



## Water chemistry and nutrient budgets in an undisturbed evergreen rainforest of southern Chile

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**Abstract.** In a pristine evergreen rainforest of *Nothofagus betuloides*, located at the Cordillera de los Andes in southern Chile (41 °S), concentrations and fluxes of nutrients in bulk precipitation, cloud water, throughfall water, stemflow water, soil infiltration and percolation water and runoff water were measured. The main objectives of this study were to investigate canopy–soil–atmosphere interactions and to calculate input–output budgets. From May 1999 till April 2000, the experimental watershed received 8121 mm water (86% incident precipitation, 14% cloud water), of which the canopy intercepted 16%. Runoff water volume amounted 9527 mm. Bulk deposition of inorganic (DIN) and organic (DON) nitrogen amounted 3.6 kg ha<sup>-1</sup> year<sup>-1</sup> and 8.2 kg ha<sup>-1</sup> year<sup>-1</sup> respectively. Occult deposition (clouds + fog) contributes for 40% to the atmospheric nitrogen input (bulk + occult deposition) of the forest. An important part of the atmospheric ammonium deposition is retained within the canopy or converted to nitrate or organic nitrogen by epiphytic bacteria or lichens. Also the export of inorganic (0.9 kg ha<sup>-1</sup> year<sup>-1</sup>) and organic (5.2 kg ha<sup>-1</sup> year<sup>-1</sup>) nitrogen via runoff is lower than the input to the forest floor via throughfall and stemflow water (3.2 kg DIN ha<sup>-1</sup> year<sup>-1</sup> and 5.6 kg DON ha<sup>-1</sup> year<sup>-1</sup>). The low concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> under the rooting depth suggest an effective biological immobilization by vegetation and soil microflora. Dry deposition and foliar leaching of base cations (K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) was estimated using a canopy budget model. Bulk deposition accounted for about 50% of the total atmospheric input. Calculated dry and occult deposition are both of equal value (about 25%). Foliar leaching of K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> accounted for 45%, 38% and 6% of throughfall deposition respectively. On an annual basis, the experimental watershed was a net source for Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>.

### Introduction

The native temperate rainforests of southern Chile represent an important reserve of temperate forests of the world, with an extraordinary genetic, phytogeographic and ecological significance (Armesto et al. 1996). These forests have high structural complexity and functional and biological diversity. Biotic components regulate the internal circulation and output of nutrients and these natural conditions give stability to the ecosystem (Arroyo et al. 1995). In Chile, the evergreen *Nothofagus betuloides* (Mirb.) Oerst forests have a surface area of 1,801,637 ha (CONAF et al.

1999) and are distributed between 40°30'–55°58'S in Cordillera de los Andes and 39°57'–46°50'S in Cordillera de la Costa.

Most studies of element fluxes in temperate forests have been carried out in the Northern Hemisphere. Research in temperate forests of the Southern Hemisphere, where *Nothofagus* spp. represents the dominant tree species, is most scarce (Veblen et al. 1996). Especially studies of pristine forest ecosystems with natural processes and undisturbed nutrient cycling are difficult to find. The chemistry of precipitation in southern Chile reflects one of the closest approximations of pre-industrial atmospheric conditions in the world (Weathers and Likens 1997). Depositions of inorganic nitrogen ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) are reported to be below  $1 \text{ kg ha}^{-1} \text{ year}^{-1}$  in coniferous forests dominated by *Fitzroya cupressoides* and *Pilgerodendron uviferum*, evergreen broad-leaved forests dominated by *Nothofagus nitida* and *Drimys winteri* (Hedin et al. 1995) and *F. cupressoides* forests (Oyarzún et al. 1998) at the Cordillera de la Costa in southern Chile. Godoy et al. (1999) found less than  $5 \text{ kg ha}^{-1} \text{ year}^{-1}$  of inorganic nitrogen deposition in a deciduous *Nothofagus pumilio* forest of the Cordillera de los Andes. Inorganic nitrogen concentrations in small streams draining evergreen broad-leaved forests of the Chiloé island are also reported to be very low (Hedin and Campos 1991; Hedin et al. 1995).

It has been proven that mountain forest ecosystems are very efficient in trapping nutrients from clouds and fog, especially in the case of nitrogen and base cations (e.g., Lovett et al. 1982; Clark et al. 1998; Heath and Huebert 1999). In cloud or fog dominated coastal and mountain regions, ecosystem hydrology and nutrient dynamics might be closely linked to occult precipitation (Weathers 1999). Godoy et al. (1999) found occult precipitation to contribute significantly to nutrient dynamics in a *N. pumilio* forest located at high altitude in the Cordillera de los Andes of southern Chile. Also Weathers and Likens (1997) and Weathers et al. (2000) state that fog and clouds can be important sources of nitrogen in N-limited forest ecosystems in southern Chile.

