

Ecohidrology and Nutrient Fluxes in Forest Ecosystems of Southern Chile

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1. Introduction

Nitrogen (N) cycling in terrestrial ecosystems is a global environmental concern. The N cycle is a complex interplay where biotic and abiotic processes interact to transform and transfer N in an ecosystem. In general, one can simplify by classifying terrestrial N cycles all over the world in two groups: 'tight' N cycles and 'open' N cycles. The 'tight' N cycle is characterized by its high efficiency in producing bioavailable N and retaining it in the plant-soil system. The 'open' N cycle, on the other hand, is then considered to be less efficient, showing significant loss of N towards aquatic ecosystems and the atmosphere. The latter losses might lead to adverse effects on stream water and air quality, contributing as such to 'global change' [1].

The movement of nutrients between ecosystems is called geochemical cycling or external cycling. Two important input processes to forests are atmospheric deposition and mineral weathering [2]. The atmospheric input to forests consists of dry, and wet deposition. Aerosol and gases can be deposited directly from the air to plant and soil surfaces during rainless periods by dry deposition. Wet deposition is defined as the input of atmospheric compounds to the earth's surface by rain, hail, snow and/or occult deposition that occurs via fogs and clouds, which can be important in mountainous regions [3]. During rain events, dry deposition is washed off from plant parts and, together with wet deposition, reaches the forest floor as throughfall and stem flow. A second input process is the weathering of soil minerals as a result of chemical dissolution. In combination with atmospheric deposition, mineral weathering is the only long-term source of base cations for terrestrial ecosystems [2].

The temperate climate region of southern Chile still reflects undisturbed, pre-industrial environmental conditions [4]. This is in strong contrast with land use, which has been altered significantly over the last decades and centuries. Only fragments of the original forest vegetation remain unaltered, and are located in the Coastal and Andes mountain ranges (CMR

and AMR, respectively). Exotic tree plantations and agricultural areas dominate the central valley of southern Chile [5]. These characteristics make this region an ideal study area to investigate human impacts on biogeochemical nutrient cycling. Temperate forests in Chile are not yet affected by elevated N deposition, as is the case for forests in Europe or northeastern North America [6]. However, anthropogenic activities such as transport, industry and agriculture have been increasing in central and southern Chile. These activities can substantially alter the atmospheric N load and enhance N input on forest ecosystems in Chile [5].

Several biogeochemical studies have been carried out most in humid temperate forest ecosystems between 40° and 43° S in southern Chile [i.e. 7; 8; 9]. The annual mean temperature is 5 to 12° C and precipitation ranges from 2000 to 7000 mm in the AMR [3]. Data from [5] reported that mean annual N composition of the rainwater in the CMR and AMR ranges (41°–43° S), varied between $< 30 - 43 \text{ NO}_3\text{-N } \mu\text{g L}^{-1}$ and $9.8 - 26.2 \text{ NO}_3\text{-N } \mu\text{g L}^{-1}$. Similarly, $\text{NH}_4^+\text{-N}$ concentrations were $< 50 \text{ NH}_4^+\text{-N } \mu\text{g L}^{-1}$ and between $39.5 - 45.4 \text{ NH}_4^+\text{-N } \mu\text{g L}^{-1}$ for CMR and AMR, respectively. Forests in the CMR, are located immediately near the ocean and are unique in this sense that external input of major elements are almost exclusively due to marine aerosols. Since trees canopy act as efficient filters, forests can capture large amounts of atmospheric deposition, especially occult deposition (i.e: fog and cloud). Normally, mountain forest ecosystems are very efficient in trapping nutrients, especially N and cations from clouds and fogs [10; 11; 4].

Stream nutrient loads are heavily dependent on catchment vegetation. Alteration of canopies and the soil under it, have a significant impact on nitrogen ($\text{NO}_3\text{-N}$; $\text{NH}_4^+\text{-N}$; DON and TDN) and phosphorus ($\text{PO}_4^{3-}\text{-P}$ and TDP) reaching the stream. Human disturbances have a direct impact on biological communities and may lead to land degradation, causing a change in ecosystem services and livelihood support. Temperate rain forest ecosystems of southern Chile have efficient mechanisms of retention for essential nutrients, especially NH_4^+ and NO_3 [7, 3]. [6] described that the dominant form of N leaching was dissolved organic nitrogen (DON) for unpolluted forests of southern Chile. Other studies in the area had reported that conversion from native forests to exotic fast-growing plantations is likely to decrease N retention on catchments [12].

1.1. Native temperate rainforests of southern Chile

Native temperate rainforests of southern Chile represent an important global reserve of temperate forest with an extraordinary genetic, phytogeographic and ecological significance [13] with a worldwide high conservation priority [14]. These forests cover an area of 13.5 million ha. and are isolated by physical and climatic barriers, resulting in high endemism in plants and animals: 28 of 82 genera of woody plants (34%) are endemic to the region, along with 50% of vines, 53% of hemiparasites and 45% of vertebrates [15]. Some taxa are derived from ancient elements in southern Gondwana. Some relict tree species of conifers have the longest recorded lifespan, reaching an age of up to 3,600 years, constituting an excellent historical document for studies in reconstruction of climatic variability [16]. Most of the Valdivian eco-region is also considered as part of the world's 25 hotspots for biodiversity conservation and some of its forest types are included among the last frontier forests in the

planet. These forests support fundamental ecological functions, which provide a range of ecosystem services and goods such as conservation of biological diversity, maintenance of soil fertility, and timber and non-timber products [17]. Also they contribute to maintain fresh water supply, which in turn supports the availability of drinkable water for cities [18].

