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Influence of canopy budget model approaches on atmospheric deposition estimates to forests

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Abstract Accurate quantification of total nitrogen and acidifying deposition is a major source of uncertainty in determining the exceedance of critical loads in forest ecosystems. Monitoring of atmospheric deposition is frequently based on throughfall measurements in combination with the canopy budget model to calculate ion-exchange fluxes between the forest canopy and incident rainfall water. Various approaches for each step in the canopy budget model have been reported and compared, but combinations of different approaches were not yet assessed. Therefore, the present study quantified the range of estimated dry deposition and total deposition resulting from all possible combinations of canopy budget model approaches for three typical case studies: (i) total nitrogen and potentially acidifying deposition onto a forest canopy, (ii) the ratio of these deposition variables between adjacent coniferous and deciduous stands and (iii) the parameters of a deposition time trend analysis. The time step, type of precipitation data and tracer ion used in the model had a significant effect on the findings in the three case studies. In addition, including or excluding canopy leaching of weak acids and canopy uptake of nitrogen during the leafless season largely affected the results, while including or excluding canopy uptake of nitrate generally showed

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no effect. In general, the use of wet-only precipitation data can be recommended, along with sodium as a tracer ion and the inclusion of weak acids. We conclude that further research should focus on the assumptions of inertness of the tracer ion and the equal deposition efficiency of base cations and the tracer ion and on the quantification of weak acids in rainfall and throughfall water. Since local or tree-species specific effects might influence the results obtained in this study, a similar analysis is recommended for other tree species and regions when using the canopy budget model.

Keywords Throughfall · Canopy budget model · Atmospheric deposition · Nitrogen · Trend analysis

Introduction

Human-induced atmospheric deposition of nitrogen (N) and sulphur (S) compounds have significantly altered nutrient cycling in temperate forest ecosystems and caused soil acidification and eutrophication. As a consequence, the quantification of atmospheric deposition has gained importance to establish cause-effect relationships, assess temporal and spatial trends and evaluate abatement measures and mitigation strategies (de Vries et al. 2003a; Erisman et al. 1994). Wet deposition can be measured with reasonable accuracy using wet-only or bulk precipitation collectors (Staelens et al. 2005), whereas for dry deposition (DD) a trade-off needs to be made between measurement accuracy and monitoring effort/costs (Erisman et al. 1994). The choice of a certain DD method depends on the purpose of the study and throughfall (TF) measurements are considered to be more suitable for long-term monitoring purposes and large scale monitoring networks than micrometeorological measurements (de Vries et al. 2003b; Erisman et al. 1994). Several studies have reported the use of TF measurements to evaluate trends in atmospheric deposition on forests (Graf Pannatier et al. 2011; Vanguelova et al. 2010). Furthermore, the method has often been used to compare deposition on different forest types, and deciduous versus coniferous forest stands in particular (De Schrijver et al. 2007; de Vries et al. 2007). An additional advantage of the TF method is that it also gives information on the internal nutrient cycle in forests (Emmett et al. 1998; Ferm and Hultberg 1999; Friedland et al. 1991; Parker 1983; Neirynck et al. 2008).

When incident precipitation passes through the canopy it is altered by wash-off of gases and particles deposited in dry periods prior to the precipitation event and by ion exchange, i.e. uptake or leaching, between canopy surfaces and the solutions passing over them (Draaijers et al. 1997). Therefore, to quantify total atmospheric deposition with TF measurements it is necessary to distinguish DD from canopy exchange (CE) (Parker 1983). This distinction is made by the canopy budget model of Draaijers and Erisman (1995), in which ion-exchange processes between the canopy and TF water are estimated. Various approaches of this model with respect to the time step, type of open-field precipitation data, tracer ion and ion exchange processes have been reviewed by Staelens et al. (2008). This review also assessed the sensitivity of atmospheric deposition onto two deciduous canopies to each approach compared to the reference model of Draaijers and Erisman (1995). The DD of base cations was meaningfully affected by the type of precipitation data and the tracer ion used, while canopy uptake of ammonium (NH_4^+) and protons (H^+) was influenced by accounting for canopy leaching of weak acids (WA). However, the authors suggested that future applications of the model could benefit from combining different approaches with each other to quantify the range of estimated DD and CE. This would also allow testing the relative influence of each approach on total N and potentially acidifying deposition.

Furthermore, Staelens et al. (2008) indicated that assuming no canopy uptake of nitrate (NO_3^-) (Harrison et al. 2000) had little effect on the total N deposition when the relative uptake efficiency of NO_3^- was considered to be low, but that more research was needed with regard to the uptake efficiency of NH_4^+ compared to NO_3^- for varying tree species and environmental conditions. Adriaenssens et al. (2012b) determined NH_4^+/NO_3^- retention ratios from wet

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deposition by means of ^{15}N labelled sources for four different tree species and phenological stadia. In this study it was also observed that inorganic N compounds were merely adsorbed to woody plant surfaces instead of being assimilated and that no relation between $^{15}NH_4^+$ uptake and net throughfall (NTF) of base cations was observed during the leafless season. This indicates that other processes than ion-exchange processes might play a role during the leafless season of deciduous species and that the ion-exchange assumptions made in the model might not be valid.

Therefore, in the present study we applied a combination of the different assumptions that can be made at each step in the canopy budget model (Draaijers and Erisman 1995) to the rainfall and TF data of three case studies. The steps containing the approaches that showed a high impact on CE and DD calculations according to Staelens et al. (2008) were included again, but now combined with each other. In addition, the effects of two new assumptions were tested, i.e. the NH_4^+/NO_3^- uptake ratio (Adriaenssens et al. 2012b) and a diameter-weighted DD factor for K^+ (Adriaenssens 2012). We explored the variation in output of 600 model variants obtained by combining different model approaches and assumptions and assessed the effect of each of these approaches on (i) the range of CE, DD and total N and acidifying deposition fluxes at the level of an individual beech tree, (ii) the ratio of total N and acidifying deposition on a coniferous and deciduous stand and (iii) a time trend analysis of total N and acidifying deposition onto a mixed deciduous stand.

Materials and methods

Study sites and sample collection (see Supplementary Material for a more extensive description)

All study sites were located in Flanders, the northern part of Belgium. The region is characterized by high atmospheric N and S deposition. The European beech (*Fagus sylvatica* L.) tree as well as the mixed deciduous stand used for the time trend analysis both were located in the Aelmoeseneie forest (50°58.5′N, 3°48′E, 16 m a.s.l.). This is a mixed deciduous forest located near Ghent in northern Belgium, approximately 60 km from the North Sea. TF water under the canopy of the individual beech tree at 1.5 m height and bulk precipitation above the canopy at 36 m height were collected every fortnight from 22 April 2009 to 22 April 2010 by six and two funnels, respectively. Based on visual observation of the beech canopy, the following phenological periods were distinguished: leaf development (22 April–20 May 2009), fully leafed period (21 May–24 September), leaf senescence (25 September–19 November) and leafless period (20 November 2009–22 April 2010).

In the mixed oak–beech stand, precipitation, TF and stemflow (SF) were collected from 1994 till 2010 according to the guidelines of Clarke et al. (2010). The different phenological stages in this study were delineated based on K^+ TF deposition, which was shown to increase during leaf development and leaf senescence (Houle et al. 1999; Neary and Gizyn 1994; Staelens et al. 2007).

The study site for the deposition ratio between a coniferous and a deciduous stand is located in the nature reserve ‘Heidebos’ in northern Belgium (Wachtebeke-Moerbeke) (51°11′N, 3°55′E, 11 m a.s.l.). Here, adjacent monospecific forest stands of pedunculate oak and Scots pine (*Pinus sylvestris* L.) were selected with the same soil type, stand history and tree age. Bulk precipitation and TF water were sampled biweekly from 7 December 2007 until 3 December 2008, by means of 4 and 15 collectors respectively. Based on visual observations of the oak canopy, the following phenological periods were distinguished for the oak TF data: leafless period (7 December 2007–7 May 2008), leaf development (8 May–5 June), fully leafed period (6 June–8 October) and leaf senescence (9 October–3 December 2008).

