There are several possible explanations for the Ni-resonance distribution. First, the amplitude of the 18-meV resonance peak might fall with rising Δ and disappear near $\Delta \approx 50$ meV. However, measurement of the peak heights shows them to be almost independent of local Δ. Second, there might be statistical fluctuations such that no Ni atoms reside in regions where $\Delta > 50$ meV. However, if the Ni atoms are distributed randomly, and if all regions can support quasiparticle scattering resonances, our non-observation (in two independent experiments on different crystals) of Ni resonances in regions with $\Delta > 50$ meV has a combined probability of no more than 3×10^{-5}. Therefore this explanation also appears to be ruled out. A third explanation could be that the Ni atoms somehow 'seed' nanoscale regions (perhaps by attracting the dopant oxygen atoms or the holes), influencing them to develop into superconducting domains with $\Delta < 50$ meV. This model seems unlikely because, in one Zn-doped sample studied, Zn impurity resonances disappear in a statistically similar fashion near $\Delta \sim 50$ meV—but it cannot be ruled out. Nevertheless, impurity atoms are clearly not necessary to create α-domains as they exist in samples with no impurity atoms (see Figs 1a, 2 and 3).

A final hypothesis is that Ni impurity atoms are in fact physically present in regions with $\Delta > 50$ meV, but that they do not create scattering resonances because these regions represent an electronically distinct phase. If Ni atoms are randomly distributed, and if the locations of particle–hole symmetric Ni resonances indicate the local existence of superconductivity, then the distribution of superconducting regions has a similar shape to the red histogram of Fig. 4b. The picture would then be of purely superconducting regions when $\Delta \lesssim 35$ meV, a mixture of two different electronic orders when $35\ \text{meV} \lesssim \Delta \lesssim 50$ meV, and an unidentified second phase (possibly the pseudogap) when $\Delta \gtrsim 50$ meV. The data in Figs 1–3 corroborate this picture, particularly because the energy where the superconducting α-domains disappear is very close to the energy where the Ni resonances disappear. Therefore, although we cannot distinguish between the possible microscopic mechanisms[2,4,5,15–22] for the phenomena reported here, the data all suggest that underdoped Bi-2212 is a granular superconductor. This provides a new and unconventional context in which to view the underdoped copper oxides. □

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Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds

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Conceptual[1–4] and numerical[5–8] models of nitrogen cycling in temperate forests assume that nitrogen is lost from these ecosystems predominantly by way of inorganic forms, such as nitrate and ammonium ions. Of these, nitrate is thought to be particularly mobile, being responsible for nitrogen loss to deep soil and stream waters. But human activities—such as fossil fuel combustion, fertilizer production and land-use change—have substantially altered the nitrogen cycle over large regions[9], making it difficult to separate natural aspects of nitrogen cycling from those

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induced by human perturbations[10]. Here we report stream chemistry data from 100 unpolluted primary forests in temperate South America. Although the sites exhibit a broad range of environmental factors that influence ecosystem nutrient cycles[11–13] (such as climate, parent material, time of ecosystem development, topography and biotic diversity), we observed a remarkably consistent pattern of nitrogen loss across all forests. In contrast to findings from forests in polluted regions, streamwater nitrate concentrations are exceedingly low, such that nitrate to ammonium ratios were less than unity, and dissolved organic nitrogen is responsible for the majority of nitrogen losses from these forests. We therefore suggest that organic nitrogen losses should be considered in models of forest nutrient cycling, which could help to explain observations of nutrient limitation in temperate forest ecosystems.

Hydrologic nutrient losses can constrain the accumulation and availability of nitrogen in terrestrial ecosystems[10], with important long-term effects on productivity and carbon storage in nitrogen-limited temperate forest ecosystems[5–8,14,15]. However, much of our understanding of nitrogen cycles in temperate forests has been developed from studies of relatively polluted and/or disturbed areas of the Northern Hemisphere. We here seek to characterize the limits to natural variations in nitrogen losses from forested ecosystems that have experienced minimal nitrogen pollution and minimal disturbances from logging and other human activities. We sampled hydrologic nitrogen losses from small watersheds that differed markedly in the principal state factors[11–13] thought to influence how ecosystem nutrient cycles develop over time: climate, geologic parent material, time, topography and biota. We specifically considered whether broad variations in these state factors could yield appreciable variation in pathways of nitrogen loss for primary (that is, never logged) temperate forests that have developed across a large, yet unpolluted geographical region (Fig. 1).

