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Hydrological Controls on Nutrient Exportation from Old-Growth Evergreen Rainforests and *Eucalyptus nitens* Plantation in Headwater Catchments at Southern Chile

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Abstract

Soil cover disturbances have a direct effect on biogeochemistry, potentially enhancing nutrient loss, land degradation and associated changes in ecosystem services and livelihood support. The objective of this study was to assess how canopy affected throughfall chemistry and how hydrology affected stream nutrient load responses in two watersheds dominated by native old-growth evergreen rainforest (NF) and exotic plantation of *Eucalyptus nitens* (EP), located at the Coastal mountain range of southern Chile (40˚S). We measured nitrogen (NO_3-N, NH_4-N, Organic-N, Total-N) and total phosphorus (Total-P) at catchment discharge, and $\delta^{18}O$ in throughfall precipitation and stream discharge in both catchments, in order to separate throughfall (or new water) contributions during storm events. It was hypothesized that all nutrients showed an increase in concentration as discharge increased (or enhanced hydrological access), in EP; but not in NF. Our results indicated that Organic-N, Total-N and Total-P concentrations were positively related to discharge. However, NO_3^--N showed a negative correlation with catchment discharge. Organic-N and Total-P

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showed a flush during storm events; the opposite was observed for NO_3^--N. However, this behavior suggested that NO_3^--N was being retained by charged particles or soil micro biota, whether Organic-N was flushed as it was more concentrated in big pore water that was not tightly attached, compared with NO_3^--N.

Keywords

Native Rainforests, Exotic Plantations, Nutrient Fluxes, Hydrological Controls, Headwater Catchments

1. Introduction

Human disturbances have a great impact on native forest communities. This may lead to land degradation, causing changes in ecosystem services and livelihood support [1]. Stream nutrient loads are very sensitive to vegetation changes due human disturbances [2]-[4], but also to variables related to ecosystem hydrology, including infiltration rates, rainfall, and surface runoff [5]. Human-induced alteration of forest canopies and their soils have a significant impact on the hydrological controls of the nutrients (nitrogen, phosphorous and base cations) that reach the stream water. In this sense, export during storm events, concentration of nutrients could exhibit one of three general trends with respect to stream discharge: 1) dilution, 2) hydrological constant, or 3) enhanced hydrological access [6].

- Dilution occurs whenever stream discharge increases, but not the chemical concentration. This type of relationship is expected for chemicals with strong internal watershed source that does not increase in magnitude as a function of increased hydrologic throughput. We expect these elements to be diluted by enhanced throughput of water.
- Hydrological constant controls are characterized by a balance between water discharge and chemical concentration. This relationship is expected for elements that are delivered with precipitation water to the watershed, but that lack significant internal production or consumption processes. In the strictest sense, such idealized hydrological constancy may be rare since evapotranspiration provides a mechanism for concentrating solutes in deeper soil waters, and thus may impart differences in the delivery of chemicals and water depending on soil water flow paths. Some form of constancy may also be expected for elements that are chemically buffered within soils (e.g. via cation exchange reactions), but only if rates of hydrologic throughput remain low enough to maintain some form of equilibrium between soils and soil solutions. This is not likely to occur in most natural soils that experience variable hydrologic inputs over time.
- Enhanced hydrological access refers to controls that exhibit increasing chemical concentration with increasing discharge. The most common enhanced hydrological access is for chemicals found in areas of a watershed that are only active during periods of high flows. For example, in the case of elements produced in the surface soil horizons, as the region of subsurface flow deepens, *i.e.* as the saturated soil boundary approaches the soil surface, the flowing water increasingly accesses these elements. In recent years, this hydrological process has often been referred to as "piston flow".

Native temperate rainforests of southern Chile covering an area of 13.5 million ha, represent an important global reserve of temperate forests with an extraordinary genetic, phytogeographic and ecological significance [7]. Native forests in the Valdivian eco-region (36˚S through 48˚S) have suffered anthropic disturbances due to fires, logging practices, or its conversion to agricultural land and exotic fast-growing plantations. Temperate rain forest ecosystems of southern Chile have efficient mechanisms of retention for essential nutrients, especially NH_4^+ and NO_3^-. [8]-[10] described that the dominant form of N leaching was dissolved organic nitrogen (DON) in unpolluted forests of southern Chile. [11] described that DIN inputs did not end up in the soil water compartment, and gave evidence that Organic-N losses, originate from bio-unavailable compounds leaching from slow-turnover soil organic matter pools. While [3] reported that conversion from native forests to exotic fast-growing plantations was likely to decrease catchment N retention.

Besides the effects over N retention, [3] [5] described that soil water infiltration rates under eucalypts plantations were lower (6.7 ± 5.0 and 23.0 ± 19.7 $mm \cdot hr^{-1}$) and higher under a second growth native evergreen forest (76.9 ± 56.7 and 703 ± 380 $mm \cdot hr^{-1}$). In the former case, these would be large amounts of rainfall reaching the catchment after storm events, therefore affect N and P dynamics.

The temperate climate region in southern Chile still reflects undisturbed environmental conditions, with total nitrogen (Total-N) bulk precipitation inputs of less than 3 $kg \cdot ha^{-1} \cdot yr^{-1}$ at the Coastal mountain range [3]. This is in strong contrast with land cover, 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 range. Agricultural areas dominate the central valley of southern Chile; however, exotic tree plantations are spreading fast over the coastal mountain range [3] [12] [13]. These observations make this region ideal to study land cover change effects on biogeochemical nutrient cycling, without biases due to increased atmospheric nutrient depositions.

