21 (4.4)
	% Retention-control	74 (11.4)	41 (4.9)	-3 (3.2)	71 (10.1)	57 (17.5)
Sod-cutting	Deposition	21.9 (0.01)	0.4 (0.01)	4.4 (0.03)	2.3 (0.01)	3.4 (0.02)
	Leaching-treatment	7.8 (1.39)	0.4 (0.02)	3.6 (0.43)	1.5 (0.12)	3.6 (0.47)
	Leaching-control	3.7 (0.13)	0.3 (0.01)	3.4 (0.22)	0.9 (0.03)	2.1 (0.19)
	Retention-treatment	14.1 (1.39)	-0.1 (0.02)	0.8 (0.43)	0.7 (0.12)	-0.2 (0.47)
	Retention-control	18.3 (0.13)	0.0 (0.01)	1.0 (0.22)	1.4 (0.03)	1.4 (0.19)
	% Retention-treatment	***64 (6.3)	***-14 (5.4)	19 (9.9)	***33 (5.2)	***-5 (13.9)
	% Retention-control	83 (0.6)	12 (2.3)	23 (5.0)	60 (1.5)	40 (5.6)

<sup>\*</sup>P < 0.05, \*\*P < 0.01, \*\*\*P < 0.001



to be equal for all of the sample plots, but differed with regard to the one-year time span within which effects of a particular treatment were analysed (since treatments were carried out at different points in time). N input ranged between 20.5 (mown plots) and 25.0 kg ha<sup>-1</sup> year<sup>-1</sup> (burned plots; Table 3). P deposition rates were low  $(<0.5 \text{ kg ha}^{-1} \text{ year}^{-1})$  and concentrations close to the analytically detectable threshold  $(0.0326 \text{ mg L}^{-1})$ . The deposition of Ca, Mg, and K ranged between 1.9 kg ha<sup>-1</sup> year<sup>-1</sup> and 4.8 kg ha<sup>-1</sup> year<sup>-1</sup> (for all three elements and for all plots; Table 3).

Soil pH<sub>H2O</sub>

For all sample plots, soil pH did not change significantly in the course of the experiment (P > 0.05). In the mown and choppered plots, the pH of the O-horizon before, immediately after, and 1 year after treatments ranged between 3.0 and 3.5. Soil pH in the burned subplots ranged between 3.2 and 4.0. Pre-treatment values for the sod-cut subplots were in the same range as values for the mown and choppered subplots. No significant changes in pH values were observed in the controls either (all values were between 3.0 and 3.5).

Fig. 1 Impact of treatments on mean annual nutrient concentrations in the leachate (a-d) and annual quantities of rainfall and seepage water (e). Note that quantities of rainfall differ for the treatments due to differences in the time when treatments took place (means of n = 12 + 1SD for rainfall measurements, means of n = 4 + 1SD for all the other measurements: asterisks and lower case letters indicate significant differences at the level of P < 0.05)

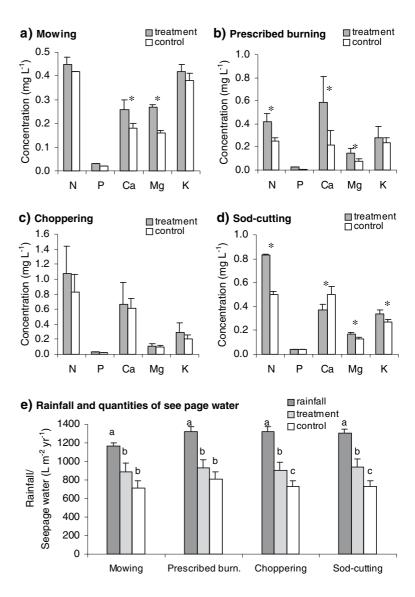




Fig. 2 Annual course (oneyear period) of nutrient deposition and leaching of N, P, Ca, Mg, and K within the first year after the treatments were carried out; deposition: thick solid line (means of n = 12), leaching treatment: thin solid line (means of n = 4), leaching control: dotted line (means of n = 4); treatments: (a) mowing, (b) prescribed burning, (c) choppering, (d) sod-cutting; abbreviations: leach = leaching, treat = treatment, con = control

