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Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes

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SUMMARY

Human activity has greatly perturbed the nitrogen cycle through increased fixation by legumes, by energy and fertilizer production, and by the mobilization of N from long-term storage pools. This extra reactive N is readily transported through the environment, and there is increasing evidence that it is changing ecosystems through eutrophication and acidification. Rothamsted Experimental Station, UK has been involved in research on N cycling in ecosystems since its inception in 1843. Measurements of precipitation composition at Rothamsted, made since 1853, show an increase of nitrate and ammonium N in precipitation from 1 and 3 kg N ha^{-1} yr^{-1}, respectively, in 1855 to a maximum of 8 and 10 kg N ha^{-1} yr^{-1} in 1980, decreasing to 4 and 5 kg N ha^{-1} yr^{-1} today. Nitrogen inputs via dry deposition do, however, remain high. Recent measurements with diffusion tubes and filter packs show large concentrations of nitrogen dioxide of *c.* 20 μg m^{-3} in winter and *c.* 10 μg m^{-3} in summer; the difference is linked to the use of central heating, and with variations in wind direction and pollutant source. Concentrations of nitric acid and particulate N exhibit maxima of 1·5 and 2 μg m^{-3} in summer and winter, respectively. Concentrations of ammonia are small, barely rising above 1 μg m^{-3}.

Taking deposition velocities from the literature gives a total deposition of all measured N species to winter cereals of 43·3 kg N ha^{-1} yr^{-1}, 84 % as oxidized species, 79 % dry deposited. The fate of this N deposited to the very long-term Broadbalk Continuous Wheat Experiment at Rothamsted has been simulated using the SUNDIAL N-cycling model: at equilibrium, after 154 yr of the experiment and with N deposition increasing from *c.* 10 kg ha^{-1} yr^{-1} in 1843 to 45 kg ha^{-1} yr^{-1} today, *c.* 5 % is leached, 12 % is denitrified, 30 % immobilized in the soil organic matter and 53 % taken off in the crop. The 'efficiency of use' of the deposited N decreases, and losses and immobilization increase as the amount of fertilizer N increases. The deposited N itself, and the acidification that is associated with it (from the nitric acid, ammonia and ammonium), has reduced the number of plant species on the 140-yr-old Park Grass hay meadow. It has also reduced methane oxidation rates in soil by *c.* 15 % under arable land and 30 % under woodland, and has caused N saturation of local woodland ecosystems: nitrous oxide emission rates of up to 1·4 kg ha^{-1} yr^{-1} are equivalent to those from arable land receiving > 200 kg N ha^{-1} yr^{-1}, and in proportion to the excess N deposited; measurements of N cycling processes and pools using ^{15}N pool dilution techniques show a large nitrate pool and enhanced rates of nitrification relative to immobilization. Ratios of gross nitrification:gross immobilization might prove to be good indices of N saturation.

Key words: Nitrogen cycling, atmospheric deposition, mineralization, nitrification, trace gas fluxes, air pollution.

INTRODUCTION

In the 56th Tansley Review, Pearson & Stewart (1993) discussed the effects of increasing ammonia deposition and linked it to acidification and nutrient imbalance in plants. They concluded that acidic habitats are particularly prone to damage from

eutrophication, and that the abilities of different plants to buffer against N enrichment would cause some species selection and ecosystem change. Vitousek (1994) calculated that (i) more N was fixed annually by human-driven than by natural processes, and (ii) that human activity mobilizes N from long-term storage pools through biomass burning, land clearance and conversion, and the drainage of wetlands. Both newly-fixed and mobilized N is readily transported in solution or via the atmosphere

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so that local perturbations spread regionally and globally. Vitousek (1994) reported evidence of increased nitrate leaching, increased emissions of N-containing trace gases and enhanced carbon storage, all in forest ecosystems. Nitrogen saturation in forest ecosystems was reviewed by Aber (1992). He described the different process responses (mineralization, immobilization, etc.) in saturated and unsaturated forest ecosystems in a search for quantitative predictors of N saturation. In particular, he suggested that a ratio of gross nitrification:gross immobilization > 1 might identify N-saturated systems