Native forests in the Valdivian eco-region (36° S through 48° S) have suffered anthropical disturbances due to inadequate logging practices, and to agricultural land or exotic fast growing plantations conversion. Rapid conversion to forest plantations between 1975 and 2000 resulted in deforestation rates of 4.5% per year within an area of 578,000 ha in the Maule region (38° S), facilitated through afforestation incentives [19]. Another important cause of deforestation has been human-set fires, with an annual average of 13,000 ha burned in the period 1995–2005 and a high interannual variability associated to rainfall variation [20]. Anthropogenic land cover change in the central depression of southern Chile (40°–42° S) is the most evident process of deforestation and agricultural expansion. A large fraction of the *Nothofagus* forests in that region has been cleared for agriculture during the last century [21]. Patches of second-growth forest cover vast areas of the regional landscape, leaving only scattered stands as a result from intensified agriculture activity. Direct effects of past land use may occur via long-term (> 50 yr) physical alteration of the rhizosphere caused by historic practices. Soil compaction is an enduring consequence of cultivation, grazing, and logging that can cause increased bulk density and reduced pore space [1]. These changes may affect the abundance of aerobic and anaerobic microorganisms and subsequently reduce the cycling of several elements, including N.

1.2. Eucalyptus plantation forests

In south-central Chile (35–40° S), the native vegetation has been converted to agricultural uses, primarily plantation forestry, which has resulted in a landscape dominated by industrial forestry plantations. The amount of land in the region classified as plantation forestry has increased by 55 % between 1998 and 2008 (116–179 thousands ha; [22]). As in other parts of Chile, over 20,000 ha of those new plantations have replaced native forests in the region [19, 23], mainly located in the CMR. The growth of exotic species in non-native environments has uncertain ecohydrological consequences [24]. Therefore, there is much concern about their water consumption. Several authors have concluded that the consequences of exotic fast growing plantations are: (i) the decrease of discharge due to higher evapotranspiration [25, 26]; and (ii) changes in the soil hydrological properties, such as infiltration rates [27] and soil hydrophobicity [28].

2. Objectives

In small headwater catchments located at the Costal mountain range (CMR), in southern Chile (40° S), concentrations and fluxes of NO_3^- -N, NH_4^+ -N, DON, TDN, TDP and base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) in bulk precipitation, throughfall and catchment discharge water were measured. The main objective of this study was to compare how hydrological variability affects

catchment nutrient load responses with different land cover of native forests and exotic plantation of *Eucalyptus* spp., in order to evaluate possible effects of land use

3. Material and methods

3.1. Description of the study sites

We selected five catchments with different land cover: (a) one with old-growth native evergreen rainforest (ONE), (b) one with native deciduous *Nothofagus obliqua* forest (ND), (c) one with secondary native evergreen forest (NE), (d) one covered with exotic fast growing *Eucalyptus nitens* (FEP) and (e) one with fast-growing exotic cover of *Eucalyptus globulus* (EG), located at CMR (40°S), near the city of Valdivia, Chile. All five catchments are located inland from the Pacific coast. The ONE catchment has an area of 2.8 ha at 336 m a.s.l. and is 20 km from the coast. The ND catchment has an area of 10.1 ha at 71–125 m a.s.l., and is 23.0 km from the coast. The NE catchment has an area of 3.1 ha at 227–275 m a.s.l. and is 2.0 km from the coast. The FEP catchment has an area of 54.8 ha and is 18 km from the coast, and the EG catchment has an area of 5.6 ha at 250–297 m a.s.l., and is 2.6 km from the coast.

3.2. Forest cover

In the catchment covered by old-growth native evergreen rainforest (ONE) the main canopy species are *Eucryphia cordifolia* Cav., *Aextoxicon punctatum* Ruiz et Pav. and *Laureliopsis philippiana* (Looser) Schodde. This last shows the highest density (718 tree ha⁻¹) and basal area (37.2 m² ha⁻¹) (Figure 1). The understorey is dominated by *Amomyrtus luma*, *Amomyrtus meli*, *Drimys winteri* and *Myrceugenia planipes*. The attributes of the old-growth native rainforests in the study area includes: increase in the proportion of successional species, the promotion of better growth rates to reach large diameters, the development of a rich understory and new regeneration cohorts, the increase of vertical structure, the development of increased wildlife habitat, and the presence of dead wood in the system (snags, and coarse woody debris) [29].

The main canopy species in the mixed ND catchment is the deciduous species *Nothofagus obliqua* (Mirb.) Oerst. reaching heights of 35 m, which covers 63.3 % of the catchment. Also, 13.8 and 7.9 percent is covered by native secondary forests of *Gevuina avellana* and *Astrocedrus chilensis* planted in 1983 and 1982, respectively, and 15.0 percent is covered by the fast-growing *Eucalyptus* sp. plantation. Understorey trees include *Luma apiculata*, *Podocarpus salignus*, *Aextoxicon punctatum*, *Amomyrtus meli*, *Gevuina avellana* and the exotic tree *Acacia melanoxylon*. Shrubs that reach heights over 3 m are mainly *Chusquea quila* Kunth with a 95% canopy cover.