The objectives of this study are: 1) to assess how canopy affected throughfall chemistry, and 2) to compare how hydrological variability of "new" or event water, and "old" or groundwater contributions during storm events affects nutrient loads under different land covers of native evergreen rainforest (NF) and exotic plantation of *Eucalyptus nitens* (EP). To find these differences we measured nutrients such as: nitrogen (NO_3^--N, NH_4^+-N, Organic-N and Total-N) and total phosphorus (Total-P) in bulk and throughfall precipitation and catchment discharge, and $\delta^{18}O$ in throughfall and storm discharge in small headwater catchments located at coastal mountain range in southern Chile (40˚S). Our hypothesis is that new water will have higher contribution in EP, but not in NF, therefore controlling nutrient exportation. NO_3^--N and NH_4^+-N will show a dilution in old-growth native evergreen (NF), but not in *Eucalyptus nitens* (EP); while Organic-N and Total-P will show an enhanced hydrological access in EP, but not in NF, due to the different water infiltration rates are higher in native forests and lower in *Eucalyptus* plantation [12].

2. Study Sites

We selected two catchments with different land cover at the Coastal mountain range (40˚S), near the city of Valdivia, Chile. NF catchment, covered by old-growth native evergreen rainforest; and EP catchment covered with exotic fast growing *Eucalyptus nitens* (**Figure 1**). The drainage area of NF is 12.5 ha with an average altitude of 336 m above sea level (a.s.l.) and average slope of 15.4%. The main canopy species in this catchment are *Eucryphia cordifolia*, *Aextoxicon punctatum* and *Laureliopsis philippiana*. This last shows the highest density (718 tree ha^{-1}) and basal area (37.2 $m^2 \cdot ha^{-1}$). The understorey is dominated by *Amormyrtus luma*, *Amomyrtus*

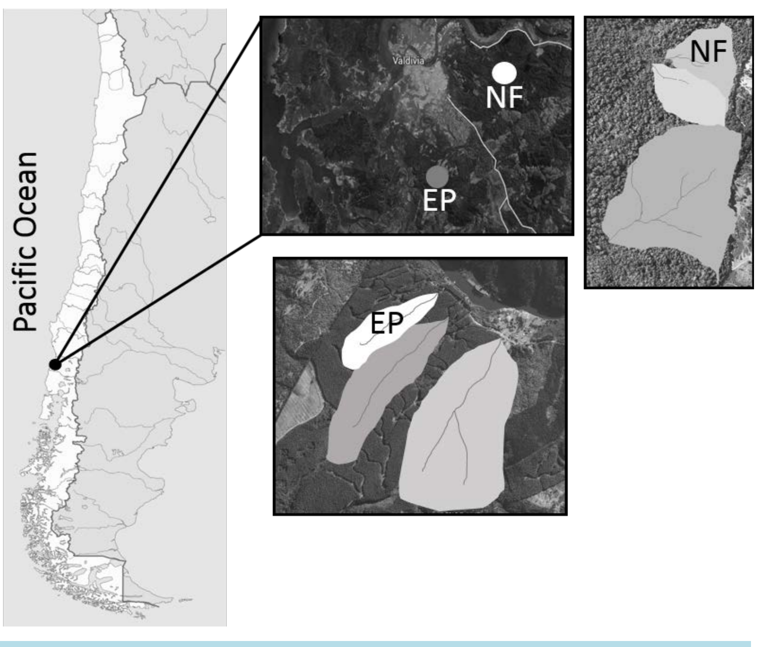

Figure 1. Old growth native forest (NF) and *Eucalyptus nitens* plantation (EP) research sites near the city of Valdivia, south central Chile (40˚S).

meli, *Drimys winteri* and *Myrceugenia planipes*. On the other hand, EP catchment has an area of 54.8 ha, an average altitude of 35 m a.s.l. and average slope of 34%. This catchment is actually covered with 6 and 16 years old *E. nitens* plantations, established on soils that already had 5 *E. nitens* rotations. Tree density equals 2911 tree ha^{-1} and the basal area is 132 $m^2 \cdot ha^{-1}$. The riparian vegetation is dominated by native species such as *Aristotelia chilensis*, *Luma apiculata*, *Fuchsia magellanica*, *Podocarpus saligna* and *Embothrium coccineum* covering not more than 15% of the whole catchment area. Both catchments are 13 km apart from each other.

The climate in the area of study is rainy temperate. In the meteorological station Isla Teja (25 m a.s.l.), 10 to 20 km away 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 2280 mm. Rainfall is concentrated in winter (May-August, 62%) and decreases strongly in summer (January-March, 9%). Soils at each catchment have approximately the same texture in the bottom of the 1 meter depth soil profile, but the top layers (0 to 15 cm; and 15 to 30 cm) have consistently 10% more clay, and 1% less sand in EP compared to NF soil profiles. Soils in these catchments are Andic Palehumult and Typic Paleudult, for NF and EP respectively. The main characteristic of these soils is that they are formed from volcanic ashes over a meteorized metamorphic complex [14]. In EP, soil clay content ranged between 37.2% - 45.1%, organic matter content ranges between 1.8% - 17.1%, inorganic-N (NO_3-N + NH_4-N) ranges between 9.8 - 21.0 $mg \cdot kg^{-1}$, Ca^{2+} between 0.19 - 0.23 $cmol \cdot kg^{-1}$ and Mg^{2+} ranges between 0.09 - 0.16 $cmol \cdot kg^{-1}$. While, NF 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 $mg \cdot kg^{-1}$, Ca^{2+} ranges between 0.23 - 1.32 $cmol \cdot kg^{-1}$ and Mg^{2+} ranges between 0.10 - 0.71 $cmol \cdot kg^{-1}$.

