

Total deposition of nitrogen on Swiss long-term forest ecosystem research (LWF) plots: comparison of the throughfall and the inferential method

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Abstract

The total deposition of nitrogen was estimated at 10 plots in the Swiss Long-Term Forest Ecosystem Research Programme for 1 year (1999/2000) using two methods: (1) the throughfall method, using bulk precipitation and throughfall measurements as input data for the canopy budget model; and (2) the inferential method, based on measurements of ammonia and nitrogen dioxide with passive samplers and deposition velocities taken from literature. The inferential method was coupled with a regression model deriving the other terms of the total deposition of nitrogen (wet deposition, dry deposition of nitric acid and dry deposition of particulate nitrogen) from measurements of the bulk deposition of nitrogen. The two methods gave estimates of the total deposition that correlated significantly with each other, in the range of 5–38 kg ha⁻¹ a⁻¹, but the inferential method tended to yield higher estimates than those obtained with the throughfall method (median difference +2.4 kg ha⁻¹ a⁻¹). In view of the overall agreement of the two methods, the use of passive samplers in the open, coupled with the measurement of bulk deposition, appears, under certain conditions, to be an interesting alternative to the throughfall method.

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1. Introduction

Quantifying nitrogen deposition has become a key issue in the long-term monitoring programmes that investigate the impact of air pollution and other environmental factors on forest ecosystems. Such programmes include the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (de Vries et al., 2003), which involves measuring nitrogen deposition at more

than 500 plots in Europe. In Switzerland, one of the 30 countries participating in ICP Forests, nitrogen deposition is being or has been assessed as part of the Swiss Long-term Forest Ecosystem Research programme (LWF) at 14 out of 17 plots (Cherubini and Innes, 2000).

While the wet deposition of nitrogen is relatively straightforward to measure, it is much more difficult to determine the dry deposition of nitrogen (aerosols and gases), because this measurement greatly depends on the properties and the structure of the receptor surface. Among the three main categories of methods available (Lovett, 1994), the micrometeorological methods (e.g. eddy correlation and gradient techniques) are usually

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not appropriate for long-term monitoring programmes as they require highly trained personnel, expensive instrumentation and a uniform area. Where long-term measurements are required, the other two types of methods, the inferential method and the surface analysis methods, are often used.

In the inferential method, the dry deposition flux is derived from measurements of atmospheric concentrations and parameterization of the rate of transfer from the atmosphere to the surface, which is usually expressed as a deposition velocity. Deposition velocities have been determined for several forest stands using, e.g. the micrometeorological method or by parameterizing dry deposition models (Wesely and Hicks, 2000).

Among the surface analysis methods, where the subject of analysis is the receptor surface rather than the air above it, throughfall sampling is widely used. The limitation of the throughfall method is that the throughfall flux of nitrogen is not the sum of the wet and dry deposition of nitrogen, as part of the nitrogen deposited is taken up by the canopy. To separate the dry deposition and the canopy exchange sources in the throughfall composition, a model, called the canopy budget model, was first developed by Ulrich (1983) and then further refined by various authors (EC-UN/ECE et al., 2001).

In this study, we estimate the total deposition of nitrogen on 10 forest permanent plots maintained within the framework of LWF. In these plots, throughfall and bulk deposition have been routinely measured for several years in order to assess atmospheric deposition with the canopy budget model (Thimonier et al., 2004). As part of a short-term project, air concentrations of NH_3 and NO_2 in the open were additionally measured for 1 year, which made it possible to estimate the dry deposition of these two compounds with the inferential method.

The canopy budget model, applied to the throughfall and bulk deposition data, usually provides reliable estimates of atmospheric deposition of sulphur or base cations. For nitrogen, however, the relative exchange efficiencies of ammonium, nitrate and proton are required, which are based on a single experiment (Van der Maas et al., 1991). They still need to be validated for species or site conditions different from those of Van der Maas and co-workers. On the other hand, the inferential method requires deposition velocities, which are not available for our sites. Therefore, to estimate the dry deposition of NH_3 and NO_2 , we applied the mean deposition velocities selected from literature (Rihm, 1996) concerning calculations of nitrogen deposition in Switzerland over a 1×1 km grid. Thus, our two methods of estimating nitrogen deposition rely on assumptions and on parameter values which have not been validated locally for our sites. However, the assumptions of the two methods are completely independent and, in this paper, we can check them roughly by comparing the two total deposition estimates.

2. Methods

2.1. Study sites

Throughfall and bulk deposition have been measured progressively on 13 LWF plots since 1994 (Thimonier et al., 2004). Measurements of NO_2 and NH_3 air concentrations in the open for 10 of these plots started in November 1999 and ended in November 2000. Measurements of both precipitation chemistry and air concentrations over 1 year are thus available. Bulk precipitation, NO_2 and NH_3 were sampled in open areas close to the forest stands at a meteorological station also run by LWF. The 10 study sites are distributed across the five main geographic regions of Switzerland (Table 1).

2.2. Field measurements

2.2.1. Bulk precipitation and throughfall

A detailed description of the field measurements is given in Thimonier et al. (2004). Bulk precipitation was sampled with three collectors. Each collector consisted of a funnel (100 cm² opening) connected to a 2 L storage bottle. The collectors were placed 1.5 m above ground in PVC tubes. In winter, in the plots where abundant snowfall was expected (BET, BEA, SCH, CEL, NAT and NOV), the funnel-type collectors were replaced by a single bucket-type snow collector (30 cm diameter).

Throughfall was sampled with two sets of eight funnel-type collectors, of the same design as the collectors used in the open area. The collectors were systematically placed 1 m above ground on two 43 m \times 43 m subplots, except at OTH (see Thimonier et al., 2004). In winter, in the plots where abundant snowfall was expected (see above), the funnel-type collectors were replaced by four bucket-type collectors.