For all samples, the volume was determined and pH and electric conductivity were measured. After filtering through a 0.45 μm nylon membrane filter, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, NH_4^+,K^+, Ca^{2+}, Mg^{2+} and Na^+ concentrations were determined. H^+ concentrations were derived from the pH measurements.

Canopy budget models

The chemical composition of TF and SF water under a forest canopy is the result of incident precipitation, wash-off of dry deposited gases, particles or cloud droplets prior to the precipitation event, and the exchange between the canopy surfaces and the solutions passing over them (Lovett et al. 1996):

$$TF + SF = TD + CE = PD + DD + CE \quad (1)$$

where TD is the total deposition, PD is the precipitation deposition, DD is the dry deposition and CE is the canopy exchange.

Total potentially acidifying deposition (TD_{ac}) can then be defined as the sum of TD of NO_3^- and NH_4^+ (TD_N), SO_4^{2-} (TD_S) and Cl^- (TD_{Cl}) corrected for the neutralizing effect of base cations (TD_{BC}; Na^+, K^+, Ca^{2+} and Mg^{2+}) (UBA 2004):

$$TD_{ac} = TD_N + TD_S + TD_{Cl} - TD_{BC} \quad (2)$$

The NTF of an ion is defined as the difference between TF (+SF; if available) and PD, and equals the sum of DD and CE.

$$NTF = TF + (SF) - PD = DD + CE \quad (3)$$

The aim of the canopy budget model is to distinguish DD from CE for all major ions. Positive values for CE represent canopy leaching (CL) and negative values canopy uptake (CU). However, we follow the convention of expressing CU as positive values (CU = −CE). In the model, all fluxes are expressed on an equivalent basis (mol_c) per unit ground surface area and time. Further on, SF is not explicitly mentioned, but is included in TF for datasets where this flux is available.

When using the model, various approaches can be chosen within each step. For a thorough overview and discussion of these approaches, we refer to Staelens et al. (2008) and the Supplementary Material. In the present study, the effect of several of these approaches reported in literature was assessed for the three case studies. Figure 1 and Table 1 give an overview of the tested approaches. The model was tested with a phenological, semi-annual and annual step and with both bulk precipitation data and wet-only precipitation data as input. Furthermore, the effect of using Na^+ and SO_4^{2-} as a tracer ion was tested. In addition, based on previous research (Adriaenssens 2012) a new approach was tested which uses a diameter-weighted DD factor for K^+. WA were first excluded from the model, and then included again but calculated with three different methods, i.e. based on (i) the cation–anion balance, (ii) DOC and alkalinity and (iii) DOC and pH. In the reference canopy budget model, no CU of NO_3^- is taken into account, although several studies have indicated that forest canopies can incorporate NO_3^- (Adriaenssens 2012; Dail et al. 2009). To calculate CU of NO_3^-, four different approaches have been reported. In the first and second approach, CU of NH_4^+ and H^+ is set equal to CL of base cations and/or CL of WA, while in the third and fourth approach only CU of NH_4^+ is set equal to CL of base cations and/or CL of WA. CU of H^+ is then set equal to CU of NO_3^-. Additionally, in the first and third approach CU of NO_3^- is calculated based on a relative uptake efficiency of NH_4^+ to NO_3^- that equals 6, while in the second and fourth approach, this relative uptake efficiency varies by tree species and phenological period based on previous studies (Table 2; Adriaenssens et al. 2012b). Finally, previous research indicated that no CU of NH_4^+ and NO_3^- occurs during the leafless season for deciduous species (Adriaenssens et al., 2012b), so this was included in as well excluded from the model.

Data analysis

The combination of all approaches listed above (Table 1) resulted in 720 model versions. Since the approach of no CU of NH_4^+ and NO_3^- during the leafless period could not be calculated with an annual time step, 600 models were retained. For the case studies on the beech tree and the coniferous versus deciduous forest stands no DOC data were available, so for these datasets we evaluated 300 different models. For the comparison of forest types, deposition ratios between the coniferous and deciduous stand were evaluated. Time trends in annual deposition fluxes on the oak–beech stand were investigated through Kendall tests (Kendall 1975) to detect monotonically increasing or decreasing trends. Kendall's tau statistic represents the non-parametric correlation between a time series of data and time. When a linear trend can be assumed, the median slope and trend line is calculated non-parametrically.

The effect of different model versions was evaluated for two summarizing variables, i.e. the total N deposition ($NH_4^+ + NO_3^-$) (TD_N) and the potentially acidifying deposition (TD_{ac}; Eq. 2 in "Canopy budget models" section). For each time step considered (Table 1), the effect of different steps in the model, i.e. the type of precipitation data, the tracer ion, the CL of WA, the NO_3^- uptake and the CU of N during the leafless season (Table 1) was assessed by means of a multi-way Analysis of Variance (ANOVA). To evaluate model steps for the time trend analysis, a semi-

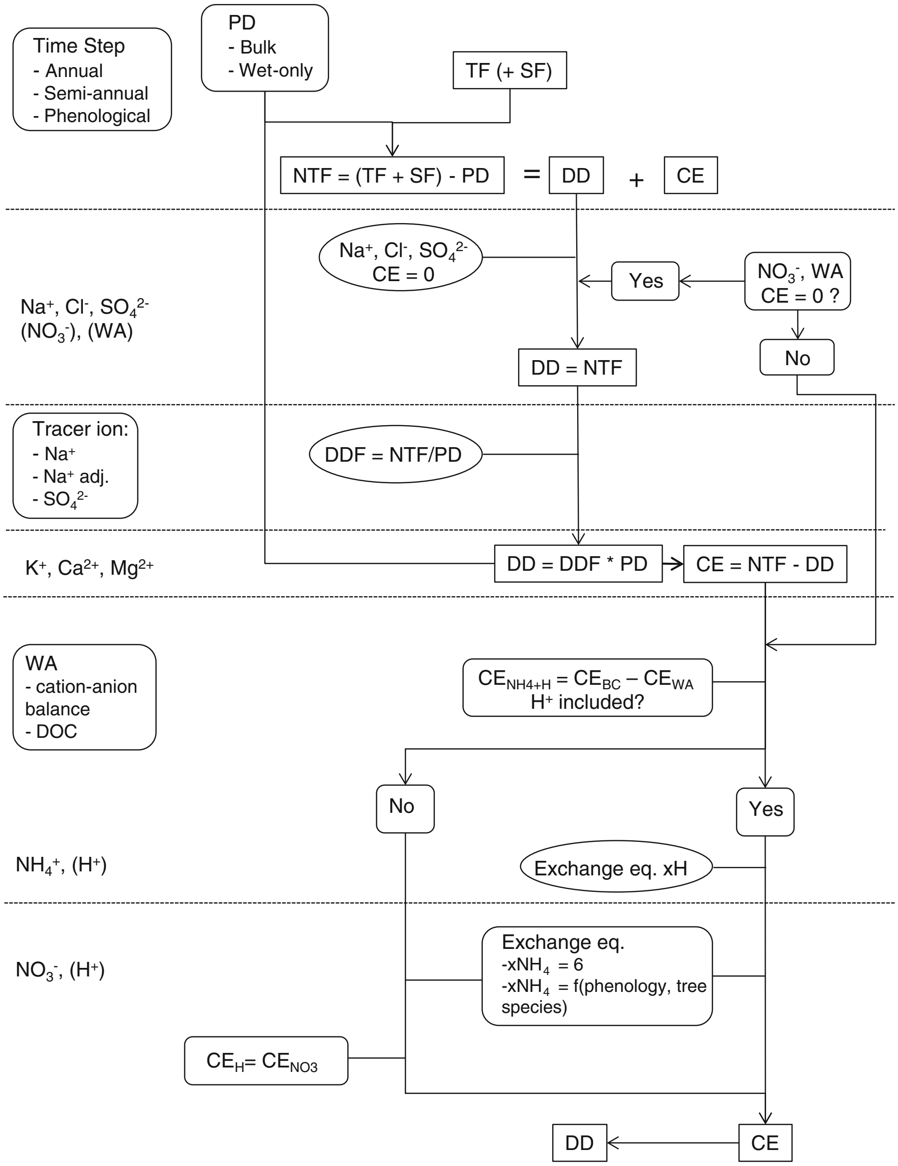

Fig. 1 Flow chart of the canopy budget model, extended from Staelens et al. (2008). The measured deposition of major ions in precipitation deposition (PD) and throughfall (+stemflow) deposition (TF (+SF)) is used to calculate NTF deposition, which consists of dry deposition (DD) and canopy exchange (CE). *Ellipses* are used to indicate model assumptions about the deposition factor (DDF) and on CE processes. *Rounded rectangles* indicate model assumptions for which various approaches were tested. *Dotted horizontal lines* separate equations used for different ions or ion groups. *WA* weak acids, *Na^+adj.* Na^+ as tracer ion with adjusted DD of K^+, *BC* base cations, *DOC* dissolved organic carbon, *xH* exchange efficiency of H^+ relative to NH_4^+, *xNH_4* exchange efficiency of NH_4^+ relative to NO_3^-