In the Cordillera de los Andes (southern Chile), *Nothofagus* evergreen forest ecosystems are situated principally on geological substratum of volcanic rocks on which soils are formed from deposits of volcanic ash (Veblen et al. 1996). This type of soil is still in an active stage of carbon and nitrogen accumulation. Therefore, retention of nitrogen should be at or near maximum capacity in these ecosystems (Edmonds et al. 1995). Consequently, and especially in case of low external input of nitrogen, leaching of nutrients is expected to be very low. However, also Gundersen et al. (1998) have suggested that forests with a C/N of  $<25$  have a high risk of nitrate leaching, and MacDonald et al. (2002) corroborates that leaching occur at European forests receiving  $<10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ , where soils are acidic or with low to intermediate C/N ratios.

This study was conducted in an evergreen *N. betuloides* (Mirb.) Oerst. rainforest located in southern Chile. The objectives were threefold: (a) to quantify the nutrient budget for a pristine catchment (b) to determine changes that occur in the chemical composition of bulk precipitation while passing through the canopy and soil and (c) to estimate the importance of cloudwater as nutrient input in an unpolluted old-growth forest. Therefore, concentrations of nitrogen ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , organic-N) and

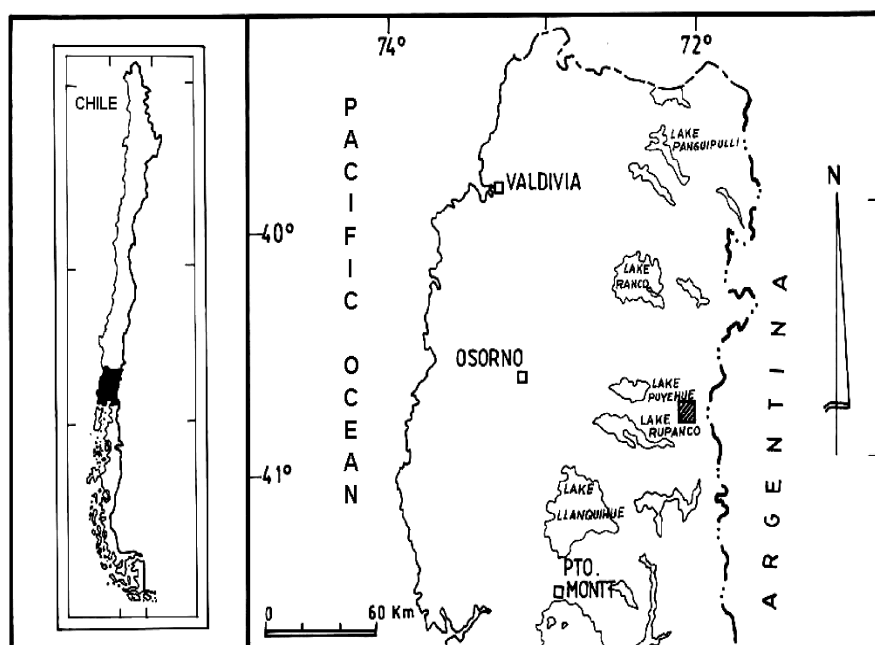


Figure 1. Location map of the study area, Puyehue National Park (Chile). Study site indicated by the black square.

base cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) in bulk precipitation, cloudwater, throughfall, stemflow, infiltration and percolation soil solution and runoff in a small watershed were studied.

### Study area

The study area is located in the Valley Antillanca, Puyehue National Park in the Cordillera de los Andes, southern Chile ( $40^{\circ}47'S$ ,  $72^{\circ}12'W$ ) (Figure 1). A watershed of 69 ha was selected with an elevation ranging from 910 to 1402 m above sea level. The orientation of the watershed is northwest and the mean slope is 39.5%. The climate is classified as rainy temperate. The annual precipitation (rain and snow) amounts about 7000 mm, with occurrence of a snow cover during June to November. During the study period (May 1999–October 2000) the annual mean temperature was  $4.5^{\circ}C$ , maximum temperature was  $24.8^{\circ}C$  and minimum temperature  $-8.7^{\circ}C$  inside the forest. The prevailing wind direction during winter was as a consequence of the Polar Front north to north-west. During summer the prevailing wind direction was west because of the presence of the South Pacific Anticyclone.

Soils of the area, originating from volcanic eruptions of different ages, are classified as Mesic, Umbric Vitrandept. The material consists of andesitic and

Table 1. Chemical characteristics of the mineral soil in the study area.

Depth (cm)	pH	N (%)	C (%)	C/N	P (ppm)	Na <sup>+</sup> (ppm)	K <sup>+</sup> (ppm)	Ca <sup>2+</sup> (ppm)	Mg <sup>2+</sup> (ppm)	Al <sup>3+</sup> (ppm)
0–10	5.0	0.56	12.3	21.9	5.9	53.0	130.0	311.0	64.0	2543
10–35	6.1	0.40	8.3	21.1	2.5	40.0	47.0	66.0	19.0	2688

basaltic tuff, scoria and sand of different particle sizes (Peralta 1975). Soil chemical characteristics are shown in Table 1. The study area is a *N. betuloides* forest of 325 year old and has a stand density of 865 trees ha<sup>-1</sup>, a mean tree height of 23 m, and a canopy cover of 69%. The overstorey is constituted of *N. betuloides* (23 m height) and *Saxegothaea conspicua* Lindl. (9 m height). The understorey (3–5 m height) is dominated by *Podocarpus nubigena* Lindl, *S. conspicua* Lindl and *Myrceugenia chrisocarpha* (Berg) Kausel with a cover of 15%. The lower understorey (2–4 m height) is comprised of *Chusquea argentina* Desv. and *Chusquea montana* Phil. with a cover of 90%. In the shrub stratum (<2 m), *C. montana*, *Blechnum magellanicum* (A.N. Desv.) Mett, *Pernettya mucronata* (L.f.) Gaud ex. Spreng., *Desfontainea spinosa* R. et P., *M. planipes* (H. et A.) Berg. and *Myrceugenia chrisocarpha* (Berg.) Kausel are dominant (Godoy et al. 2001).

