were higher than the background levels used in the model.

When the convection was vigorous, the intensifying echo top usually rose above the 0 °C isotherm and the spectra in the rain tended towards that usually observed in mature clouds, but on one occasion (28 June 1986) it was possible to observe the evolution of an echo to over 50 dBZ without ice forming in the cloud. The average values of Z_{DR} for each 2-dBZ step in Z for three successive scans are shown in Fig. 2. The time resolution is rather poor because the radar was executing 360° surveillance scans. At 12:21 the maximum Z value was 17 dBZ, associated with a Z_{DR} value of ~1.5 dB, and inferred concentrations are more than two orders of magnitude (equivalent to 20 dB) below the curve for 'average' rain. Six minutes later, at 12:27, Z had reached nearly 40 dBZ and Z_{DR} was ~3 dB, indicating that the biggest drops had grown in diameter by 2 mm. The concentration of these large drops is still two orders of magnitude below average. By 12:40 the highest Z was over 55 dBZ, but the picture is then dramatically different, the inferred raindrop size distribution being that found in mature clouds.

To support our contention that drop collisions are responsible for this abrupt change in the spectra, the dashed line in Fig. 2 represents values of Z and Z_{DR} for which a 5-mm droplet would have an average lifetime of 1,000 s before it collided with another droplet greater than 1 mm in diameter. Collisions between two raindrops which are both larger than 1 mm are generally followed by disruption and shattering to produce many small fragments[11]. For a given Z_{DR}, the value of d_0 is constant and the number of drops is proportional to Z; accordingly, the lifetime of each large raindrop is inversely proportional to Z. We note that in Fig. 1 the data lie in a region where the large drops have a lifetime of several hours before they suffer collision-induced rupture. In Fig. 2 the initial concentrations are somewhat higher, and by 12:27 the drop lifetimes are slightly shorter than 20 min; finally, at 12:40 h the spectrum has changed to the 'mature' mode, with a high concentration of smaller drops, so that the large drops contributing to a Z_{DR} of 3–4 dB would have a lifetime of only a few seconds and would be continuously regenerated.

Some measurements[12,13] made from aircraft within developing clouds have also indicated raindrop spectra different from those found in mature clouds, although Z values were higher and the spectra were not as extreme as those reported here. Measurements in Texas[12] revealed low values of n_0 in early echoes and an implied absence of collision-induced break-up. The authors attributed the low values of n_0 to drop sorting in the updraft, but this does not seem compatible with the time evolution of the Z_{DR} RHI scans from the MIST data. In Hawaii[13] raindrops 8 mm in size were observed. The existence of such large raindrops had been questioned because in Marshall–Palmer rain they would rapidly suffer collision-induced break-up, but the authors showed that when total drop concentrations are low, the lifetimes are sufficiently long. The very low concentrations inferred from the radar data of the MIST project would be difficult to confirm by aircraft penetrations because of the limited sample volume of most precipitation-sizing probes.

Other mechanisms for the production of the raindrops must be considered. There is always the possibility that a few ice crystals (which would have a Z value below −20 dBZ and would be undetectable by radar) could fall from higher levels, melt, and then grow into large raindrops. This seems unlikely: the air was very dry at these colder levels and no bright band in Z_{DR} was observed. (It is our experience that as small ice crystals start to melt there is a sudden jump in Z_{DR} as they become wet and change their dielectric constant, followed by an equally sudden drop to zero Z_{DR} as they melt completely to become small spherical raindrops.)

In his initial report on the existence of ultra-giant nuclei, Junge[3] remarked that they were so rare that they could not be important in the warm-rain process. Such a view seems eminently sensible, but this new radar evidence shows that warm rain does indeed first form in such low concentrations. It may be that a fortunate combination of collection efficiencies and droplet sizes results in just one cloud droplet in 10^8 being able to capture its neighbours and grow into a raindrop. It is evident that further modelling and observations are needed, but I propose meanwhile that cloud droplet capture by ultra-giant nuclei is a simple and equally plausible mechanism.