parametric Permanova test was performed on Kendall's tau and the median slope (Anderson 2001). The effect of time step was assessed by a one-way ANOVA. All calculations and statistical analyses were performed with R version 2.13.0 (R Development Core Team 2011).

The obtained range in TD_N and TD_{ac} of the different stands in this study was compared with site-specific critical loads of acidity and nutrient N (eutrophication), determined with the widely-used simple mass balance model (UBA 2004). Input data were as much as possible derived from site-specific measurements or regional data, as described by Staelens et al. (2009).

Results

Deposition onto an individual beech canopy

Application of the 300 different canopy budget models on the data for the beech canopy resulted in CE ranging from −20 to 0 kg N ha^{-1} yr^{-1} and DD ranging from 6 to 28 kg N ha^{-1} yr^{-1} (see

Table 1 Overview of the different tested approaches at each step of the canopy budget model (see also Fig. 1)

Step	Tested approaches
Time step (3)	Phenological
	Semi-annual
	Annual
Precipitation deposition (2)	Wet-only data derived from bulk deposition measurements
	Bulk deposition measurements
Tracer ion (3)	Na^+
	Na^+ with adjustment for a lower DD rate of K^+
	SO_4^{2-}
Canopy leaching of weak acids (4)	Not included
	Weak acids estimated based on cation–anion balance
	Weak acids estimated based on DOC measurements and alkalinity
	Weak acids estimated based on DOC measurements and pH
Canopy uptake of NO_3^- (5)	Not included
	$CU(NH_4 + H) = CL(BC); xNH_4 = 6$
	$xNH_4^{i,t} = f(\text{phenology, tree species})$ (Table 2)
	$CU(NH_4) = CL(BC); xNH_4 = 6$
	$xNH_4^{i,\ t} = f(\text{phenology, tree species})$ (Table 2)
Canopy uptake of NH_4^+ and NO_3^- in The leafless season (2)*	Included
	Not included

The number of approaches per step is given in parentheses, which resulted in a total of 720 different canopy budget models. Since the approach of no canopy uptake of NH_4^+ and NO_3^- during the leafless period could not be calculated with an annual time step, 600 models were retained

*Not applicable to coniferous species

CU canopy uptake, *BC* base cations, *xNH_4* relative uptake efficiency of NH_4^+ compared to NO_3^-

Table 2 Ammonium to nitrate uptake ratios used for the calculation of the different canopy budget model versions, based on the results of Adriaenssens et al. (2012b)

Period	Beech	Pedunculate oak	Scots pine	Oak–beech
Leaf development	2.1	2.9	93.6	2.6
Fully leafed	4.7	4.1	4.0	4.3
Leaf senescence	7.7	3.9	9.2	5.3
Leafless	4.3	5.1	39.6	4.8
Leafed	5.0	4.2	16.7	4.5*
Annual	4.8	3.7	49.2	4.1*

For semi-annual and annual time steps a time-weighted average of the ratios was used. For the oak-beech stand a weighted average of values for beech and pedunculate oak was used, based on basal area reported by De Coucк (2011)

*Approximate value, ratios used in the time trend analysis vary between years depending on the length of each period

Supplementary Material Fig. S1). The highest CU was calculated using Na^+ as a tracer (without adjustment for a different DD rate of K^+), excluding CL of WA and including CU of N during the leafless season. The lowest CU was obtained with SO_4^{2-} as a tracer ion, including CL of WA, using bulk precipitation data and with a phenological time step. This lower CU of N was caused by occasionally negative CL of base cations or a high value for the estimated CL of WA, especially during leaf development. Lowest DD of N was calculated using SO_4^{2-} as a tracer ion, including CL of WA and using bulk precipitation data, while the highest DD was obtained with Na^+ as a tracer ion, excluding CL of WA, using wet-only precipitation data and including CU of N during the leafless season. When using a phenological time step, calculated DD of N during the leaf development period was negative when CL of WA was included.

The highest variance in total N deposition (TD_N) could be explained by CL of WA, followed by CU of

N during the leafless season (in case of a phenological or semi-annual time step), the tracer ion used and the precipitation data. For total acidifying deposition (TD_{ac}) the highest variance could be explained by the tracer ion used, CL of WA and CU of N during the leafless season (Table 3). For TD_N, all factors were significant while for TD_{ac} the effect of NO_3^- uptake was not significant in the semi-annual and annual time step. The time step itself had no significant effect on TD_N ($p = 0.838$) and TD_{ac} ($p = 0.998$). Including CL of WA significantly lowered CU of NH_4^+ and consequently lowered DD_N, TD_N and TD_{ac} (Fig. 2). The use of SO_4^{2-} as a tracer ion increased estimated DD of base cations compared to Na^+, hereby decreasing CL of these base cations and CU and DD of NH_4^+. This decreased TD_N but increased TD of base cations and consequently reduced TD_{ac}. Using bulk precipitation data decreased TD_N and TD_{ac} estimates. The CU of NO_3^- explained the least variance in the model results. A significant difference between excluding and including CU of NO_3^- was only found for TD_N.

Deposition ratio between a coniferous and a deciduous stand

Application of the 300 canopy budget models resulted in a ratio of TD_N (coniferous to deciduous forest stand) between 1.02 and 1.75 and a ratio of TD_{ac} (coniferous to deciduous) between 0.68 and 1.46 (see Supplementary Material Fig. S2). The highest variance on the ratios of TD_N and TD_{ac} could be explained by CU of N in the leafless season followed by the CL of WA and the tracer ion (Table 3). No significant effect of NO_3^- uptake was found, except with an annual time step, and the type of precipitation data only significantly affected TD_N deposition ratios for an annual time step. The time step significantly affected TD_{ac} ($p < 0.001$) but not TD_N ($p = 0.128$). Including CL of WA increased the coniferous to deciduous ratio of TD_N and TD_{ac} because TD_N decreased relatively more for pedunculate oak than for Scots pine (Fig. 3). The use of SO_4^{2-} also increased the ratio of TD_N and TD_{ac} because the deposition ratio of SO_4^{2-} was lower than of Na^+. Excluding CU of N during the leafless season

Table 3 *p* Values of the multi-way ANOVA analysis assessing the effect of different steps in the canopy budget model on total nitrogen (N) and total acidifying deposition to an individual beech tree (Case 1), the ratio of total N and total acidifying deposition to a coniferous and a deciduous stand (Case 2); The effect on Kendalls tau of total N and total acidifying deposition on a deciduous oak–beech stand (Case 3) was assessed by a semi-parametric Permanova test

Source of variation	Df	Total N deposition			Total acidifying deposition		
		Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
Phenological time step							
Precipitation	1	**<0.001**	0.479	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Tracer ion	2	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Weak acids	1	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
NO_3^- uptake	4	**0.001**	0.143	0.374	**0.023**	0.216	0.777
Canopy uptake leafless	1	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Semi-annual time step							
Precipitation	1	**<0.001**	0.418	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Tracer ion	2	**<0.001**	0.103	**<0.001**	**<0.00**	**<0.001**	**<0.001**
Weak acids	1	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
NO_3^- uptake	4	**0.008**	0.780	0.316	0.084	0.705	0.220
Canopy uptake leafless	1	**<0.001**	**<0.001**	0.320	**<0.001**	**<0.001**	**<0.001**
Annual time step							
Precipitation	1	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Tracer ion	2	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Weak acids	1	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.00**
NO_3^- uptake	4	**0.002**	**0.038**	0.084	0.163	**0.011**	0.495