## Materials and methods

### Field sampling

Precipitation quantities (rainfall and snow) were determined from hourly rain-gauge data recorded with a Heater Recording HOBO (Ben Meadows Company). Bulk precipitation was sampled using three plastic rain gauges (surface area = 200 cm<sup>2</sup>) attached to a 2-liter collection bottle. Both rain gauge and bulk precipitation collectors were installed in an open area (no trees were within 20 m of the sampling point), about 1000 m from the experimental plot at approximately 1120 m elevation. Cloudwater samples were collected during 12 events of both fog and cloud using passive collectors (Schemenauer and Cereceda 1994). Collectors (0.5 m tall, 1 m width) consisted of a panel frame with polypropylene Raschel mesh (2.5 mm diameter) installed 1.5 m above the ground.

Within the watershed, a representative plot of 45 m × 30 m was selected. To collect throughfall water, 12 pluviometers (surface area = 200 cm<sup>2</sup>) were installed along two transects. The collectors were placed at 5 m intervals, 1.2 m above the forest floor. The collectors of bulk precipitation and throughfall water were installed inside opaque tubes in order to avoid light penetration that could promote algae growth. They were covered with plastic nets in order to prevent insects and leaves entering the collection bottles, and designed with a plastic ring in order to exclude bird droppings (Kleemola and Soderman 1993). Stemflow collectors were installed at 12 trees of average diameter: four of *N. betuloides* (27.5–117.5 cm dbh)

and eight of *S. conspicua* (7.5–37.5 cm dbh). Stemflow collectors were constructed with plastic collars of 2.5 cm diameter, with the flow passing into a plastic container of 100 l. Six small zero-tension lysimeters (900 cm<sup>2</sup>) were used for the collection of soil infiltration water. These collectors were installed at 0.1 m depth and were covered by an undisturbed soil layer. Percolation water (0.8 m depth) was collected using a Pressure Vacuum Soil Water Sampler (Soil Moisture Equipment Corp., Santa Barbara, CA). Sixty centibars of soil suction was applied 24 h before collection. A water level recorder was installed on the catchment to measure stream water discharge. Runoff water samples were collected in the stream in a place adjacent to the water level recorder.

The volume of water in each collector was measured in the field on a weekly basis. Because of logistic considerations and difficulties of working in remote areas, all water samples for chemical analysis were, according to recommendations of Kleemola and Soderman (1993), collected monthly for the period May 1999–October 2000. Samples of stream water were collected fortnightly. On each sampling occasion, the water volume of each collector was measured in the field and the bottles were replaced by bottles rinsed with distilled water. For each water fraction, samples were pooled to one sample for chemical analyses at the analytical laboratory of Water Chemistry, Universidad Austral de Chile.

#### *Chemical analyses*

The samples were analyzed within 48 h after collection. Samples were filtered through a borosilicate glass filter (Whatman) of 0.45 µm. pH and electrical conductivity were determined using specific electrodes. NO<sub>3</sub>-N was determined by a colorimetric method based on the reduction of cadmium (Clesceri et al. 1998). NH<sub>4</sub>-N was measured by the phenate method (Clesceri et al. 1998). Organic-N was calculated by subtracting NH<sub>4</sub><sup>+</sup>-N concentration of total Kjeldahl nitrogen (sum of organic nitrogen and NH<sub>4</sub>-N) measured by the Kjeldahl method (Clesceri et al. 1998). K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were measured by atomic emission spectrometry.

The quality of chemical analyses was checked by including method blanks, repeated measurements of internal and certified reference samples and by inter-laboratory tests. The detection level was 1 mg l<sup>-1</sup> for base cations and 1 µg l<sup>-1</sup> for nitrate, ammonium and organic-N.

#### *Calculation of water fluxes*

Soil percolation flux at 0.8 m depth was not calculated since no validated soil water transport model was available. Stream water ion export was calculated using continuous discharge and biweekly grab samples according to the methods 2 and 4 of Swistock et al. (1997). Cloud water volume was estimated using the model of Walmsley et al. (1996), considering the water volume, the cross-sectional area of

the collector, the collection efficiency and the sampling period. According to Schemenauer and Cereceda (1994), the collection efficiency of the mesh was assumed to be about 35–50% increasing with higher wind speeds. In our study site, the average wind speed is high (data from Aguas Calientes meteorological station indicates daily maximum values of about  $30 \text{ m s}^{-1}$ ). The average cloud immersion frequency was estimated to be about  $5 \text{ h day}^{-1}$  and 10–20 days per month with cloud/fogs between March and February, from data observed in Aguas Calientes meteorological station (Puyehue National Park).

