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Organic and inorganic nitrogen in precipitation and in forest throughfall at the Bílý Kříž site (Beskydy Mts., Czech Republic)

I. Drápelová

Institute of Forest Ecology, Faculty of Forestry and Wood Technology, Mendel University in Brno, Brno, Czech Republic

ABSTRACT: Organic nitrogen is an important but yet not very well explored component of nitrogen deposition. In this study concentrations and fluxes of organic and inorganic nitrogen in bulk precipitation in an open field (BOF) and in throughfall (THR) were evaluated at the Bílý Kříž experimental site (Moravian-Silesian Beskydy Mts., Czech Republic, 908 m a.s.l.) with a young Norway spruce stand. The results of a two-year study (2008 and 2009) were compared with the results obtained during the same time period on forest plots included in ICP Forests Programme in the Czech Republic. Total nitrogen deposition in BOF at the Bílý Kříž site amounted to about 918 $mg \cdot m^{-2} \cdot a^{-1}$, the contribution of organic nitrogen was about 8%. Total nitrogen flux with THR at Bílý Kříž was about 1,305 $mg \cdot m^{-2} \cdot a^{-1}$ during the studied years and organic N accounted for 12% of this amount. The ranges of the two-year average values found for total nitrogen flux on ICP Forests plots throughout the Czech Republic were as follows: 759–1,857 $mg\ N \cdot m^{-2} \cdot a^{-1}$ with 7–38% contribution of organic N in BOF and 928–3,816 $mg\ N \cdot m^{-2} \cdot a^{-1}$ with 7–20% contribution of organic N in THR. The share of organic nitrogen in THR nitrogen fluxes at Bílý Kříž proved clear seasonality with maxima in July. A highly significant correlation between $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ concentrations in BOF suggested the common anthropogenic source of these substances at the Bílý Kříž site. No significant correlation was found either between organic N and $N\text{-}NH_4^+$ or between organic N and $N\text{-}NO_3^-$ concentrations in BOF. Cumulative deposition charts showed different behaviour of particular nitrogen deposition components while passing through the canopy.

Keywords: nitrogen deposition; throughfall; dissolved organic nitrogen; DON; inorganic nitrogen; Bílý Kříž; Moravian-Silesian Beskydy Mts.

Long-term research has pointed out the increasing impact of humans on the environment and natural balance on this planet. We can expect that interactions between the nitrogen cycle, carbon cycle and climate will become an increasingly important determinant of the Earth system (Gruber, Galloway 2008). Nitrogen deposition is a part of the nitrogen global cycle which has been significantly influenced by anthropogenic inputs produced in industry, agriculture and transport (Vitousek et al. 1997; Galloway 1998). Atmospheric deposition of nitrogen and its influence on forest ecosystems have attracted attention of scientific research for a long time especially in connection with solving the problems of acid deposition (Taylor et al. 1994; Hordijk, Kroeze 1997; Schöpp et al. 2003), eutrophication of the environment (Paerl et al. 2002), nitrogen saturation of forests (Dise, Wright 1995; Aber et al. 1989, 1998, 2003; Bobbink et al. 1998; Fenn et al. 1998), ground-level ozone production (DiGiovanni, Fellin 2006) and recently also in relation to carbon sequestration (Magnani et al. 2007; de Schrijver et al. 2008; de Vries et al. 2008; Sutton et al. 2008). Interesting studies revealing the impact of various industrial, agricultural and other human activities on nitrogen deposition and fluxes mapped

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the situation both on the global scale (Holland et al. 1999; Galloway et al. 2003, 2004; Glibert et al. 2006) and in the Czech Republic (Kopáček et al. 2001; Kopáček, Veselý 2005).

Until recently most papers addressing the nitrogen cycle and nitrogen deposition focused on inorganic nitrogen forms in deposition fluxes and did not take into consideration the organic component of nitrogen deposition. This holds true also of the studies mentioned above. Not even did Krupa's comprehensive review, published in 2002, cover the analysis of organic nitrogen in precipitation (describing only determination of total amines) in spite of the fact that nitrogen incorporated into organic compounds can contribute to a relatively large portion of the total nitrogen deposition budget (Neff et al. 2002; Cornell et al. 2003). One of the causes of a difference between well mapped inorganic nitrogen deposition fluxes and only fragmentary information on organic nitrogen deposition could be the fact that organic nitrogen in water samples cannot be measured directly. It is neither a single compound nor a single class of compounds but it includes a complex mixture of compounds of various origin: natural (amino acids, urea, amines – Cornell et al. [2003], macromolecular humic-like substances – Kieber et al. [2005]), anthropogenic (nitrophenols – [Lüttke et al. 1997]) or mixed origin (organic nitrates are formed as a result of photochemical reactions of NO_x with volatile anthropogenic or biogenic organic carbon compounds – Cornell et al. [2003], Altieri et al. [2009]). The only way to determine the amount of organic nitrogen in an aqueous sample is to measure separately amounts of nitrate, ammonium and total nitrogen and to calculate the amount of organic nitrogen as the difference between the total nitrogen and inorganic nitrogen concentrations in the sample. The subtraction of independently measured concentrations results in the accumulation of analytical variance in organic nitrogen determination as arises from the error propagation law (Vandebruwane et al. 2007). The precision of the dissolved organic nitrogen (DON) measurement also depends on the inorganic nitrogen concentrations being lower when samples with high inorganic nitrogen concentrations are processed (Hansell 1993). The tendency for organic nitrogen is to be underestimated because the methods used for total dissolved nitrogen determination: UV photolysis, wet chemical persulphate oxidation, high-temperature catalytic combustion (to name the three most common techniques used for the conversion of organic nitrogen compounds into quantifiable N forms) are not able to transform all nitrogen in the sample to the analyte measured (Bronk et al. 2000). As a re-

Table 1. Characteristics of the experimental site at Bílý Kříž (bold) and characteristics of the sites included in deposition monitoring during 2008 and 2009 within the framework of ICP Forests programme in the Czech Republic.