2.2.2. Passive samplers

Concentrations of atmospheric NH_3 and NO_2 were measured using Palmes-type diffusion tubes (Palmes and Gunnison, 1973). For NH_3 , “Zürcher” passive samplers were used (Thöni et al., 2003), which consisted of a polypropylene cylinder with a cap and a Teflon gasket on the top and an opening at the bottom. A Teflon membrane (0.2 mm) separated the ambient air from the absorbent. Three NH_3 diffusion tubes per site and period were placed in a box that prevented wind influence. The NO_2 sampler consisted of a PMA tube with a polyethylene cap and three stainless steel grids coated by dipping them in a 25% v/v triethanol-amine/acetone solution. A PTFE membrane was placed at the inlet as a windshelter to keep the diffusion path constant (Brunner and Schlatter, 2002). Three NO_2 diffusion tubes were placed in an open cover which protected

Table 1
Site description

Region	Site code	Site name	Longitude	Latitude	Altitude a.s.l. (m)	Main tree species on the plot	Situation of the open area and land use in its direct neighborhood	Sampling period
Jura Plateau	BET	Bettlachstock	07°25	47°14	1149	<i>Fagus sylvatica</i>	Meadow	17.11.1999–15.11.2000
	JUS	Jussy	06°17	46°14	501	<i>Quercus robur</i>	Forest clearing	24.11.1999–23.11.2000
	OTH	Othmarsingen	08°14	47°24	484	<i>Fagus sylvatica</i>	Forest clearing	12.11.1999–14.11.2000
	LAU	Lausanne	06°40	46°35	807	<i>Fagus sylvatica</i>	Open fields with intensive agriculture	09.11.1999–07.11.2000
	VOR	Vordemwald	07°53	47°17	480	<i>Abies alba</i>	Open fields with intensive agriculture	16.11.1999–14.11.2000
Lower Alps	BEA	Beatenberg	07°46	46°43	1511	<i>Picea abies</i>	Pasture	09.11.1999–07.11.2000
	SCH	Schänis	09°04	47°10	733	<i>Fagus sylvatica</i>	Meadow, sheep grazing	16.11.1999–30.10.2000
Alps	CEL	Celerina	09°53	46°30	1871	<i>Pinus cembra</i>	Meadow	15.11.1999–13.12.2000
	NAT	National Park	10°14	46°40	1899	<i>Pinus mugo</i>	Grassland	16.11.1999–20.11.2000
Southern Alps	NOV	Novaggio	08°50	46°01	950	<i>Quercus cerris</i>	Pasture	09.11.1999–07.11.2000

them from sun radiation and rain. The shelter boxes were installed 2 m above ground at the meteorological station.

The bulk deposition, the throughfall and the passive samplers were exposed for 2 weeks (4 weeks at CEL and BET in winter), and were replaced by new samplers afterwards.

2.3. Chemical analyses

2.3.1. Bulk precipitation and throughfall

Samples were usually processed within 3 days after arrival at the laboratory (Thimonier et al., 2004). The samples were weighed, and then pooled to obtain composite samples of either bulk precipitation or throughfall. The conductivity and the pH were measured, and the solution was then filtered (0.45 µm). Ammonium (NH₄⁺) was determined colorimetrically through automated flow injection analysis. Calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺) and sodium (Na⁺) were determined by inductively coupled plasma-mass spectrometry. From March 2000 onwards, these elements were determined by inductively coupled plasma-atomic emission spectrometry. Nitrate (NO₃⁻), sulphate (SO₄²⁻) and chloride (Cl⁻) concentrations were analysed by ion chromatography (IC).

Missing values were estimated by multiple regressions (Thimonier et al., 2004).

2.3.2. Passive samplers

The samplers were stored at <4 °C before and after exposure and analyses were carried out within 1–4 weeks after the end of exposure. The ammonium in the absorption solution of the NH₃-diffusion tube was analysed by ion chromatography (Dionex DX-100, Dionex column CS 12). The nitrite absorbed on the coated grids of the NO₂ sampler was extracted into aqueous solution, quantified by the Saltzman reaction and analysed by UV/Vis spectrophotometry (in the visible range). Blank samples were systematically analysed together with the exposed samples and intercomparisons with independent measuring systems were carried out. The mean NO₂ concentration over the period was calculated according to Fick's first law of diffusion. The NH₃ concentration was determined from the diffusion resistance, calculated according to Fick's first law, to which the membrane resistance, which had been determined experimentally (Thöni et al., 2003), was added. The air temperature measured at the LWF meteorological stations and interpolated atmospheric pressures measured at NABEL stations (e.g. NABEL, 2002) were used to correct the diffusion coefficient.

One missing value (NO₂ at VOR in June) was replaced by the mean concentration of NO₂ at this plot for the period April–October.

2.4. Calculation of N concentrations and fluxes

The mean annual concentrations in bulk precipitation and throughfall for the period November 1999–November 2000 were calculated by weighting concentrations with the precipitation volume. Mean annual concentrations of NH₃ and NO₂ for the same period were calculated by weighting concentrations with the lengths of the exposition periods. Annual fluxes were standardized to 365 days.

2.5. Estimation of the total and dry deposition of nitrogen

2.5.1. Throughfall method

In the throughfall method, total nitrogen deposition (TD_N) was estimated by adding an estimated canopy uptake (CU_N) to the throughfall flux (TF_N).

CU_N was estimated using the canopy budget model described in detail in EC-UN/ECE et al. (2001). In this model, a balance is assumed between the total canopy leaching of base cations (Ca²⁺, Mg²⁺ and K⁺), corrected for the leaching of weak acids, on the one hand, and the canopy uptake of NH₄⁺ and H⁺, on the other hand. The fluxes of Ca²⁺, Mg²⁺ and K⁺ in canopy leaching were estimated using Na⁺ as a tracer, assuming that the ratios of total deposition over bulk deposition are similar for Ca²⁺, Mg²⁺, K⁺ and Na⁺. The weak acid concentration was estimated as the difference in concentration of cations minus strong acid anions. The canopy leaching of weak acids was estimated by assuming that the total deposition of weak acids was equal to twice their bulk deposition. H⁺ was assumed to have per mole an exchange capacity six times larger than NH₄⁺, and NH₄⁺ an exchange capacity six times larger than NO₃⁻ (Van der Maas et al., 1991; EC-UN/ECE et al., 2001).

The wet deposition of nitrogen (WD_N) was derived from bulk deposition (BD_N) measurements by applying average wet-only to bulk ratios given in the literature (Draaijers et al., 1998). The dry deposition of nitrogen (DD_N) was estimated as the difference between total and wet deposition.