In the NE catchment, the vegetation cover is characterized as a second growth native evergreen forest, dominated by *Myrtaceae* spp., *Amomyrtus luma* (Mol.) Legr. et. Kaus (29%), *Amomyrtus meli* (Phil.) Legr. et. Kaus (25%), *Laureliopsis philippiana* (Mol.) Mol. (14%), *Myrceugenia planipes* (Hook. et Arn.) Berg. (13%), *Dyasaphillum diacanthoides* (Less.) Cabrera (7%), *Gevuina avellana* (Molina) Molina (6%), *Lomatia ferruginea* (Cav.) R. Br., *Persea lingue* (Ruiz et Pav.) Nees ex Koop. and *Myrceugenia exucca* (DC.) Berg. (2% each) and *Aextoxicon punctatum* (1%). This

catchment is also used as a source of wood by local residents and as an occasional grazing ground for animals during the winter.

The FEP catchment is covered with *Eucalyptus nitens* of 4 and 14 yr-old. However, this catchment has had already 5 *E. nitens* rotations; density of 2911 tree ha⁻¹ and the basal area is 131.9 m² ha⁻¹. In FEP, the highest density was observed in the diameter 20-25 and 25-30 cm (Figure 2). The total density ranges between 2911-2733 tree ha⁻¹ in the sites. Basal area ranges between 131.9 and 144.4 m² ha⁻¹, and the mean height of the trees was 25.4 m. The riparian vegetation of the catchment with *Eucalyptus nitens* plantation has a large proportion of small trees and shrubs with a diameter distribution between 5-10 cm (Figure 3). The main tree species is *Luma apiculata* with 2180 tree ha⁻¹ and the shrub *Aristotelia chilensis* with 815 tree ha⁻¹ (Figure 3).

In EG catchment, the vegetation cover is composed of 80% exotic plantation of *Eucalyptus globulus* and 20% native evergreen remnant as a buffer zone. This is composed of *Berberis darwini* (Hooker) and *Ovidia pillopillo* (Gray) Hohen ex Meissn. (both with 29% cover), *Eucryphia cordifolia* Cav. (25.8%), *Lomatia ferruginea* (Cav.) R. Br. (9.7%), *Dasyphyllum diacanthoides* (Less.) Cabrera and *Raphitamnus spinosus* (Juss.) Mold. (both with 3.2%). Originally this catchment was a native evergreen forest. However it was cleared (35 years ago) with fire to open areas for grazing animals, and in some areas, for the extraction of wood. Recently (9 years ago) the grassland was replaced by exotic trees (*Eucalyptus globulus*). Local residents use the forest as a source of wood and also allow animals to graze on the grass as well as on tree shoots.

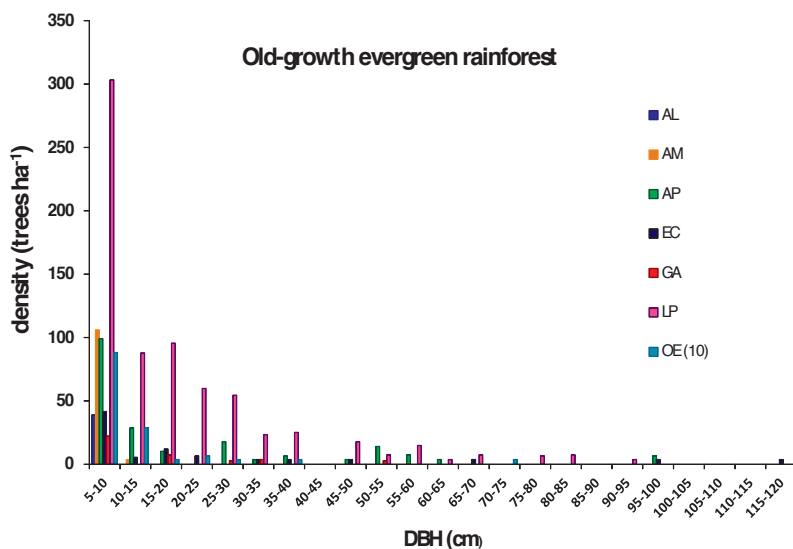


Figure 1. Diameter distributions by species (AL=Amomyrtus luma, AM=Amomyrtus meli, AP=Aextoxicon punctatum, EC=Eucryphia cordifolia, GA=Gevuina avellana, LP=Laureliopsis philippiana, OE=other species) in the catchment with native old-growth evergreen rainforests.

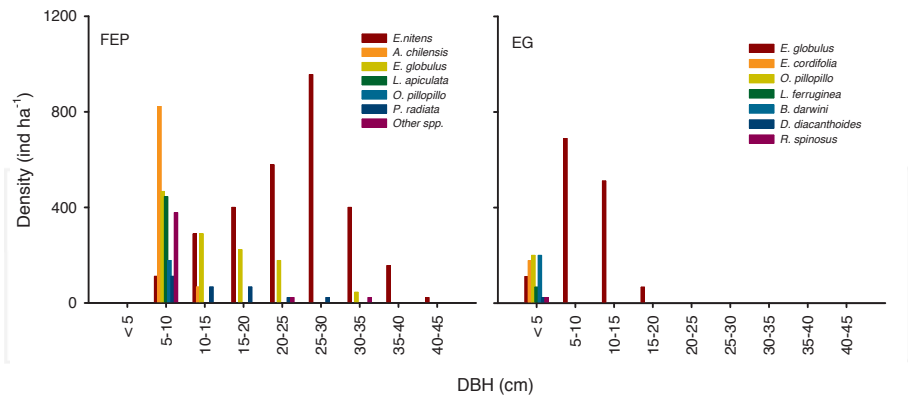


Figure 2. Diametric classes of species found on FEP and EG catchments.