Locality	International code within ICP Forests	Latitude	Longitude	Altitude (m)	Number of trees ha^{-1}	Dominant storey established	The main species
Bílý Kříž, FD plot		**49'30° N**	**18'32° E**	**908**	**1,430 in 2008**	**1981**	***Picea abies***
Benešovice	CZ2061	49'44° N	12'51° E	385	884 in 2002	1918	*Pinus silvestris*
Březka	CZ2102	49'54° N	14'33° E	435	436 in 2000	1952	*Quercus robur*
Dolní Mísečky	CZ2015	50'44° N	15'32° E	940	224 in 2002	1787	*Fagus sylvatica*
Horní Lazy	CZ521	50'02° N	12'37° E	875	376 in 2004	1887	*Picea abies*
Jizerka	CZ2211	49' 02° N	14'59° E	910	780 in 2005	1948	*Picea abies*
Klepačka	CZ2401	49'27° N	18'24° E	650	444 in 2005	1925	*Picea abies*
Lásenice	CZ2163	49'01° N	14'58° E	592	484 in 2001	1914	*Picea abies*
Luisino údolí	CZ2251	50'49° N	15'20° E	940	796 in 2004	1913	*Picea abies*
Medlovice	CZ2361	49'04° N	17'17° E	350	388 in 2002	1900	*Quercus petrae*, *Fagus sylvatica*
Nová Brtnice	CZ561	49'15° N	15'40° E	640	548 in 2000	1902	*Picea abies*
Všeteč	CZ2103	49'14° N	14 '8° E	615	404 in 2001	1894	*Fagus sylvatica*
Želivka	CZ2161	49'41° N	15'14° E	440	824 in 2000	1902	*Picea abies*

Data on ICP Forests plots were retrieved from the Czech Hydrometeorological Institute web site (www.chmi.cz) or taken from Boháčová et al. (2010)

sult we can find papers reporting negative organic nitrogen concentrations (physically impossible) in up to 15% of the measurements (Solinger et al. 2001; Siemens, Kaupenjohann 2002).

In the last decade the number of research papers addressing the evaluation of organic nitrogen in precipitation has increased and the mosaic of our knowledge is being continuously supplemented (Neff et al. 2002; Cornell et al. 2003; Cape et al. 2004; Zhang et al. 2008; Bencs et al. 2009; Benitez et al. 2009, 2010; Pelster et al. 2009; Sleutel et al. 2009; Violaki et al. 2010).

The aims of this study are:

– to evaluate the contribution of organic nitrogen to nitrogen fluxes with bulk precipitation in an open field and with throughfall and to describe relationships among the components of nitrogen deposition at the mountainous study site Bílý Kříž in the Beskydy Mts. (Czech Republic),

– to compare the results acquired at Bílý Kříž site with available data measured on the Level II plots (i.e. intensively monitored plots) included in the network of ICP Forests in the Czech Republic.

MATERIAL AND METHODS

The area of interest is situated in the top part of the Moravian-Silesian Beskydy Mts. in the Czech Republic at an altitude of 908 m a.s.l. The geographical coordinates of the site are 49°30'N latitude and 18°32'E longitude (Table 1). As for the climate, the region is moderately cold, wet and rich in precipitation. Mean air temperature was 5.5°C, mean annual precipitation was 1,300 mm, the number of days with precipitation above 1 mm was 140–160, and the length of growing season was 120–140 days during the period of 1993–2003 (Janouš et al. 2004). Snow precipitation accounts for 16–24% of the annual precipitation amount (Červený et al. 1984). Mean relative air humidity is about 80%. Although the precipitation totals are rather high, occasional droughts can occur in the area (Hadaš 2007). The mild NW wind blowing mainly in January and February brings the air pollutants from the Ostrava industrial agglomeration. The open plot meadow with the bulk precipitation collector was surrounded by spruce stands (*Picea abies* [L.] Karst.). The monoculture was set out in 1981 using 4-year-old plants and the average height of trees was about 12.5 m and stand density 1,428 trees·ha^{-1} in 2008 (Marková et al. 2010), the stand age in 2008 was 31 years. A more detailed description of the climatic conditions at the experimental plot was given by Drápelová et al. (2010).

Bulk precipitation and throughfall samplings were carried out during 2008 and 2009. The sampling period for the first year covered the period from 18. 12. 2007 to 15. 12. 2008, the sampling period for the second year covered the period from 16. 12. 2008 till 13. 12. 2009. Permanently open polyethylene sampling vessels of an area of 335 cm^2 were used for throughfall sampling in the spruce stand and atmospheric precipitation in the open area (Block, Bartels 1985; Niehus, Bruggemann 1995). The vessels were inserted into thick-walled plastic pipes in order to shield the samples from solar radiation and to hold the funnels approximately 1 m above ground level. There were 7 collectors randomly distributed in the spruce stand. During the winter the number of throughfall collectors was reduced to 5. Bulk atmospheric precipitation was sampled with one collector installed in the nearby open area. Samples were taken once a month in the winter season and in 14-day intervals in the other seasons. The samples were transferred to the laboratory and prepared for the analyses usually the next day after sampling. During winters, when samples were frozen, it was sometimes necessary to wait one day for their melting. One proportionally pooled sample was prepared at each sampling event from waters collected in all installed throughfall samplers.