2.5.2. Inferential method combined with regression on bulk deposition (passive samplers)

The second method for estimating the total deposition of nitrogen relies on measuring the NH₃ and NO₂ concentrations in the air outside the forest, as well as the bulk deposition. The dry deposition of NH₃ (DD_{NH₃}) and NO₂ (DD_{NO₂}) was then estimated with the inferential method. From the bulk deposition, which is a deposition pathway that is comparatively easy to measure, the remaining deposition components were derived using a regression model (Thöni, unpublished): the sum of wet deposition (WD_N), dry deposition of HNO₃ (DD_{HNO₃}), of particulate NH₄⁺ (DD_{NH₄}) and of

particulate NO₃⁻ (DD_{NO₃}) was estimated with

$$WD_N + DD_{HNO_3} + DD_{NH_4} + DD_{NO_3} = aBD_N + b, \quad (1)$$

where *a* and *b* are regression coefficients.

TD_N was then estimated with

$$TD_N = aBD_N + b + DD_{NH_3} + DD_{NO_2}. \quad (2)$$

2.5.2.1. Estimating DD_{NH₃} and DD_{NO₂} using the inferential method. The dry deposition of NH₃ (DD_{NH₃}) and NO₂ (DD_{NO₂}) was estimated by multiplying air concentrations with mean annual deposition velocities obtained from literature (Table 2). In a first run of calculations, we used the deposition velocities selected by Rihm (1996) in his computation of nitrogen deposition in Switzerland at a 1 × 1 km spatial resolution. In Rihm's model, the values of the deposition velocities for NH₃ and NO₂ for forests depended only on the type of stand (coniferous or broadleaved). These values, as well as the deposition velocities for the other land-use types, were set so that the total nitrogen deposition in Switzerland approximately matched the deposition calculated by EMEP with a resolution of 50 × 50 km (77.4 kt N a⁻¹ in 1998, corresponding to 19 kg N ha⁻¹ a⁻¹ on average, EMEP, 2000).

In a second run of calculations, we adjusted Rihm's deposition velocities for NH₃ and NO₂ for the plots at higher elevations (BEA, CEL, NAT, which are coniferous stands) by making it empirically dependent on the length of the winter period, following the observation that, in most studies, the deposition velocity is reported as lower in winter (Fischer-Riedmann, 1995). With the variable *W*, ranging from 0 to 1, and representing the proportion of the winter period related to the whole year, the following empirical equation was used for the coniferous stands:

$$v_{d(x)} = v_d^{\text{veg}}(1 - W) + \frac{v_d^{\text{veg}}}{5} W, \quad (3)$$

where *v_{d(x)}* is the mean annual deposition velocity of either NH₃ or NO₂, *v_d^{veg}* is the deposition velocity during the vegetation period, with *v_d^{veg}* = 40 and 5.4 mm s⁻¹ for NH₃ and NO₂, respectively (Table 2b).

2.5.2.2. Estimating WD_N + DD_{HNO₃} + DD_{NH₄} + DD_{NO₃} using the regression model (*aBD_N*+*b*). The model (Eq. (1)) we used to estimate the other components of N deposition was established using detailed measurements of the different forms of nitrogen at four sites in Switzerland (Table 3). At these sites, precipitation in the open field was sampled by both wet-only and bulk collectors, and analysed for NH₄⁺ and NO₃⁻. Gaseous HNO₃ was measured with a denuder system (Alean-Kirkpatrick and Hertz, 1992). NO₃⁻ and

Table 2
Deposition velocities (V_d , in mm s^{-1}) used in the calculations

(a) Deposition velocities after Rihm (1996)					
Compound	Altitude (m)	Deposition velocity (mm s^{-1})			
		Coniferous forests	Broadleaved forests		
Gases					
NO ₂		4	3		
NH ₃		30	22		
HNO ₃		15	15		
Aerosols					
NH ₄ ⁺	400	2	2		
	800	4	4		
	2000	4	4		
NO ₃ ⁻	400	2	2		
	800	4	4		
	2000	4	4		
(b) Adjusted deposition velocities					
		Regression model			
LWF plots with conifers		NH ₄ ⁺ and NO ₃ ⁻ (aerosol)			
	NH ₃	NO ₂	Coniferous forests	Broadleaved forests	
VOR	30	4	Plateau	2	1.5
BEA	24	3.3	Lower Alps	4	3
CEL	22	3	Jura	3	2.5
NAT	22	3	Valley in the Alps	3	2.5

Between 400 m and 800 m the deposition velocity of aerosols is calculated by linear interpolation. V_d , for NO₂ and NH₃ are average values obtained from the literature (Hertz and Bucher (1990), Riedmann and Hertz (1991), Harwell Laboratory (1990)). Only the values differing from those in Rihm (1996) are shown.

NH₄⁺ aerosols were determined with coated filters, which were connected in series to denuders, sampling the gases HNO₃ and NH₃, respectively. For each site, DD_{HNO₃}, DD_{NH₄} and DD_{NO₃} on forests were estimated by multiplying the measured monthly concentrations with the mean annual deposition velocities for forests taken from literature (Table 2).

Again, a first run of calculations was made using the deposition velocities of Rihm (1996) (Table 2a), and a second using adjusted deposition velocities (Table 2b).

The dry deposition of these N compounds was then grouped together with the wet deposition of N (WD_N) into a single term, which was linearly regressed against the bulk deposition of N (BD_N). The following equations were obtained ($n = 77$ monthly values, $R^2 = 0.92$; all values are, e.g. in $\text{kg N ha}^{-1} \text{ month}^{-1}$):

First run of calculation (deposition velocities v_d for forests selected by Rihm (1996), independent of the type of stand; Table 2a):

$$\text{WD}_N + \text{DD}_{\text{HNO}_3} + \text{DD}_{\text{NH}_4} + \text{DD}_{\text{NO}_3} = 1.037\text{BD}_N + 0.773. \quad (4)$$

Second run of calculation (adjusted deposition velocities according to the type of stand, Table 2b):

Using v_d for broadleaved stands:

$$\text{WD}_N + \text{DD}_{\text{HNO}_3} + \text{DD}_{\text{NH}_4} + \text{DD}_{\text{NO}_3} = 1.022\text{BD}_N + 0.397. \quad (5)$$