3. Methods

3.1. Sampling and Sample Analysis

Bulk precipitation was sampled using four plastic rain collectors attached to a 2.5-liter bottle. Bulk precipitation collectors (surface area 200 cm^2) 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 4 collectors (surface area 254 cm^2) which were installed under each type forest (evergreen and *E. nitens* plantation). 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 [15]. Soil water was sampled at two different depths (0.3 and 0.6 m) with low-tension porous-cup lysimeters (max 60 kPa of tension was applied) (Soil Moisture equipment corp. Santa Barbara, CA., USA).

Discharge from each catchment was constantly measured by a pressure transducer paired with a baro diver (Schlumberger Water Services). We sampled 5 rainfall events during the period March-November 2013 (**Table 1**). However, in this work we present detailed data from the events of April 4th (2nd event) and August 2nd (4th event) corresponding to events occurring at the end of dry season, and to mid rainy season respectively.

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, and were determined for: NH_4-N using the phenate method (blue indophenol), and NO_3-N as (NO_3^--N + NO_2^--N) using the cadmium reduction method, NO_2^--N was always below detection limit (DL), which was 1.5 $\mu g \cdot L^{-1}$, for nitrate, nitrite and ammonia. Dissolved Inorganic Nitrogen (DIN) was calculated as follows: DIN = NO_3^--N + NO_2^--N + NH_4^+-N. Total dissolved nitrogen (Total-N) was determined by the sodium hydroxide and persulfate digestion method (DL < 15 $\mu g \cdot L^{-1}$). Organic nitrogen (Organic-N) was calculated as follows: Organic-N = Total-N-DIN. Total phosphorous (Total-P) was measured by the sodium hydroxide and persulfate digestion method (DL < 3 $\mu g \cdot L^{-1}$) at LIMNOLAB (Limnology Laboratory, Universidad Austral de Chile).

In order to separate water fluxes in pre-event and event water during a storm event, we used stream samples sampled each hour with an ISCO-6512 automatic sampler; and 5 mm sequentially sampled throughfall using a modified version of the passive sequential sampler by [16], during the events. If two end members have a distinct difference in their isotopic signature, the stormflow hydrograph can be separated in their contributions based on a mass balance approach [17]:

Table 1. Mean discharge (Q), concentrations of dissolved inorganic nitrogen (DIN), organic nitrogen (Organic-N), total nitrogen (Total-N) and total phosphorus (Total-P) for the rainfall events in old growth native forest (NF) and *Eucalyptus nitens* plantation (EP).

	NF					EP				
Rainfall events	Q ($L \cdot s^{-1}$)	DIN ($\mu g \cdot L^{-1}$)	Organic-N ($\mu g \cdot L^{-1}$)	Total-N ($\mu g \cdot L^{-1}$)	Total-P ($\mu g \cdot L^{-1}$)	Q ($L \cdot s^{-1}$)	DIN ($\mu g \cdot L^{-1}$)	Organic-N ($\mu g \cdot L^{-1}$)	Total-N ($\mu g \cdot L^{-1}$)	Total-P ($\mu g \cdot L^{-1}$)
1st										
Mean	4.6	12.1	161.3	174.2	19.3	nd	nd	nd	nd	nd
±1 SD	1.4	5.9	151.0	150.5	15.2	nd	nd	nd	nd	nd
2nd										
Mean	3.8	7.3	254.5	262.0	22.5	2.0	14.7	155.7	32.0	1.9
±1 SD	0.9	3.0	215.8	216.3	26.0	0.4	5.9	224.3	30.5	0.3
3th										
Mean	17.8	19.3	392.0	411.4	37.0	20.1	28.7	363.9	63.2	2.0
±1 SD	10.3	3.8	315.6	313.7	37.0	15.5	9.9	560.7	102.4	0.3
4th										
Mean	13.8	3.2	246.0	251.0	28.9	10.7	22.2	246.4	63.9	2.2
±1 SD	5.9	1.2	191.2	190.5	20.5	9.1	3.0	374.2	108.1	0.2
5th										
Mean	8.3	5.5	268.3	273.5	27.9	3.4	19.2	144.1	44.9	1.2
±1 SD	2.7	1.8	175.4	168.6	17.0	1.8	2.0	255.2	87.1	0.1

$$Q_t = Q_p + Q_e \tag{1}$$

$$C_t Q_t = C_p Q_p + C_e Q_e \tag{2}$$

$$F_O = \left(\frac{C_T - C_E}{C_P - C_E} \right) \tag{3}$$

where Q_T is the streamflow, Q_P is the contribution from pre-event water, Q_E is the contribution of event water, C_T, C_P and C_E are the δ values of streamflow, pre-event water and event water, and F_P is the fraction of pre-event water in the stream. Abundance of stable water isotopes is based on the isotopic ratios ($^{18}O/^{16}O$). The abundance is reported in the δ notation and often expressed as parts per thousand (‰ or per mil). $\delta^{18}O$ values were determined on a Picarro Cavity Ring-Down Spectrometer (CRDS) L2120-i. Standard deviations were equal to or lower than 0.03‰ for $\delta^{18}O$. All isotopic analyses were made in ISOFYS Laboratory, Ghent University, Belgium.

The contributions of event and pre-event water can be determined based on Equation (3). The equation is constrained so that C_T falls between C_P and C_E and that Q_P and Q_E are between zero and Q_T. Several assumptions underlie Equations (1) and (2):

1) The isotopic content of event and pre-event water are significantly different.

2) The event water maintains a constant isotopic signature in space and time, or any variations can be accounted for.

3) The isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for.

4) Contributions from the vadose zone must be negligible, or the isotopic signature of the soil water must be similar to that of groundwater.

5) Surface storage contributes minimally to the streamflow.