#### *Calculation of element fluxes*

Element fluxes were calculated for the period May 1999–April 2000, by multiplying the measured amount of water in the different compartments of the forest with the element concentration (volume-weighted averages).

Compared to bulk precipitation, the chemical composition of throughfall and stemflow water is generally altered with respect to most chemical elements, and it is widely acknowledged that this transformation results from (i) washing of dry deposition of aerosols and gases as well as (ii) canopy leaching, that is, release of ions from plant tissues or canopy uptake (Parker 1983). The total effect of the canopy on depositions is obtained by subtracting the incident precipitation deposition from throughfall deposition and is designated as net throughfall water (NTF). Negative NTF values indicate retention by the canopy, positive NTF values indicate release from the canopy. The canopy budget method was used (Ulrich 1983; De Vries et al. 1998) to estimate the contribution of dry deposition and canopy leaching or uptake to net throughfall water. Following Parker (1983), we calculated the deposition quantity of net throughfall water (NTW,  $\text{kg ha}^{-1} \text{ year}^{-1}$ ) to obtain the total effect of the canopy on deposition in the forest:

$$\text{NTW} = \text{TF} - \text{BD} = \text{DD} + \text{CL} \quad (1)$$

where BD = bulk deposition, TF = throughfall, DD = dry deposition, and CL = canopy leaching.

In the canopy budget method,  $\text{Na}^+$  is assumed to be inert with respect to the canopy, that is, neither uptake nor leakage occurs. Furthermore, particles containing  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are assumed to have the same deposition velocity as  $\text{Na}^+$ , as expressed by a dry deposition factor (DDF):

$$\text{DDF} = \frac{(\text{TF} - \text{BD})_{\text{Na}}}{\text{BD}_{\text{Na}}} \quad (2)$$

Dry deposition of  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is then calculated as bulk deposition multiplied by this dry deposition factor:

$$\text{DD}_X = \text{BD}_X \cdot \text{DDF} \quad (3)$$

where  $X = \text{K}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ .

Table 2. Water (mm year<sup>-1</sup>) and nutrient (kg ha<sup>-1</sup> year<sup>-1</sup>) fluxes from *N. betuloides* forest in southern Chile. Bulk precipitation (B), occult deposition (O), throughfall (TF), stemflow (SF), soil water infiltration (SI) and runoff (R).

	Water	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Org-N	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
B	7111	0.6	3.0	8.2	26.8	18.3	11.3	3.7
O	1010	1.0	1.4	n.d.	10.7	8.8	7.0	1.9
B + O	8121	1.6	4.4	–	37.5	27.1	18.3	5.6
TF	6715	2.6	0.5	5.5	51.1	66.8	39.5	8.0
SF	100	0.1	0.0	0.1	0.7	1.1	1.1	0.2
TF + SF	6815	2.7	0.5	5.6	51.8	67.9	40.6	8.2
SI	6930	6.0	1.1	8.2	47.0	118.8	43.3	10.2
R	9527	0.6	0.3	5.2	106.0	43.8	90.2	37.8

### Data analyses

One-way ANOVA and LSD tests were applied to find differences in nutrient concentrations in precipitation, throughfall water, stemflow water, soil solution, soil water percolation and runoff water (Sokal and Rohlf 1981). Differences among means were determined at the  $p < 0.05$  level. These tests were conducted after testing the preconditions of normality, homoscedasticity and autocorrelation.

## Results and discussion

### Hydrologic fluxes

From May 1999 to April 2000, the experimental watershed received 7111 mm of incident precipitation, of which 90% was rainfall and 10% was snowfall. The annual input of cloudwater was calculated to be 1010 mm. The forest floor received 6715 mm of throughfall water and 100 mm of stemflow water (Table 2).

Canopy interception, taking into account the calculated flux of cloudwater, amounted 1306 mm, which is 16% of the input of rain, snow and cloudwater. This interception value is lower compared to literature values from native forests in southern Chile (Huber and Oyarzún 1992) due to the open structure of the forest. The forest is as a consequence of natural disturbances characterized by a high number of small gaps (<1000 m<sup>2</sup>) (Veblen et al. 1996). The highest intercepted fractions were observed during spring and summer months. In winter and autumn, calculated interception was negative, since throughfall exceed precipitation measured in the clearing. This is due to the effect of fogs and clouds on the forest canopy (Figure 2). Cereceda and Schemenauer (1991) have reported the occurrence of fog in Chile, and they observed an average of 45 fog days per year about 40°S at coastal stations. However, fog frequencies as high as 189 days per year with another 84 days of patchy fog were reported at an altitude of 860 m a.s.l. There are several uncertainties in estimating atmospheric cloud/fog deposition to remote forest ecosystems.