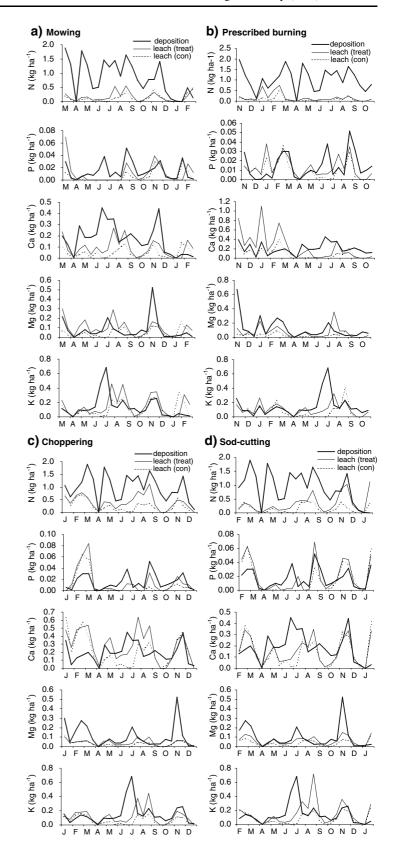




Table 4 Spearman rank correlation between rainfall, atmospheric nutrient deposition, and nutrient leaching in treatments and corresponding controls

Comparison of	Nutrient	Mowing	Prescribed burning	Choppering	Sod-cutting
Rainfall versus leaching treatment	N	0.72**	0.56*	0.81**	0.65**
	P	0.25**	0.87**	0.38*	0.65**
	Ca	0.67**	0.49*	0.83**	0.85**
	Mg	0.63**	0.76**	0.84**	0.74**
	K	0.70**	0.89**	0.86**	0.74**
Deposition versus leaching treatment	N	0.60**	0.45*	0.64**	0.34*
	P	0.15	0.28	0.55**	0.61**
	Ca	0.46*	0.29	0.45*	0.38*
	Mg	0.70**	0.62**	0.57**	0.63**
	K	0.48**	0.61**	0.48**	0.53**
Deposition versus leaching control	N	0.47*	0.46*	0.47*	0.44*
	P	0.43*	0.18	0.35*	0.55**
	Ca	0.23	0.22	0.21	0.24
	Mg	0.48**	0.49**	0.67**	0.56**
	K	0.39*	0.32	0.32	0.30
Leaching treatment versus leaching control	N	0.92**	0.83**	0.83**	0.79**
	P	0.63**	0.90**	0.73**	0.86**
	Ca	0.60**	0.89**	0.84**	0.92**
	Mg	0.60**	0.89**	0.87**	0.90**
	K	0.64**	0.81**	0.90**	0.90**

<sup>\*</sup>*P* < 0.05, \*\**P* < 0.01

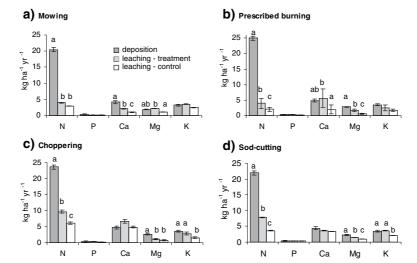


Fig. 3 Annual amounts of atmospheric nutrient deposition and nutrient leaching (treatments and corresponding controls) within the first year after the treatments were carried out; treatments: (a) mowing, (b) prescribed burning, (c) choppering, (d) sodcutting; means  $\pm$  SE (n of deposition measurements = 12, n of

treatments and corresponding controls = 4); lower-case letters indicate significant differences. Common or missing letters indicate that means were not significantly different at P < 0.05 (one-way ANOVA with post-hoc Tukey's test)



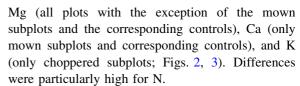
Effects of deposition and management on seepage water and leaching