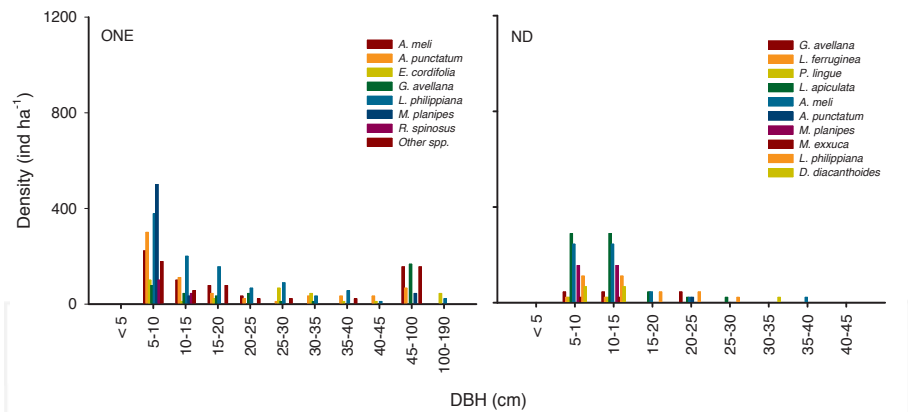


Figure 3. Diametric classes and density of trees for ONE and ND. Note that since ONE had the oldest trees, the last two classes comprise trees within 45 to 100, and 100 to 190 cm diameter at breast high.

3.3. Soils and climate

Climate in the area of study, is rainy temperate. In the meteorological station Isla Teja (25 m a.s.l.), 10 to 20 km from the study sites, the mean annual temperature is 12.0 °C (January mean

is 17 °C and July mean is 7.6 °C) and the mean annual precipitation is 2,280 mm. Rainfall is concentrated during winter (May–August, 62 %) and decreases strongly in the summer (January–March, 9 %). Soils in the study area are red clayish derivatives from ancient volcanic ashes, deposited over a metamorphic geological substratum, dominated by micaceous schist and quartz lenses. The soils are shallow (< 1.0 m depth) in EG and NE catchments, and predominantly deep (> 1.0 m) in ND catchment. Soils in the EG catchment are characterized by poor infiltration rates, and in the NE and ND catchments by high infiltration rates [27].

Soils at ONE and FEP catchments have approximately the same texture in the bottom of the 1 meter depth soil profile, however the top layers (0 to 15; and 15 to 30) have consistently 10% more clay, and 1% less sand in FEP compared to ONE soil profiles. In the FEP catchment, clay content ranges between 37.2 – 45.1 %, organic matter content ranges between 1.8 – 17.1%, inorganic-N (NO_3^- -N and NH_4^+ -N) ranges between 9.8 – 21.0 mg kg⁻¹, Ca^{2+} between 0.19 – 0.23 cmol kg⁻¹ and Mg^{2+} ranges between 0.09 – 0.16 cmol kg⁻¹. While, ONE soil clay content ranges between 31.1 – 37.3 % and organic matter content ranges between 5.9 – 17.8 %, inorganic-N ranges between 11.2 – 57.4 mg kg⁻¹, Ca^{2+} ranges between 0.23 – 1.32 cmol kg⁻¹ and Mg^{2+} ranges between 0.10 – 0.71 cmol kg⁻¹.

4. Methods

Bulk precipitation was sampled using four plastic rain collectors attached to a 2.5-liter bottle. Bulk precipitation collectors (surface area 200 cm²) were installed in open areas (no trees were within 20 m of the sampling point), located between a distance of 100 – 500 m. Throughfall water was collected, using 2–4 collectors (surface area 254 cm²) were installed inside each type forest. All collectors were installed 1.2 m above the forest floor and installed inside opaque tubes in order to avoid light penetration that could promote algae growth. Throughfall collectors had a thin mesh at the beginning of the neck of the funnel, in order to prevent insects and leaves entering the collection bottles, and designed with a plastic ring in order to exclude bird droppings [30]. Soil water was sampled at two different depths (0.3, 0.6 m) with low-tension porous-cup lysimeters (max 60 kPa of tension was applied) (Soil Moisture equipment corp.).