Using v_d for coniferous stands:

$$\text{WD}_N + \text{DD}_{\text{HNO}_3} + \text{DD}_{\text{NH}_4} + \text{DD}_{\text{NO}_3} = 1.033\text{BD}_N + 0.770. \quad (6)$$

3. Results

3.1. Concentrations of NH₃ and NO₂ in the air and N in precipitation

The NO₂ concentrations were clearly highest at the four LWF plots located on the Plateau (JUS, LAU, OTH and VOR, Table 4, Fig. 1). On these four plots and SCH, all below 900 m a.s.l., the highest NH₃ concentrations were also measured. The highest mean annual NO₂

Table 3

Description of the sites where data were obtained for the development of the model that derives the sum of the wet deposition of nitrogen and the dry deposition of HNO₃ and particulate NH₄⁺ and NO₃⁻ from the bulk deposition of N

Region	Altitude a.s.l. (m)	Land use in the direct neighborhood	Sampling period	Precipitation (mm a ⁻¹)	Air concentrations (µg m ⁻³)		Wet deposition (kg ha ⁻¹ a ⁻¹)	Bulk deposition (kg ha ⁻¹ a ⁻¹)
					HNO ₃	NO ₃ ⁻ _{3aerosol}		
Jura	560	Rural, agriculture and pasture	Apr. 1998–Mar. 1999	840	0.6	3.5	5.4	6.2
Plateau	470	Agriculture in urban area	Dec. 1998–Dec. 2000	1010	0.5	4.3	9.3	11.0
Lower Alps	970	Rural, meadows and pasture	Jan. 1994–Jun. 1995	1670	0.6	2.9	14.3	16.8
			Jan. 2001–Oct. 2002	1920	0.4	2.9	12.5	14.5
Valley in the Alps	510	No agricultural activity	Oct. 1997–Sep. 1998	1150	0.3	2.1	7.1	7.4

concentrations were measured at OTH (18.7 µg m⁻³), which is near the motorway between Zurich and Berne (about 1.5 km away), where traffic is usually dense. Yet, even at OTH, the mean annual NO₂ concentration did not exceed the annual limit value of 30 µg m⁻³ set by the Swiss Federal Ordinance of 16 December 1985 on Air Pollution Control (OPair). The highest NH₃ concentrations were measured at LAU (3.2 µg m⁻³) and VOR (2.7 µg m⁻³). Low concentrations of both NH₃ (0.27 µg m⁻³) and NO₂ (<3.1 µg m⁻³) were measured at the two high-elevation sites (CEL, NAT).

At plots below 900 m, NO₂ concentrations were higher in winter than in summer (Fig. 1a), due to higher emissions (heating) and the temperature inversions, frequently observed on the Plateau at this time of the year, which result in a very stable air layer where pollutants are trapped. NH₃ concentrations followed the opposite pattern, with values tending to be higher in summer than in winter. However, NH₃ concentrations occasionally reached peak values at LAU and VOR both in summer and in winter (Fig. 1b).

The highest N concentrations in bulk precipitation were measured at NOV (1.23 mg L⁻¹), LAU (0.97 mg L⁻¹) and VOR (0.96 mg L⁻¹) (Table 4). The lowest N concentrations were measured at CEL (0.42 mg L⁻¹) and NAT (0.41 mg L⁻¹). Under the forest canopy, VOR and OTH exhibited the highest N concentrations in throughfall (>2 mg L⁻¹), while CEL and NAT were again the sites where N concentrations were lowest (<0.40 mg L⁻¹). N concentrations in precipitation followed no distinct seasonal pattern. NH₃ and NO₂ air concentrations were usually not or only weakly correlated with NH₄⁺ and NO₃⁻ concentrations in precipitation.

3.2. Estimates of total nitrogen deposition

In the following, TD_{N(TF)} refers to the total N deposition estimated with the throughfall method. TD_{N(PS)} and TD_{N(PS)}^{*} refer to the total deposition derived from passive sampling of NH₃ and NO₂ and bulk deposition. TD_{N(PS)} is the output of a first run of calculations using deposition velocities as selected by Rihm (1996); TD_{N(PS)}^{*} is the output of a second run of calculations with adjusted deposition velocities.

TD_{N(PS)} and TD_{N(PS)}^{*} correlated significantly with TD_{N(TF)} ($r = 0.84$, $p < 0.01$ between TD_{N(PS)} or TD_{N(PS)}^{*} and TD_{N(TF)}).

TD_{N(PS)} was systematically higher than TD_{N(TF)} for all the 10 plots except NOV, with a median difference of +3.2 kg N ha⁻¹ a⁻¹ (Table 5, Fig. 2). TD_{N(PS)}^{*} was, up to 1.1 kg N ha⁻¹ a⁻¹ (at BEA), lower than TD_{N(PS)}. The median difference between TD_{N(PS)}^{*} and TD_{N(TF)} was +2.4 kg N ha⁻¹ a⁻¹.

The values of TD_{N(PS)} and TD_{N(TF)} were closest to each other at BET, OTH, BEA, and NOV, with absolute

Table 4
Mean annual NH₃ and NO₂ concentrations in the open areas, mean annual NH₄⁺ and NO₃⁻ concentrations in bulk deposition and throughfall, and annual precipitation volume