Post-management nutrient concentrations in the seepage water increased for some of the nutrients (Fig. 1a– d). Quantities of seepage water increased significantly in the choppered and sod-cut subplots (Fig. 1e). Deposition and leaching patterns showed a pronounced temporal variability (Fig. 2). Leaching patterns were well correlated with rainfall, but showed a moderate correlation with atmospheric inputs and varied for the nutrients considered (Table 4). Correlations tended to be more pronounced for the treated subplots (Fig. 2, Table 4), but only for some of the nutrients (e.g. for K). In the controls, correlations between atmospheric deposition and leaching were highest for Mg, as indicated by the similar course of corresponding curves in Fig. 2 and highly significant correlations (i.e. P mostly < 0.01; Table 4). No significant correlation between deposition and leaching was found for Ca (controls). However, correlations between leaching rates in the treatments and the corresponding controls were significant for all the nutrients considered (r between 0.60 and 0.92, P < 0.01; Table 4).

In the first year after treatment, leaching rates were significantly elevated for some of the elements compared with the controls (Figs. 2, 3). With the exception of mowing, all treatments caused a significant increase in N leaching (Fig. 3). For example, in the subplots subjected to high-intensity management measures N leaching increased by 3.6 and 4.1 kg ha<sup>-1</sup> year<sup>-1</sup> (choppered and sod-cut subplots, respectively; Table 3). This corresponds to an increase of 59% and 111%, respectively. As shown in Fig. 2, N leaching was particularly high in summer. Treatments also significantly affected the leaching of Mg (with the exception of choppering), Ca (prescribed burning; Fig. 3b), and K (choppering; Fig. 3c). No management effects on leaching rates of P were observed. As with deposition rates for this element, P leaching was below 0.5 kg ha<sup>-1</sup> year<sup>-1</sup> and concentrations close to the analytically detectable threshold value (0.0326 mg  $L^{-1}$ ).

Input-output comparison and retention rates of nutrients

Rates of atmospheric nutrient inputs significantly exceeded nutrient losses via leaching for N (all plots),



For most of the elements, retention of atmospheric nutrient input was significantly lower in the treatments than in the controls, with the exception of N, Ca, Mg, and K in the choppered subplots and Ca in the sod-cut subplots (Table 3). Retention rates were highest for N, ranging between 74% and 92% in the controls and 59% and 84% in the treatments. High retention was also found for Mg in the controls (42–78%). Retention was lowest for most of the nutrients (N, P, Ca, K) in the choppered and sod-cut subplots. Negative values were found for Mg and K in the mown subplots, for Ca in the burned and choppered subplots, and for P and K in the sod-cut subplots.

#### Discussion

Atmospheric deposition

Atmospheric nutrient input in the study area was comparable to other regions in NW Germany (Herrmann et al. 2005). It was also in the range reported by studies conducted in the UK (Kirkham 2001; Power et al. 2001; Schmidt et al. 2004), and was somewhat lower than deposition rates in many regions in the Netherlands (Bakema et al. 1994; Erisman and de Vries 2000; Schmidt et al. 2004). By contrast, deposition rates reported from Denmark were somewhat lower than in our study area (Hansen and Nielsen 1998; Schmidt et al. 2004). However, N deposition in the study area exceeded critical load values for dry heathlands (10–20 kg ha<sup>-1</sup> year<sup>-1</sup>; Bobbink et al. 2003) by up to 5 kg ha<sup>-1</sup> year<sup>-1</sup>. This emphasises the need for appropriate management prescriptions which aim at the removal of nutrients on a long-term basis, although effects of atmospheric deposition may differ between regions due to differing precipitation levels (Britton et al. 2001).

Soil pH<sub>H2O</sub>

Soil pH values indicated that there was no significant change in soil acidity in the course of the experiment.



Although one would expect the deposition of basic ash to have raised pH values in the subplots subjected to burning (Forgeard 1990), increased nitrification rates and, thus, liberation of protons may in fact have compensated for a pH increase (Brady and Weil 2002; Mohamed et al. 2006). In our experiment, soil pH proved to be an inappropriate indicator of internal turnover processes. This may apply to acid soils in particular (Härdtle et al. 2004).