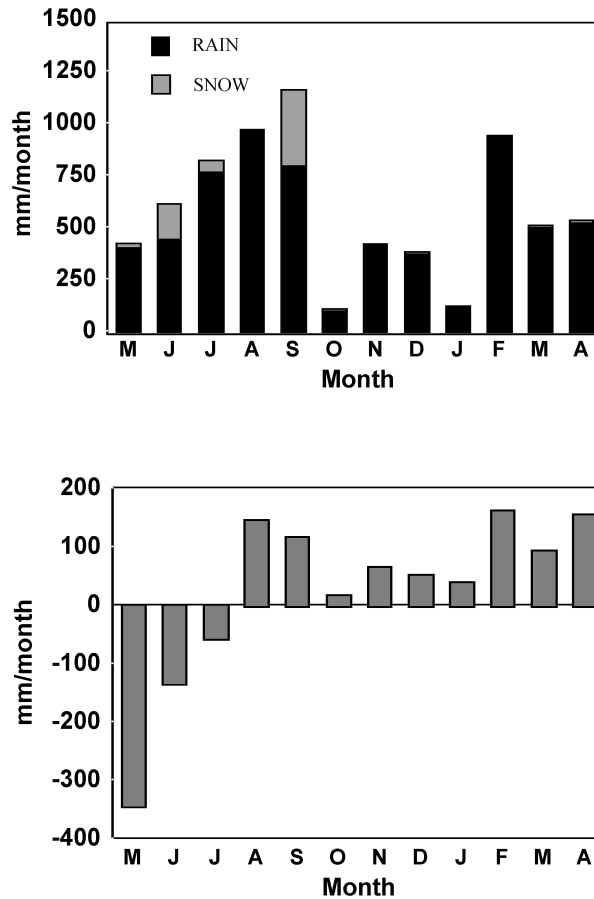


Figure 2. Monthly precipitation (upper) and crown interception (lower) of the *N. betuloides* forest.

Stemflow volume was very low and amounted only 1.2% of the incident precipitation. This low contribution to stand precipitation can be explained by the low density of trees, the geometry of the branches in this old-growth evergreen forest, the trunk surface roughness and the great capacity of water absorption by the bark of *N. betuloides* trees. Older trees have a higher trunk surface roughness and have a tendency to generate less stemflow (Houle et al. 1999; Levia and Frost 2003). Similar values have been reported for a temperate forest dominated by *Nothofagus obliqua* and *Eucryphia cordifolia*, located near Valdivia at 50 m a.s.l. (40 °S) (Huber and Oyarzún 1992), and a coniferous native forest of *F. cupressoides* in the Cordillera de la Costa (40 °S) at 820 m a.s.l. (Oyarzún et al. 1998). In south-central Chile, the native broad-leaved trees have a rough bark as well as abundant epiphytes and mosses which increase the interception storage and reduce the stemflow volume (Huber and Iroumé 2001).



Runoff water amounted 9527 mm, which is about 17% higher than the precipitation through rain and cloudwater (Table 2). This is probably due to the groundwater transfer in the volcanic soils of the Cordillera de los Andes. Research conducted in southern Chile showed that groundwater can deliver an important contribution to the water yield at catchment level (Pérez and Helms 2002). Values of annual water yield higher than one have also been observed in other small experimental watersheds nearby the study site. Data from forested and agricultural watersheds of the Rupanco lake basin located at the Cordillera de los Andes indicated that runoff volume was higher than precipitation (Oyarzún et al. 1995). On a catchment scales of several square kilometers, runoff is necessarily smaller than incident precipitation, since no water can be generated in the catchment. But, in this small experimental catchment of 69 ha probably the phreatic boundaries not correspond with the topographic divides and the deep seepage of the nearby catchments are high. Infiltration rates about  $400\text{--}650\text{ mm h}^{-1}$  have been measured in volcanic soils at the Cordillera de los Andes in southern Chile (Oyarzún et al. 1997). Another possible source of error is the underestimation of the precipitation measurements since when the precipitation falls as liquid or snow combined with high wind speed the deficit can be more than 50% (Allerup et al. 1997). We estimated this error using the model of Allerup et al. (1997) and the corrected precipitation could be 9463 mm, about 33% more than the rainfall amount.

#### *Nutrient fluxes in aboveground water fractions*

During the period May 1999 to October 2000, average pH of bulk precipitation, throughfall water and stemflow water was higher than the natural acidity of rainwater ( $\text{pH} = 5.6$ ), while the average pH of cloudwater was slightly lower. Electrical conductivity was very low in all water fractions (Table 3). Electrical conductivity was highest in cloudwater ( $20.2\text{ }\mu\text{S cm}^{-1}$ ).