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Deforestation alters denitrification in a lowland tropical rain forest

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Nitrogen gas loss from terrestrial ecosystems is the most poorly quantified component of the global nitrogen cycle[1–3]. Particularly little is known about gas losses from tropical rain forests, which may be an especially important source of nitrogen gases worldwide[3,4], and one that is changing rapidly because of tropical deforestation. Here we report measurements of denitrification (N_2+N_2O production), an important mechanism of nitrogen loss in most ecosystems[5–7], at a set of sites in Central America. Measurements were made to determine whether nitrogen gas loss is related to the successional status of rain-forest vegetation. Denitrification is high in primary forest and early successional sites and substantially lower in mid-successional sites. This implies that denitrification can be a major route of nitrogen loss from recently cleared and primary forest sites, and that global denitrification losses from humid tropical regions today are probably much smaller than losses in pre-colonial times, when a smaller proportion of sites were in mid-successional growth phases.

Recent work in temperate forests suggests that rates of denitrification may be closely related to the successional status of the existing plant community[8,9]. Results suggest that nitrogen gas losses from old-growth and early successional communities may be much greater than from communities in which much of the vegetation is in a nitrogen-immobilizing, mid-successional growth phase. This pattern, if true, could have important consequences for the management of soil nitrogen resources in the humid tropics. It could also have important consequences for estimates of the impacts of human activity on global nitrogen gas fluxes[10]: if denitrification is an important source of N_2O in these ecosystems[5–7], then the worldwide loss of primary tropical

rain forests may be attenuating rather than contributing to some of the recently documented increases in atmospheric concentrations of nitrogen trace gases[11,12].

Over the past two years we have measured denitrification rates in rain-forest soils at several sites at the La Selva field station of the Organization for Tropical Studies in the wet Atlantic lowlands of north-east Costa Rica, Central America (10°26′ N, 84°00′ W, 50 m elevation). Rainfall at La Selva is weakly seasonal (mean annual precipitation is 4,000 mm) and temperature is relatively constant year-round, with an annual mean of 24 °C. Soils at the station vary from relatively fertile entisols developed on recent alluvial deposits of volcanic origin to highly weathered, base-poor inceptisols and ultisols derived from alluvium and lava flows[13–15]; all of our sample sites were on the older soils, dominated by low-charge-density, variable-charge clays. Three of the sites were on typic (site SWT) and andic (sites WP, SOC) Humitropept soils; the remainder were on oxic (sites GC, GBF, FBF) and andic (sites BP, PAS) Dystropepts[13]. Soils from all sites exhibited low *p*H (4.2–5.0), were well aggregated, and nitrified readily (2–4 $\mu g\ g^{-1}\ d^{-1}$ NO_3^--N) in 10-day potential mineralization assays (G.P.R. and J.M.T., unpublished results).

We measured denitrification at ten sites: four primary-forest sites which had never been cleared, two mid-successional sites cleared from primary forest about 25 years before sampling, two mid-successional sites cleared from successional vegetation about two years before sampling, and two early-successional sites cleared from successional vegetation several weeks before sampling. The maximum distance between sites was 2 km. Our primary-forest sites were typical for La Selva, where in intact forest a very diverse mixture of species form a 30–40-m-high canopy with 50-m emergents[16]. The two older mid-successional sites were on sites that had been first cleared of primary forest at around 1970; one site (PAS) was, at the time of sampling, a 2-m-high stand of grass and woody shrubs; the other site (GC) was a mixture of 2-m-high grass and fern. The two younger mid-successional sites (GBF and FBF) also had been cleared of primary forest around 1970, but in 1984, 18 months before their mid-successional sampling dates, they had also been cleared of regrowth (2-m-high grass and grass plus fern, respectively) and were maintained vegetation-free thereafter. Several weeks after their 1984 clearing, these two sites were our early-successional sites (early GBF and early FBF, respectively). All four of the mid-successional sites had similar pre-1984 land-use histories in that all were cleared around 1970, grazed for 5–8 years, and then abandoned. Rates of re-vegetation on these sites have been slower than those reported for other wet tropical sites in Costa Rica[17]; this is probably because our sites are on highly weathered, base-poor soils and, after cutting, were grazed for a number of years before abandonment.