Bold $p < 0.05$

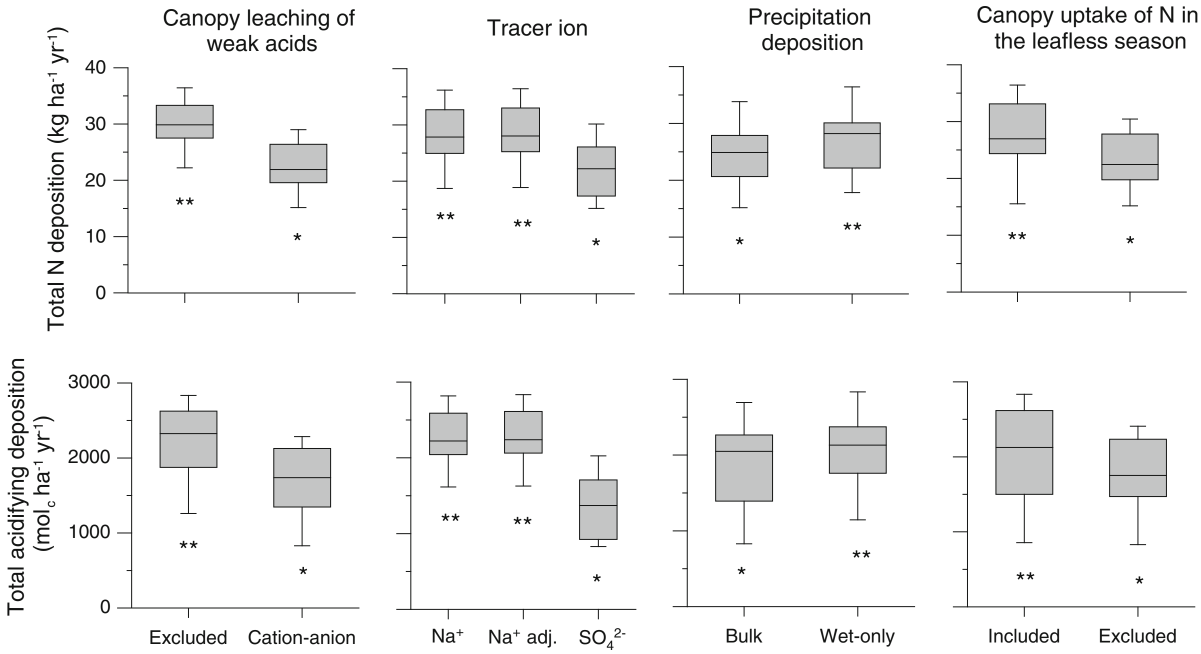

Fig. 2 *Box plots* showing the effect of each step in the canopy budget model on total nitrogen (N) deposition (kg ha^{-1} yr^{-1}) and total potentially acidifying (mol_c ha^{-1} yr^{-1}) deposition on the individual beech tree. *Stars* indicate significant differences between different levels of each step

significantly decreased TD_N on the pedunculate oak stand and consequently increased the ratio of TD_N and TD_{ac}. Wet-only precipitation data yielded a higher TD_{ac} ratio than bulk precipitation data and a phenological time step significantly decreased the TD_{ac} ratio compared to an annual or semi-annual time step. It needs to be mentioned that in the pedunculate oak stand calculated DD values of N during leaf development were negative when CL of WA was included. For the Scots pine stand, CE of Ca^{2+} and/or Mg^{2+} was always negative during leaf development and senescence and CE of NO_3^-, NH_4^+ and H^+ was always positive during leaf development and when CL of WA was included also during other phenological periods.

Determination of trends in deposition

According to the Kendall tests, yearly TD_N on the beech site calculated by the 600 different canopy budget models showed a significant ($p < 0.05$) time trend over 1999–2010 for 66 % of the models. Kendall's tau value varied from −0.76 for the highly significant time trends to −0.03 for non-significant time trends. The median slope varied from −1.75 to −0.05 mol_c N ha^{-1} yr^{-1} (Fig. 4). Yearly TD_{ac} showed a significant ($p < 0.05$) time trend for 58 % of the tested models. Kendall's tau value varied from −0.70 to −0.12 and the median slope from −197 to −26 mol_c N ha^{-1} yr^{-1} (see Supplementary Material Fig. S3).

The variation in Kendall's tau values for TD_N and TD_{ac} could mainly be explained by the CL of WA followed by the type of precipitation data, the tracer ion and the CU of N in the leafless season, although the last factor was not significant for a semi-annual time step (Table 3). Choices regarding the CU of NO_3^- had no significant effect on the tau value of TD_N and TD_{ac}. Using wet-only precipitation data decreased TD_N by 13 % from 1999 to 2010, while TD_N was reduced by 11 % with bulk precipitation data. Similarly, TD_{ac} decreased by 22 and 19 % using wet-only and bulk data, respectively (Fig. 4). Using SO_4^{2-} as a tracer reduced TD_N and TD_{ac} with 21 and 34 %, respectively, compared to 8 and 13 %, respectively, for Na^+. Furthermore, no significant trend was found for TD_N and TD_{ac} when CL of WA was estimated from the difference between cations and anions (−15 % TD_N and −3.5 % TD_{ac}; in 12 years). In contrast, this trend was highly significant when WA were estimated from

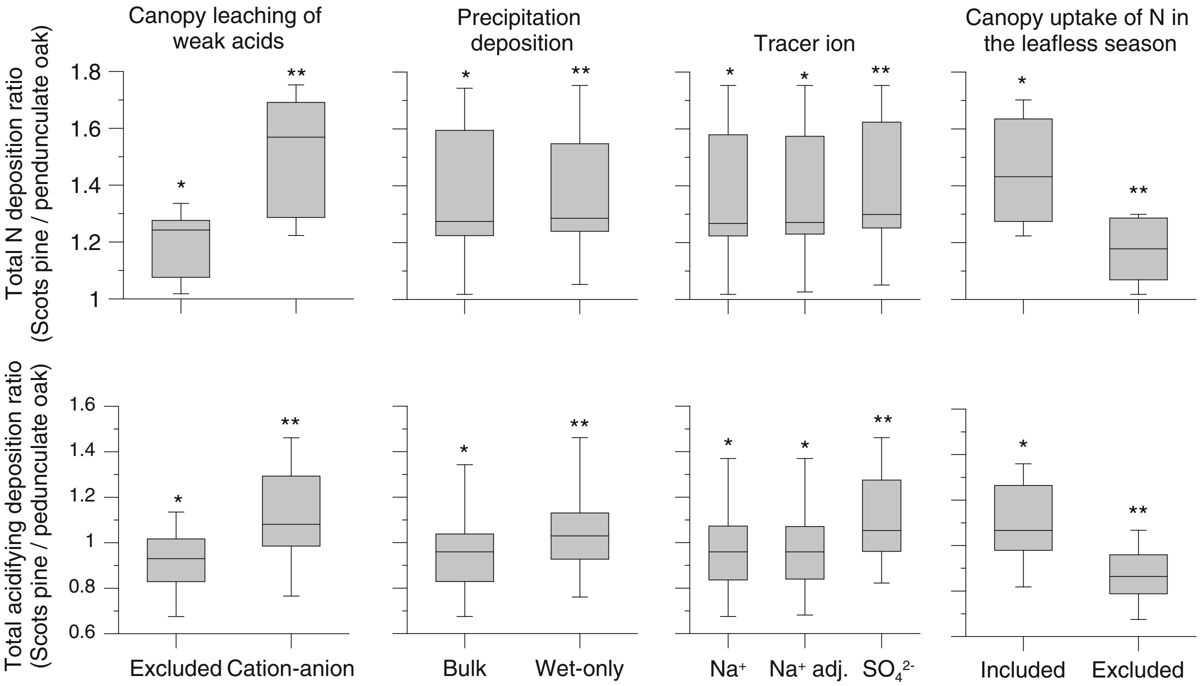

Fig. 3 *Box plots* showing the effect of each step in the canopy budget model on the ratio of total nitrogen (N) deposition and total potentially acidifying deposition between a Scots pine and a pedunculate oak stand. *Stars* indicate significant differences between different levels of each step

DOC and alkalinity measurements (−25 % TD_N and −30 % TD_{ac}). Excluding CL of WA and including WA estimated from DOC and pH measurements resulted in intermediate but significant time trends. Estimated WA in TF were similar in magnitude for DOC combined with alkalinity measurements compared with the cation–anion balance, while in PD estimated WA from DOC and alkalinity were approximately four times higher. Excluding CU of N during the leafless season reduced TD_N and TD_{ac} with 12 and 20 %, respectively, and including with 14 and 22 %, respectively.