Table 2. List of methods and instruments used for the analysis of precipitation and throughfall water samples

Analyte	Analytical method	Instrumentation
NH_4^+	spectrophotometry at the wave-length of 650 nm or flow injection analysis with diffusion chamber	UV/VIS spectrophotometer or flow injection analyzer FIAlab 2500
NO_3^-	high performance ion exchange liquid chromatography with gradient elution	chromatograph DX-600 DIONEX with gradient pump GP50
TDN	high temperature catalytic combustion with chemiluminescence detection	total N analyzer SHIMADZU TOC-VCSH

TDN – total dissolved nitrogen

Table 3. Mean annual concentrations (mg·l^{-1}) and two-year average of THR/BOF concentration ratios for various forms of nitrogen at the Bílý Kříž experimental site (bold) and at experimental sites included in deposition monitoring during 2008 and 2009 in the framework of ICP Forests programme in the Czech Republic

Locality	Year	BOF concentrations (mg·l^{-1})				THR concentrations (mg·l^{-1})				THR/BOF concentration ratio			
		N-NH$_4^+$	N-NO$_3^-$	TDN	DON	N-NH$_4^+$	N-NO$_3^-$	TDN	DON	N-NH$_4^+$	N-NO$_3^-$	TDN	DON
Benešovice	2008	0.6	0.57	1.30	0.13	1.10	1.23	2.57	0.24	1.92	2.22	2.08	2.48
	2009	0.72	0.57	1.36	0.07	1.45	1.31	2.97	0.21				
Bílý Kříž	**2008**	**0.5**	**0.36**	**0.91**	**0.05**	**0.67**	**0.74**	**1.59**	**0.19**	**1.20**	**1.94**	**1.57**	**2.84**
	2009	**0.52**	**0.33**	**0.96**	**0.1**	**0.55**	**0.62**	**1.34**	**0.17**				
Březka	2008	0.69	0.55	1.41	0.16	0.85	0.65	2.2	0.71	0.88	1.62	1.43	2.77
	2009	0.58	0.59	1.32	0.15	0.31	1.23	1.71	0.17				
Dolní Mísečky	2008	0.48	0.54	1.13	0.1	0.51	0.70	1.37	0.17	1.08	1.31	1.25	1.68
	2009	0.39	0.42	0.92	0.11	0.44	0.56	1.18	0.19				
Horní Lazy	2008	1.31	0.66	2.14	0.17	0.95	1.7	2.97	0.32	0.83	2.20	1.28	1.13
	2009	0.94	0.75	2.03	0.34	0.87	1.36	2.39	0.16				
Jizerka	2008	0.55	0.66	1.28	0.08	0.67	0.87	1.74	0.20	1.13	1.28	1.24	1.83
	2009	0.49	0.46	1.09	0.14	0.51	0.56	1.22	0.14				
Klepačka	2008	0.41	0.59	1.04	0.04	0.38	0.57	–1.18	0.23	0.97	1.04	1.11	3.29
	2009	0.35	0.5	0.95	0.1	0.36	0.55	1.03	0.12				
Lásenice	2008	1.07	0.59	1.95	0.29	1.18	1.58	3.06	0.30	1.16	2.55	1.56	0.82
	2009	0.93	0.74	2.01	0.34	1.14	1.79	3.13	0.20				
Luisino údolí	2008					1.42	1.69	3.23	0.11				
	2009					1.30	1.02	2.61	0.30				
Medlovice	2008	0.54	0.45	1.95	0.96	1.53	1.12	2.97	0.32	1.95	2.53	1.56	0.68
	2009	0.52	0.5	1.37	0.35	0.54	1.29	2.18	0.35				
Nová Brtnice	2008	0.67	0.66	1.55	0.22	3.87	2.41	7.1	0.82	6.45	3.61	5.03	4.38
	2009	0.61	0.5	1.23	0.12	4.37	1.79	6.75	0.59				
Všeteč	2008	0.63	0.57	1.38	0.18	1.56	1.48	3.41	0.37	2.14	2.98	2.5	2.19
	2009	0.49	0.44	1.03	0.11	0.87	1.47	2.6	0.25				
Želivka	2008	1.08	0.74	1.98	0.16	1.80	1.75	3.94	0.40	1.51	2.01	1.82	2.86

BOF – bulk precipitation in open field, THR – throughfall, TDN – total dissolved nitrogen, DON – dissolved organic nitrogen
Data on ICP Forests plots were taken from Boháčová et al. (2010).

Samples of water were filtered through a 0.45 µm membrane filter prior to analysis.

Determination of N-NH$_4^+$ was done immediately in freshly prepared samples; subsamples for total N determination were stored in a refrigerator and analyzed within a week, the aliquots for N-NO$_3^-$ determination were frozen and kept in a freezer until analyzed (usually within a month after the sample preparation). The methods used for the determination of total dissolved nitrogen (TDN), NO$_3^-$ and NH$_4^+$ are listed in Table 2.