3.2. Data Analysis

We used Spearman correlations and also fitted models to determine whether catchment discharge or new water contributions had an influence on nutrient concentration. Then, catchment discharge and nutrient concentrations during the study period and each event were plotted in order to observe the behavior in the increase, decrease and peak flows. Sigmaplot 12.5 (Systat Software, inc.) was used for all regressions. Statistical differences were considered if $p \le 0.05$. Since Total-N concentration was almost 95% conformed by Organic-N, we decided to plot only NO_3^--N, DIN, Total-N and Total-P.

4. Results and Discussion

4.1. Canopy Effects on Nutrient Concentration

There was a trend for Total-N and Total-P concentrations to be higher in throughfall than in bulk precipitation for both NF and EP (**Figure 2**). The enrichment concentration ratios of throughfall to precipitation were as follows: 3.03 and 4.48 for Total-N and Total-P, respectively, in NF; and 1.43 (Total-N) and 2.31 (Total-P) in EP. 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 [18]. The old-growth evergreen forests are multi-stratified and have an understory of high diversity, resulting in a complex and diverse structure and species composition. The particular structural features of old-growth forests in southern Chile include the presence of old individuals of late-successional species, canopy gaps, and large-sized coarse woody detritus [19].

Total-N concentrations from soil water at 30 and 60 cm were higher in NF (1125 and 1265 $\mu g \cdot L^{-1}$, respectively), and EP plantation (399 $\mu g \cdot L^{-1}$, for 30 cm only) than in bulk precipitation (169 $\mu g \cdot L^{-1}$). Also, Total-P concentrations in soil water at 30 and 60 cm depth were higher in NF (172 and 157 $\mu g \cdot L^{-1}$, respectively) and EP plantation (57 $\mu g \cdot L^{-1}$, for 30 cm only) than in bulk precipitation (18 $\mu g \cdot L^{-1}$). The same pattern was found in water soil infiltration at 10 cm depth in a native *Nothofagus obliqua* forest and in a *Pinus radiata* plantation located at the Central Valley of southern Chile (40˚S) [20]. Compared to bulk precipitation, the Total-N increased in both stands by passing through the humus and soil layers. This can be attributed to mineralization, nitrification and plant uptake occurring in the top soil [20]. There was a general trend for lower Total-N (127 $\mu g \cdot L^{-1}$ and 100 $\mu g \cdot L^{-1}$, for NF and EP respectively) and Total-P concentrations (11.1 $\mu g \cdot L^{-1}$ and 11.0 $\mu g \cdot L^{-1}$ for NF and EP,

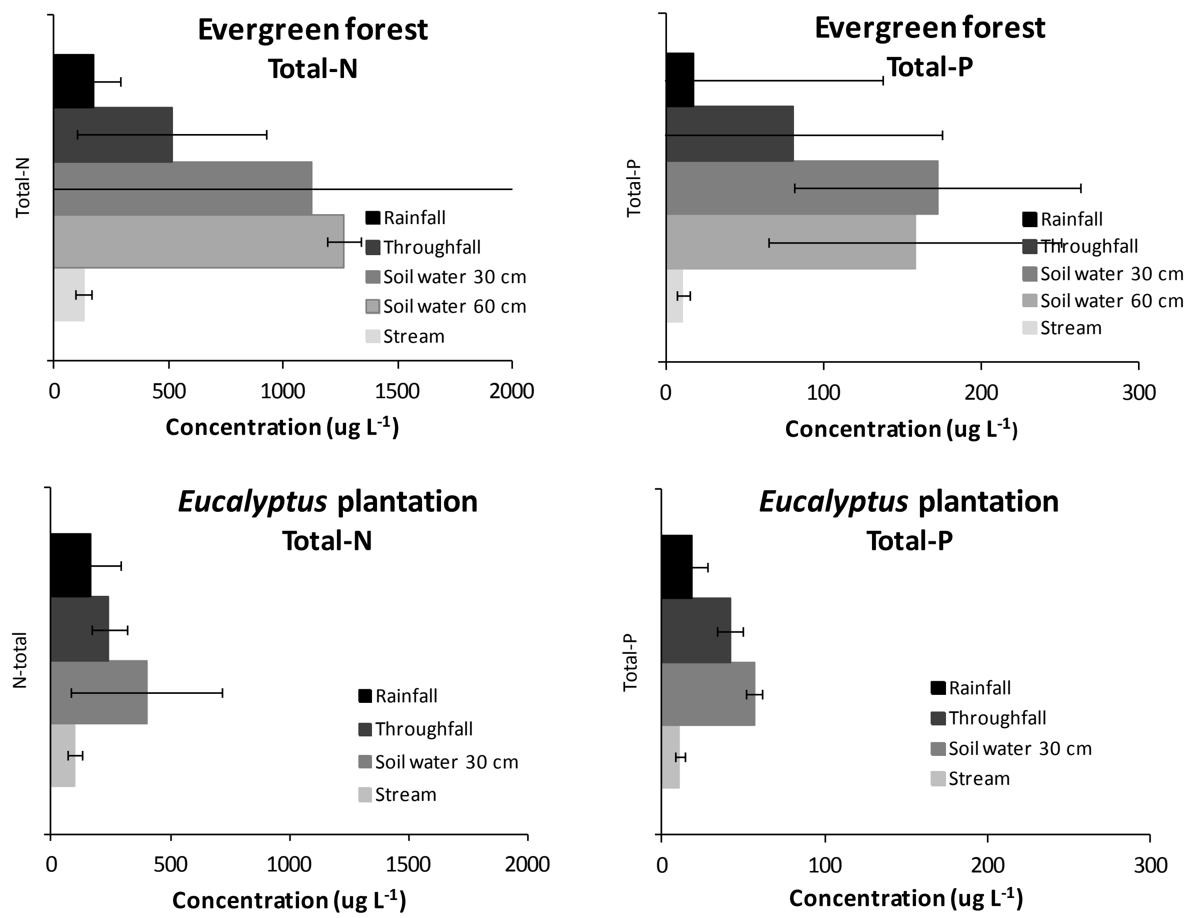

Figure 2. Total-N and Total-P concentrations in rainfall, throughfall, soil water and streams for old growth native forest (NF) and *Eucalyptus nitens* plantation (EP).

respectively) in streams than in bulk precipitation (Total-N: 169 μg·L^{-1}; Total-P: 18.1 μg·L^{-1}) (**Figure 2**).