Effects of deposition and management on seepage water and leaching

Nutrient leaching may be controlled by several parameters, such as nutrient deposition, sorption behaviour of nutrients and nutrient immobilisation, exchange capacity of humus horizons, nutrient uptake by plants and type of nutrient limitation, as well as internal nutrient turnover (Nielsen et al. 2000; Pilkington et al. 2005). In our study, deposition and leaching in the controls were only moderately correlated and correlation coefficients only slightly or not at all increased (at least for some of the nutrients) for the treatments (Table 4). Ca leaching, for example, was not at all related to deposition rates either in the controls or in the burning treatments (r = 0.22 and 0.29, respectively; Table 4). In contrast, K immobilisation proved to be strongly affected by the presence of a vegetation cover and humus horizons, since deposition-leaching relationships were low in the controls, but significant for all treatments (P < 0.01). As regards N, in a study by Dise et al. (1998b) deposition rates explained about 50% of the variability of N leaching. In addition to deposition rates, the C/N ratio of the organic layer has proven a useful predictor for the susceptibility of sites to N leaching (Dise et al. 1998a; Evans et al. 2006b). According to the model of Dise et al. (1998a), which allows for the prediction of nitrate leaching at a given site, expected N losses with seepage water should exceed 10 kg ha<sup>-1</sup> year<sup>-1</sup> in the Lüneburger Heide (based on current deposition rates and organic layer C/N ratios of 22.1; see Table 2). However, the actual mean of N leaching was 3.7 kg ha<sup>-1</sup> year<sup>-1</sup> for the controls. This finding suggests that other factors need to be considered when refining models aimed at predicting N leaching. For all the plots, P leaching was low and fell below a threshold of 0.5 kg ha<sup>-1</sup> year<sup>-1</sup>. This may be attributable to low deposition rates, generally low concentrations of plant available phosphate in heathland soils, as well as to the sorption behaviour of ortho-phosphate in the A- and B-horizons (Olff and Pegtel 1994; Manning et al. 2006).

As would be expected, post-management leaching rates were increased for all the nutrients considered, particularly for N in subplots subjected to highintensity management. Several factors may account for this: (i) Quantities of percolating soil water may increase due to reduced evapotranspiration rates, (ii) post-management nutrient uptake by plants was reduced, and (iii) nutrient exchange capacity of the humus horizons decreased in plots where treatments affected the humus layers (Gimingham et al. 1981; Niemeyer et al. 2005). In our study, treatments affected both nutrient concentrations in the leachate and quantities of seepage water. In the subplots subjected to low-intensity management, increased losses of Ca and Mg (mowing experiment) and N, Ca and Mg (burning experiment) were attributable to increased concentrations of these elements in the seepage water, as quantities of seepage water showed no significant post-treatment increase (Figs. 1a, b and 3a, b). In the choppered subplots, leaching rates increased due to increased water fluxes, as choppering had no significant effects on seepage water nutrient concentrations (Fig. 1c). In the sod-cut subplots, increased leaching losses (of N, Ca, Mg and K) were attributable to both an increase in nutrient concentrations and increased quantities of seepage water. However, an increase in rainfall always contributes to higher leaching losses, as indicated by high correlation coefficients between rainfall and leaching rates (Table 4). Rainfall variability, thus, is also responsible for the temporal variability of leaching patterns found during the course of the experiments.

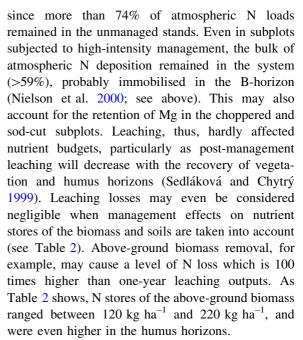
The close relationship between leaching in the treatments and the corresponding controls (Table 4) showed that leaching patterns were controlled to a considerable extent by internal nutrient turnover processes, which in turn are affected by parameters such as soil temperature and soil moisture (Chapman et al. 2001; Herrmann et al. 2005). In podzols, the exchange capacity decreases, in particular if organic layers are removed. Moreover, mineralisation rates may increase after management (Berendse 1990; Bakema et al. 1994). With the exception of the mown