The mean amount of throughfall water was calculated for every particular sampling date as the arithmetic average of water amounts captured in parallel collectors on the plot. Mean annual concentrations for TDN, N-NO$_3^-$ and N-NH$_4^+$ in bulk precipitation in an open field (BOF) and in throughfall (THR) were calculated as weighted means of TDN, N-NO$_3^-$ and N-NH$_4^+$ concentrations, respectively, measured in particular sampling events during the year on the particular plot (precipitation amounts in particular sampling events were used

Table 4. Results of correlation analysis among concentrations of ammonium, nitrate and organic nitrogen in bulk precipitation in open field precipitation and in throughfall samples taken during 2008 and 2009 at the Bílý Kříž experimental site

	BOF N-NO_3^-	BOF N-NH_4^+	BOF DON	THR N-NO_3^-	THR N-NH_4^+	THR DON
BOF N-NO_3^-	1.0000	0.5518**	0.2752	0.6270**	0.4602**	0.3054
BOF N-NH_4^+	0.5518**	1.0000	0.2816	0.2429	0.5601**	0.6368**
BOF DON	0.2752	0.2816	1.0000	0.4461**	0.3136*	0.5064**
THR N-NO_3^-	0.6270**	0.2429	0.4461**	1.0000	0.7233**	0.3206*
THR N-NH_4^+	0.4602**	0.5601**	0.3136*	0.7233**	1.0000	0.4958**
THR DON	0.3054	0.6368**	0.5064**	0.3206*	0.4958**	1.0000

BOF – bulk precipitation in an open field, THR – throughfall, DON – dissolved organic nitrogen,*Spearman correlation coefficient indicates statistically significant correlations between corresponding variables ($P < 0.05$), **Spearman correlation coefficient indicates statistically significant correlations between corresponding variables ($P < 0.01$)

as weights). DON concentrations were calculated by subtraction of N-NO_3^- and N-NH_4^+ concentrations from TDN concentration. The fluxes of TDN, DON, N-NO_3^- and N-NH_4^+ in mg·m^{-2} in bulk precipitation in an open field and in throughfall for each sampling event were calculated as a product of the amount of water (in l·m^{-2}) and the relevant element concentration (in mg·l^{-1}) and summed for each single year and plot to give the annual flux (in mg·m^{-2}·a^{-1}). Statistical software STATISTICA 9.0 (StatSoft 2008) was used for result evaluation.

Data on deposition and nitrogen species concentrations in precipitation and throughfall on ICP Forests plots were taken from Boháčová et al. (2010), precipitation and throughfall amounts were taken from the web pages of the Czech Hydrometeorological Institute (www.chmi.cz). Characteristics of these plots (summarized in Table 1) were retrieved from the web site of the Czech Hydrometeorological Institute or taken from Boháčová et al. (2010). Measuring of deposition was done by standard methods on ICP Forests plots as described in Boháčová et al. (2010) and in the ICP Forests Manual (www.icp-forests.org).

RESULTS

Water fluxes at the Bílý Kříž site

Annual precipitation totals at the Bílý Kříž site were 1,033 and 934 mm for the years 2008 and 2009, respectively. These values were below the long-term average (which was 1,318 mm for the period of 1998–2009, according to Marková et al. (2011)). Throughfall annual totals amounted to 895 mm and 884 mm and interception values were about 13% and 5% in the two years, respectively.

Concentration of nitrogen in precipitation and throughfall water

Mean annual open field and throughfall concentrations of N-NH_4^+, N-NO_3^- , DON and TDN on the Bílý Kříž experimental plot and on several ICP Forests plots throughout the Czech Republic are presented in Table 3. As can be seen, mean annual total nitrogen concentrations were always higher under the canopy than in BOF. This holds true with one exception (see data for Klepačka) for nitrate nitrogen, with several exceptions (see data for Horní Lazy, Jizerka, Lásenice, Medlovice sites) for organic nitro-

Table 5. *P*-values as results of the Wilcoxon nonparametric paired test used to assess differences between concentrations of nitrogen species concentrations in bulk precipitation in an open field and in throughfall for 42 sampling events during 2008 and 2009 at the Bílý Kříž site, Beskydy Mts. Highly significant differences were found in all cases ($P < 0.01$)

Concentrations compared	*P*-value
BOF TDN & THR TDN	0.000005
BOF N-NH_4^+ & THR N-NH_4^+	0.006
BOF N-NO_3^- & THR N-NO_3^-	0.000008
BOF DON & THR DON	0.00001

BOF – bulk precipitation in an open field, THR – throughfall, DON – dissolved organic nitrogen