4.2. Relationships between Discharge and Nutrient Concentration

Table 1 summarizes measured concentrations for stream discharge and nutrient concentrations for the different rainfall events. In both catchments, the highest values of discharge and nutrients concentration were observed during the 3rd event (June 21-22, 2013). In NF, mean discharge was 17.8 ± 10.3 L seg^{-1}. On average, Organic-N amounted to 392.0 ± 315.6 μg·L^{-1}, whereas DIN was only 19.3 ± 3.8 μg·L^{-1} resulting in a Total-N concentration of 411.4 ± 313.7 μg·L^{-1}; while Total-P was 37.0 ± 37.0 μg·L^{-1} (**Table 1**). In EP, mean discharge was 20.1 ± 15.5 L·s^{-1}. Organic-N was much higher than inorganic nitrogen (363.9 ± 560.7 μg·L^{-1} and 28.7 ± 9.9 μg·L^{-1}, respectively) (**Table 1**). The lowest values of discharge and nutrient concentration were in the 2nd event (April 4-5, 2013). On **Table 2**, we summarized the Spearman correlation (r values) and model fitting analysis (adjusted r^2) for the 2nd and 4th events, corresponding to the end of dry (April 4-5, 2013) and in middle of the rain seasons (August 2, 2013), respectively.

In general, Total-N (and Organic-N) and Total-P showed an increase in concentration with increasing discharge and were best described by exponential and linear models for 2nd and 4th event respectively. Catchment discharge showed higher correlation and r^2 values compared to new water (see **Table 2**, for details). This means that Total-N and Total-P shows an enhanced hydrological access on 2nd and 4th events. Presumably this behavior is due to the fact that the majority of Organic-N reaching the stream is present in the mobile water compartment (or big pore water). The slope decrease from 2nd to 4th event could be the effect of several rainfall events previous the 4th event. We hypothesized that these relations were due to these nutrients were more concentrated in mobile (or big pore) water in soil, and not retained by soil particles or by biological activity.

According to the "piston flow" theory, during storm events, water reaching the soil pushes mobile soil water into the stream. This explains the stronger relations that Total-N (and Organic-N) and Total-P have with catch-

Table 2. Results of Spearman correlations (r); and of best fitted models adjusted r^2 (Adj r^2): Linear models (L, $y = y0 + a \times x$); 2 parameter exponential decay (ED2, $y = a \times e^{(-b\times x)}$), and 3 parameter exponential decay (ED3, $y = y0 + a \times e^{(-b\times x)}$), for old growth native forest (NF) and *Eucalyptus nitens* plantation (EP).

		Total discharge				New water			
Site	Nutrient	M	r	Adj r^2	p	M	r	Adj r^2	p
					2nd event				
EP	NO_3^--N	ED2	0.66	0.41	p < 0.001	ED2	0.78	0.59	p < 0.001
	DIN	ED2	0.31	0.06	NS	ED3	0.69	0.43	p < 0.01
	Total-N	ED2	0.73	0.51	p < 0.001	L	0.52	0.23	p < 0.01
	Total-P	ED2	0.81	0.63	p < 0.001	ED3	0.67	0.42	p < 0.001
NF	NO_3^--N	ED2	0.73	0.51	p < 0.001	ED2	0.77	0.57	p < 0.001
	DIN	L	0.22	0.01	NS	L	0.34	0.08	NS
	Total-N	ED3	0.58	0.31	p < 0.01	L	0.42	0.14	p < 0.05
	Total-P	ED3	0.60	0.34	p < 0.01	L	0.39	0.12	p < 0.06
					4th event				
EP	NO_3^--N	ED2	0.51	0.23	p < 0.01	L	0.14	0.01	NS
	DIN	ED3	0.72	0.47	p < 0.001	L	0.43	0.14	p < 0.05
	Total-N	L	0.86	0.73	p < 0.001	L	0.92	0.84	p < 0.001
	Total-P	L	0.93	0.85	p < 0.001	L	0.95	0.9	p < 0.001
NF	NO_3^--N	ED2	0.68	0.44	p < 0.001	ED2	0.92	0.84	p < 0.001
	DIN	ED2	0.67	0.43	p < 0.001	ED2	0.92	0.83	p < 0.001
	Total-N	L	0.60	0.33	p < 0.01	L	0.37	0.10	NS
	Total-P	L	0.74	0.52	p < 0.001	L	0.46	0.18	p < 0.05

ment discharge during the 2nd event, on both catchments. Nevertheless, the 4th event shows that Total-N and Total-P concentrations are highly related to both, catchment discharge ($r = 0.86$; $p < 0.001$ and $r = 0.93$; $p < 0.001$, for Total-N and Total-P respectively), and new water ($r = 0.92$; $p < 0.001$ and $r = 0.95$; $p < 0.001$, for Total-N and Total-P respectively) in EP. This was not observed in NF, where the relation between N and P was explained mainly by catchment discharge ($r = 0.60$; $p < 0.01$ and $r = 0.74$; $p < 0.001$, for Total-N and Total-P respectively), than new water ($r = 0.37$; ns and $r = 0.46$; $p < 0.05$, for Total-N and Total-P respectively). The higher relation and slopes of the model, shown by Total-P vs catchment discharge and new water in EP, could reflect higher erosion rates that are taking place in EP, but not in NF. Several studies have described high erosion rates in *Eucalyptus* spp. covered catchments [5]. [21] described that 85% and 79% of exported sediment was coming from the stream bed in an *E. nitens* (100% coverage), and an *E. nitens* and *Pinus* spp. (66% and 33% of catchment cover respectively) covered catchment in a nearby study site.