Region	Site	# periods	Air concentrations						Bulk deposition						Throughfall					
			NH ₃ (µg m ⁻³)		NO ₂ (µg m ⁻³)		[NH ₄ ⁺] (µeq L ⁻¹)		[NO ₃ ⁻] (µeq L ⁻¹)		Precipitation volume (mm a ⁻¹)		[NH ₄ ⁺] (µeq L ⁻¹)		[NO ₃ ⁻] (µeq L ⁻¹)		Precipitation volume (mm a ⁻¹)			
			Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE		
Jura Plateau	BET	20	0.47	0.07	4.32	0.22	21.57	3.25	24.00	2.48	1306	2.48	26.08	5.20	43.81	6.15	1206			
	JUS	26	1.21	0.15	11.54	1.20	24.75	3.34	27.93	3.96	1011	3.96	35.45	14.31	30.41	4.81	770			
	LAU	26	3.15	0.33	12.47	1.09	35.97	4.94	33.14	5.56	1341	5.56	48.24	11.43	49.92	8.43	1091			
	OTH	26	1.22	0.10	18.74	1.22	37.39	4.01	34.04	3.36	1070	3.36	82.40	9.54	75.77	7.87	779			
	VOR	26	2.66	0.34	11.88	0.95	38.80	4.20	30.10	3.66	1162	3.66	71.92	11.08	72.14	9.24	869			
Lower Alps	BEA	26	0.58	0.09	2.33	0.13	23.37	2.95	23.40	2.22	1282	2.22	28.53	3.92	47.52	5.63	1116			
	SCH	25	1.45	0.18	6.64	0.63	33.10	3.32	29.97	2.33	2529	2.33	42.91	5.37	44.52	4.06	2095			
Alps	CEL	20	0.27	0.04	3.08	0.17	12.40	2.57	17.83	2.38	1063	2.38	9.66	2.52	18.06	3.08	1023			
	NAT	26	0.27	0.03	1.87	0.08	12.92	2.67	16.35	2.25	1242	2.25	9.86	2.28	18.40	2.57	1170			
Southern Alps	NOV	26	0.59	0.08	4.94	0.33	45.42	10.64	42.12	7.90	2335	7.90	44.34	12.08	60.38	14.81	2050			

differences not exceeding 2.3 kg N ha⁻¹ a⁻¹, and differences relative to TD_{N(TF)} lower than 10.3% (OTH). For these four plots, when TD_{N(PS)} was replaced by the estimates resulting from the second run of calculations TD_{N(PS)}^{*}, the range of absolute differences was reduced (from -1.1 (NOV) to 1.7 kg N ha⁻¹ a⁻¹ (OTH)). At SCH, the absolute difference between the two methods was greater than 3 kg N ha⁻¹ a⁻¹, but the relative difference between TD_{N(PS)} or TD_{N(PS)}^{*} and TD_{N(TF)} was acceptable (+12.2% and +9.9%, respectively). The absolute difference between TD_{N(PS)} (or TD_{N(PS)}^{*}) and TD_{N(TF)} at CEL and NAT, the two high-elevation plots, was of the same magnitude as at SCH, but, in contrast, the relative difference was very high. The largest differences, both relative and absolute, were obtained at LAU, VOR and JUS.

The highest TD_{N(PS)} were calculated at VOR and LAU, due to the very high N dry deposition, while the highest TD_{N(TF)} were obtained at NOV and SCH. Both estimation methods showed a gradient of deposition with altitude north of the Alps, with lower TD_N values at CEL and NAT (above 1800 m), moderate TD_N between 1000 and 1600 m in the Jura (BET) and the Lower Alps (BEA), and higher TD_N below 900 m on the Plateau (LAU, OTH, VOR) and at SCH. The two methods were also in agreement in indicating high deposition at the plot south of the Alps (NOV).

4. Discussion

Although independent methods were used for estimating dry deposition, we obtained a strong correlation between the estimates of the total N deposition obtained with the inferential method (TD_{N(PS)} and TD_{N(PS)}^{*}), on the one hand, and the estimates obtained with the throughfall method (TD_{N(TF)}), on the other hand. Yet TD_{N(PS)} and TD_{N(PS)}^{*} tended to be higher than TD_{N(TF)}. Using adjusted deposition velocities as in our second run of calculations (TD_{N(PS)}^{*}) improved the agreement with TD_{N(TF)}, but differences between the two methods were still noticeable, depending on the site considered.

Several factors may account for these differences. In the inferential method, the accuracy of the dry deposition of NH₃ and NO₂ depends on the accuracy of both the measured atmospheric concentration and the deposition velocity. A number of studies have recognized potential sources of errors in the use of passive samplers. Heal et al. (2000), e.g. observed, in urban conditions, systematic biases in measurements of NO₂ with passive samplers compared to those made with a continuous analyser. Yet the deviation of the annual mean NO₂ concentrations measured with our passive samplers from the means obtained with continuous measuring systems during a comparison exercise in a rural area were <3% (Thöni, unpublished data). Ammonia concentrations

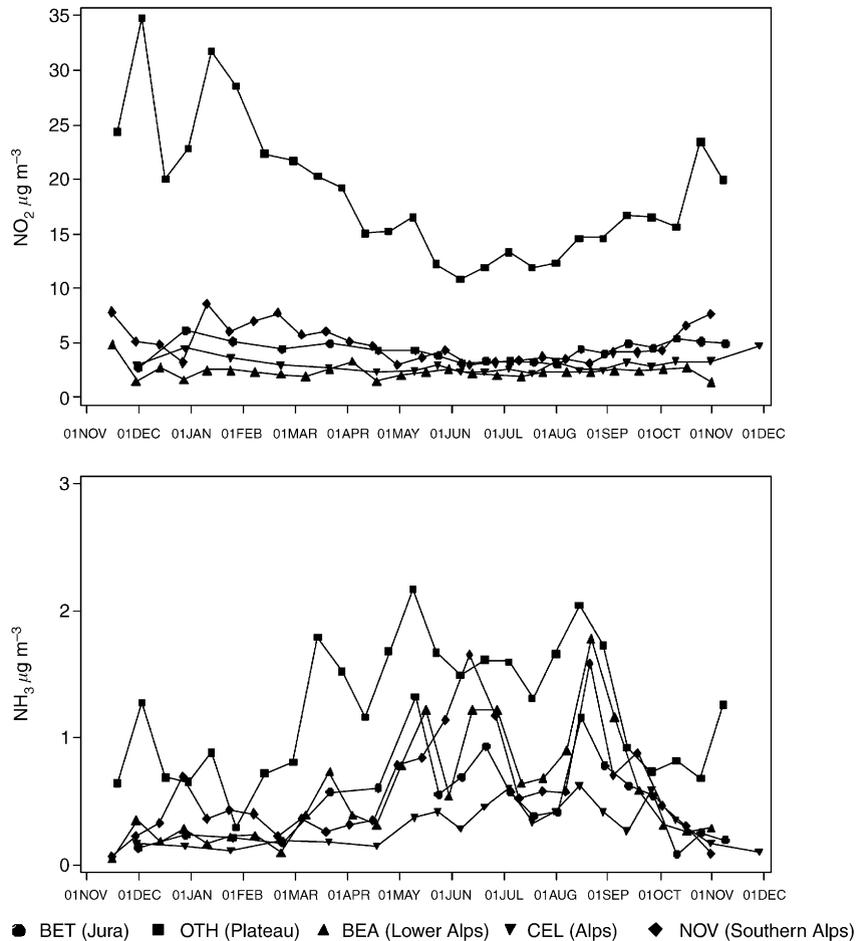


Fig. 1. (a) NO_2 concentrations and (b) NH_3 concentrations in the open areas of selected LWF plots (BET, OTH, BEA, CEL, NOV) from each region of Switzerland between November 1999 and November 2000.

determined by the Zürcher passive sampler also proved to be in good agreement with concentrations obtained from denuder systems (deviation $<7\%$, Thöni et al., 2003). It must be mentioned, however, that the ammonia passive sampler provided less accurate measurements for mean concentrations below $1 \mu\text{g m}^{-3}$, which were frequently measured at most of the LWF plots in winter or even throughout the whole year in the Alps.