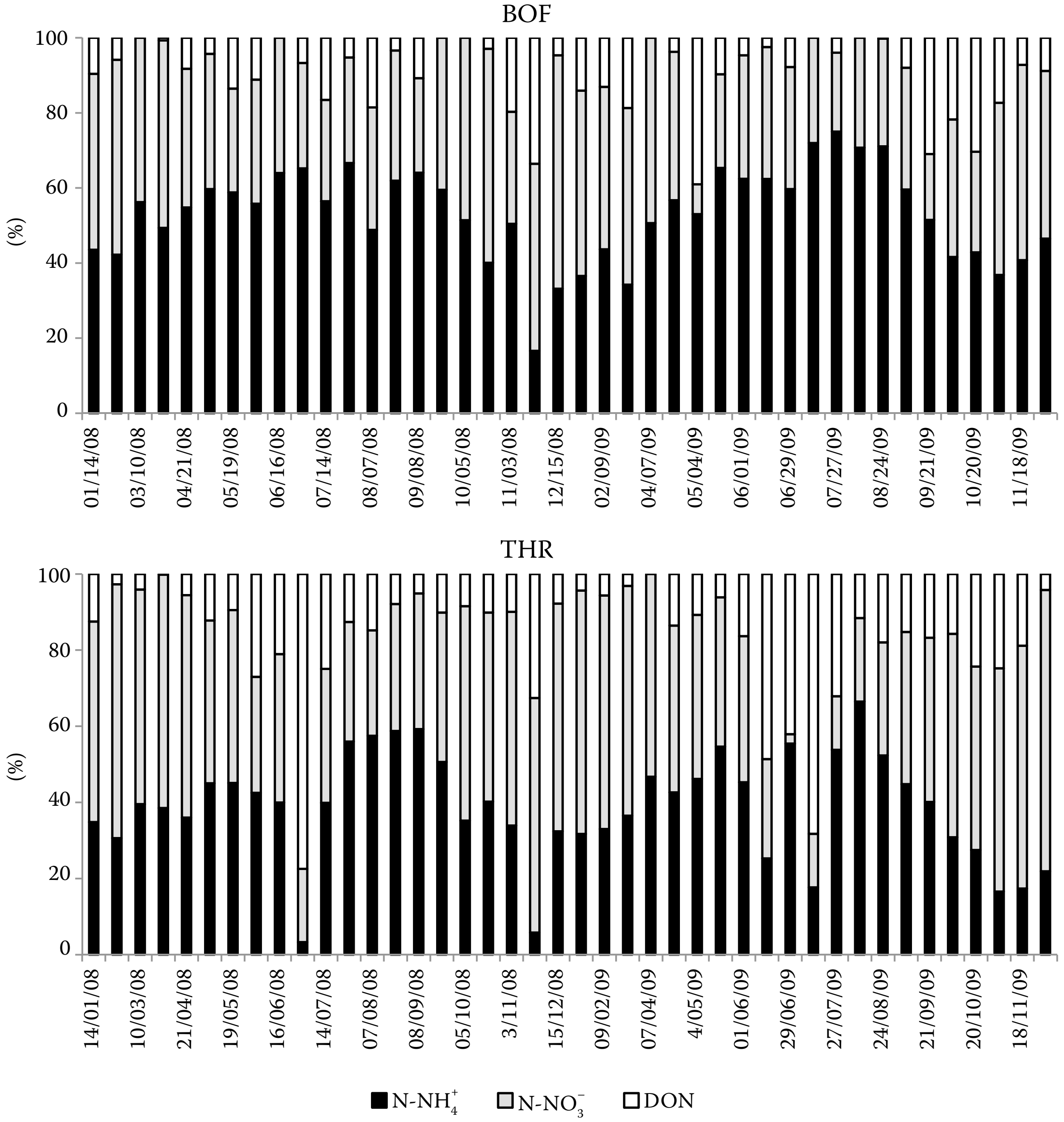

Fig. 1. The share of various nitrogen forms in the total nitrogen concentration in bulk precipitation in an open field (BOF) and in throughfall (THR) at the Bílý Kříž site for particular sampling events during 2008 and 2009. Negative dissolved organic nitrogen (DON) concentrations were substituted by zero value

gen, and with only two exceptions (at Březka, Horní Lazy and Klepačka) also for ammonium nitrogen.

During the two sampling seasons (2008 and 2009) 42 samplings were performed at the Bílý Kříž site. Nonnormal distribution of concentrations was observed for all parameters (N-NH$_4^+$, N-NO$_3^-$, TDN, DON) on either of the plots (open field and forest stand) as was confirmed by the Shapiro-Wilk test (with $P < 0.001$ in all cases). The highest variability was observed in TDN concentrations in throughfall. In BOF in seven cases (16.7%) negative concentrations within the range between –0.064 and –0.015 mg DON per litre were recorded, the highest DON concentration in BOF was 1.6 mg·l^{-1}. In throughfall the negative concentration of DON was calculated for one sampling event only (i.e. 2% of all cases), the highest DON concentration in THR was 2.9 mg·l^{-1}.

Correlations between the concentrations of various components of nitrogen deposition were investigated. Results of this statistical evaluation are described in Table 4. In the open field precipitation samples only concentrations of N-NH$_4^+$ and N-NO$_3^-$ were significantly correlated, in the throughfall samples concentrations of all forms of nitrogen were mutually correlated. Statistically significant correlations were also found between

$N\text{-}NO_3^-$ in BOF and THR, between $N\text{-}NH_4^+$ in BOF and THR, between organic nitrogen in BOF and THR. $N\text{-}NO_3^-$ concentrations in THR were correlated also with BOF concentration of DON. $N\text{-}NH_4^+$ concentrations in THR were correlated with both BOF $N\text{-}NO_3^-$ and DON concentrations. DON concentrations in throughfall seem to be influenced by $N\text{-}NH_4^+$ concentrations in BOF but not by $N\text{-}NO_3^-$ concentrations in BOF.

The Wilcoxon nonparametric paired test was used to assess differences between the concentrations of individual nitrogen forms in BOF and THR for all sampling events during 2008 and 2009. Results summarized in Table 5 confirm highly significant statistical differences in concentrations between the BOF and THR for all nitrogen forms.

The share of nitrogen forms in the total nitrogen concentration for individual sampling events in bulk precipitation in an open field and in throughfall is depicted in Fig. 1. Seasonal character could be observed in the relative share of $N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and DON in total nitrogen deposition.

In BOF the highest share of $N\text{-}NH_4^+$ was observed in June–August, the lowest share of $N\text{-}NH_4^+$ during winter months. The share of $N\text{-}NO_3^-$ in the total nitrogen concentration assumed the highest values during the winter months. No clear seasonal trend was observed for DON relative shares.

In throughfall the highest share of $N\text{-}NH_4^+$ was observed in May and August sampling events. The share of $N\text{-}NO_3^-$ in the total nitrogen concentration assumed the highest values during the winter months again. The highest share of DON in total N concentration and fluxes for throughfall samples was observed during July sampling events.

The concentration enrichment factor for $N\text{-}NH_4^+$ at the Bílý Kříž site was lower than the enrichment factor for $N\text{-}NO_3^-$ and this was lower than the enrichment factor for DON (the last four columns in Table 3). Similar relationships among the enrichment factors for the three nitrogen forms were found also at Benešovice, Březka, Dolní Mísečky, Jizerka and Želivka ICP Forests sites (Table 3).