We sampled 100 first-order streams that drained small watersheds[1,10] within 13 different geographical areas (n = 2–14 streams per area) between latitudes 40° S and 54° S in Chile and Argentina (Fig. 1). This region receives little or no nitrogen input from anthropogenic sources[16], and encompasses wide variations in state factors that produce an array of temperate forest ecosystems[11,17–21] (Table 1). Climate ranged between 4 and 11 °C mean annual temperature, and 500 to 5,840 mm mean annual precipitation across the different study areas[18,19]. Geologic parent material varied widely, from highly metamorphosed schists in the Coastal Cordillera of Chile (study areas HU, PE, CP, MF), to glacial till in low-lying southern coastal regions (SC, TF), to recently deposited tephra over glacial till (CE, LP) or igneous rocks (SK, LF) in the Argentinean Andes, to deep tephra in the northern Lake District Chilean Andes (AN, PU), and a mixture of basalts, andesites and granites in the southern Lake District Chilean Andes (AA)[20]. Time of ecosystem development ranged from ≤ 4,000 years since retreat of glaciers at TF and volcanic activity at AN, to ≤ 18,000 years at PY, SC, AA, CE, SK, LF and LP since retreat of the Llanquihue glacier, to ≫20,500 years in the unglaciated areas HU, PE, CP and MF[20]. Old-growth forests with little or no evidence of human disturbance dominated the watersheds in all but one area; LF watersheds contained mixtures of young and old forests recovering from natural and human-ignited fires. Areas were dominated by either one (TF, CE) or two (LP, SK) species of deciduous broadleaf tree, a single deciduous and single evergreen broadleaf species (AN), two species of coniferous evergreen trees (CP), or by higher diversity (greater than 3 species) mixtures of broadleaf evergreen (HU) or mixed coniferous and broadleaf evergreen (MF, PE, AA, PU, SC, LF) trees[21].

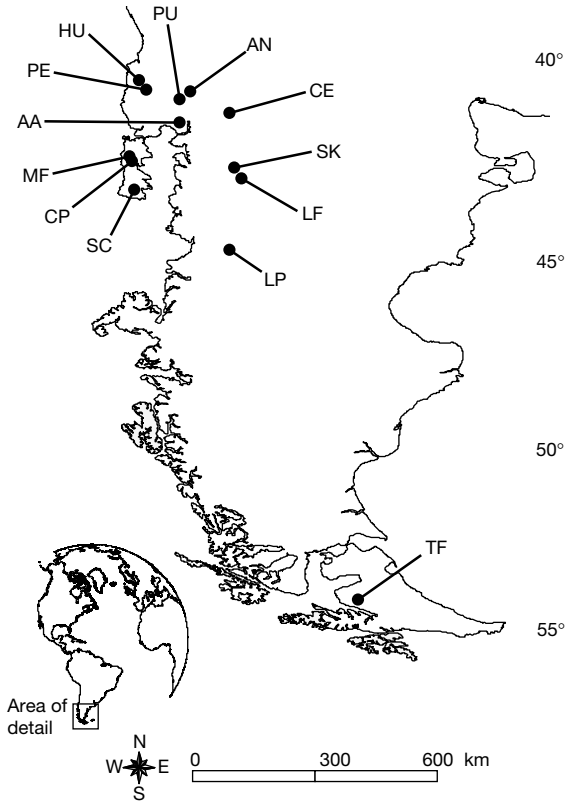

Figure 1 Map showing locations of study areas in South America.