When large differences, due to unreliable measurements by passive samplers, are thus excluded, there are other cases where the concentration term in the inferential equation, even accurately measured, may lead to a substantial bias: the high NH_3 concentrations at LAU and VOR led to high rates of NH_3 deposition ($18 \text{ kg ha}^{-1} \text{ a}^{-1}$ at LAU, $20.7 \text{ kg ha}^{-1} \text{ a}^{-1}$ at VOR) and accordingly high $\text{TD}_{\text{N(PS)}}$ values ($35\text{--}38 \text{ kg ha}^{-1} \text{ a}^{-1}$). LAU and VOR, both located on the Plateau, are greatly influenced by the intensively cultivated fields in the

direct neighbourhood of the open areas. The peaks of NH_3 concentrations measured were most likely caused by manure spreading in the agricultural fields around the open areas, which is a typical practice in these regions. NH_3 is readily deposited locally (e.g. Singles et al., 1998), which leads to considerable spatial variability. In this context, measuring NH_3 in open areas subjected to high local emissions to derive deposition on the forest stand with the inferential method is not appropriate, or can only be used to estimate the deposition at the forest edge, as suggested by Spangenberg (2002). In a forest stand subjected to high emissions of NH_3 due to poultry farming, Spangenberg measured decreasing NH_3 concentrations inside the stand with increasing distances from the forest edge ($25 \mu\text{g m}^{-3}$ at the edge, 13 and $4 \mu\text{g m}^{-3}$ at 200 and 500 m, respectively, from the edge). At VOR, we simultaneously measured NH_3 concentrations below

Table 5
Annual nitrogen fluxes (in kg N ha⁻¹ a⁻¹)

Region	Site	BD _N	WD _N	Throughfall method				Inferential method—1st run					Inferential method—2nd run				
				DD _{N(TF)}	TD _{N(TF)}	TF _N	CU _N	DD _{NH₃}	DD _{NO₂}	DD _{N(PS)}	TD _{N(PS)}	CU _{N(PS)}	DD _{NH₃} *	DD _{NO₂} *	DD _{N(PS)} *	TD _{N(PS)} *	CU _{N(PS)} *
Jura Plateau	BET	8.3	7.2	5.9	13.1	11.8	1.3	2.7	1.2	6.2	13.4	1.6	2.7	1.2	5.7	12.9	1.1
	JUS	7.5	6.4	2.5	9.0	7.1	1.8	6.9	3.3	12.3	18.7	11.6	6.9	3.3	11.8	18.2	11.1
	LAU	13.0	11.2	8.2	19.3	15.0	4.4	18.0	3.6	24.7	35.8	20.8	18.0	3.6	24.1	35.3	20.3
	OTH	10.7	9.2	12.7	22.0	17.2	4.7	7.0	5.4	15.0	24.2	7.0	7.0	5.4	14.5	23.7	6.5
	VOR	11.2	9.7	11.7	21.4	17.5	3.9	20.7	4.6	28.0	37.6	20.1	20.7	4.6	27.9	37.6	20.1
Lower Alps	BEA	8.4	7.2	6.7	13.9	11.9	2.0	4.5	0.9	7.7	14.9	3.0	3.6	0.7	6.6	13.8	1.9
	SCH	22.3	19.2	11.2	30.4	25.6	4.8	8.3	1.9	14.9	34.1	8.5	8.3	1.9	14.2	33.4	7.8
Alps	CEL	4.5	3.8	1.4	5.2	4.0	1.3	2.1	1.2	4.8	8.7	4.7	1.5	0.9	4.0	7.8	3.8
	NAT	5.1	4.4	1.6	6.0	4.6	1.4	2.1	0.7	4.5	8.9	4.3	1.6	0.5	3.7	8.1	3.5
Southern Alps	NOV	28.6	24.6	10.9	35.5	30.1	5.5	3.4	1.4	10.6	35.2	5.2	3.4	1.4	9.8	34.4	4.3

Bulk deposition (BD); throughfall (TF); wet deposition (WD); dry deposition (DD) and total deposition (TD). Estimates of the dry and total deposition derived from the throughfall method are indexed as TF, and estimates from the inferential method combined with regression are indexed as PS. In the inferential method, two runs of calculations were done, the first with deposition velocities as in Rihm (1996), the second (outputs identified by a*) with adjusted deposition velocities. DD_{N(PS)} (resp. DD_{N(PS)}*) is calculated as the difference between TD_{N(PS)} (resp. TD_{N(PS)}*) and WD_N, CU_{N(PS)} (resp. CU_{N(PS)}*) as the difference between TD_{N(PS)} (resp. TD_{N(PS)}*) and TF_N.