Discussion

Effect of time step, type of precipitation data and tracer ion

Using different time steps in the canopy budget model allowed introducing different CE approaches, which are discussed further in this paragraph. However, there was also an effect of time step as such, with phenological or semi-annual time steps generally resulting in lower N and potentially acidifying deposition (TD_N and TD_{ac}, respectively), lower TD_{ac} ratios between a coniferous and deciduous stand and in more steeply decreasing deposition time trends, i.e. lower Kendall tau values and median slopes. The negative DD values of NO_3^-, NH_4^+ and H^+ calculated during leaf development may be caused by 1) underestimated CL of base cations which is in turn caused by overestimated DD of base cations or 2) overestimated CL of WA by the cation–anion balance. The first cause was confirmed by negative CE values of Ca^{2+} and Mg^{2+} during leaf development. This indicates that both Na^+ and SO_4^{2-} may be subject to leaching during leaf development (Reiners and Olson 1984; Staelens et al. 2007), which makes them less suitable as tracer ion. Staelens et al. (2007; 2008) suggested solving this by calculating the DDF of Na^+ for the fully leafed period and using this factor for the periods of leaf development and senescence. However, for the Scots pine stand this would not be sufficient as CE of Ca^{2+} and Mg^{2+} was also negative during the leafless period. Hence, more research is needed on the assumption of inertness of the tracer ion and the deposition efficiency of different particles.

Although the type of precipitation data was generally not the main source of variation between model

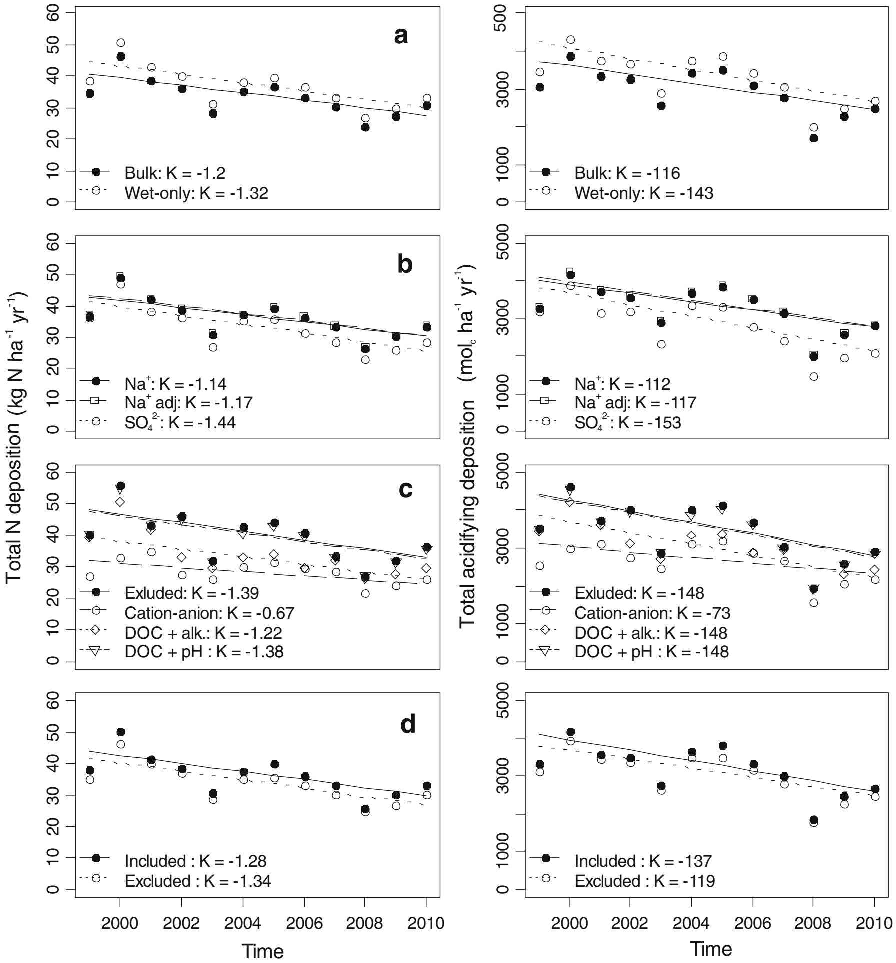

Fig. 4 Time series of total nitrogen (N) deposition and total potentially acidifying deposition calculated with canopy budget models using varying **a** precipitation data, **b** tracer ion, **c** canopy leaching of weak acids and **d** canopy uptake of N during the leafless season. The estimated median slope K (kg N ha^{-1} yr^{-1}) of each approach is given

versions, it significantly affected the calculated TD_N and TD_{ac} in the three case studies. In particular for Na^+, Cl^-, K^+, Ca^{2+} and Mg^{2+}, which had low wet-only to bulk ratios, the NTF was significantly reduced using bulk instead of wet-only precipitation deposition. This in turn reduced CE of base cations and consequently CE and DD of N. As the wet-only to bulk ratios used in this study were generally in line with other reports (see Table 2 in Staelens et al. 2005), this conclusion may held true for other studies as well. In general, the difference in TD_N or TD_{ac} between bulk and wet-only precipitation data increased when TF deposition increased, i.e. TF of Scots pine was higher than of pedunculate oak and higher in 1999 compared to 2010.

Using SO_4^{2-} as tracer ion may significantly overestimate DD of base cations if meaningful gaseous SO_2 deposition occurs, and consequently underestimate DD of N (see also Sect. 1.3.3 in the Supplementary Material). This is confirmed by the present study: TD_N to the beech canopy was significantly lower with SO_4^{2-} than with Na^+ as a tracer ion; and SO_2 deposition at this site was estimated to be 50 mmol$_c$ m^2 yr^{-1}, while almost no particulate SO_4^{2-} was deposited on artificial foliage (Adriaenssens 2012). The TD_N and TD_{ac} ratios between a coniferous and deciduous stand were significantly affected by the tracer ion due to the fact that the TF deposition ratio of SO_4^{2-} was lower than for Na^+. In the time trend analysis of the oak–beech stand, more steeply decreasing trends were observed with SO_4^{2-} as tracer ion since the precipitation and TF deposition decreased more significantly from 1999 to 2010 for SO_4^{2-} than for Na^+. It is clear that for regions with high SO_2 deposition, Na^+ can be considered to be a more reliable tracer ion. In some cases, such as in coastal regions (Adriaenssens et al. 2012a) the use of SO_4^{2-} may be justified if particle deposition dominates DD of S, but then still the generally finer SO_4^{2-} particles (Lindberg et al. 1986; Ruijgrok et al. 1997) will be deposited with lower deposition efficiency (Slinn 1982) and results need to be handled with care.