Denitrification rates were measured by an aerobic, short-term intact-core assay[18]. On any given sample date (see below), 10–20 soil cores of 2.2-cm diameter ×15-cm depth were removed from each site at random intervals along three 10-m transects within a 1-hectare area. Cores were collected in individual acrylic tubes, which were then taken to a field laboratory, flushed with a (10 kPa C_2H_2 + 90 kPa air) atmosphere, and stoppered. N_2O accumulation over the ensuing 12 hours was monitored in each tube at three-hour intervals by injecting headspace gas into a gas chromatograph fitted with a ^{63}Ni electron-capture detector. Denitrification activity ($N_2 + N_2O$ production) was calculated from the linear portion of the N_2O accumulation curve[19,20]. Rates measured in this manner have been shown to directly reflect *in situ* denitrification rates in temperate-region forest, grassland and agricultural sites[21,22]; we assume that the same is true for our tropical site.

Sample dates varied somewhat between sites, with all except the early-successional sites sampled 2–3 times at 4–6-month intervals over the course of a year. The early-successional sites were sampled twice in the 6-month interval following clearing.

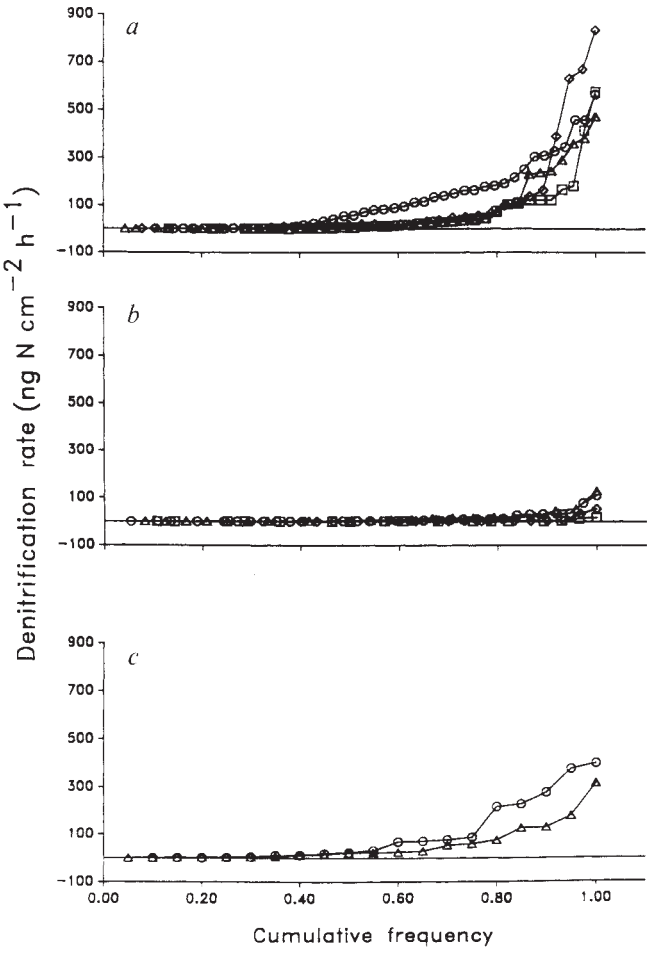

Fig. 1 Cumulative frequency distributions for denitrification rates ($N_2 + N_2O$ production) in individual soil cores from the 8 rain-forest sites sampled. Primary-forest sites have never been cut; all four mid-succession sites had been cut about 15 years before sampling, and two sites (FBF and GBF) had been cut again 1.5 years before sampling and maintained vegetation-free (vf). Values for the early-succession sites FBF and GBF represent samplings at 1 and 6 months following clearing. *a*, Primary-forest sites: ○ WP, △ SOC, □ SWT, ◇ BP. *b*, Mid-succession sites: ○ PAS, △ GC, □ FBF (vf), ◇ GBF (vf). *c*, Early-succession sites: ○ early GBF, △ early FBF.