subplots, dead plant roots and a considerable amount of organic material remained in the soil, all of which started to decompose after vegetation had been burned or removed (Mitchell et al. 2000; Dorland et al. 2004). Elevated soil temperatures, following the removal of shading vegetation, may also have affected mineralisation rates (Mallik and FitzPatrick 1996; Anderson and Hetherington 1999). Beside the increase in mineralisation rates, elevated NH<sub>4</sub><sup>+</sup> concentrations following high-intensity management (Dorland et al. 2004) may have led to a replacement of cations at exchange sites and thus may have contributed to an increase in K and Mg leaching (choppered and sod-cut subplots, respectively; Brady and Weil 2002). The significant increase in Ca and Mg leaching in the burned subplots can be attributed to the deposition of ash containing high amounts of Ca and Mg (Niemeyer et al. 2005). Since plant uptake was limited and amounts of seepage water increased after burning, post-management leaching of these cations significantly increased (Mohamed et al. 2006). The high leaching rates for Ca found for the choppering controls were probably due to slightly higher loam contents at these sites. Internal turnover processes as described above may account for the moderate correlations found between nutrient deposition and leaching. However, management effects on leaching may be masked in soils with well developed B-horizons functioning as a trap for nutrients dissolved in seepage water. At these sites, the B-horizon may partly replace the function of the organic layer as ion exchanger, if the organic layer has been removed due to management (Nielsen et al. 2000; Manning et al. 2006).

Input-output comparison and retention rates of nutrients

The comparison of input and output rates (via deposition and leaching, respectively) showed that controls had positive nutrient balances (with the exception of Ca in the choppering controls). Even after treatment, most of the balances remained positive, and negative balances were found only for some of the nutrients (e.g. Ca in the choppered and burned subplots). Thus, leaching did not counterbalance atmospheric nutrient loads (at least for most of the nutrients), despite increased leaching rates following management. This applied to N in particular,



However, N accumulation is known to cause longterm changes in the structure and functioning of heathland ecosystems (Power et al. 2006). As long as the functioning of the system remains undisturbed, heath nutrient budgets are characterised by a strong internal cycling with a relative independence of nutrients released from the mineral soil (Nielsen et al. 2000; Kristensen 2001). At N limited sites, incoming N will be sequestered by soil microbes or plant root uptake, and Calluna vulgaris responds positively to improved N supply (i.e. higher biomass production; Uren et al. 1997; Bobbink et al. 2003). In the study area, N leaching (mean in the controls: 3.7 kg ha<sup>-1</sup> year<sup>-1</sup>) has doubled in the Lüneburger Heide since 1980, despite unchanged input rates (cf. Matzner and Ulrich 1980). This may indicate an early stage of N saturation (Kaste and Skjelkvåle 2002; Pilkington et al. 2005). However, according to Evans et al. (2006a) it may take decades for N saturation to be achieved. Assessing the level of N saturation of the sites analysed, the status of the Lüneburger Heide is between that described for heaths in Denmark and UK (with N leaching below 2 kg ha<sup>-1</sup> year<sup>-1</sup>; Nielson et al. 2000; Schmidt et al. 2004) and that of sites in the Netherlands (with N leaching of 24.5 kg ha<sup>-1</sup> year<sup>-1</sup>; Schmidt et al. 2004). In the latter sites, N deposition has exceeded critical load values for half a century and sites, thus, may be saturated with N (Heil and Bobbink 1993).



#### Management implications

Our study provides evidence that leaching has negligible effects on nutrient budgets of heath, even when leaching increases as a result of management. As plant growth and competition in heathlands is considered to be controlled by N or P (Härdtle et al. 2006), management effects on N and P budgets are of particular interest. At sites covered with 10-15 year old Calluna vulgaris, leaching may compensate for about 16% of atmospheric N loads, whilst N loss via leaching after sod-cutting amounts to 34% of atmospheric N deposition. Leaching may, thus, affect N flows in heaths, but is insufficient to counterbalance current atmospheric loads. In contrast, P leaching was hardly affected by management. As a consequence, atmospheric N deposition may cause a shift from N to P limitation of plant growth in the long term (Verhoeven et al. 1996). In order to maintain both a diverse structure and balanced nutrient budgets on a long-term basis, management will be an indispensable tool for the long-term preservation of heathland ecosystems (Barker et al. 2004). In this context, management schemes are needed that cause high outputs of N, but avoid an increasing P shortage (e.g. prescribed burning, Niemeyer et al. 2005).