Deposition fluxes of nitrogen with bulk precipitation in open field and with throughfall

The mean annual total nitrogen deposition with BOF precipitation at the Bílý Kříž site for the two-year period was 918 $mg \cdot m^{-2} \cdot a^{-1}$. About 74 $mg \cdot m^{-2} \cdot a^{-1}$ of this amount was deposited as DON (i.e. 8.1% of the total N deposited), about 501 $mg \cdot m^{-2} \cdot a^{-1}$ as $N\text{-}NH_4^+$ (54.6%) and about 344 $mg \cdot m^{-2} \cdot a^{-1}$ as $N\text{-}NO_3^-$ (37.5%). After passage through the canopy the nitrogen flux increased reaching the two-year annual mean of about 1,305 mg $N \cdot m^{-2} \cdot a^{-1}$. About 160 mg $N \cdot m^{-2} \cdot a^{-1}$ was deposited as DON, 543 mg $N \cdot m^{-2} \cdot a^{-1}$ as $N\text{-}NH_4^+$ and 603 mg $N \cdot m^{-2} \cdot a^{-1}$ as $NN\text{-}NO_3^-$, accounting for 12.3, 41.6 and 46.2% of the total nitrogen deposition, respectively. The share of DON and $N\text{-}NO_3^-$ increased and the share of $N\text{-}NH_4^+$ decreased after passage through the canopy. A comparison of the fluxes of various forms of nitrogen is apparent also from the graphs (Fig. 2) where cumulative amounts of deposited nitrogen are depicted. In the case of $N\text{-}NH_4^+$ the fluxes in an open field and under the canopy were almost the same while cumulative fluxes of $N\text{-}NO_3^-$ were always higher in throughfall. Curves of cumulative fluxes of DON in BOF and THR were copying each other from the beginning of the particular year to June and then, from July on, the difference between BOF and THR increased in favour of throughfall cumulative deposition. The deposition fluxes of various forms of nitrogen at the Bílý Kříž site and on ICP Forests plots throughout the Czech Republic are summarized in Table 6.

DISCUSSION

Water fluxes

Precipitation and throughfall totals measured at the Bílý Kříž site during 2008 and 2009 can be compared with the values measured on ICP Forests plots throughout the Czech Republic (Table 6). At most sites higher totals were found in 2009, only at Jizerka and Dolní Mísečky the totals were higher in 2008 as was also the case of the Bílý Kříž plot. It is noticeable that all these sites lie at higher altitudes (Table 1). Our precipitation total values for 2008 and 2009 correspond well with the totals of 1,149 mm and 930 mm measured in 2008 and 2009, respectively (Marková et al. 2011) at the climatological station situated on the open plot at the Bílý Kříž site within 5 m from our sampler. The fact that periods of sampling at the Bílý Kříž site were slightly shifted and did not cover precisely the calendar years must be taken into consideration while comparing annual totals.

Concentrations of nitrogen in precipitation and throughfall water

Results in Table 3 show that the Bílý Kříž, Dolní Mísečky and Klepačka were the sites with the low-

Table 6. Open field and throughfall fluxes of nitrogen at the Bílý Kříž experimental site (bold) and at experimental sites included in deposition monitoring during 2008 and 2009 in the framework of ICP Forests programme in the Czech Republic

Locality	Year	Rainfall amount (mm)	Open field fluxes (mg·m^{-2})				Throughfall amount (mm)	Throughfall fluxes (mg·m^{-2})			
			N-NH_4^+	N-NO_3^-	TDN	DON		N-NH_4^+	N-NO_3^-	TDN	DON
Benešovice	2008	663	400	376	860	84	484	534	593	1,243	116
	2009	717	519	410	978	49	558	809	730	1,656	117
Bílý Kříž	**2008**	**1,033**	**518**	**375**	**944**	**51**	**895**	**598**	**659**	**1,426**	**169**
	2009	**934**	**484**	**312**	**892**	**97**	**884**	**487**	**546**	**1,183**	**151**
Březka	2008	492	341	272	693	80	390	330	253	859	276
	2009	625	363	370	824	91	583	181	716	997	100
Dolní Mísečky	2008	1,740	842	939	1,959	178	1,362	689	948	1,872	235
	2009	1,702	665	713	1,568	190	1,418	622	791	1,679	266
Horní Lazy	2008	813	1,062	536	1,740	142	714	680	1,214	2,119	225
	2009	971	915	724	1,973	334	859	748	1,172	2,054	134
Jizerka	2008	1,312	721	860	1,681	100	1,275	852	1,109	2,217	256
	2009	1,277	630	587	1,395	178	1,185	609	668	1,446	169
Klepačka	2008	1,180	479	698	1,227	50	948	357	544	1,117	216
	2009	1,287	450	641	1,223	132	950	338	525	980	117
Lásenice	2008	771	828	452	1,506	226	468	550	739	1,426	142
	2009	979	915	724	1,973	334	655	748	1,172	2,054	134
Luisino údolí	2008	1,186					1,172	1,669	1,981	3,783	133
	2009						1,473	1,911	1,503	3,849	435
Medlovice	2008	591	317	266	1,152	569	379	579	424	1,126	123
	2009	711	367	357	971	247	476	258	614	1,040	168
Nová Brtnice	2008	633	425	417	979	137	411	1,590	991	2,920	339
	2009	810	496	406	998	96	574	2,512	1,027	3,876	337
Všeteč	2008	573	359	329	792	104	395	616	584	1,346	146
	2009	778	378	339	801	84	553	481	815	1,436	140
Želivka	2008	562	607	416	1,112	89	328	590	574	1,294	130
	2009	738	519	457	1,072	96	439	416	451	1,051	184