Average concentration of ammonium-N in bulk precipitation was higher than average concentration of nitrate-N (Table 3). The ratio of  $\text{NH}_4^+/\text{NO}_3^-$  was about 5, what can be attributed to the agricultural livestock activities in the Central Valley (100 m a.s.l.), located between 50 and 80 km west from the studied forest ecosystem. In bulk precipitation of the agricultural-livestock region of the Central Valley, average concentration of ammonium-N ( $753\text{ }\mu\text{g l}^{-1}$ ) is high compared with the average nitrate-N concentration ( $56\text{ }\mu\text{g l}^{-1}$ ) (Oyarzún et al. 2002). As a consequence of this agricultural-livestock activity, high amounts of  $\text{NH}_3$  are emitted from pastures, cowsheds, dungholds and manure or mineral fertilizer application, which can be trapped as dry, wet or occult deposition by the mountain forests. Nevertheless, the input of inorganic nitrogen via bulk deposition ( $7\text{ kg N ha}^{-1}\text{ year}^{-1}$ ) is low compared to more polluted forest ecosystems in Europe and North-America (Dise and Wright 1995). Average ammonium-N concentrations in throughfall and stemflow water were significantly lower than in precipitation (Table 3). Concentration of ammonium-N in cloudwater was significantly ( $p < 0.05$ ) higher than in precipitation (Table 3).

Bulk and stand (throughfall + stemflow) deposition amounted 3.0 and 0.5 kg  $\text{NH}_4\text{-N ha}^{-1}\text{ year}^{-1}$  respectively (Table 2). The contribution of stemflow to total stand deposition was lower than 2%. Occult deposition of  $\text{NH}_4\text{-N}$  was calculated to be  $1.4\text{ kg ha}^{-1}\text{ year}^{-1}$ . Net throughfall deposition (stand deposition minus bulk and occult deposition) amounted  $-3.9\text{ kg ha}^{-1}\text{ year}^{-1}$ , indicating that the canopy acts as a net sink for ammonium. Compared to precipitation, a net  $\text{NO}_3^-$  enrichment was observed in throughfall and stemflow water. Average  $\text{NO}_3\text{-N}$  concentrations in throughfall and stemflow water were significantly higher ( $p < 0.001$ ) than in precipitation (Table 3). Also concentrations in cloudwater were significantly ( $p < 0.001$ ) higher than in precipitation (Table 3). Nitrate fluxes in bulk, occult and stand deposition (Table 2) were 0.6, 1.0 and  $2.7\text{ kg NO}_3^-\text{-N ha}^{-1}\text{ year}^{-1}$  respectively. Stemflow contributed less than 5% to stand deposition. Net throughfall deposition of nitrate due to dry deposition and/or canopy leaching was  $1.1\text{ kg ha}^{-1}\text{ year}^{-1}$ .

Concentrations of organic nitrogen in throughfall and stemflow water were lower than concentrations in bulk precipitation, but without showing significant differences (Table 3). Organic-N concentrations in cloud water were not determined. Bulk and stand deposition (Table 2) amounted 8.2 and  $5.6\text{ kg organic-N ha}^{-1}\text{ year}^{-1}$ , respectively. The net throughfall flux of organic nitrogen was negative, indicating organic nitrogen is retained in the canopy.

It is clear that occult deposition contributes to a considerable extent to nutrient input of the forest. Our results indicate that 40% of the total atmospheric input of inorganic-N originated from cloud deposition (Table 2). Weathers et al. (2000) estimated occult deposition to be between  $0.3$  and  $2.0\text{ kg ha}^{-1}\text{ year}^{-1}$  for dissolved inorganic and between  $1$  and  $9\text{ kg ha}^{-1}\text{ year}^{-1}$  for dissolved organic nitrogen in a *Nothofagus* forest at the Cordillera de la Costa in southern Chile ( $41^\circ\text{S}$ ). High concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in cloud water have been measured at a remote site in southern Chile (Weathers and Likens 1997) and a coastal site in northern Chile (Schemenauer and Cereceda 1992).

An important part of the atmospheric inorganic nitrogen deposition can be retained within the canopy, particularly in the case of ammonium. In general, the aboveground retention of inorganic nitrogen by forests was reported to be between  $2.8$  and  $4.2$  up to  $11.9\text{ kg N ha}^{-1}\text{ year}^{-1}$  (Lovett 1992). Beside the active uptake of ammonium within the canopy, it is speculated that also epiphytic lichens play an important role in the nitrogen balance of this *Nothofagus* forest. According to Reiners and Olson (1984), ammonium might be converted to nitrate by epiphytic bacteria or to organic nitrogen by microepiphytes or lichens. Guzmán et al. (1990) indicated lichens to be important sources of nutrients because of their high biomass and rapid decomposition rate. Also Galloway (1996) reported that talophytes are important sources of nitrogen and carbon in the forests of southern Chile. The temperate forests of southern Chile have lichen floras that have the richest and highest biological diversity. Their lichen floras are the most productive and prolific, and present the highest biomass, which has resulted in one the best-developed lichen floras in the world (Galloway 1996, Galloway and Quilhot 1998).