The fixation over land of unreactive dinitrogen gas (N_2) by lightning and biological N fixation in the pre-industrial world has been estimated at 90–130 Tg N yr^{-1} (Delwiche, 1970; Galloway *et al.*, 1995; Vitousek *et al.*, 1997). This fixation into reactive forms (NO_y, NH_x and organic N; where $NO_y = NO + NO_2 +$ any other single N species with an oxygen atom, and $NH_x = NH_3 +$ aerosol NH_4^+) was balanced by denitrification to N_2. Galloway *et al.* (1995) calculated that human activity has resulted in the fixation of an additional 140 Tg N yr^{-1} by energy production (20 Tg N yr^{-1}), fertilizer production (80 Tg N yr^{-1}) and the cultivation of legumes and other crops (40 Tg N yr^{-1}). About 55 % of this anthropogenic fixed N is redistributed back to the atmosphere as NO_y and NH_3, much more widely than in pre-industrial times. In turn, 70–80 % of this emitted N is deposited back on land. There is great concern over the ultimate fate of this extra fixed N. Much of it, as with much of the extra mobilized carbon dioxide, is 'missing', i.e. current measurements and calculations cannot account for it. It could be denitrified to N_2 or be accumulating in the atmosphere, soils, groundwater, land vegetation, oceans and marine sediments, changing ecosystems through eutrophication and acidification.

Rothamsted Experimental Station, UK has been involved in research into N cycling in ecosystems since its inception in 1843 (see, for example, Johnston (1994); Powlson, (1994)). Nitrogen deposition in precipitation has been measured since 1853 when the first rain gauge was built (Goulding *et al.*, 1986), and dry-deposited forms and total deposition since 1986 (Goulding, 1990). There is a wealth of short-, medium- and long-term data on N deposition and its effects on managed and unmanaged ecosystems. This paper presents the most recent measurements of N deposition at Rothamsted, the effects that this deposited N has on local ecosystems – arable farmland, traditional grass meadow and woodland – and on N-cycling processes in soil, and possible quantitative measures of N saturation developed as part of the current N-cycling research programme. Together with modelling predictions of the fate of deposited N, the research has begun to answer some of the questions regarding the

amount of N deposited and recycled to the atmosphere and waters, and the impacts of that which stays in the soil/plant ecosystem.

ATMOSPHERIC DEPOSITION

Wet (bulk) deposition

The first rainfall gauge was constructed at Rothamsted in 1852/3 and partial data are available from that time. The gauge was constructed of lead-lined wood, exactly 1/1000th of an acre (4·04 m²) in area and at ground level. Precipitation was also collected in a simple funnel-and-bottle bulk gauge 1·2 m above ground from 1969 to 1986 (Goulding *et al.*, 1986). Rothamsted and Rothamsted-managed sites at Woburn Farm (Husborne Crawley, Bedfordshire, UK) and Broom's Barn Experimental Station (Bury St Edmunds, Suffolk, UK), joined the UK Secondary Precipitation Composition Network (UKSPCN) in 1986. All data are now collected using the UKSPCN gauge and rigorous protocols. Comparisons between the gauges show that the simple funnel-and-bottle and UKSPCN gauges give identical results. There are systematic differences between the 1/1000th acre and other gauges owing mainly to the collector height. All data for N in precipitation in this paper, apart from Figure 1, are from the UKSPCN gauge and so are comparable with other UK Precipitation Composition data (UKRGAR, 1990).

A long-term data set of N and sulphur deposition in precipitation is in Figure 1. Sulphur deposition in precipitation increased from 5 kg ha^{-1} yr^{-1} in 1855 to a maximum of 25 kg ha^{-1} yr^{-1} in 1980, when the switch from coal to natural gas and from high-S to low-S coals, and industrial decline, led to a sudden and precipitous decrease (see McGrath & Goulding, 1990; McGrath & Zhao, 1995). The deposition of nitrate and ammonium has increased more slowly from 1 and 3 kg ha^{-1} yr^{-1}, respectively, in 1855 to 8 and 10 kg ha^{-1} yr^{-1}, respectively, in 1980; their deposition has also been decreasing recently for reasons that are not yet clear.
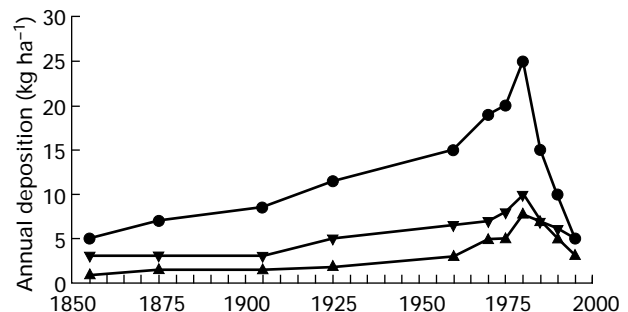