Preliminary experiments suggested that individual rainfall events had no discernible effect on denitrification activity in these moist, extremely well-drained soils; nevertheless, no sites were sampled within 12 hours of the most recent rainfall. On the last sample date, the effects of added nitrate on denitrification were evaluated by adding either 0 or 100 μg $NaNO_3$-N in 10 ml H_2O to each core and monitoring N_2O accumulation as above.

Within any given site, denitrification rates were quite variable even within individual sample dates. Rates among cores from within a site tended to vary by an order of magnitude or more, with frequency distributions of rates tending towards the log-normal (Fig. 1). This was true regardless of whether maximum rates within the site were low (for example, the mid-successional PAS site, with a mean rate of 3.61 ng N $cm^{-2}\ h^{-1}$) or high (for example, the primary-forest WP site, with a mean rate of 24.3 ng N $cm^{-2}\ h^{-1}$), and is typical of rates in many temperate-region sites[9,23]. Partly because of this high within-site variability, there were no significant differences between different sample dates for any given site, and the date-by-site interaction term was negligible (probability $P > 0.10$). Consequently, for each site we pooled data across dates for subsequent statistical analyses.

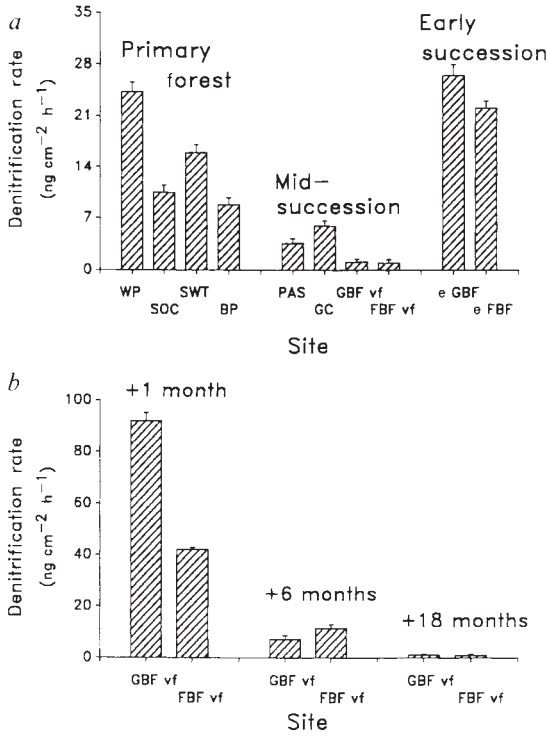

Fig. 2 *a*, Mean denitrification rates (N_2+N_2O production) in rain-forest sites at different stages of secondary succession (see Fig. 1 legend). Values were log-normal-transformed before analysis to satisfy homogeneity of variance assumptions; vertical lines in bar centres represent 1 standard error. *b*, Denitrification rates in the successional sites described in Fig. 1 legend. Times refer to months following secondary vegetation clearing. vf, vegetation-free; e denotes early.

Despite high within-site variability, several trends were significant. First, denitrification differed significantly ($P<0.001$) among vegetation groups (primary-forest sites, mid-succession sites and early-succession sites). Rates of denitrification were significantly higher in our primary-forest and early-succession sites than in any of the mid-succession sites ($P<0.05$) (Fig. 2*a*).

The rates of denitrification shown in Fig. 2*a* extrapolate to a mean of 0.11 g N m^{-2} per month in the primary-forest sites, to 0.16 g N m^{-2} per month in the early-successional sites, and to <0.034 g N m^{-2} per month in the mid-successional sites. These values are within the range of those reported for temperate-region forests[8,9,18], although in individual cores denitrification occurred at rates substantially higher than any yet reported. For example, in the primary forest a number of cores denitrified at rates of 300–900 ng N cm^{-2} h^{-1} (Fig. 1), values that extrapolate to 2.1–5.4 g N m^{-2} per month.