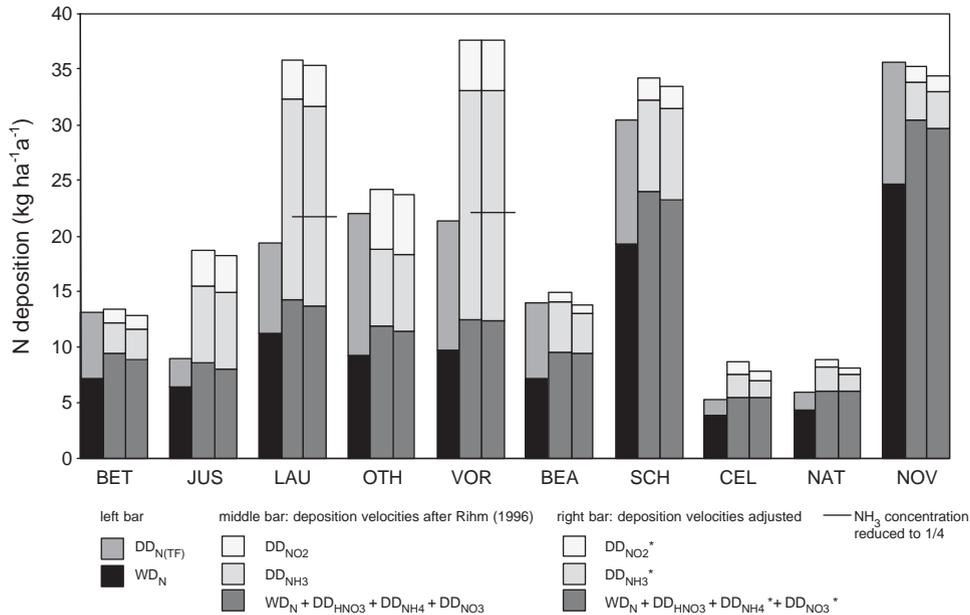


Fig. 2. Nitrogen deposition on the LWF plots estimated with the throughfall method (WD_N and $DD_{N(TF)}$) and with the inferential method combined with regression ($WD_N + DD_{NH_4} + DD_{NO_3} + DD_{HNO_3}$, DD_{NH_3} and DD_{NO_2}). Left bar: throughfall method; middle bar: inferential method with deposition velocities as in Rihm (1996); right bar: inferential method with Rihm (1996)'s deposition velocities adjusted.

the canopy and in the open area. The mean annual concentration below the canopy was $<25\%$ of the mean annual concentration measured in the open. Measurements directly above the canopy are not available, but the concentration gradient with distance observed by Spangenberg (2002), and measurements at a forest site in Switzerland (Hofstetten, Jura) showing little difference between NH_3 concentrations above and below the canopy (Thöni and Seitler, 2003) suggest that the NH_3 concentrations above the forest stand of VOR, and most likely of LAU as well, are in fact considerably lower than those measured in the open area. Assuming that the NH_3 concentration above the canopy at VOR and LAU is only a quarter of the concentration measured in the open area, $TD_{N(PS)}^*$ would amount to approx. $22 \text{ kg ha}^{-1} \text{ a}^{-1}$ at both plots, which would considerably reduce the difference between $TD_{N(TF)}$ and $TD_{N(PS)}^*$ ($TD_{N(PS)}^*$ still exceeding $TD_{N(TF)}$ by $0.7\text{--}2.5 \text{ kg ha}^{-1} \text{ a}^{-1}$, Fig. 2).

Other sites where concentrations are being measured relatively accurately, but may not be representative of the emission context, could be CEL and NAT. At these two sites, the NH_3 concentrations are low and might be actually lower than the compensation point for NH_3 , below which NH_3 is emitted instead of being deposited (e.g. Andersen and Hovmand, 1999).

The second source of uncertainty in the inferential method is the deposition velocity. The use of a mean

deposition velocity to which a mean annual concentration is applied involves large uncertainties. For the most reliable assessments of dry deposition, deposition velocities and concentrations should be determined on a time scale where these two parameters do not change significantly, which is at a maximum of about 3 h above the forest according to Andersen and Hovmand (1999). However, the significant correlation between $TD_{N(PS)}$ and $TD_{N(TF)}$ seems to validate the approach based on concentrations and deposition velocities averaged over longer periods.

The systematically higher values of $TD_{N(PS)}$ compared with $TD_{N(TF)}$, especially when calculating the dry deposition with the deposition velocities as selected in Rihm (1996), suggest that the deposition velocities applied by Rihm in his Swiss model are too high. The estimates of the canopy uptake of nitrogen $CU_{N(PS)}$, derived from the difference between $TD_{N(PS)}$ and the throughfall flux TF_N , range from $1.6 \text{ kg ha}^{-1} \text{ a}^{-1}$ (BET) to 11.6 (JUS), when LAU and VOR are not considered (Table 5). These values are within the range of the estimates of canopy uptake reported in literature ($1\text{--}12 \text{ kg ha}^{-1} \text{ a}^{-1}$, e.g. Lovett and Lindberg, 1993). However, Rihm's selected deposition velocities are rather in the upper range of the deposition velocities found in literature. For NH_3 , the annual deposition velocities reported in literature range from approximately 8 mm s^{-1} (Puxbaum and Gregori, 1998, in an oak

forest), which is a considerably lower value than the deposition velocity we used for our broadleaved stands, to approx. 30 mm s^{-1} (the upper range of the annually averaged deposition velocity in a Douglas fir stand in Duyzer et al., 1994). In a Norway spruce stand, Horváth (2003) obtained a mean deposition velocity of NH_3 , averaged for the whole year, of 24 mm s^{-1} , which lies below the 30 mm s^{-1} we applied on all our coniferous stands in our first run of calculations. For NO_2 , the deposition velocities reported in the literature are usually of the order of $1\text{--}3 \text{ mm s}^{-1}$ (references in Smith et al., 2000, and e.g. Puxbaum and Gregori, 1998). In comparison, the deposition velocities selected by Rihm (3 mm s^{-1} for broadleaved stands, 4 mm s^{-1} for conifers) are rather high. Another argument further supports our suspicion that the deposition velocities selected by Rihm were too high: occult deposition is included in through-fall measurements, as compounds deposited during fog or cloud events are subsequently washed out by rainfall. In contrast, occult deposition should be added to the dry deposition estimated with the inferential method. This should lead to an underestimation of the total deposition of nitrogen with the inferential method on plots where fog events are frequent (on the Plateau) or where cloud deposition occurs (at higher elevations). Yet $\text{TD}_{\text{N(PS)}}$ is almost always higher than $\text{TD}_{\text{N(TF)}}$.