Figure 1. Annual deposition (kg ha^{-1}) of nitrate-N (▲), ammonium-N (▼) and sulphate-S (●) in precipitation (bulk deposition) at Rothamsted Experimental Station from 1855 to 1995. Data points are 5-yr means.
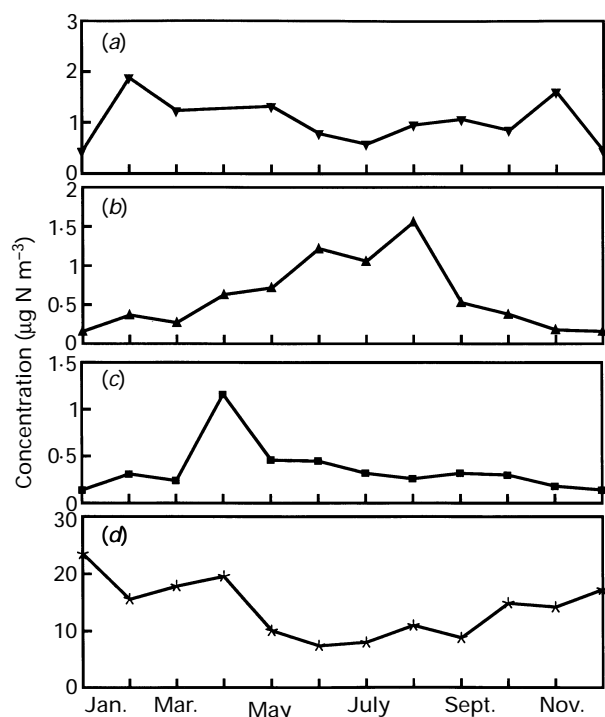
Figure 2. Monthly concentrations (μg N m^{-3}) of (*a*) particulate nitrogen (▼); (*b*) nitric acid (▲); (*c*) ammonia (■); (*d*) nitrogen dioxide (★), at Rothamsted Experimental Station in 1996.

Dry deposition

Measurements of concentrations of ammonia and nitrogen dioxide began at Rothamsted in 1986 (Goulding, 1990). Diffusion tubes were used as part of a test of the technique, coordinated by the Harwell Laboratory, UK (Campbell, 1988; Atkins, Jeffry & Law, 1989*a*; Atkins, Law & Sandalls, 1989*b*). Some research has found good agreement between measurements of ammonia concentrations made with diffusion tubes and those made with other techniques such as filter packs and denuders; other work has found that diffusion tubes give consistently higher values, especially outdoors (Atkins & Lee, 1993). Measurements at Rothamsted are being made using the latest version of the ammonia diffusion tubes, with a gas porous membrane covering the end to limit the effects of wind speed. Since early 1997, a simple denuder has formed part of the ITE-coordinated measurements of ammonia at Environmental Change Network sites, but data are not yet available. In addition, ammonia, nitric acid aerosol and particulate-N concentrations have been measured since April 1996 using a filter-pack technique. A comparison between diffusion tubes and filter packs shows poor agreement (data not shown). For this paper, all ammonia, nitric acid and particulate concentration data are from filter packs exposed for a month at a time.

The diffusion-tube technique for nitrogen dioxide has also recently been criticized as overestimating concentrations in urban air by up to 70 % (Heal &

Cape, 1997); in rural areas the overestimate was no more than 10 %. All of the diffusion tube, filter pack and wet deposition measurements reported in this paper were made in the meteorological enclosure at Rothamsted, 200 m from the nearest house and 300 m from the nearest major road and so free of any urban interferences.

Figure 2 shows monthly concentrations of nitrogen dioxide, ammonia, nitric acid and particulates in 1996. Maximum concentrations for nitrogen dioxide of 15–25 μg m^{-3} were observed in winter; concentrations were largest when the wind was from the north, bringing more polluted air from Harpenden, the Luton/Dunstable conurbation and the Midlands. Nitrogen dioxide concentrations were almost exactly halved in summer, coinciding with the switching off of central heating systems. These data compare well with those of UKRGAR (1990), UKPORG (1993) and Campbell, Stedman & Stevenson (1994).