NO_3^--N and DIN, on the other hand, showed a different behavior, being best fitted with exponential decay models (**Table 2**), showing a clear dilution behavior. During 2nd event NO_3^--N and DIN concentrations were best explained by new water and by an exponential decay models in both catchments. However, the model fitting was similar only for NO_3^--N (adjusted $r^2 = 0.59$; $p < 0.001$ and adjusted $r^2 = 0.57$; $p < 0.001$, for EP and NF respectively), but not for DIN (adjusted $r^2 = 0.43$; $p < 0.01$ and adjusted $r^2 = 0.08$; ns, for EP and NF catchments respectively). During the 4th event, in EP, NO_3^--N and DIN concentrations were more related with catchment discharge ($r = 0.51$; $p < 0.01$ and $r = 0.72$; $p < 0.001$, respectively), rather new water ($r = 0.14$; ns and $r = 0.43$; $p < 0.05$ for NO_3^--N and DIN respectively). However, native evergreen forest showed the opposite behavior NO_3^--N was highly related to new water ($r = 0.92$; $p < 0.001$) than catchment discharge ($r = 0.68$; $p < 0.001$). DIN concentrations showed the same behavior as NO_3^--N, being more related to new water than catchment discharge ($r = 0.92$; $p < 0.001$; $r = 0.67$; $p < 0.001$, for new water and discharge respectively).

The dilution observed for NO_3^--N and DIN, as catchment discharge and new water increases suggests that these nutrients have a strong internal source. Even though, throughfall is highly enriched in NO_3^--N and DIN, it is known that inorganic forms of nitrogen are used in several biological processes occurring at soil level. Also, [22] described that acid soils formed by volcanic ashes had the capability of retaining anions, like NO_3^- and PO_4^{-2}. On the other hand, [11] described that DIN inputs did not end up in the soil water compartment (mobile water). If the rate of NO_3^--N and DIN supply remains relatively unchanged during precipitation events, we expect these elements to be diluted by the enhanced throughput of water, therefore we could say that NO_3^--N and DIN are either highly consumed by microorganisms or is being retained by soil particles. This last suggests that the accessibility of moving water to NO_3^--N and DIN is difficult, maybe due to the fact that is strongly attached to soil particles.

Figure 3 and **Figure 4** show the relationship between catchment discharge and nutrient concentration for the 2nd event and for the 4th event. The correlations between nutrient fractions and catchments discharge were significant in both catchments for most of the nutrients (see **Table 2**). In general, when discharge increases also Total-N and Total-P concentrations increase and this is generally observed during all events (data not shown). Total-N increases are mostly due to Organic-N concentrations increase and for all N forms, except for DIN in NF (**Figure 3**). On the other hand, [23] observed both positive and negative correlations between stream discharge and NO_3-N in an old-growth evergreen rainforest located at Andean mountain range (40˚S) which was attributed to differences in peak flow. Nitrate has different behaviors during storm events because the streamflow can dilute the nitrate at the peak flows, but when the streamflow increases slowly, usually the nitrate also increases [23]. Our results show that when stream discharge increases, NO_3^--N concentrations decreases (**Figure 3** and **Figure 4**). Organic-N flushes, along with the dilution of NO_3^--N, have been previously described in literature [24] [25].

4.3. Total-N and Total-P Concentrations in Stream Water for Forest Ecosystems of Southern Chile

Total-N and Total-P concentrations in stream water are variable in forest ecosystems of southern Chile (see **Table 3**). In general, the highest values of Total-N and Total-P concentrations are in *Fitzroya cuppressoides* forest (176.5 µg Total-N L^{-1}) located in Coastal mountain range and in *Nothofagus pumilio* forest (67.3 µg Total-P L^{-1}) located in Andean mountain range, while the lowest values are found in an evergreen forest (36.8 µg Total-N L^{-1}), located in Coastal range and in *Fitzroya cuppresoides* forest (4.6 µg Total-P L^{-1}) located in the Coastal