In the three case studies there was no significant effect between using Na^+ as a tracer ion and using Na^+ adjusted for a lower DD of K^+. This was mainly due to the fact that atmospheric K^+ deposition was low, so that the impact of a reduced DD of K^+ was not detectable in the output of the canopy budget model (here summarized by TD_N and TD_{ac}). However, TD_{ac} for the individual beech tree and the ratio of TD_{ac} between the coniferous and deciduous stand were slightly increased when using Na^+_{adj}. We only adjusted the DDF of K^+ as this was suggested by several authors (Ruijgrok et al. 1997; Staelens et al. 2008) and also concluded from own results (Adriaenssens 2012). Furthermore, the ratio between the MMD of K^+ and Na^+ was based on data of Ruijgrok et al. (1997) assuming a linear and 1:1 relationship between particle diameter and deposition efficiency for particles larger than 0.1 μm, while, according to the model of Slinn (1982) or other models (Ruijgrok et al. 1995), this relationship is more exponential. Since the steepness of this curve varies considerably among existing models that all show a large uncertainty due to variable input parameters (Ruijgrok et al. 1995) and since a more linear pattern was observed from deposition measurements (Garland 2001), our choice for a linear and 1:1 relationship in this study seems justifiable. However, future research could benefit from assessing the influence of different MMD – deposition velocity relationships for various conditions, e.g. particular meteorological conditions or different surface geometry (Garland 2001) if information on the MMD of the different aerosols is available. Further studies may suggest an adjusted DDF for Ca^{2+} and Mg^{2+} too, which will increase the impact on TD_N and particularly TD_{ac}.

Effect of canopy exchange calculations: canopy leaching of weak acids, NO_3^- uptake and CU of N during the leafless season

In the three case studies, a strong effect of in- or excluding CL of WA estimated by the cation–anion balance was observed. Especially for beech and oak significant CL of WA was calculated, while this was less important for the pine stand. This is in agreement with a higher base cation leaching from deciduous than coniferous canopies, as was found in our case study of a paired deciduous–coniferous stand and in other reports (De Schrijver et al. 2007; Rothe et al. 2002). In the trend analysis, CL of WA decreased significantly from 1999 to 2010, hereby decreasing the downward trend of TD_N. This high impact of including WA in the canopy budget model illustrates its importance, especially in deciduous stands where CL of WA contributed on average 50 % to CL of base cations. Estimating WA by means of the cation–anion balance was considered to be a reliable approach by de Vries et al. (2001), given that all other major ions are analysed precisely and accurately (Staelens et al. 2008). However, in the trend analysis the cation–anion approach differed significantly from the two DOC-based approaches. In general, measuring WA can be preferred above estimating them. However, estimated HCO_3^- from alkalinity may contain some organic acids and calculated HCO_3^- from pH may be less accurate due to the uncertainty in pH measurements of weakly buffered water samples like precipitation samples. Hence, more research is needed with regard to the estimation of WA in precipitation and TF samples.

Adriaenssens et al. (2011; 2012b) observed low but significant uptake of wet deposited NO_3^- by tree leaves, particularly during leaf development. Incorporating NO_3^- uptake in the canopy budget model significantly increased the calculated TD_N on the individual beech tree and is recommended given the clear experimental evidence. Nevertheless, including NO_3^- uptake had neither effect on the comparison between a coniferous and a deciduous stand nor on the trend analysis and TD_N did not differ between the different calculation NO_3^- uptake approaches. This suggests that the proposed xNH_4 efficiency factor of six by de Vries et al. (2001) may also be suitable and that no differentiation according to leaf phenology is necessary. However, the studied tree species were all shown to preferentially retain NH_4^+ compared to NO_3^-. The effect of the different calculation approaches of NO_3^- uptake will likely increase for species that have been shown to preferentially retain NO_3^- in their foliage instead of NH_4^+, such as red spruce (*Picea rubens* Sarg.) (Dail et al. 2009; Gomez-

Guerrero et al. 2008). Therefore, it is still suggested to use a tree species specific xNH_4 at a phenological time step when available. Furthermore, attributing CE of H^+ and NH_4^+ to CL of WA often resulted in (impossible) negative DD values of H^+ for the individual beech tree and the trend analysis, while this was generally not the case when CE of H^+ was determined via the CE of NO_3^-.

In this study we introduced the new concept of excluding the CU of NH_4^+ and NO_3^- during the leafless season for deciduous species, based on previous observations that twigs and stems of deciduous trees retained almost no N (Adriaenssens et al. 2012b). As expected, this significantly reduced TD_N and TD_{ac} for the individual beech tree (Fig. 2) and the ratios of TD_N and TD_{ac} between a coniferous and deciduous stand (Fig. 3). It also decreased the estimated tau value and estimated slope in the trend analysis for TD_N. However, in mature temperate deciduous stands some N can be retained by microbial assimilation processes and lichens (Reiners and Olson 1984), which mainly occur on older trees (Fritz et al. 2008; Ranius et al. 2008). Several studies have reported a significant contribution of N assimilation by epiphytic lichens to total CU in coniferous (Johansson et al. 2010; Lang et al. 1976) and tropical forests (Clark et al. 2005; Wanek and Hinko-Najera Umana 2010), but not in deciduous stands. If the latter is also significant, which needs to be investigated, attributing all NTF of N to DD during the leafless period will likely underestimate TD_N. For the Scots pine stand used in this study, CU of N in winter was not excluded since needles are then still present and since significant amounts of ^{15}N were found to be adsorbed to the bark surface, as suggested by Dail et al. (2009) and Wilson and Tiley (1998). This retained N is likely not subject to ion exchange processes with K^+, Ca^{2+} and Mg^{2+} as assumed in the canopy budget model. However, this remains to be investigated.

It should also be mentioned that the CU of N calculated by the canopy budget model does not comprise immediate uptake of gases like HNO_3, but only ion exchange between the water layer on the canopy surface and the canopy itself. As a consequence, DD_N, TD_N and TD_{ac} could be underestimated. However, the few available studies that compared N uptake from dry and wet deposition concluded that foliar retention from the liquid phase is much more important than from the gaseous phase (Harrison et al. 2000; Sievering et al. 2007), although dry deposited N may significantly contribute to canopy retention (Horvath 2004). Dry deposited N to the canopy during the dry period prior to a wet deposition event is generally mobilized by canopy wetness, after which the dissolved N is available to canopy foliage for use in photosynthesis (Sievering et al. 2007). From this we conclude that the canopy budget model takes into account most of the canopy N uptake.

Comparison with literature data and site-specific critical loads

Based on this study and other literature data (Ignatova and Dambrine 2000; Staelens et al. 2008; Zhang et al. 2006), some canopy budget model approaches can be considered more reliable than others, e.g. Na^+ is a more suitable tracer ion than SO_4^{2-}, and the use of wet-only precipitation data and including CL of WA is recommended. If we only consider these models, DD to the beech canopy was 10–20 kg N ha^{-1} yr^{-1},TD_N was 19–29 kg N ha^{-1} yr^{-1} and TD_{ac} 1664–2285 mol_c ha^{-1} yr^{-1}. This range was comparable at the Heidebos site for the oak stand (DD_N: 8–16 kg N ha^{-1} yr^{-1}; TD_N: 20–28 kg N ha^{-1} yr^{-1}; TD_{ac}: 1357–1902 mol_c ha^{-1} yr^{-1}) but higher for the pine stand with regard to N (DD_N: 23–24 kg N ha^{-1} yr^{-1}; TD_N: 34–35 kg N ha^{-1} yr^{-1}; TD_{ac}: 1612–1895 mol_c ha^{-1} yr^{-1}). For the oak–beech stand in the Aelmoeseneie forest in 2010 DD_N was 15–31 kg N ha^{-1} yr^{-1}, TD_N was 25–41 kg N ha^{-1} yr^{-1} and TD_{ac} was 2228–3382 mol_c ha^{-1} yr^{-1}. For the individual beech tree, DD_N covers the results obtained by multi-layer artificial foliage and by passive sampler measurements multiplied with a fixed deposition velocity (Adriaenssens 2012). Neirynck et al. (2008) reported much higher DD_N and TD_N values for a Scots pine stand in the same region, however, this stand was 70 years old and consequently had a higher collecting surface for DD. Moreover, the proximity of a harbour causes higher local emissions of NO_x and SO_2. Canopy N uptake by the individual beech tree ranged from 4 to 14 kg N ha^{-1} yr^{-1}, which is within the range of 1–57 kg N ha^{-1} yr^{-1} reported in literature (Sievering et al. 2007; Neirynck et al. 2008). The ratio of TD_N between a coniferous and deciduous stand was within the range reported in meta-analyses on this topic (De Schrijver et al. 2007; Rothe et al. 2002). To our knowledge, no such comparison has been done for TD_{ac}.