Epiphytic lichens are reported to be active absorbers of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (Reiners and Olson 1984). Also Houle et al. (1999) have measured significant decreases in

Table 3. Average concentrations ( $\pm$  standard deviation) of nutrients in different water fractions of the *N. betuloides* forest (Puyehue National Park, southern Chile).

	pH	EC ( $\mu\text{S cm}^{-1}$ )	$\text{NO}_3\text{-N}$ ( $\mu\text{g l}^{-1}$ )	$\text{NH}_4\text{-N}$ ( $\mu\text{g l}^{-1}$ )	Org-N ( $\mu\text{g l}^{-1}$ )	$\text{Na}^+$ ( $\mu\text{g l}^{-1}$ )	$\text{K}^+$ ( $\mu\text{g l}^{-1}$ )	$\text{Ca}^{2+}$ ( $\mu\text{g l}^{-1}$ )	$\text{Mg}^{2+}$ ( $\mu\text{g l}^{-1}$ )
Precipitation	6.1 (0.6)	8.5 (5.5)	10 (12)	49 (58)	115 (110)	445 (363)	195 (254)	161 (168)	55 (59)
Cloud water	5.5 (0.5)	20.2 (14.8)	87 (42)	109 (111)	n.d.	883 (471)	945 (456)	525 (436)	147 (77)
Throughfall water	6.1 (0.7)	12.9 (11.1)	38 (31)	10 (11)	82 (37)	766 (537)	967 (1043)	485 (482)	125 (133)
Stemflow water	6.0 (0.7)	17.9 (13.6)	112 (53)	14 (20)	77 (32)	621 (336)	1066 (633)	1091 (546)	158 (144)
Soil water infiltration	6.1 (0.5)	15.5 (11.2)	90 (61)	27 (25)	103 (59)	558 (314)	1318 (679)	585 (319)	144 (107)
Percolation water	6.2 (0.3)	19.7 (7.5)	46 (47)	28 (23)	94 (59)	1345 (313)	684 (731)	1462 (304)	573 (151)
Runoff water	6.4 (0.3)	14.3 (3.4)	4 (4)	3 (3)	55 (31)	1127 (307)	305 (297)	976 (243)	387 (110)

Table 4. Nutrient fluxes ( $\text{kg ha}^{-1} \text{ year}^{-1}$ ) split up in bulk and calculated occult deposition (BD + OD), calculated dry deposition (DD), total atmospheric deposition (BD + OD + DD), estimated canopy leaching (–)/uptake (+) (CL), and total stand deposition (TF + SF).

	BD + OD	DD	BD + OD + DD	CL	TF + SF
$\text{Na}^+$	37.5	14.3	51.8	0.0	51.8
$\text{K}^+$	27.1	10.3	37.4	30.5	67.9
$\text{Ca}^{2+}$	18.3	7.0	25.3	15.3	40.6
$\text{Mg}^{2+}$	5.6	2.1	7.7	0.5	8.2

nitrogen concentrations (both  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) relative to precipitation in coniferous stemflow water due to epiphytic lichens and associated microorganisms. Since epiphytic lichens are present in significant amounts on the stems and branches of the *Nothofagus* species, it is probable that the chemistry of throughfall and stemflow water is affected. Preliminary sampling (Godoy et al. 1999) indicated a higher cover degree of epiphytic lichens of the genus *Peltigera*, *Pseudocyphellaria* and *Sticta* living on the trunks and branches of the *N. betuloides* compared with *S. conspicua* trees. The bark of *S. conspicua* trees is smooth and is renewed periodically, not permitting the establishment of epiphytic lichens. Preliminary results indicate that average  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations were higher in stemflow of the *Nothofagus* specie (respectively 176 and  $21 \mu\text{g l}^{-1}$ ) compared to *Saxegothaea conspicua* (respectively 45 and  $11 \mu\text{g l}^{-1}$ ) trees, although the stemflow volume was similar.

Throughfall deposition of base cations was higher than the sum of bulk and occult deposition (Table 2). Occult deposition contributed 24–29% of base cations in total deposition. The contribution of stemflow deposition to total stand deposition was lower than 5%. Net throughfall deposition was positive for all base cations ( $\text{Na}^+ = 14.3 \text{ kg ha}^{-1} \text{ year}^{-1}$ ,  $\text{K}^+ = 40.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ ,  $\text{Ca}^{2+} = 22.3 \text{ kg ha}^{-1} \text{ year}^{-1}$  and  $\text{Mg}^{2+} = 2.6 \text{ kg ha}^{-1} \text{ year}^{-1}$ ). Relative to total atmospheric deposition, stand depositions of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were enriched by a factor 1.4, 2.5, 2.2 and 1.5, respectively. Canopies were sources of base cations both during the growing and dormant season. This can be attributed to the wash off of dry deposition captured by the canopy and to element leaching from the leaves. The foliar leaching of  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  accounted for 45%, 38% and 6% of throughfall deposition respectively (Table 4), corresponding to results for other temperate forests (Parker 1983; Ragsdale et al. 1992; Van Ek and Draaijers 1994; Houle et al. 1999).