Discharge from each catchment was constantly measured by a pressure transducer paired with a baro diver (Schlumberger Water Services). Water samples were taken directly from the streams with an ISCO-6712 automatic sampler in each catchment. Stream samples were composed by two 250 mL aliquots taken each 30 minutes (1 h compound sample per bottle). Samples were filtered through a borosilicate glass filter (Whatman) of 0.45 µm. NO_3^- -N (NO_3^- -N+ NO_2^- -N) was determined by the cadmium reduction method, where NO_2^- -N was always below detection limits. NH_4^+ -N was determined with the phenate method (blue indophenol), detection limit (DL) was < 2 µg L⁻¹, for nitrite, nitrate and ammonia. Dissolved Inorganic Nitrogen (DIN) was calculated as follows: $\text{DIN} = \text{NO}_3^-$ -N + NO_2^- -N + NH_4^+ -N. Total dissolved nitrogen (TDN) was determined by the sodium hydroxide and persulfate digestion method (DL < 15 µg L⁻¹). Organic nitrogen (DON) was calculated by subtracting ($\text{DON} = \text{TDN} - \text{DIN}$)

concentration from TDN. Total dissolved phosphorous (TDP) was measured by the sodium hydroxide and persulfate digestion method ($DL < 3 \mu\text{g L}^{-1}$) at LIMNOLAB (Limnology Laboratory, Universidad Austral de Chile). Ca^{2+} and Mg^{2+} ($\pm 0.05 \text{ mg L}^{-1}$) were analyzed by AAS, while Na^+ and K^+ ($\pm 0.05 \text{ mg L}^{-1}$) by AES in the Forestry Nutrition and Soil Laboratory, Universidad Austral de Chile.

Canopy enrichment factors were calculated as the ratio between throughfall and bulk precipitation from different forest covers (throughfall / bulk precipitation). Fluxes were calculated using discharge and rainfall volumes. While nutrient retention (R) was calculated as follows:

$$\text{Retention} = (\text{Input} - \text{Output}) / \text{Input}$$

Where, $\rightarrow R > 0$, + Retention

$R = 0$, Equilibrium

$R < 0$, - Retention

5. Results and discussion

5.1. Throughfall enrichment factors

Canopy enrichment factors are presented in Figure 4. ND and ONE forests showed the highest enrichment and variability, whereas the EG plantation showed the lowest. The nutrient which presented the lowest annual enrichment in all throughfall samples was NO_3^- -N ranging from 0.8 for EG, through 1.5 for FEP. The highest enrichment was DON (10.3 times) for ONE and TDP (10.7 times) for ND forests. This enrichment is due to two processes: the washing off of the unquantified N input by dry deposition, on the one hand, and the N uptake from wet, dry particulate and gaseous deposition by leaves, twigs, stem surfaces, and lichens, on the other hand [31]. The old-growth evergreen forests (like ONE catchment) are multi-stratified and have an understory of high diversity, resulting in a complex and diverse structure and species composition. Also, [32] reported that DIN and DON concentrations were higher in throughfall than in bulk precipitation, particularly for nitrate, in a native *Nothofagus obliqua* forest and a *Pinus radiata* plantation, located near of the study sites. [8] observed 3.7 times throughfall enrichment for NO_3^- -N, in an evergreen *Nothofagus betuloides* forest ($9.8 \mu\text{g L}^{-1}$ and $36.5 \mu\text{g L}^{-1}$ for bulk precipitation and throughfall, respectively) and a 1.7 throughfall enrichment under a deciduous *Nothofagus pumilio* forest ($26.2 \mu\text{g L}^{-1}$ and $43.5 \mu\text{g L}^{-1}$ for bulk precipitation and throughfall, respectively) at cordillera de los Andes (40°S , 1120 m a.s.l.). However, NH_4^+ -N was retained by canopies. Data from forested sites in the USA and Europe [33] showed that net canopy exchange of N (throughfall plus stemflow minus bulk precipitation) was negative for NH_4^+ and NO_3^- at all sites, indicating that canopies were clearly sinks for inorganic N.

5.2. Annual nutrient fluxes

TDN annual retention and net annual fluxes (in $\text{kg N ha}^{-1} \text{ yr}^{-1}$) was 0.58 (1.43); 0.90 (9.31) and -4.79 (-7.14) for NE, ND and EG forests, respectively. TDP annual retention and net annual

fluxes (in $\text{kg P ha}^{-1} \text{ yr}^{-1}$) were 0.70 (0.08); 0.96 (0.06) and -1.44 (0.4) for NE, ND and EG, respectively (Figure 4). Studies in watersheds in the United States [34] reported that thin or porous soils and high infiltration rates have less capacity to retain N. However, in our study, catchments with high infiltration rates, such as NE and ND showed greater N retention than soils with very low infiltration rates, such as EG. In our study, the differences in DIN retention were evident between native forests and *Eucalyptus* plantation, as also has been described previously by [12]. However, [35] observed using land cover, watershed area and precipitation as predictors for water quality (nitrate, ammonia, DON, TDP and electric conductivity) for local models explained 79.5% of the variance.

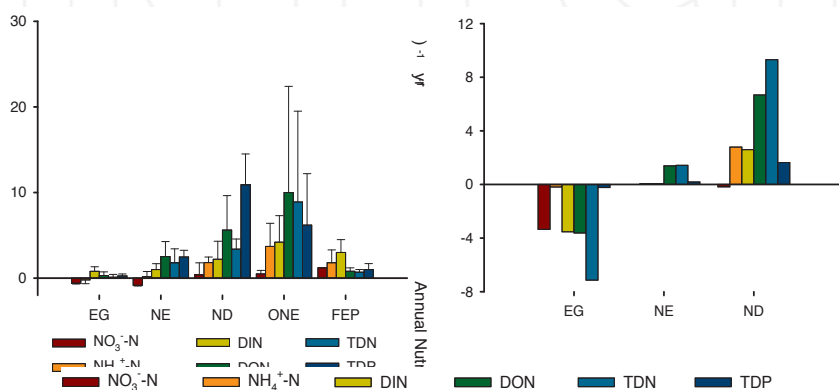


Figure 4. Throughfall enrichment factors for the five catchments (left) and annual nutrient fluxes for three catchments (right). EG=*Eucalyptus globulus* plantation, NE= native secondary evergreen ND= native deciduous, ONE= native old-growth evergreen, FEP=*Eucalyptus nitens* plantation.