Concentrations of ammonia were small, with a maximum in spring of *c*. 1 μg m^{-3}. There are no major livestock enterprises near Rothamsted. Concentrations of nitric acid and particulate N were of the same order as those of ammonia, with maxima of 1·5 μg m^{-3} (summer) and 2 μg m^{-3} (winter), respectively. They also compare well with those of the United Kingdom Review Group (UKRGAR, 1990).

Total deposition

Measuring deposition in precipitation is simply a matter of multiplying the concentration of N in precipitation by the amount of precipitation. Uncertainty lies mostly in the spatial variation of precipitation amount and composition. Campbell *et al*. (1988) measured the variation between the precipitation-weighted mean concentrations of nitrate and ammonium in two collectors 4 m apart to be *c*. 5 %. Thus the local variation of N species in precipitation is quite small. The site must still be representative of the local ecosystem, however; bulk deposition in woodland is much larger than that to grass or arable land (Beier & Gundersen, 1989). The Rothamsted gauge is in the meteorological enclosure and representative of the arable land surrounding it.

Calculating depositions of ammonia, nitrogen dioxide, nitric acid and particulates from concentrations is much more uncertain and depends on the use of deposition velocities. Those used in this paper are in Table 1 and are the same as those used by Goulding (1990). They were obtained from Voldner, Barrie & Sirois (1986), Voldner & Sirois (1986), Dollard *et al*. (1987) and Derwent, Dollard & Metcalf (1988). However, for this paper the growth of the cereal has been taken into account. Data from Prew *et al*. (1986) were used to estimate the surface area of the crop for each month of the year and deposition velocities from those for bare soil to a full crop

Table 1. *Deposition velocities, V_d for various nitrogen species*

		Deposition velocity (m s^{-1})			
Reference	Surface	Ammonia	Nitrogen dioxide	Nitric acid	Particulate N
This paper*	Winter wheat	0·008–0·02	0·0012–0·0025	0·035–0·135	0·004–0·01
Harrison & Allen (1991)	Arable	0·022	0·001	0·022	0·0015
Sievering *et al.* (1994)	Forest	n.d.	n.d.	0·02–0·09	0·02–0·09
Erisman *et al.* (1994)	Heathland	0·008	0·001–0·004	n.d.	n.d.
Duyzer *et al.* (1994)	Forest	0·02–0·03	n.d.	n.d.	n.d.
Wyers & Duyzer (1997)	Forest	n.d.	n.d.	> 0·1	0·01
Yamulki *et al.* (1996)	Arable	0·002–0·026	n.d.	n.d.	n.d.
Yamulki *et al.* (1997)	Grass	n.d.	0·004–0·007	n.d.	n.d.

Values for this paper are for deposition to a bare soil, regarded as the minimum, through to deposition to a cereal crop in full leaf, regarded as the maximum.

* Deposition velocities for this paper taken from Dollard *et al.* 1987), Voldner & Sirois (1986), Voldner *et al.* (1986), Derwent *et al.* (1988).

Table 2. *Nitrogen deposition to a winter cereal crop at Rothamsted in 1996*

	Monthly total depostion (kg N ha^{-1})												Annual total deposition (kg N ha^{-1})
Form of nitrogen	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	
Wet													
Nitrate	0·25	0·34	0·47	0·48	0·22	0·13	0·50	0·18	0·47	0·25	0·30	0·18	3·77
Ammonium	0·31	0·29	0·60	0·88	0·39	0·14	0·85	0·23	0·49	0·41	0·36	0·23	5·18
Dry													
Nitrogen dioxide	1·85	1·23	1·60	2·06	1·23	0·97	1·05	0·35	0·28	0·47	1·12	1·36	13·57
Nitric acid	0·17	0·39	0·57	1·98	2·55	4·32	3·76	1·43	0·49	0·35	0·19	0·17	16·37
Particulates	0·06	0·25	0·19	1·11	0·35	0·21	0·16	0·10	0·11	0·09	0·17	0·05	2·85
Ammonia	0·04	0·08	0·08	0·46	0·24	0·24	0·17	0·05	0·07	0·06	0·04	0·03	1·56
Sub-totals													
Reduced	0·35	0·37	0·68	1·34	0·63	0·38	1·02	0·28	0·56	0·47	0·40	0·26	6·74
Oxidized	2·33	2·21	2·83	5·63	4·35	5·63	5·47	2·06	1·35	1·16	1·78	1·76	36·56
Total	2·68	2·58	3·51	6·97	4·98	6·01	6·49	2·34	1·91	1·63	2·18	2·20	43·30

obtained or interpolated from those in the references listed above. This provides a much more reasonable estimate of deposition, with concentrations and crop size interacting to give maximum deposition rates for ammonia and particulate N in spring, nitrogen dioxide in late winter through to early spring, and nitric acid in summer (Table 2).