Second, very high rates of denitrification in those sites recently cleared of secondary vegetation tapered off to rates close to those in the mid-successional site within a few months after clearing (Fig. 2*b*). In one of the sites, rates averaged 90 ng N cm^{-2} h^{-1} shortly after clearing; within 4 months, mean denitrification rates had fallen to <10 ng N cm^{-2} h^{-1}. A year later, in the absence of vegetation which might have even further depressed denitrification rates as a result of plant–denitrifier competition for nitrate[24,25], rates had fallen to <2 ng N cm^{-2} h^{-1}, perhaps because of nitrate immobilization during decomposition of grass or fern roots.

Third, in the primary-forest sites, denitrifiers did not respond to added nitrate, whereas nitrate added to soils from mid-successional sites with vegetation stimulated denitrification substantially (Table 1). This suggests that competition for nitrate may be a principal factor in keeping denitrification low in the

Table 1 Response of denitrifiers in intact soil cores from primary-forest and mid-successional sites to added water and water plus nitrate

	N_2O–N (ng cm^{-2} h^{-1})	
Primary forest		
WP	87.7 (5.4)	77.2 (4.4)
SOC	111.0 (5.1)	91.6 (5.2)
BP	12.3 (3.9)	12.7 (0.9)
SWT	49.9 (4.0	38.1 (9.0)
Mid-succession		
PAS (regrowth)	2.7 (1.5)	9.0 (2.2)*
GC (regrowth)	0.2 (1.4)	148.0 (5.4)*
FBF (vegetation-free)	1.0 (2.5)	0.03 (1.0)
GBF (vegetation-free)	1.1 (1.9)	0.3 (1.3)

Cores were assayed for nitrate response after the initial non-amendment denitrification assay described in the text. Values are means of 10 cores ±1 standard error; * indicates significant differences at $P<0.05$.

vegetated (non-bare fallow) mid-successional sites, an explanation consistent with results from temperate-region studies and with general theory concerning factors that regulate denitrification in non-agricultural sites[25,26]. In other primary-forest sites, such as those in the Amazon, nitrate has been shown to stimulate N_2O fluxes[27,28]. Presumably in these very infertile soils nitrogen is in short supply even in primary forest.

This study represents the first systematic measurement of denitrification in humid tropical ecosystems. Because of the initial nature of this endeavour, because humid tropical soils are diverse[29,30], and because system-wide responses to disturbance such as clear-felling can be dependent on many factors, including the type and severity of disturbance[31], caution should be exercised in generalizing our results to humid tropical ecosystems worldwide. Before general conclusions can be drawn, we need a broad database covering a variety of tropical ecosystems, and careful consideration of historical patterns of change in clearing rates. Nevertheless, successional theory suggests that similar trends ought to occur in other parts of the humid tropics following similar sorts of disturbance. If this is so, then our results suggest that denitrification may represent an important but transient source of nitrogen loss following tropical-rainforest clearing, and that deforestation in the past few decades should lead to lower rates of nitrogen gas emission worldwide, as high-activity primary forest is converted to lower-activity mid-successional vegetation.

The importance of these results to our understanding of global N_2O fluxes *per se* is clouded by a generally poor understanding of the biological sources of N_2O in most ecosystems. Denitrifiers—both heterotrophs such as *Pseudomonas* spp. and chemoautotrophs such as *Nitrosomonas* spp.—probably comprise the greatest single source of N_2O in most ecosystems, but evidence for the importance of other biological sources is growing[32]. Furthermore, we have no evidence that the N_2O portion of the total N_2+N_2O gas flux evolved by denitrifiers is constant among sites in our ecological sequence. This makes it difficult to infer patterns for denitrifier-derived N_2O fluxes with confidence even for these sites. However, because N_2O and denitrification (N_2+N_2O) fluxes in the systems studied so far appear to be under similar system-level controls[8,9,18,28,33], it is conceivable that N_2O fluxes *per se* may be related to plant succession in the same way that denitrification appears to be. Given this likelihood, and the importance of N_2O fluxes to atmospheric processes such as ozone depletion in the stratosphere[34–36] and infrared transmissivity in the troposphere[11], we believe that the relationship between plant succession and both denitrification and N_2O fluxes *per se* deserves clarification in additional tropical and other globally-important ecosystems.