#### *Belowground and run-off nutrient fluxes*

Average pH and electrical conductivity of infiltration water, soil water percolation and runoff water was slightly higher than those of throughfall water (Table 3). Although concentration values of soil percolation water are difficult to interpret due to influence of possible dilution or concentration effects, the low concentrations of

$\text{NO}_3^-$  and  $\text{NH}_4^+$  under the rooting depth are an indication for an effective biological immobilization (Fernández et al. 1995) by vegetation and soil microflora. In winter, an increase in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations in soil water percolation was probably related to a decrease of biological uptake in the forest floor. In summer and autumn,  $\text{NO}_3^-$  concentrations increased in the soil water infiltration (10-cm depth), probably as a result of higher temperatures promoting litter decomposition and mineralization of organic matter. Average concentrations of organic nitrogen in runoff water are significantly higher ( $p < 0.001$ ) than inorganic nitrogen concentrations (Table 3). Also Hedin et al. (1995) reported the dominance of organic nitrogen in streamwater of the unpolluted forested catchments of the Cordillera de la Costa in southern Chile (40–42 °S). In soil water percolation, concentrations of cations generally decreased in the order  $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$ , and in the runoff in the order  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  (Table 3).

#### *Watershed nutrient fluxes*

Export of inorganic ( $0.9 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) and organic ( $5.2 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) nitrogen via streamflow water is lower than the input to the forest floor via throughfall and stemflow water ( $3.2$  and  $5.6 \text{ kg ha}^{-1} \text{ year}^{-1}$  respectively). In other words, 72% of the total deposited N was retained in the soil and vegetation. Export of inorganic nitrogen was negligible compared to organic N, in agreement with previous research in southern Chile (Hedin et al. 1995; Perakis and Hedin 2002), demonstrating that dissolved organic nitrogen is responsible for the majority of nitrogen losses from unpolluted forest ecosystems. Also, very low rates of N mineralization have been found in temperate forests of southern Chile (Pérez et al. 2003) indicating a relatively tighter internal N cycle in unpolluted forests, and the smaller amounts of inorganic N produced may be rapidly taken up by plants and microorganisms, with minimum losses to downstream ecosystems.

On an annual basis, the experimental watershed was a net source for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Table 2). The export via stream flow of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  was about two times higher than the input to the forest floor, for  $\text{Mg}^{2+}$  even 4.6 times higher. Only for potassium, export was only 65% of the throughfall and stemflow input. The large differences between input and output fluxes of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in this *Nothofagus* forest suggest internal sources for these elements in the stream. The bedrock of the study area is composed of coarse ferromagnesian compounds with high weathering capacity. These results are in contrast with input–output nutrient budgets calculated for coniferous forests of *F. cupressoides* located at Cordillera de la Costa (41 °S) (Oyarzún et al. 1998). The budget for base cations was positive, indicating the stability of the bedrock of the Cordillera de la Costa with negligible input from the geological substratum. Nutrient release in this type of soil is originating from forest floor decomposition and weathering of the mineral soil is negligible (Pérez 1995).

However, calculated input–output budgets are difficult to interpret. Besides weathering processes, also groundwater transfer from outside the watershed can be

an important factor controlling stream chemistry. In these types of watersheds located at the Cordillera de los Andes in southern Chile, external input from outside the watershed via groundwater is difficult to measure. External groundwater contribution to the hydrologic fluxes was estimated to be 2500 mm, indicating that the calculated output of nutrients via streamflow water could be overestimated with 20–30%.

### General conclusions

The evergreen *Nothofagus* forests, located at the Cordillera de los Andes in southern Chile, are receiving  $3.6 \text{ kg ha}^{-1} \text{ year}^{-1}$  of inorganic-N and  $8.2 \text{ kg ha}^{-1} \text{ year}^{-1}$  of organic-N via bulk deposition. Export of  $\text{NO}_3\text{-N}$  ( $0.6 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) and  $\text{NH}_4\text{-N}$  ( $0.3 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) via streamflow water represented negligible quantities. It is possible that runoff fluxes are overestimated for about 20–30% because of the inputs from outside the watershed via groundwater. Inorganic-N concentrations in runoff water were generally within the lowest range of those reported from other temperate forests in the world. However, according to the data from European forests, the low values of C/N ratio of  $<25$  and the acidic soils of these old-growth forests means a potential risk of nitrate leaching under increase future nitrogen deposition scenarios.

Significant changes were observed in throughfall, stemflow and soil solutions chemistry compared to bulk precipitation. The canopy was a net source for nitrate and base cations, and a net sink for ammonium and organic-N. Epiphytic lichens of the genus *Peltigera*, *Pseudocyphellaria* and *Sticta* living on the trunks and branches of the *N. betuloides* trees can play an important role in the nitrogen balance of *Nothofagus* forests due to their high biomass and rapid decomposition rates, especially *Sticta* sp. that has been identified as a species fixing of nitrogen.

It was estimated that this montane forests received  $2.4 \text{ kg ha}^{-1} \text{ year}^{-1}$  of inorganic-N via occult deposition, indicating that 40% of the total atmospheric input of inorganic-N originated from cloud deposition. The input via cloud water represented also an important source of base cations ( $10.7 \text{ kg ha}^{-1} \text{ year}^{-1}$  for  $\text{Na}^+$ ,  $8.8 \text{ kg ha}^{-1} \text{ year}^{-1}$  for  $\text{K}^+$ ,  $7.0 \text{ kg ha}^{-1} \text{ year}^{-1}$  for  $\text{Ca}^{2+}$  and  $1.9 \text{ kg ha}^{-1} \text{ year}^{-1}$  for  $\text{Mg}^{2+}$ ).

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