**Acknowledgements** This ecosystem research project was funded by the German Ministry for Education and Research. We acknowledge the support of the Alfred Toepfer Academy for both the field experiments and the project coordination.

#### References

- Aerts R, Chapin FS (2000) The mineral nutrition of wild plants revisited: a re-evaluation of processes and patterns. Adv Ecol Res 30:1–67
- Anderson JM, Hetherington SL (1999) Temperature, nitrogen availability and mixture effects on the decomposition of heather (*Calluna vulgaris* (L.)Hull) and bracken (Pteridium aquilinum (L.)Kuhn) litters. Funct Ecol 13:116–124
- Bakema AH, Meijers R, Aerts R, Berendse F, Heil GW (1994) HEATHSOL: a heathland competition model. National Institute of Public Health and Environmental Protection Report 259102009
- Barker CG, Power SA, Bell JNB, Orme CDL (2004) Effects of habitat management on heathland response to atmospheric nitrogen deposition. Biol Conserv 120:41–52
- Berendse F (1990) Organic matter accumulation and nitrogen mineralization during secondary succession in heathland ecosystems. J Ecol 78:413–427

- Bobbink R, Heil GW, Raessen MBAG (1992) Atmospheric deposition and canopy exchange processes in heathland ecosystems. Environ Pollut 75:29–37
- Bobbink R, Ashmore M, Braun S, Fluckiger W, van den Wyngaert IJJ (2003) Empirical nitrogen critical loads for natural and semi-natural ecosystems: 2002 update. In: Achermann B, Bobbink R (eds) Empirical critical loads for nitrogen. Environmental Documentation No. 164.
  Swiss Agency for the Environment, Forest and Landscape, pp 43–170
- Brady NC, Weil RR (2002) The nature and properties of soils. Prentice Hall, London
- Britton AJ, Pakeman RJ, Carey PD, Marrs RH (2001) Impacts of climate, management and nitrogen deposition on the dynamics of lowland heathland. J Veg Sci 12:797–806
- Chapman PJ, Williams BL, Hawkins A (2001) Influence of temperature and vegetation cover on soluble inorganic and organic nitrogen in a spodosol. Soil Biol Biochem 33:1113–1121
- Chen XY, Mulder J (2007) Indicators for nitrogen status and leaching in subtropical forest ecosystems, South China. Biogeochemistry 82:165–180
- Diemont WH (1996) Survival of Dutch heathlands. IBN Scientific Contribution 1, Wageningen
- Dise NB, Matzner E, Forsius M (1998a) Evaluation of organic horizon C:N ratio as an indicator of nitrate leaching in conifer forests across Europe. Environ Pollut 102:453–456
- Dise NB, Matzner E, Gundersen P (1998b) Synthesis of nitrogen pools and fluxes from European forest ecosystems. Water Air Soil Pollut 105:143–154
- Dorland E, van den Berg LJL, van den Berg AJ, Vermeer M, Roelofs JGM, Bobbink R (2004) The effects of sod cutting and additional liming on potential net nitrification in heathland soils. Plant Soil 265: 267–277
- Erisman JW, de Vries W (2000) Nitrogen deposition and effects on European forests. Environ Rev 8:65–93
- 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 (2006a) Evidence that soil carbon pool determines susceptibility of semi-natural ecosystems to elevated nitrogen leaching. Ecosystems 9:453–462
- Evans CD, Caporn SJM, Carroll JA, Pilkington MG, Wilson DB, Ray N, Cresswell N (2006b) Modelling nitrogen saturation and carbon accumulation in heathland soils under elevated nitrogen deposition. Environ Pollut 143:468–478
- Forgeard F (1990) Development, growth and species richness on Brittany heathlands after fire. Acta Oecologia 11: 191–213
- Gauger T, Köble R, Anshelm F (2000) Kritische Luftschadstoff-Konzentrationen und Eintragsraten sowie ihre Überschreitung für Wald und Agrarökosysteme sowie naturnahe waldfreie Ökosysteme. Studie im Auftrag des Umweltbundesamtes Berlin. Institut für Navigation der Universität Stuttgart. Bericht Nr. 29785079, Berlin
- Gimingham CH, Hobbs RJ, Mallik AU (1981) Community dynamics in relation to management of heathland vegetation in Scotland. Vegetatio 46:149–155