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Origin of Messel Oil Shale kerogen

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Despite many investigations concerning the insoluble organic matter in sediments (kerogen), its chemical nature and origin are only poorly understood. Here we report the results of a combined microscopy and chemical study of the Messel Oil Shale which shed light on the mechanism of kerogen formation. Scanning electron microscopy revealed the overwhelming presence of cell-wall remains of *Tetraedron-like* microalgae which are virtually indistinguishable from those of the widely occurring extant *Tetraedron minimum* (Chlorococcales). Flash-pyrolysis gas chromatography/mass spectroscopy indicated the presence of an insoluble, non-hydrolysable highly aliphatic biopolymer in both fossil and extant *Tetraedron* species. The bulk of the Messel Oil Shale kerogen probably consists of selectively preserved cell-wall material of *Tetraedron* algae, mainly made up of this newly discovered biopolymer. We therefore suggest that this polymer, and similar types of recently discovered highly aliphatic biopolymers in other algae and plant cuticles, are important precursors of *n*-alkanes in crude oils.

The Messel Oil Shale (near Darmstadt, West Germany) represents an organic-matter-rich lacustrine deposit of Mid-Eocene (~48-Myr) age[1]. This sediment (in particular, its fossil content) has been studied extensively by palaeontologists and organic geochemists[2], but despite these efforts, the origin and nature of the bulk of the organic matter is poorly understood.

Microscopic examinations of a large number of samples, obtained from outcrops within the open-cast mine at the aforementioned location as well as samples from cores, revealed that the organic matter in the Messel Oil Shale (~30% on a dry-weight basis) is mainly concentrated in distinct laminae. These organic-rich laminae alternate with laminae that are rich in clay and which also contain minor amounts of terrestrially derived organic debris (Fig. 1). Such units of microlaminae are commonly ~0.1-0.2 mm thick and their abundant occurrence throughout the Messel Oil Shale sequence suggests a cyclic sedimentation pattern (K.G., manuscript in preparation). The lack of vertical circulation within the lake, probably caused by density stratification, prevented bioturbation, thus permitting the preservation of these laminae. The occurrence of pyrite and siderite[3,4] supports the suggestion of an oxygen-depleted deep water body. Further evidence for density stratification is provided by the presence of porphyrins related to the bacteriochlorophyll *d* series, which originate from the anaerobic phototrophic bacteria *Chlorobiaceae*[5].

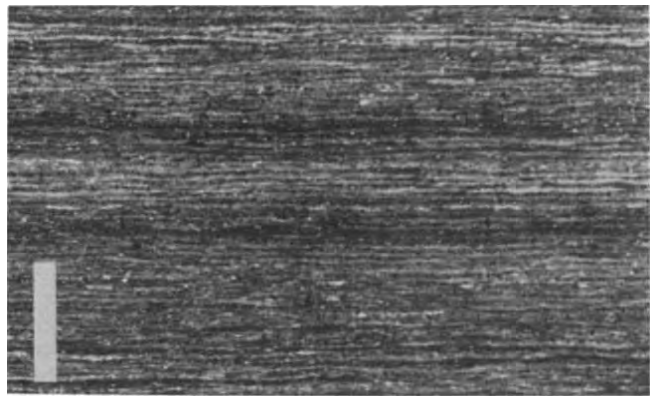

Fig. 1 Cross-section of a typical laminated oilshale from the Messel Formation. Light-coloured microlaminae are composed of *Tetraedron* remains, and dark layers represent background sediment. Scale bar, 2.0 mm.

Examination of a large number of the organic-rich laminae by scanning electron microscopy (SEM) revealed a predominance of small sculptured bodies, relatively uniform in size (5-10 μm, Fig. 2), which are considered to be the cell-wall remains of unicellular algae[4]. A sharp delineation was observed between the base of these nearly pure algal laminae and the inorganic laminae. This alternating sequence results from the sedimentation of algal debris, originating in annual blooms of these organisms, superimposed on the mainly inorganic, terrestrially derived background (K.G., manuscript in preparation).