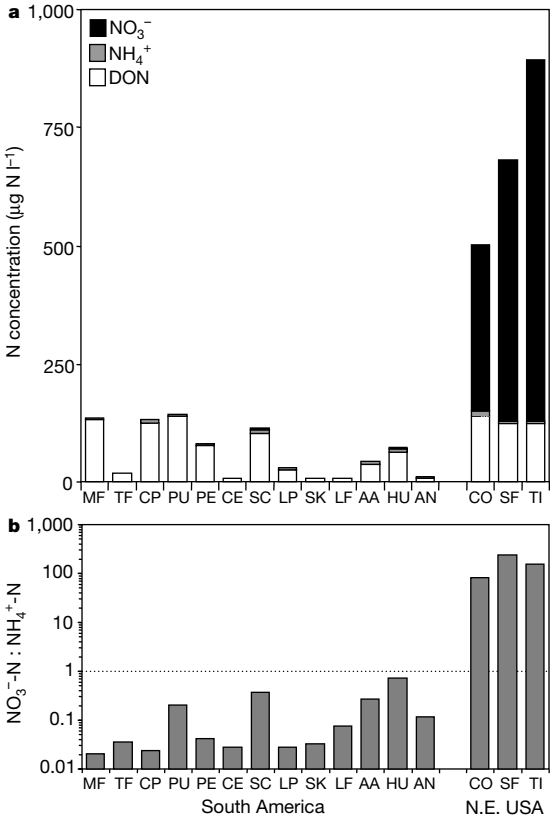

Figure 2 Hydrologic nitrogen losses from temperate forest watersheds in 13 areas of South America and 3 areas of eastern North America. **a,** Average concentrations of NH_4^+, NO_3^- and DON; **b,** Ratios of NO_3^--N:NH_4^+-N. Sites arranged from left to right in order of increasing contribution of NO_3^--N to total dissolved nitrogen. Dashed line in **b** indicates equal concentrations of NO_3^--N and NH_4^+-N.

We also sampled streams draining five old-growth forests from three chronically polluted areas of eastern North America. Watersheds located in the Tionesta National Forest in north-central Pennsylvania (TI) contained *Tsuga–Fagus* forests developed on sandstone[22]. Watersheds in Great Smoky Mountains National Park in eastern Tennessee[23] contained *Liriodendron–Fagus* (CO) and *Picea–Abies* forests (SF) developed on sandstone. All five North American watersheds escaped the Last Glacial Maximum.

We found that nitrate (NO_3^-) was consistently only a small fraction (average 5%, range 0.1–18%) of total dissolved nitrogen losses from unpolluted forests in southern Chile and Argentina, comprising less than 5% in 10 of 13 areas (Fig. 2a). Nitrate concentrations were uniformly low in the 13 different sample areas, ranging from 0.02 to 7.7 $\mu g\,N\,l^{-1}$ (average 1.9 $\mu g\,N\,l^{-1}$). Concentrations of dissolved ammonium (NH_4^+) were also low (average 4.9 $\mu g\,N\,l^{-1}$, range 0.5–11 $\mu g\,N\,l^{-1}$) and contributed 3–36% (average 15%) of total nitrogen. In contrast to these inorganic forms of nitrogen, dissolved organic nitrogen (DON) was the dominant vector of hydrologic nitrogen loss in all sampled areas of southern Chile and Argentina, accounting for 61–97% of total N (average 80%). The range in DON concentrations among areas (8–135 $\mu g\,N\,l^{-1}$) was much greater than for dissolved inorganic nitrogen (DIN; range 0.5–18 $\mu g\,N\,l^{-1}$), with lowest DON ($< 26\ \mu g\,N\,l^{-1}$) restricted to dry (mean annual precipitation $< 1{,}500$ mm; LP, SK, CE, LF) or young ($< 4{,}000$ years; TF and AN) areas.

The overall pattern of nitrogen loss from these South American forests contrasts sharply with losses from chronically polluted old-growth forests in eastern North America (Fig. 2a). Nitrate dominated (70–86%) total dissolved nitrogen losses from all North American watersheds, with concentrations (350–766 $\mu g\,N\,l^{-1}$) that were between 40 and 95 times greater than the highest concentrations among the South American forest areas. In addition, the average ratio of nitrate to ammonium expressed as N (NO_3^--N:NH_4^+-N) was very low (< 1) in all Chilean and Argentinean forests compared to ratios in the primary North American forests considered here (> 80; Fig. 2b), and compared to ratios in primary and secondary forests elsewhere in eastern North America[23–26]. Concentrations of DON did not differ significantly between unglaciated areas of South and North America ($P = 0.17$, t-test), although DON comprised a much smaller proportion of total nitrogen (20%) in North American forests. Variations in DON across South American watersheds were positively related to dissolved organic carbon (DOC; $r^2 = 0.70$, $P < 0.001$), and from the linear regression slope we estimate a DOC:DON ratio of 61 (s.e. = 4.0, $n = 100$) in hydrologic losses (see Supplementary Information). In comparison, DOC:DON ratios in losses from old-growth eastern North American forests are substantially lower (median 27, $n = 9$ watersheds[24,25]), possibly as a result of chronic nitrogen deposition[26].