5.3. Nutrient concentration in stream water

Nitrogen and phosphorous concentrations in stream water are variable in forest ecosystems of southern Chile (see Table 1). In general, the highest values of TDN and TDP concentrations are in *Fitzroya cupressoides* forest ($176.5 \mu\text{g N L}^{-1}$) located in Coastal mountain range and in *Nothofagus pumilio* forest ($67.3 \mu\text{g P L}^{-1}$) located in Andean mountain range. The lowest values were found in an evergreen forest ($36.8 \mu\text{g N L}^{-1}$), located in Coastal mountain range and in *Fitzroya cupressoides* forest ($4.6 \mu\text{g P L}^{-1}$), and located in the Coastal mountain range. Concentrations of inorganic N were smaller in the evergreen forest ($33.2 \mu\text{g L}^{-1}$) and in *E. nitens* plantation ($33.6 \mu\text{g L}^{-1}$) compared to organic N (94.4 and $67.0 \mu\text{g L}^{-1}$, respectively), in agreement with previous research in southern Chile [6; 3] demonstrating that dissolved organic nitrogen is responsible for the majority of nitrogen losses from unpolluted forest ecosystems.

Type of forest	Forest description	Location	TDN	TDP	References
Native deciduous	<i>Nothofagus pumilio</i>	AMR	nd	67.3	[8]
Native deciduous	<i>Nothofagus betuloides</i>	AMR	nd	9.2	[8]
Native deciduous	<i>Nothofagus betuloides</i>	AMR	62	nd	[3]
Native deciduous	<i>N.nervosa-N. obliqua</i>	AMR	73.3	44	Unpublished
Native evergreen	Evergreen forest	AMR	157	18	Unpublished
Native evergreen	Evergreen forest	AMR	67.3	37.4	Unpublished
Native evergreen	<i>S. conspicua</i> - <i>L. philippiana</i>	AMR	109	4.9	Unpublished
Native conifer	<i>Fitzroya cupressoides</i>	CMR	177	4.6	[9]
Native evergreen	Evergreen forest	CMR	36.8	24.1	[12]
Native evergreen	Evergreen forest	CMR	127	11.1	Unpublished
Native deciduous	<i>Nothofagus dombeyi</i>	CMR	153	nd	[32]
Exotic monoculture	<i>Eucalyptus spp.</i>	CMR	94.8	30.1	[12]
Exotic monoculture	<i>Eucalyptus nitens</i>	CMR	100	11	Unpublished
AMR average			85.6	30.1	
CMR average			115	16.2	

Table 1. Mean concentrations ($\mu\text{g L}^{-1}$) of TDN and TDP in stream water for different forest ecosystems under a low-deposition climate, southern Chile. At the end of the table 1, is the average for each location: Andean mountain range (AMR) and Coastal mountain range (CMR).

5.4. Relationships between discharge and nutrient concentrations

Nutrient exportation is related to hydrology, since water transports chemical compounds and particles. The relations of TDN and TDP with catchment discharge were positive for all nutrients except DIN, which showed a negative relation with discharge, during wet season (Figure 5). This negative relation is due to the dilution of nitrate with rainfall water which has higher concentrations of $\text{NH}_4^+\text{-N}$.

For dry season, the fitted models showed relatively high adjusted r^2 values for the *E. nitens* covered catchment for TDN and TDP (0,952 and 0,826, respectively; both with $p < 0.05$). However, the old growth covered catchment showed much lower values for TDN and TDP (0.317 and 0.519, respectively). Nevertheless, only TDP was significant. Dry season event DIN exportation was best fitted with a linear model. However, the fit was poor and not significant for both catchments. During wet season, the adjusted r^2 values were higher for *E. nitens* covered catchment than the old growth covered catchments (Table 2). On figure 5, is clearly seen that during dry season TDN, TDP and DIN increase rapidly as discharge increases in *E.*

nitens covered catchment (FEP). However this is not observed for the old growth covered catchment (ONE). However, during wet season TDP shows greater increase in concentrations in ONE, rather than FEP. TDN and DIN shows the same behaviour in both catchments.