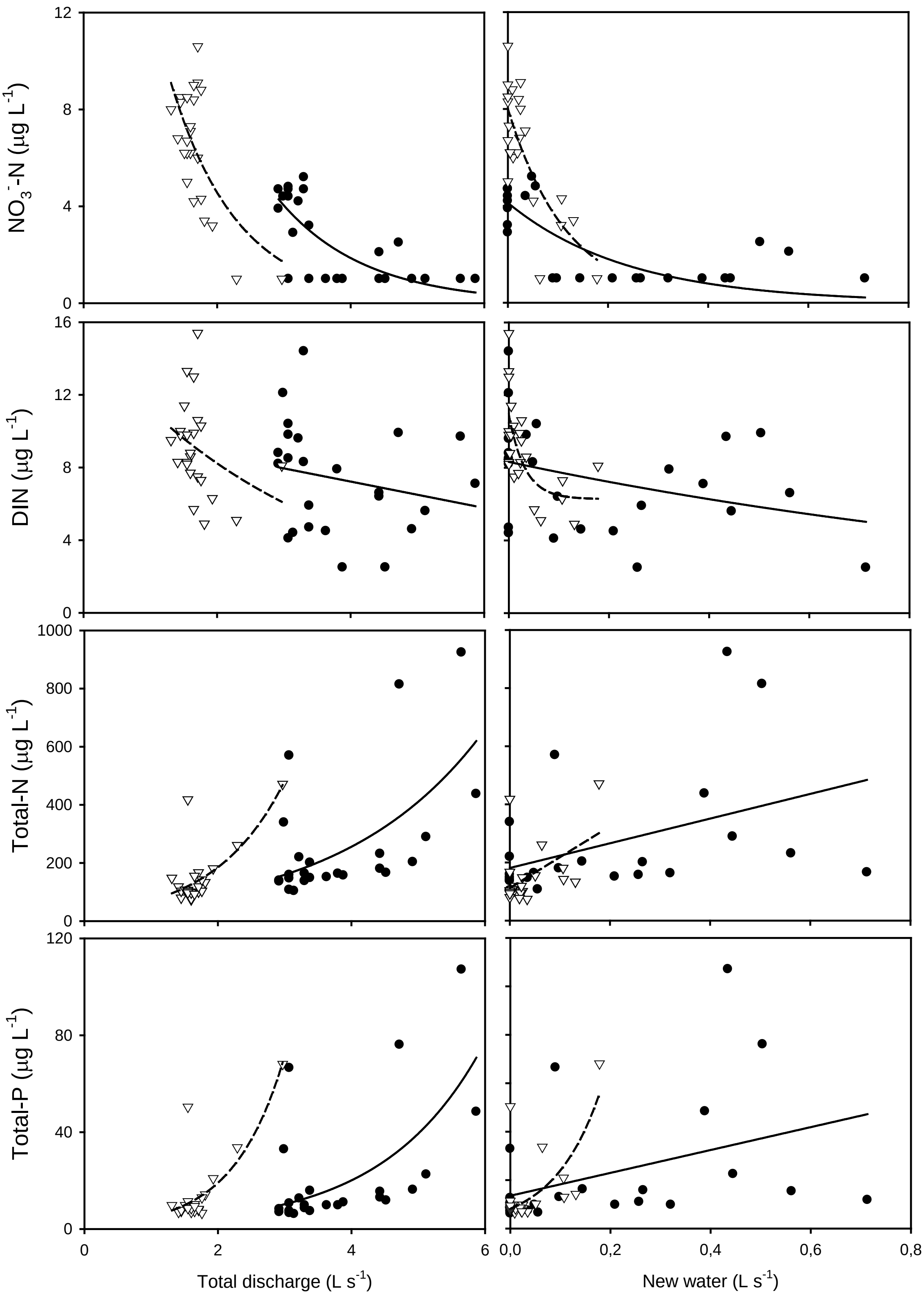

Figure 3. Nutrient concentrations (NO_3^--N, DIN, Total-N and Total-P) vs catchment dicharge (left side) and new water (L seg^{-1}) (right side), for both studied catchments during the 2nd event: old growth native forest (NF), in black round dots and *Eucalyptus nitens* plantation (EP) in white inverted triangles.