TDN – total dissolved nitrogen, DON – dissolved organic nitrogen

Data on ICP Forests plots were taken from Boháčová et al. (2010), precipitation and throughfall amounts were found at the web site of the Czech Hydrometeorological Institute

est concentration of DON and TDN both in BOF and THR when compared with ICP Forests sites throughout the Czech Republic in 2008 and 2009. Michalzik et al. (2001) summarized the published results of DON concentrations in throughfall in a comprehensive review: the range of DON concentrations in various forest ecosystems was 0.25 to 1.11 mg N·l^{-1}. The values calculated for throughfall DON concentrations at the Bílý Kříž site in our study were lower (namely 0.19 and 0.17 mg N·l^{-1}

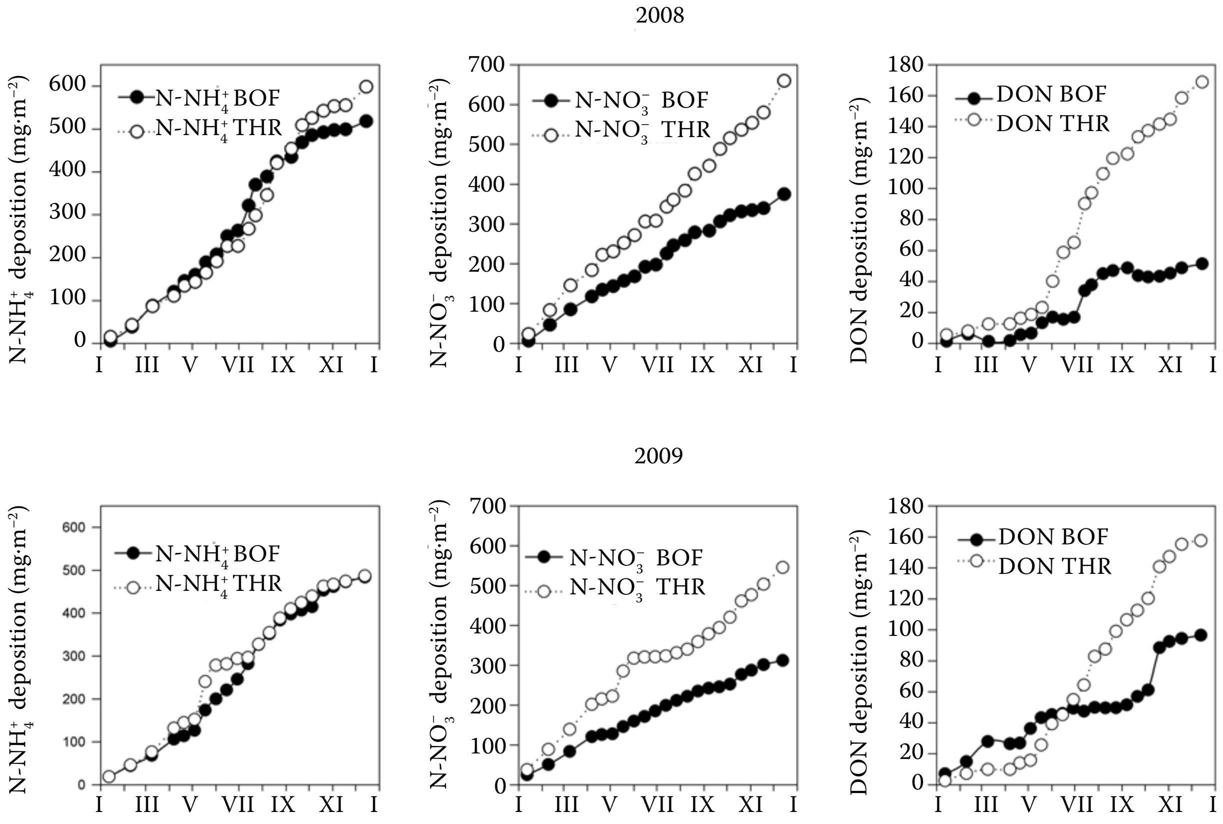

Fig. 2. Cumulative deposition of various forms of nitrogen at Bílý Kříž site in 2008 and 2009 (BOF – bulk precipitation in an open field, THR – throughfall, DON – dissolved organic nitrogen)

for the two monitored years, respectively) as well as the values measured at several ICP Forests sites (Benešovice, Dolní Mísečky, Jizerka, Klepačka, Luisino údolí). It indicates that variability in the mean annual DON concentration in THR could be even higher than that reported in the above-mentioned review. As was mentioned in the Introduction, DON concentrations could be underestimated on account of the analytical methods used for TDN determination. The negative concentrations of DON calculated for several sampling events in BOF and at one occasion in THR seem to bear evidence of this.

Concentrations of N-NO$_3^-$ and N-NH$_4^+$ in BOF were significantly correlated, which may indicate a common anthropogenic source of these compounds at the Bílý Kříž site. However, the seasonal patterns (Fig. 1) and the results of correlation analysis suggest that the sources of DON in BOF were not related to the sources of N-NO$_3^-$ and N-NH$_4^+$. On the contrary, the content of DON in THR was significantly correlated with both N-NO$_3^-$ and N-NH$_4^+$ in BOF (and of course with DON in BOF). These results are consistent with the findings of Cape et al. (2010), who showed in two large-scale field manipulation experiments in Scotland that a small fraction of dry deposited NH$_3$ was transformed to organic nitrogen in forest canopy under summer conditions and that artificial rain containing ammonium nitrate enhanced the release of organic nitrogen from the canopy. The concentration enrichment factor for total N (calculated as nitrogen concentration in THR divided by nitrogen concentration in BOF) was 1.57 (see Table 3) at the Bílý Kříž site, which is in a good agreement with the value of 1.6 derived by Parker (1983) from many reviewed studies.