The modelled critical load of acidification was 1960–2285 $mol_c\ ha^{-1}\ yr^{-1}$ for the deciduous species at the two sites and 1294 eq $ha^{-1}\ yr^{-1}$ for pine at the Heidebos site (Table 4) The critical loads for eutrophication amounted to 13–14 (deciduous species) and 8 (pine) kg N $ha^{-1}\ yr^{-1}$. The obtained ranges for TD_N reported above all exceed the critical loads for eutrophication, indicating that eutrophication is very likely in all three cases. Yet, critical loads for acidification are not all exceeded by the ranges of TD_{ac}. For instance, for the Heidebos site the obtained ranges are below the critical loads and for the beech canopy approximate around the critical load values. This highlights again, especially for the latter case, that the approaches and assumptions of the canopy budget model used to calculate atmospheric deposition on forest ecosystems are crucial when evaluating critical load exceedances.

Local effects

The three case studies for which the different CE approaches were tested are all situated in the region of Flanders. In the majority of the forests in this region, critical loads for acidifying and eutrophying deposition are exceeded (Craenen et al. 2000; Staelens et al. 2009). It is therefore certainly relevant to quantify total deposition, evaluate trends or compare different forest types for mitigation strategies in this region. However, different effects of the CE calculations might be observed in regions such as China or India, where N and particularly S deposition have started to rise more recently than in Western Europe (Fowler et al. 2009), or in unpolluted boreal forests in Northern Europe (Ukonmaanaho and Starr 2002). The canopy budget model has not been properly evaluated for subtropical and tropical forests, where large amounts of N are shown to be assimilated by epiphytic and bryophytic lichens (Wanek and Hinko-Najera Umana 2010). Furthermore, even within temperate forests different results might be obtained for different tree species, e.g. when NO_3^- is retained preferentially compared to NH_4^+ (see "Effect of canopy exchange calculations: canopy leaching of weak acids, NO_3^- uptake and canopy uptake of N during the leafless season" section).

Table 4 Modelled critical loads of acidification [$CL_{max}(S)$] and eutrophication [$CL_{nut}(N)$]

Site	Tree species	$CL_{max}(S)$ ($mol_c\ ha^{-1}\ yr^{-1}$)	$CL_{nut}(N)$ (kg N $ha^{-1}\ yr^{-1}$)
Aelmoeseneie	Beech	1960	13.9
	Oak–beech	2285	14.4
Heidebos	Oak	1294	13.4
	Pine	1982	8.4

Conclusion

In this study varying approaches to calculate the canopy budget model were used. As such we explored the range in total and potentially acidifying deposition onto a deciduous forest canopy, deposition ratios between a coniferous and deciduous forest stand and the characteristics (Kendalls tau and median slope) of a deposition time trend analysis. The time step, type of precipitation data, tracer ion, CL of WA and CU of N during the leafless season all had a significant effect on the results, whereas the CU of NO_3^- generally had no influence. A correction of bulk to wet-only precipitation data is recommended when available. Sodium can be considered as the most suitable tracer ion, but more research for different tree species is needed on the assumption of inertness during leaf development. Furthermore, an adjustment according to the mean mass diameter for each base cation could improve the estimated DD of these elements. Including CL of WA in the canopy budget model had usually the highest impact in all three case studies, but this could mainly be attributed to the fact that weak acid concentrations in water samples were estimated from a cation–anion balance. The strong effect of including weak acid leaching disappeared when calculating WA from DOC and bicarbonate measurements, which indicates that the accuracy of analytical measurements is of high importance, in particular for rainfall samples in which ion concentrations are generally low.

Some indications with regard to the most suitable approach were derived and since the results of this approach were in line with literature data, we may conclude that the canopy budget model can be a suitable approach to calculate total N and acidifying deposition. However, it is important to consider the various possible options of the canopy budget model when setting-up an experiment or starting data analysis. Also, this study presents evidence of the importance of CE calculations for three relevant case studies in Flanders, a region with enhanced N deposition due to anthropogenic emissions. Since local and tree species-specific effects may play a role here, similar model evaluations in other regions are recommended. Finally, it is recommended for future research to compare this approach to results obtained by other methods to estimate atmospheric deposition.

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References

Adriaenssens S (2012) Dry deposition and canopy exchange for temperate tree species under high nitrogen deposition. PhD thesis, Ghent University, Ghent, Belgium

Adriaenssens S, Staelens J, Wuyts K, De Schrijver A, Van Wittenberghe S, Wuytack T, Kardel F, Verheyen K, Samson R, Boeckx P (2011) Foliar nitrogen uptake from wet deposition and the relation with leaf wettability and water storage capacity. Water Air Soil Pollut 219:43–57

Adriaenssens S, Hansen K, Staelens J, Wuyts K, De Schrijver A, Baeten L, Boeckx P, Samson R, Verheyen K (2012a) Throughfall deposition and canopy exchange processes along a vertical gradient within the canopy of beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst.). Sci Total Environ 420:168–182

Adriaenssens S, Staelens J, Wuyts K, Samson R, Verheyen K, Boeckx P (2012b) Canopy retention of dissolved inorganic nitrogen by foliage and twigs of four temperate tree species. Ecosystems, in press, DOI: 10.1007/s10021-012-9568-5

Anderson MJ (2001) A new method for non-parametric multivariate analysis of variance. Austral Ecol 26:32–46

Clark KL, Nadkarni NM, Gholz HL (2005) Retention of inorganic nitrogen by epiphytic bryophytes in a tropical montane forest. Biotropica 37:328–336

Clarke N, Zlindra D, Ulrich E, Mosello R, Derome J, Derome K, König N, Lövblad G, Draaijers GPJ, Hansen K, Thimonier A, Waldner P (2010) Sampling and analysis of deposition. Part XIV. In: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. UNECE ICP Forests Programme Co-ordinating Centre, Hamburg, Germany (www.icp-forests.org/Manual.htm)

Craenen H, Van Ranst E, Tack FMG, Verloo MG (2000) Calculation and mapping of critical loads of sulfur and nitrogen in Flanders, Belgium. Sci Total Environ 254:55–64

Dail DB, Hollinger DY, Davidson EA, Fernandez I, Sievering HC, Scott NA et al (2009) Distribution of nitrogen-15 tracers applied to the canopy of a mature spruce-hemlock stand, Howland, Maine, USA. Oecologia 160:589–599

De Couck N (2011) Veranderingen in de boomlaag in het Aelmoeseneiebos en de impact op strooisel, bodem en kruidlaag. Ghent University, M.Sc. thesis

De Schrijver A, Geudens G, Augusto L, Staelens J, Mertens J, Wuyts K, Gielis L, Verheyen K (2007) The effect of forest type on throughfall deposition and seepage flux: a review. Oecologia 153:663–674

de Vries W, Reinds GJ, van der Salm C, Draaijers G, Bleeker A, Erisman JW (2001) Intensive monitoring of forest ecosystems in Europe. Technical report 2001. Brussels, Geneva: EC-UN/ECE

de Vries W, Vel E, Reinds GJ, Deelstra H, Klap JM, Leeters EEJM, Hendriks CMA, Kerkvoorden M, Landmann G, Herkendell J, Haussmann T, Erisman JW (2003a) Intensive monitoring of forest ecosystems in Europe - 1. Objectives, set-up and evaluation strategy. For Ecol Manage 174:77–95

de Vries W, Vel EM, Reinds GJ, Deelstra H, Klap JM, Leeters EEJM et al (2003b) Intensive monitoring of forest ecosystems in Europe. 1. Objectives, set-up and evaluation strategy. For Ecol Manage 174:77–95

de Vries W, van der Salm C, Reinds GJ, Erisman JW (2007) Element fluxes through European forest ecosystems and their relationships with stand and site characteristics. Environ Pollut 148:501–513