- Grasshoff H, Ehrhardt M, Kremling K (1983) Methods of seawater analysis. Verlag Chemie, Weinheim
- Hansen B, Nielsen KE (1998) Comparison of acidic deposition to semi-natural ecosystems in Denmark-Coastal heath, inland heath and oak wood – Forest decline in West Germany. Atmos Environ 32:1075–1086
- Härdtle W, Niemeyer M, Niemeyer T, Assmann T, Fottner S (2006) Can management compensate for atmospheric nutrient deposition in heathland ecosystems? J Appl Ecol 43:759–769
- Härdtle W, von Oheimb G, Friedel A, Meyer H, Westphal C (2004) Relationship between pH-values and nutrient availability in forest soils the consequences for the use of ecograms in forest ecology. Flora 199:134–142
- Heil GW, Bobbink R (1993) "Calluna", a simulation model for evaluation of impacts of atmospheric nitrogen deposition on dry heathlands. Ecol Model 68:161–182
- Herrmann M, Pust J, Pott R (2005) Leaching of nitrate and ammonium in heathland and forest ecosystems in Northwest Germany under the influence of enhanced nitrogen deposition. Plant Soil 273:129–137
- Kaste Ø, Skjelkvåle BL (2002) Nitrogen dynamics in runoff from two small heathland catchments representing opposite extremes with respect to climate and N deposition in Norway. Hydrol Earth Syst Sci 6:351–362
- Kirkham FW (2001) Nitrogen uptake and nutrient limitation in six hill moorland species in relation to atmospheric nitrogen deposition in England and Wales. J Ecol 89:1041–1053
- Kristensen HL (2001) High immobilization of NH<sup>+</sup><sub>4</sub> in Danish heath soil related to succession, soil and nutrients: implications for critical loads of N. Water Air Soil Pollut Focus 1:211–230
- Mallik AU, FitzPatrick EA (1996) Thin section studies of *Calluna* heathland soils subject to prescribed burning. Soil Use Manage 12:143–149
- Manning P, Putwain PD, Webb NR (2006) The role of soil phosphorus sorption characteristics in the functioning and stability of lowland heath ecosystems. Biogeochemistry 81:205–217
- Marcos E, Calvo L, Luis-Calabuig E (2003) Effects of fertilization and cutting on the chemical composition of vegetation and soils of mountain heathlands in Spain. J Veg Sci 14:417–424
- Matzner E, Ulrich B (1980) The transfer of chemical elements within a heath ecosystem (*Calluna vulgaris*) in northwest Germany. Z Pflanz Bodenkunde 143:666–678
- Mitchell RJ, Auld MHD, Hughes JM, Marrs RH (2000) Estimates of nutrient removal during heathland restoration on successional sites in Dorset, southern England. Biol Conserv 95:233–246
- Mohamed A, Härdtle W, Jirjahn B, Niemeyer T, von Oheimb G (2006) Effects of prescribed burning on plant available nutrients in dry heathland ecosystems. Plant Ecol 189:279–289
- Nielsen KE, Ladekarl UL, Nørnberg P (1999) Dynamic soil processes on heathland due to changes in vegetation to oak and Sitka spruce. For Ecol Manage 114:107–116
- Nielsen KE, Hansen B, Ladekarl UL, Nørnberg P (2000) Effects of N-deposition on ion trapping by B-horizons of Danish heathlands. Plant Soil 223:265–276