The pattern of low NO_3^-, high DON losses across South American forests is further supported by analyses of > 30 watershed streams[10], and by five years of continuous measures of hydrology, stream nutrient losses (sampled twice a month), soil N transformations[27], and 24 soil lysimeters within four watersheds at the MF and CP sites (Table 1). These intensive local measures have shown that variations in relative losses of NO_3^-, NH_4^+ and DON across seasons and along soil-to-stream flow paths are small (less than about 25%) when compared to differences between South and North American forests (Fig. 2).

Our results show that narrow and characteristic patterns of nitrogen loss (DON $\gg$ NH_4^+-N $>$ NO_3^--N) can emerge throughout large geographical regions of unpolluted temperate forests, despite considerable variation in natural ecosystem state factors. These loss patterns differ substantially from traditional inorganic-based models and support studies that have previously identified DON as a vector of N loss from forests[10,24–26,28]. Our findings have implications for understanding nitrogen fluxes at scales of ecosystems to landscapes in regions with minimal human impact. Using average N concentrations (65 $\mu g\,N\,l^{-1}$; range 11–140 $\mu g\,N\,l^{-1}$) from our sample areas, and assuming that evapotranspiration scales linearly with annual precipitation, we conservatively estimate that N losses range from 0.2 to 3.5 $kg\,N\,ha^{-1}\,yr^{-1}$ (minimum 0.03 and maximum 7.5 $kg\,N\,ha^{-1}\,yr^{-1}$) as a function of precipitation amount

Table 1 Characteristics of study areas

Study area	Code	Watersheds sampled	Longitude Latitude	Elevation (m)	MAT* (°C)	MAP† (mm)	Dominant vegetation	Age‡ (kyr)	Parent material§
Piuchué mixed forest	MF	10	42° 21′ S 74° 06′ W	500	6	5,840	*Nothofagus nitida, Drimys winteri, Podocarpus nubigena, Laurelia philippiana, Saxe-Gothaea conspicua*	≫20.5	PC
Cordillera Piuchué	CP	2	42° 22′ S 74° 03′ W	600	6	5,840	*Fitzroya cupressoides, Pilgerodendron uviferum*	≫20.5	PC
Tierra del Fuego	TF	2	54° 20′ S 69° 15′ W	100	4	500	*Nothofagus pumilio*	<4	GL
Cordillera Pelada	PE	13	40° 10′ S 73° 35′ W	800	8	4,000	*N. nitida, D. winteri, P. nubigena, S. conspicua, F. cupressoides*	≫20.5	PC
Puyehue	PU	11	40° 46′ S 72° 17′ W	600	9	3,600	*P. nubigena, S. conspicua, D. winteri* var. *andina, Nothofagus dombeyi*	<18	T
Southern Chiloé	SC	5	42° 52′ S 73° 49′ W	200	8	2,500	*N. nitida, S. conspicua, L. philippiana, P. nubigena*	<18	GL
Antillanca	AN	6	40° 47′ S 72° 11′ W	1,100	4	5,400	*N. pumilio, Nothofagus betuloides*	<4	T
Alerce Andino	AA	8	41° 32′ S 72° 30′ W	600	7	4,000	*N. nitida, Luma apiculata, S. conspicua, L. philippiana, D. winteri* var. *andina*	<18	I
Hueicolla	HU	7	40° 09′ S 73° 37′ W	300	11	2,500	*N. nitida, D. winteri, L. apiculata, Amomyrtus luma, Weinmannia trichosperma*	≫20.5	PC
Lago La Plata	LP	9	44° 50′ S 71° 44′ W	1,000	7	770	*N. pumilio, Nothofagus antarctica*	<18	T, GL
Lago Futalaufquen	LF	14	42° 51′ S 71° 38′ W	600	9	1,200	*Austrocedrus chilensis, N. dombeyi, Lomatia hirsuta*	<18	T, I
Senda Kruger	SK	5	42° 50′ S 71° 41′ W	1,000	7	1,200	*N. pumilio, N. antarctica*	<18	T, I
Lago Los Cesares	CE	8	41° 18′ S 71° 41′ W	1,150	7	1,500	*N. pumilio*	<18	T, GL

*MAT, mean annual temperature.
†MAP, mean annual precipitation.
‡Substrate age in kyr. ≫20.5 indicates that the area escaped the Llanquihue glacial (18–20.5 kyr before present).
§PC, pre-Cambrian mica-schists; GL, glacial till; T, tephra; I, igneous basalt, granite and andesite.