In our second run of calculations, deposition velocities for NH_3 and NO_2 for coniferous stands were adjusted according to the length of the period where winter conditions prevail. This led to less divergence between $\text{TD}_{\text{N(PS)}}$ and $\text{TD}_{\text{N(TF)}}$. Further adjustments of the deposition velocities are, however, possible. For example, lower deposition velocities could be selected in our calculations for plots with open canopies, such as CEL and NAT. At these two plots, the leaf area index of the forest stand, measured with a LI-COR LAI 2000 plant canopy analyser, and uncorrected for the clumping of needles on shoots, is lower than 1.5 (Thimonier, unpublished data). Simple calculations illustrate the impact of selecting lower deposition velocities on the estimated total deposition: if we selected, e.g. a 50% lower deposition velocity for NH_3 , $\text{TD}_{\text{N(PS)}}$ would be 5% (at NOV) to 27.5% (at VOR) lower, with an average of 16% for all plots. Selecting lower deposition velocities of NO_2 would have comparatively lower impact on the estimates of $\text{TD}_{\text{N(PS)}}$. For example, a 50% lower deposition velocity for NO_2 would lead to a decrease in $\text{TD}_{\text{N(PS)}}$ by only 5.5%, on average.

A last uncertainty in estimating the total N deposition with the inferential method lies not in the inferential method itself, but in the regression model to which it is coupled. The model simulating the wet and dry deposition of nitrogen compounds other than NH_3 and NO_2 from the bulk deposition of N may not be valid for high-elevations sites, as the sites used for the calibration of the model are all below 1000 m. This

would be a further explanation for the differences between $\text{TD}_{\text{N(PS)}}$ and $\text{TD}_{\text{N(TF)}}$ at CEL and NAT. Furthermore, the deposition velocity of HNO_3 applied in the regression model is lower than the values found in literature (e.g. in Pryor and Klemm, 2004), but we expect the impact on the estimates of $\text{TD}_{\text{N(PS)}}$ to be limited due to the low concentrations of HNO_3 .

The throughfall method also involves a number of uncertainties. Sources of uncertainties specifically related to the LWF measurements (see also Thimonier et al., 2004) include: (1) the reduced number of collectors in winter on the plots where abundant snowfall is expected (1–4 collectors, see e.g. Houston et al., 2002); (2) the fact that stemflow was not included in the calculation of the total deposition, which leads to an underestimation of $\text{TD}_{\text{N(TF)}}$, especially in beech stands (BET, LAU, OTH, SCH); (3) the fact that organic nitrogen was not included, which could lead to an underestimation of $\text{TD}_{\text{N(TF)}}$ due to the possible transformation of mineral nitrogen into organic forms in the collectors, especially in view of the rather long collection interval (2–4 weeks). The assumptions underlying the canopy budget model should also be experimentally tested for our site conditions. In particular, the relative exchange efficiencies of H^+ , NO_3^- and NH_4^+ should be determined for the main tree species on the plots. The fluxes of the weak acids, which are involved in the balance between canopy uptake and canopy leaching, should also be better quantified.

In one case, at JUS, we find it difficult to explain the quite large discrepancy between $\text{TD}_{\text{N(PS)}}$ and $\text{TD}_{\text{N(TF)}}$ and to ascribe the divergence to one method or the other. At this plot, in spite of rather high average concentrations of NH_3 and NO_2 in the atmosphere, the throughfall fluxes and the total deposition derived from the canopy budget model $\text{TD}_{\text{N(TF)}}$ were rather low. One explanation of the low $\text{TD}_{\text{N(TF)}}$ may be the relatively low annual precipitation volume, which is one of the lowest of all the LWF plots. But this factor alone is unlikely to account for the entirety of the difference between $\text{TD}_{\text{N(TF)}}$ and $\text{TD}_{\text{N(PS)}}$.

4.1. Regional variation

Regional patterns in site characteristics were identified. The lowest N deposition (both $\text{TD}_{\text{N(TF)}}$ and $\text{TD}_{\text{N(PS)}}$ or $\text{TD}_{\text{N(PS)}}^*$) and, correspondingly, the lowest NH_3 and NO_2 air concentrations were measured at the two high-elevation sites (CEL and NAT). The two sites located between 1000 and 1600 m (BET in the Jura, BEA in the Lower Alps) had moderate levels of N deposition and low air concentrations of NH_3 and NO_2 , which supports the hypothesis that pollution load decreases as altitude increases, since sites at higher altitudes are usually further away from major anthropogenic emission sources. Located on the Plateau, which is

characterized by dense population and intensive agriculture, LAU, VOR and OTH had high N-air concentrations, moderate precipitation and rather high N deposition. The highest values of $TD_{N(TF)}$ and accordingly high values of $TD_{N(PS)}$ and $TD_{N(PS)}^*$ were measured in the southern part of Switzerland (NOV) and on a plot located in the lower Alps but below 900 m (SCH). These high values were related to both high precipitation and high concentrations in precipitation. For these two plots, the wet deposition represented the major pathway for atmospheric deposition: this process accounted for 63% (at SCH) and 69% (at NOV) of the total nitrogen deposition derived from throughfall measurements. N concentrations in the air, on the other hand, were moderate, which indicates that high deposition at these two plots originates in higher proportion from the rainout process and long-range transport than from local emissions. The high nitrogen deposition at NOV is related to the high level of emissions which come from the industrialized, intensively cultivated and densely populated Po Basin to which the southern part of Switzerland is subjected (Della Lucia et al., 1996). The high nitrogen deposition at SCH, on the northern flank of the Alps, is mainly related to the livestock farming carried out in the densely populated plain and to an orographic barrier effect.

5. Conclusion

The throughfall method and the inferential method combined with a regression model gave consistent estimates of the total deposition of nitrogen on the LWF plots. However, the total deposition of N estimated with the inferential method tended to exceed the deposition values estimated with the throughfall method. We suspect that the deposition velocities we used are actually too high. However, to test this hypothesis, and to find out which of our estimates is closer to the true deposition, alternative, more accurate (but also more expensive) measurements of N-dry deposition, such as the micrometeorological methods, should be explored.

In view of the overall satisfactory agreement of the inferential method with the throughfall method, and provided that adjusted annual deposition velocities are used, the passive sampling of NH_3 and NO_2 coupled with the collection of bulk deposition in an open area could be a reliable alternative to throughfall measurements. The throughfall method, however, still has most advantages when the site-specific quantification of fluxes of elements other than nitrogen (e.g. sulphur, base cations) is needed.

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