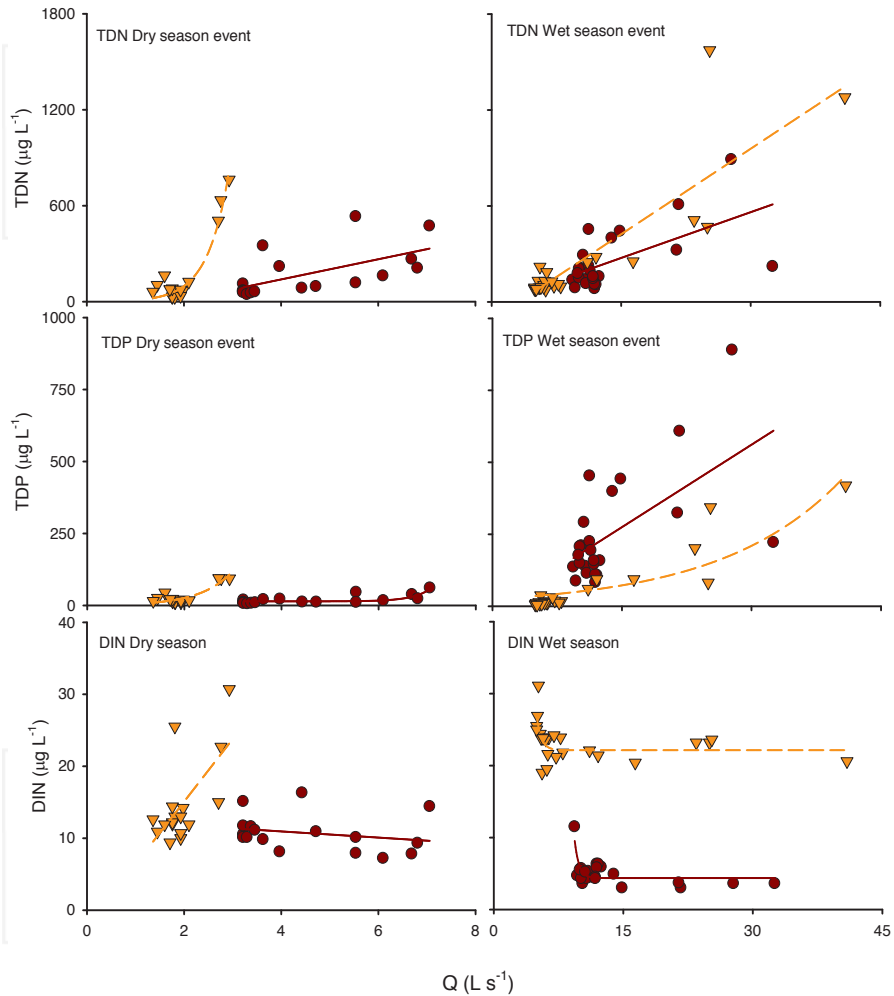


Figure 5. Total dissolved nitrogen (TDN), Total dissolved phosphorus (TDP) and Dissolved inorganic nitrogen (DIN) concentrations during one dry and wet season events (for the period March – November 2013), for the catchments covered with old growth native evergreen (ONE, in dark red circles) and catchment covered with *Eucalyptus nitens* (FEP, inverted orange triangles).

Dry season event				Wet season event		
Catchment	TDN	TDP	DIN	TDN	TDP	DIN
ONE	0,317 (L)	0,519 (3EG)	0,170 (L)	0,331 (L)	0,331 (L)	0,05 (L)
FEP	0,952 (1EG)	0,826 (2EG)	0,04 (L)	0,728 (L)	0,765 (2EG)	0,388 (L)

Table 2. Adjusted r^2 values after fitting linear (L, $f=y0+a \cdot x$); single parameter exponential growth (1EG, $f=e^{(a \cdot x)}$); 2 parameter exponential growth (2EG, $f=a \cdot e^{(b \cdot x)}$) and 3 parameter exponential growth (3EG, $f=y0+a \cdot e^{(b \cdot x)}$) models.

Dry season event			Wet season event	
Catchment	Ca ²⁺	Mg ²⁺	Ca ²⁺	Mg ²⁺
ONE	nd	nd	0,554 (L)	0,184 (L)
FEP	nd	nd	0,026 (L)	0,857 (ED)

Table 3. Ca²⁺ and Mg²⁺ vs. discharge during events for each catchment. Adjusted r^2 values after fitting linear (L, $f=y0+a \cdot x$) and exponential decay (ED, $f=a \cdot e^{(b \cdot x)}$) models.

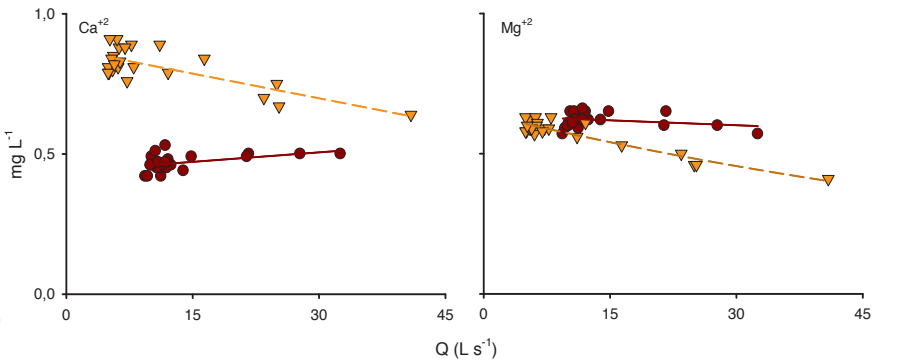


Figure 6. Ca²⁺ and Mg²⁺ concentrations vs discharge for the wet season event. Dark red dots and continuous line stands for old growth evergreen covered catchment (ONE), while inverted orange triangles and segmented line stand for *Eucalyptus nitens* covered catchment (FEP).

Typically, products of mineral weathering (e.g. Ca²⁺ and Mg²⁺) decline in concentration when the discharge increases caused by rainfall (stream water dilutes). This was observed during wet season event, and only in FEP, for both cations. ONE showed an increase in concentration for Ca²⁺ and a slightly reduced concentration for Mg²⁺.