- Niemeyer M, Niemeyer T, Fottner S, Härdtle W, Mohamed A (2007) Impact of sod-cutting and choppering on nutrient budgets of dry heathlands. Biol Conserv 134: 344–353
- Niemeyer T, Niemeyer M, Mohamed A, Fottner S, Härdtle W (2005) Impact of prescribed burning on the nutrient balance of heathlands with particular reference to nitrogen and phosphorus. Appl Veg Sci 8:183–192
- Nilsen LS, Johansen L, Velle LG (2005) Early stages of *Calluna vulgaris* regeneration after burning of coastal heath in central Norway. Appl Veg Sci 8:57–64
- Olff H, Pegtel DM (1994) Characterisation of the type and extent of nutrient limitation in grassland vegetation using a bioassay with intact sods. Plant Soil 163:217–224
- Pilkington MG, Caporn SJM, Carroll JA, Cresswell N, Lee JA, Emmett BA, Johnson D (2005) Effects of increased deposition of atmospheric nitrogen on an upland moor: leaching of N species and soil solution chemistry. Environ Pollut 135:29–40
- Power SA, Ashmore MR, Cousins DA (1998) Impacts and fate of experimentally enhanced nitrogen deposition on a British lowland heath. Environ Pollut 102 S1:27–34
- Power SA, Barker CG, Allchin EA, Ashmore MR, Bell JNB (2001) Habitat management: a tool to modify ecosystem impacts of nitrogen deposition? Sci World 1:714–721
- Power SA, Green ER, Barker CG, Bell JNB, Ashmore MR (2006) Ecosystem recovery: heathland response to a reduction in nitrogen deposition. Global Change Biol 12:1241–1252
- Rode MW (1999a) Influence of forest growth on former heathland on nutrient input and its consequences for nutrition and management of heath and forest. For Ecol Manage 114:31–43
- Rode MW (1999b) The interaction between organic layer and forest growth and forest development on former heath-land. For Ecol Manage 114:117–127
- Schmidt IK, Tietema A, Williams D, Gundersen P, Beier C, Emmett BA, Estiarte M (2004) Soil solution chemistry and element fluxes in three European heathlands and their responses to warming and drought. Ecosystems 7:638–649
- Sedláková I, Chytrý M (1999) Regeneration patterns in a Central European dry heathland: effects of burning, sodcutting and cutting. Plant Ecol 143:77–87
- Steubing L, Fangmeier A (1992) Pflanzenökologisches Praktikum. Parey Verlag, Berlin
- Sverdrup H, Thelin G, Robles M, Stjernquist I, Sorensen J (2006) Assessing nutrient sustainability of forest production for different tree species considering Ca, Mg, K, N and P at Bjornstorp Estate, Sweden. Biogeochemistry 81:219–238
- Terry AC, Ashmore MR, Power SA, Allchin EA (2004) Modelling the impacts of atmospheric nitrogen deposition on *Calluna*-dominated ecosystems in the UK. J Appl Ecol 41:897–909
- Uren SC, Ainsworth N, Power SA, Cousins DA, Huxedurp LM, Ashmore MR (1997) Long-term effects of ammonium sulphate on *Calluna vulgaris*. J Appl Ecol 34:208–216
- van Diggelen R, Marrs RH (2003) Restoring plant communities Introduction. Appl Veg Sci 6:106–110
- Verhoeven JTA, Koerselman W, Meuleman AFM (1996) Nitrogen- or phosphorus-limited growth in herbaceous,



wet vegetation: relations with atmospheric inputs and management regimes. Trends Ecol Evol 11:494–497

Webb NR (1998) The traditional management of European heathland. J Appl Ecol 35:987–990

Werger MJA, Prentice IC, Helsper HPH (1985) The effect of sod-cutting to different depth on *Calluna* heathland regeneration. J Environ Manage 20:181–188

White CC, Dawod AM, Cresser MS (1996) Nitrogen accumulation in surface horizons of moorland podzols: evidence from a Scottish survey. Sci Total Environ 184:229–237