Deposition fluxes of nitrogen with bulk precipitation in open field and with throughfall

The results of the nitrogen deposition speciation in the open field at the Bílý Kříž site, 8.1% DON, 54.6% N-NH$_4^+$ and 37.5% N-NO$_3^-$, and in throughfall, 12.3% DON, 41.6% N-NH$_4^+$ and 46.2% N-NO$_3^-$, are comparable with those from the Czech ICP Forests sites (comparison of two-year averages in Fig. 3) but the contribution of DON to TDN in BOF is lower than the average value reported by Cornell et al. (2003) for Europe (23 ± 8% of TDN). Nevertheless, there are studies reporting an even lower contribution of DON (e.g. Cape et al. (2004) found the share of DON

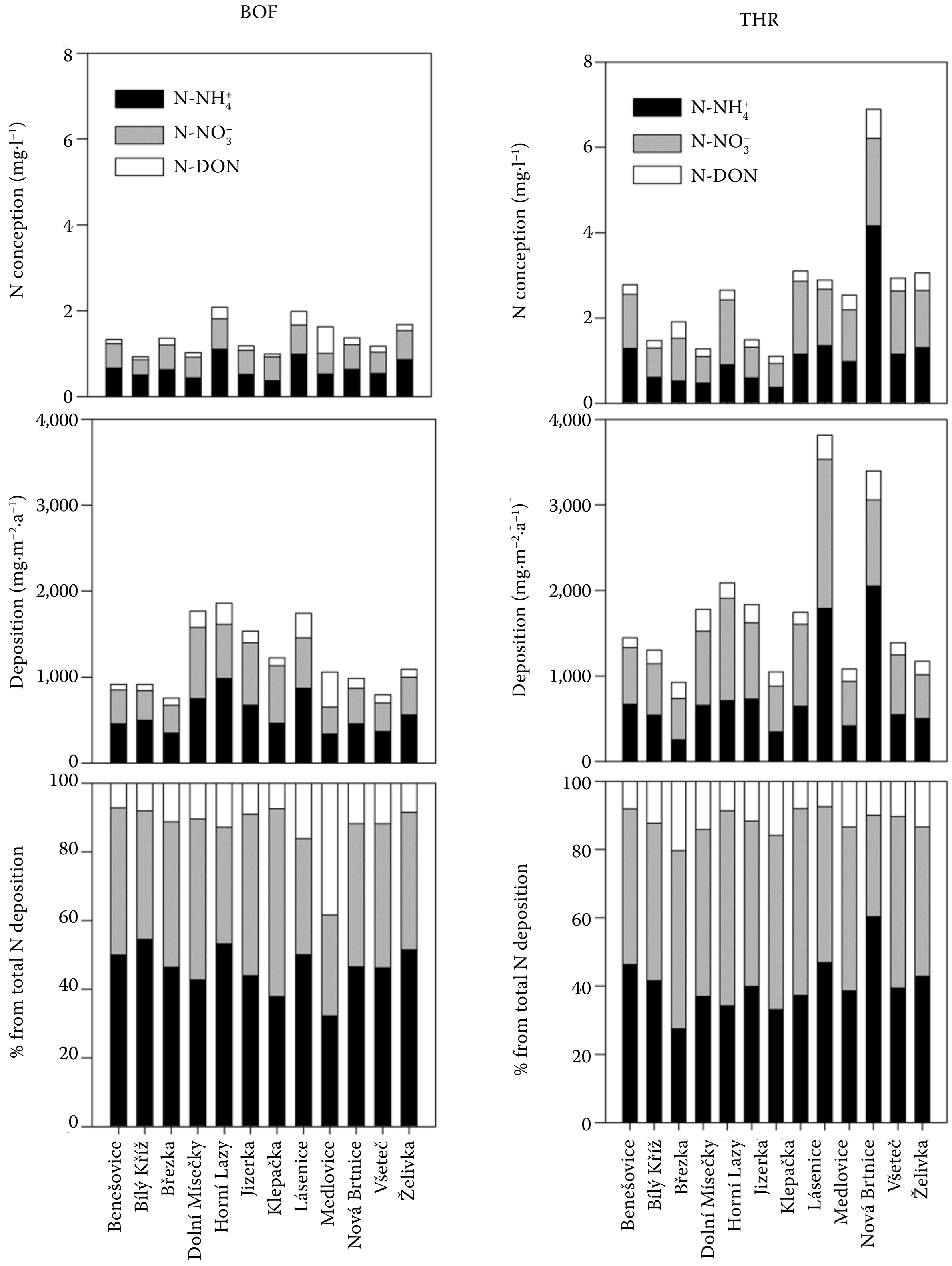

Fig. 3. Average annual concentrations and fluxes of various forms of nitrogen on the Bílý Kříž and ICP Forests plots and the share of N-NH$_4^+$, N-NO$_3^-$ and DON in the total nitrogen deposition for a two-year period (2008 and 2009)

of about 5% at Cairngorm, northeast Scotland). It indicates that the DON contribution is highly variable and site specific. In any case, it should not be omitted when nitrogen budgets are calculated.

From the DON cumulative deposition charts in Fig. 2 it can be deduced that the DON flux with throughfall is coupled with seasonal changes in the canopy. The disconnection of cumulative deposition curves for BOF and THR organic nitrogen fluxes in June coincides with the time of spruce blooming. The difference between the two curves increased from June to December in both studied years suggesting that biological processes in canopy (pollen and honeydew production, insect activities) were sources of DON in THR during that time of year.

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Corresponding author:
RNDr. Ida Drápelová, Mendel University in Brno, Faculty of Forestry and Wood Technology,
Institute of Forest Ecology, Zemědělská 3, 613 00 Brno, Czech Republic
e-mail: idad@mendelu.cz