We observed negative correlations between stream discharge and base cations concentrations (Figure 6). Typically, products of mineral weathering (e.g. Ca²⁺ and Mg²⁺) decline in concen-

tration when the discharge increases caused by rainfall (stream water dilutes). [36] reported inverse relationship between stream discharge and concentrations of Ca^{2+} and Mg^{2+} . However, [37] reported that during storms, both positive and negative relationships were observed between stream discharge and Ca^{2+} and Mg^{2+} concentrations and in some storms an initial increase in concentration was followed by dilution. On the other hand, [38] reported in an undisturbed old-growth Chilean forest that Ca^{2+} concentration demonstrated dilution when stream discharge increase and enhanced hydrological access occurred only for H^+ . According to [39], mica schists, present in the geological substrate at the coastal mountain range, are rich in micas and minerals and contain high levels of iron and magnesium. Hence, concentration levels of magnesium in stream water probably are influenced by the geological substrate. However, the dilution and increase in concentration (on FEP and ONE, respectively) is mostly due to the dilution of stream water discharge with throughfall.

6. Conclusions

We conclude that the mixed-deciduous (ND) and old-growth evergreen (ONE) forests show the highest canopy enrichment for throughfall, while the *Eucalyptus* plantations (FEP and EG) showed the minimum enrichment. The highest enrichment was DON (10.3 times) for ONE; and TDP (10.7 times) for ND catchment. In general, the differences in enrichment are attributed to high LAI (Leaf Area Index) values in both native forests: the old-growth evergreen forests are multi-stratified and have an understory of high diversity, and particularly in the mixed-deciduous forest the presence of a thick layer of bamboo (*Chusquea quila*), which covered the soil. Our results differing from forested sites in North America and Europe which indicates that the canopies are generally acting as sinks for inorganic-N [33]. Also [40] have reported that NO_3^- -N concentrations decreased in stemflow and throughfall relative to precipitation in old-growth forest in North America. However, in a data compilation from 126 European sites with high deposition climate in Scandinavia, Netherlands and Germany, [41] reported that inputs are enhanced by up to 3-5 times in throughfall through addition of dry deposition. On the other hand, our results show that the highest canopy enrichment was DON (dissolved organic nitrogen) especially in both native evergreen and deciduous forests. Also, DON was the most important nutrient fluxes in the native forested catchments, according to the literature [6] that reported that the dominant form of N leaching is dissolved organic nitrogen (DON) in unpolluted forests of southern Chile.

Annual retention of TDN in native deciduous and evergreen forests was 0.90 and 0.58, and TDP retention was 0.96 and 0.70, respectively. While the exotic *Eucalyptus* plantation there was a net release or loss of 4.79 and 1.44 for TDN and TDP, respectively. Studies in watersheds in the United States [34, 42] reported that thin or porous soils and high infiltration rates have less capacity to retain N. However, in our study, catchments with high infiltration rates, such as evergreen and deciduous forests showed greater N retention than soils with very low infiltration rates, such as *Eucalyptus globulus* plantation. Our results suggests that in native forests, rainfall water was infiltrating and percolating (subsurface flow) exporting less N in contrast to *Eucalyptus* plantation in which as soil has less porosity and infiltration rates due to land use

history. The *Eucalyptus* plantation catchment was cleared (35 years ago) with fire to open areas for grazing animals, and in some areas, for the extraction of wood, and recently (9 years ago) the grassland was replaced by exotic trees (*Eucalyptus globulus*).

Nutrients (TDN and TDP) shows the same behavior in both catchments, their concentration tends to increase as catchment discharge increases. DIN however, showed a different behavior for dry and wet season events. In the native old growth evergreen forest (ONE), DIN lower its concentrations as discharge increased, however in *E. nitens* covered catchment (FEP) increased its concentration. The latter is mostly due to the dilution or the increase of $\text{NO}_3^- \text{N}$ in stream discharge. However, during wet season both catchments showed the same DIN exportation behavior, though FEP had twice as much DIN when compared to ONE.

We are aware that modelling help to unravel and understanding hydrological processes and therefore nutrient exportation occurring within soil catchments. However there are many things to take in to account for, like biota (trees and microorganisms). However, discharge appeared to be a good predictor for TDN and TDP, for both events shown here. This was only seen in FEP, and not in ONE. DIN on the other hand showed poor model fitting. This means that there is still one or several unknowns on the control of DIN exportation during events.

The studies of events provide us with a much detailed perspective of what's happening within the catchment as an ecosystem, either pristine or heavily intervened. The reality is that ecosystems are going to keep "developing", each time with more and more relation to rural and city population. These pristine environments are in great danger and have to be protected from the inhabitants and other anthropic pressures, mostly cattle and land cover change to agricultural lands and exotic species.

Pristine study sites are recognized by being scarce and require a lot of efforts (monetary, time and struggle). In Chile, we have the luxury to have such areas near by some cities, nevertheless it will require more effort to keep it as pristine as possible. The prize for keeping this areas are many, from biodiversity hotspots to be able to unravel some of the black boxes that still exists regarding nutrient exportation and what are the effects of land cover change.

We would like also to address that soil use/cover change history, also plays an important role in N and P retention. Therefore before planting or doing forestry and agricultural activities, soil should be treated in order to enhance nutrient and water retention capabilities.

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