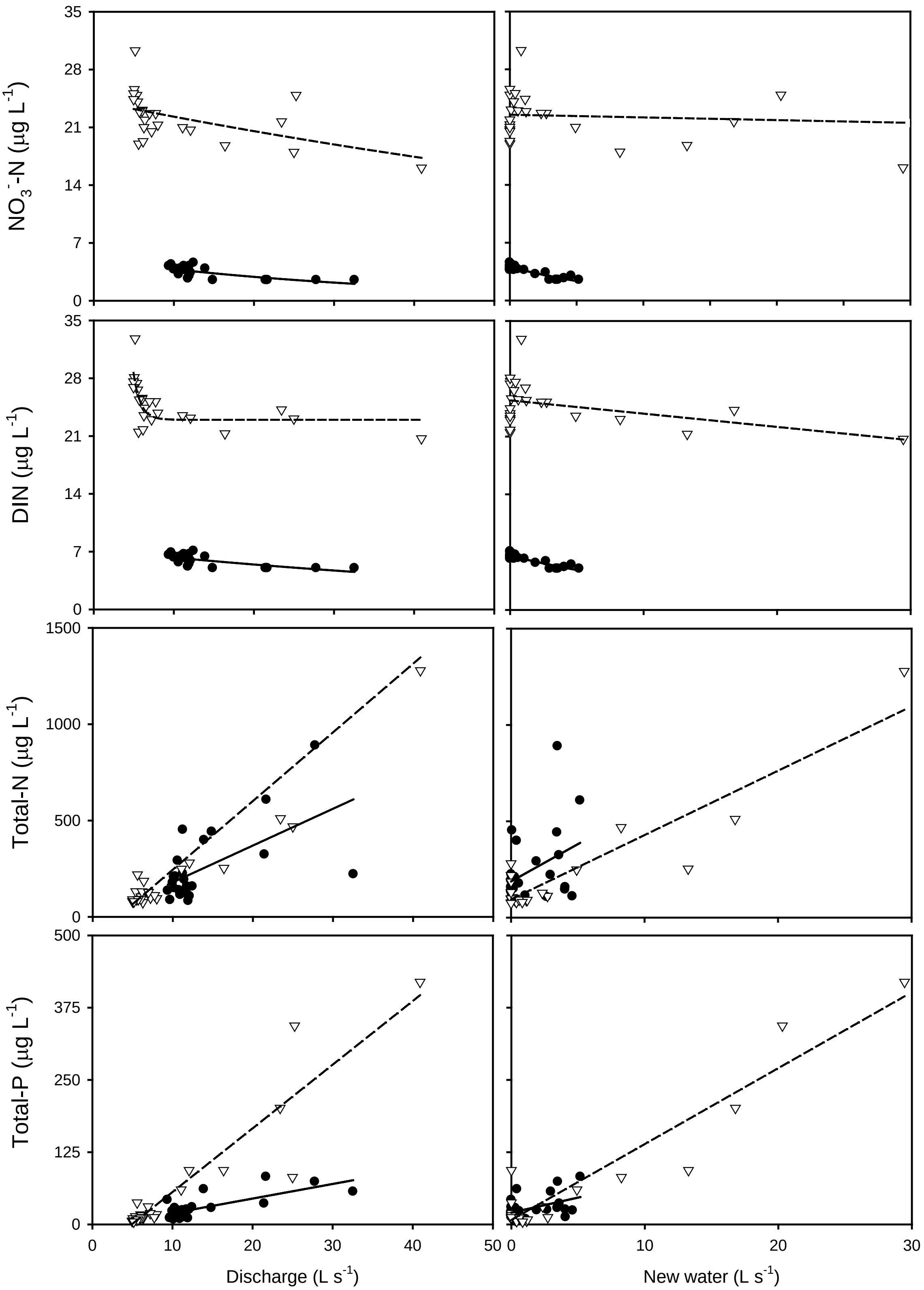

Figure 4. Nutrient concentrations (NO_3^- -N, DIN, Total-N and Total-P) vs catchment dicharge (figures on the left side) and new water (figures on the right side), both on L·s^{-1} for the 4th event. Old growth native forest (NF), in black round dots and *Eucalyptus nitens* plantation (EP) in white inverted triangles.

Table 3. Mean concentrations ($\mu g \cdot L^{-1}$) of total nitrogen (Total-N) and total phosphorous (Total-P) in stream water for different forest ecosystems under a low-deposition climate, southern Chile.

Forest description	Location	Total-N	Total-P	References
Nothofagus pumilio	Andean range	nd	67.3	[26]
Nothofagus betuloides	Andean range	nd	9.2	[26]
Nothofagus betuloides	Andean range	62.0	nd	[9]
Fitzroya cuppressoides	Coastal range	176.5	4.6	[27]
Evergreen forest	Andean range	157.1	18.0	[28]
Evergreen forest	Coastal range	36.8	24.1	[3]
Evergreen forest	Andean range	67.3	37.4	Unpublished data
Nothofagus nervosa-Nothofagus obliqua	Andean range	73.3	44.0	Unpublished data
Nothofagus dombeyi	Coastal range	153.0	nd	[29]
Old-growth native forest	Andean range	45.0	nd	[30]
Saxegothaea conspicua-Laureliopsis philippiana	Andean range	108.6	4.9	[23]
Eucalyptus spp.	Coastal range	94.8	30.1	[3]
Evergreen forest	Coastal range	127.2	11.1	This study
Eucalyptus nitens plantation	Coastal range	100.1	11.0	This study

nd = not determined.

range. Concentrations of inorganic-N were smaller than Organic-N concentration in NF (33.2 μg DIN L^{-1} versus 94.4 μg Organic-N L^{-1}) and EP (33.6 μg DIN L^{-1} versus 67.0 μg Organic-N L^{-1}), in agreement with previous research in southern Chile [9] [10], demonstrating that dissolved organic nitrogen is responsible for the majority of nitrogen losses from unpolluted forest ecosystems. According to [3], the DIN: DON ratio is smaller in evergreen native forests than in exotic plantation forests.

5. Conclusions

We conclude that the native evergreen forest shows higher enrichment concentration ratios of throughfall to precipitation with respect to *Eucalyptus* plantation. The differences in enrichment are attributed to the multi-stratified canopies and an understory of high diversity in the evergreen forests resulting in a complex and diverse structure and species composition. The Total-N and Total-P concentrations increased in both stands, especially in native evergreen forest, by passage through by the humus and upper soil layer (30 and 60 cm depth).

DIN and NO_3^--N showed a dilution during the 2nd event and hydrologically constant as discharge and/or new water apportionment increased during the 4th event. Since our study sites are in a region which is constantly under nutrient limitation, with very low N inputs (<3 $kg \cdot ha^{-1} \cdot yr^{-1}$), forest ecosystems in this region have developed strategies of high nutrient retention. In this case NO_3^--N and DIN are rapidly retained (biotic or abiotic) by the soil ecosystem. Both catchments showed very similar behaviors on all measured nutrients. However, it was clear that during the 4th event, DIN (therefore NO_3^--N) and Total-P showed higher concentrations in *Eucalyptus nitens* than native evergreen forest. Nevertheless, the 2nd event showed similar concentrations at catchment discharge for nutrients like Total-N, DIN and Total-P. These results support what [11] described for NO_3^--N and Organic-N losses in volcanic soil catchments.

Total-N and Total-P concentrations were more related to catchment discharge and not to new water. During the 4th event the pattern repeats only for NF. Whether in EP, Total-N and Total-P concentrations are more related to new water rather than catchment discharge. This is expected since *Eucalyptus* covered catchments are described and known to have low water infiltration rates, in addition P is attached to soil particles. This relation is sustained actually by the soil erosion during the 4th event.

We would like also to address that even though, we only measured throughfall nutrient concentrations, our results indicate that Total-N (DIN and Organic-N) are highly controlled by atmospheric inputs. However, we should start to observe whether other inputs (*i.e*. bacterial atmospheric fixation) of nitrogen are taking place in the understory of native forest and plantations (*Pinus* spp., and *Eucalyptus* spp.). Only then we will have a clearer picture of what is happening inside these forest ecosystems. So far, most of the differences between native forests and exotic plantations are exemplified by different water infiltration rates (higher in native forests), soil erosion (lower in native forests) and nutrients (higher exportation, especially for nitrate and Total-P, in exotic plantations). Further studies need to be done in order to unravel the different pathways and sources of nitrogen and phosphorous in this complex ecosystems in which one is decreasing and the other one is growing each year.

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