Draaijers G, Erisman JW (1995) A canopy budget model to assess atmospheric deposition from throughfall measurements. Water Air Soil Pollut 85:2253–2258

Draaijers GPJ, Erisman JW, VanLeeuwen NFM, Romer FG, teWinkel BH, Veltkamp AC, Vermeulen AT, Wyers GP (1997) The impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes. Atmos Environ 31:387–397

Emmett BA, Boxman D, Bredemeier M, Gundersen P, Kjonaas OJ, Moldan F, Schleppi P, Tietema A, Wright RF (1998) Predicting the effects of atmospheric nitrogen deposition in conifer stands: evidence from the NITREX ecosystem-scale experiments. Ecosystems 1:352–360

Erisman JW, Beier C, Draaijers G, Lindberg S (1994) Review of deposition monitoring methods. Tellus Series B-Chem Phys Meteorol 46:79–93

Ferm M, Hultberg H (1999) Dry deposition and internal circulation of nitrogen, sulphur and base cations to a coniferous forest. Atmos Environ 33:4421–4430

Fowler D, Pilegaard K, Sutton MA, Ambus P, Raivonen M, Duyzer J et al (2009) Atmospheric composition change: ecosystems-atmosphere interactions. Atmos Environ 43: 5193–5267

Friedland AJ, Miller EK, Battles JJ, Thorne JF (1991) Nitrogen deposition, distribution and cycling in a subalpine spruce-fir forest in the Adirondecks, New York, USA. Biogeochemistry 14:31–55

Fritz O, Niklasson M, Churski M (2008) Tree age is a key factor for the conservation of epiphytic lichens and bryophytes in beech forests. App Veg Sci 12:93–106

Garland JA (2001) On the size dependence of particle deposition. Water Air Soil Pollut Focus 1:323–332

Gomez-Guerrero A, Chavez-Aguilar G, Fenn ME, Vargas-Hernandez J, Horwath WR (2008) Foliar nitrogen uptake in simulated wet deposition in *Abies religiosa*. Interciencia 33:429–434

Graf Pannatier E, Thimonier A, Schmitt M, Walthert L, Waldner P (2011) A decade of monitoring at Swiss Long-Term Forest Ecosystem Research (LWF) sites: can we observe trends in atmospheric acid deposition and in soil solution acidity? Environ Monitor Asses 174:3–30

Harrison AF, Schulze E-D, Gebauer G, Bruckner G (2000) Canopy uptake and utilization of atmospheric pollutant nitrogen. Pages 171-188 in Schulze E-D, ed. Carbon and Nitrogen Cycling in European Forest Ecosystems, vol. 142 Ecological Studies

Horvath L(2004) Determination of the nitrogen compound balance between the atmosphere and a Norway spruce forest ecosystem. Nutrient Cycling in Agroecosystems 70: 143-146

Houle D, Ouimet R, Paquin R, Laflamme J (1999) Interactions of atmospheric deposition with a mixed hardwood and a coniferous forest canopy at the Lake Clair Watershed (Duchesnay, Quebec). Can J For Res 29:1944–1957

Ignatova N, Dambrine E (2000) Canopy uptake of N deposition in spruce (*Picea abies* L Karst) stands. Ann For Sci 57: 113–120

Johansson O, Nordin A, Olofsson J, Palmqvist K (2010) Responses of epiphytic lichens to an experimental whole-tree nitrogen-deposition gradient. New Phytol 188:1075–1084

Kendall M (1975) Multivariate analysis. Charles Griffin & Company, London

Lang GE, Reiners WA, Heier RK (1976) Potential alteration of precipitation chemistry by epiphytic lichens. Oecologia 25:229–241

Lindberg SE, Lovett GM, Richter DD, Johnson DW (1986) Atmospheric deposition and canopy interactions of major ions in a forest. Science 231:141–145

Lovett GM, Nolan SS, Driscoll CT, Fahey TJ (1996) Factors regulating throughfall flux in a New Hampshire forested landscape. Can J For Res 26:2134–2144

Neary AJ, Gizyn WI (1994) Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario. Can J For Res 24:1089–1100

Neirynck J, Janssens IA, Roskams P, Quataert P, Verschelde P, Ceulemans R (2008) Nitrogen biogeochemistry of a mature Scots pine forest subject to high nitrogen loads. Biogeochemistry 91:201–222

Parker GG (1983) Throughfall and stemflow in the forest nutrient cycle. Adv Ecol Res 13:57–133

Ranius T, Johansson P, Berg N, Niklasson M (2008) The influence of tree age and microhabitat quality on the occurrence of crustose lichens associated with old oaks. J Veg Sci 19: 653–662

Reiners WA, Olson RK (1984) Effects of canopy components on throughfall chemistry - an experimental-analysis. Oecologia 63:320–330

Rothe A, Huber C, Kreutzer K, Weis W (2002) Deposition and soil leaching in stands of Norway spruce and European Beech: results from the Höglwald research in comparison with other European case studies. Plant Soil 240:33–45

Ruijgrok W, Davidson CI, Nicholson KW (1995) Dry deposition of particles. Implications and recommendations for mapping of deposition over Europe. Tellus 47B:587–601

Ruijgrok W, Tieben H, Eisinga P (1997) The dry deposition of particles to a forest canopy: a comparison of model and experimental results. Atmos Environ 31:399–415

Sievering H, Tomaszewski T, Torizzo J (2007) Canopy uptake of atmospheric N deposition at a conifer forest: part I - Canopy N budget, photosynthetic efficiency and net ecosystem exchange. Tellus B59:483–492

Slinn WGN (1982) Predictions for particle deposition to vegetative canopies. Atmos Environ 16:1785–1794

Staelens J, De Schrijver A, Van Avermaet P, Genouw G, Verhoest N (2005) A comparison of bulk and wet-only deposition at two adjacent sites in Melle (Belgium). Atmos Environ 39:7–15

Staelens J, De Schrijver A, Verheyen K (2007) Seasonal variation in throughfall and stemflow chemistry beneath a European beech (*Fagus sylvatica*) tree in relation to canopy phenology. Can J For Res 37:1359–1372

Staelens J, Houle D, De Schrijver A, Neirynck J, Verheyen K (2008) Calculating dry deposition and canopy exchange with the canopy budget model: review of assumptions and application to two deciduous forests. Water Air Soil Pollut 191:149–169

Staelens J, Neirynck J, Genouw G, Roskams P (2009) Dynamic modelling of target loads of acidifying deposition for forest ecosystems in Flanders (Belgium). Iforest-Biogeosci For 2:30–33

R Development Core Team (2011) R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria (www.R-project.org)

UBA (2004) Mapping manual 2004. Manual on methodologies and criteria for modelling and mapping critical loads & levels and air pollution effects, risks and trends. Source: www.icpmapping.org

Ukonmaanaho L, Starr M (2002) Major nutrients and acidity: budgets and trends at four remote boreal stands in Finland during the 1990s. Sci Total Environ 297:21–41

Vanguelova EI, Benham S, Pitman R, Moffat AJ, Broadmeadow M, Nisbet T, Durrant D, Barsoum N, Wilkinson M, Bochereau F, Hutchings T, Broadmeadow S, Crow P, Taylor P, Houston TD (2010) Chemical fluxes in time through forest ecosystems in the UK - Soil response to pollution recovery. Environ Pollut 158:1857–1869

Wanek W, Hinko-Najera Umana N (2010) Large canopy exchange fluxes of inorganic and organic nitrogen and preferential retention of nitrogen by epiphytes in a tropical lowland rainforest. Ecosystems 13:367–381

Wilson EJ, Tiley C (1998) Foliar uptake of wet-deposited nitrogen by Norway spruce: an experiment using N-15. Atmos Environ 32:513–518

Zhang G, Zeng GM, Jiang YM, Du CY, Huang GH, Zeng M, Su XK, Xiang RJ (2006) Exchange of proton and major elements in two-layer canopies under acid rain in a subtropical evergreen forest in central-south China. J Integ Plant Biol 48:1154–1162