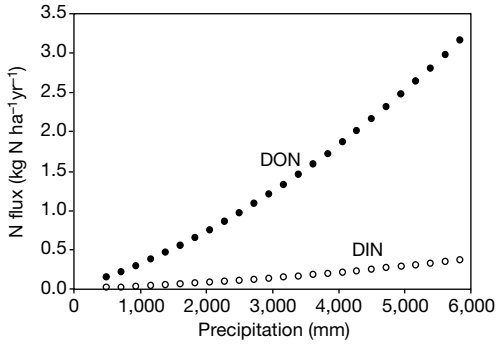

Figure 3 Hydrologic losses of dissolved inorganic and organic nitrogen, DIN and DON, estimated across the range of precipitation inputs to unpolluted forests of South America. Rates of hydrologic N flux from forest ecosystems were calculated by multiplying concentrations of DIN (average 6.8 μg N l^{-1}) and DON (average 58.6 μg N l^{-1}) by estimates of water flux. We calculated water fluxes as precipitation volume minus potential evapotranspiration losses. We assumed that percentage losses due to evapotranspiration decreased linearly from 50% to 10% across the range of precipitation from 500 to 5,840 mm.

(500–5,840 mm). We show in Fig. 3 that these rates of nitrogen loss are controlled by export of organic nitrogen compounds (DON), with little contribution from dissolved inorganic compounds (DIN). Our intensive hydrologic monitoring of watersheds at CP and MF further support these patterns; $>90\%$ of nitrogen losses occurred as DON, and volume-weighted losses of nitrogen averaged 5.7 (s.e. = 0.09, $n = 3$ years) and 5.9 (s.e. = 0.50, $n = 3$ years) kg ha^{-1} yr^{-1}, respectively.

We conclude that unpolluted forests can display unexpectedly high rates of N output, primarily in the form of DON. We expect the influence of DON loss on ecosystem N balances to increase in importance along gradients from dry to moist forests (Fig. 3). Over longer periods, such nitrogen losses must be balanced by inputs from either nitrogen fixation[29] or natural atmospheric deposition[30]. Our results suggest that DON losses from unpolluted forests can rival rates of NO_3^--N loss in regions[1–4,23–25] where N balances have been strongly biased in favour of recent anthropogenic inputs. Our findings support the idea[10,31] that in regions with naturally low inputs of nitrogen from atmospheric deposition and nitrogen fixation, export of DON offers a mechanism to explain why nitrogen commonly limits plant productivity and carbon sequestration in moist temperate forests. We consider that models of forest ecosystems therefore should include DON as a central pathway of nitrogen loss, and should take into account the effects that such losses may have on nutrient limitation and carbon balances[5–8]. □

Methods

We intensively sampled the chemistry and hydrology of small watershed streams at CP and MF every other week for over 5 years (1993–98). For the broader comparison between areas reported here, we included only results from December 1994 and January 1995, to coincide with collection efforts throughout southern Chile. However, results from these periods do not differ from long-term averages at CP and MF. For other locations in Chile, we collected duplicate samples from small watershed streams in December 1994 and January 1995, or in March 1997 for sites in the TF area. We sampled locations in Argentina in January and February 2001. Samples were filtered in the field through rinsed Gelman A/E glass-fibre filters (<1-μm nominal pore size, ref. 10) into 60-ml clean and leached polyethylene bottles. One replicate was immediately treated with 0.2 ml $CHCl_3$ to prevent biological activity, and all samples were kept cool and dark until analysis at Cornell University, generally within 2 weeks of collection. TI samples are averages from collections on October 1994 and May 1995. Data from CO and SF are averages of 9–23 sample collections per stream[23] throughout the entire year of 1998. These samples were stored frozen, and subsequently thawed and filtered through Gelman A/E glass-fibre filters. Details of analytical methods are given in ref. 10: NH_4^+ was analysed by Alpkem continuous-flow colorimetry, NO_3^- by Dionex ion chromatography, total dissolved nitrogen by colorimetry as NO_3^- following high-temperature persulphate digestion, and DOC by Shimadzu high-temperature platinum combustion. DON was calculated as total dissolved nitrogen minus NH_4^+-N and NO_3^--N.

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