The deposition velocities (V_d) used are compared with those from other research in Table 1. The values used here for ammonia, nitrogen dioxide and particulate N are comparable with those found elsewhere in the literature. The value used for the deposition of nitric acid to a cereal crop in full leaf, growth stage 51, of 0·135 m s^{-1} is larger than most others reported, with the exception of Dollard *et al.* (1987) from which it was taken. However, Wyers & Duyzer (1997) obtained very large values of V_d, up to 0·13 m s^{-1}, for nitric acid deposition to a forest and ascribed this to chemical reactions between the nitric acid and other N and S species. Sievering *et al.* (1994) measured deposition velocities of particulate nitrate and nitric acid to a forest of 0·02–0·09 m s$^{-1} \pm 65\%$, and again ascribed the larger values to chemical reactions.

Amounts of the various forms of N deposited are

in Table 2. In total, some 43·3 kg N ha^{-1} were deposited to winter cereals at Rothamsted in 1996. This is less than that measured for the mid-1980s, and with a different distribution: in 1996 there was less wet-deposition and reduced N than in 1986; the main components were nitrogen dioxide and nitric acid, and dry deposition comprised 79% and oxidized species 84% of the total. The calculated small deposition of ammonia agrees with micrometeorological measurements at Rothamsted of a small net *emission* of 1·76 kg N ha^{-1} yr^{-1} from cereals (Yamulki, Harrison & Goulding, 1996).

The total measured deposition agrees well with three other independent estimates of deposition (see also Goulding (1990)): Jenkinson (1982) calculated from a long-term N balance that 38 kg N ha^{-1} yr^{-1} were deposited to the very poor crop of winter wheat, yielding only 1–2 t ha^{-1} yr^{-1}, on the unfertilized 'Nil' plot of the Broadbalk Continuous Wheat experiment (Johnston, 1994); Powlson *et al.* (1986) estimated, from an ^{15}N balance, a mean deposition of 48 kg N ha^{-1} yr^{-1} to several plots of the Broadbalk experiment; an N balance calculation for the bare soil of the 127-yr-old Drain Gauges at Rothamsted (Addiscott, 1988), assuming equilib-

rium for the soil N cycle, i.e. 'N in' equals 'N out', gave a deposition of 37 kg N ha^{-1} for 1986 (Goulding, 1990). Thus, from these very different methods a reliable estimate can be made of N depositions of 35–40 kg N ha^{-1} yr^{-1} to bare or poorly-yielding arable crops, and 45–50 kg N ha^{-1} yr^{-1} to a good arable crop.

MODELLING THE FATE OF DEPOSITED NITROGEN

It is not currently possible to trace the path and ultimate fate of the N deposited from the atmosphere. However, isotopic labelling with the stable heavy isotope of nitrogen, ^{15}N, has made it possible to label other pools of N and, from the dilution of the label in these pools as reactions proceed and N enters from various sources, calculate rates of N-cycling processes (Powlson & Barraclough, 1993). Some results of such experiments will be discussed later because they are very relevant to understanding the effects of the extra anthropogenic N entering ecosystems. However, instead of experiments the now well developed N-cycle model, SUNDIAL (Bradbury *et al.*, 1993) has been used to simulate the fate of N deposited to the Broadbalk experiment, and its predictions of nitrate leached, denitrified and taken up by the crop tested against measured values from the experiment.

SUNDIAL simulates the flow of N through all the major N-cycling processes, including that which cycles through the soil microbial biomass (turnover time 1·5 yr) and soil humus (turnover time 66 yr). Each year's addition of fertilizer (and atmospheric N) might be taken up by the crop and partitioned between roots, grain and straw. It might be denitrified, leached or subject to loss from the system as ammonia. Any N in the crop not removed at harvest is then returned to the soil in residues. The biomass and humus compartments in the model have a fixed C:N ratio of 8·5, but that of the residues can vary; the balance between these ratios determines whether or not crop residues immobilize or mineralize N. Weekly rainfall, evaporation and soil temperature modify the base rates of turnover.

The model conveniently allows us to study the fate of atmospheric N because of its ability to handle *labelled* N inputs. Measured amounts of atmospheric N deposited on land were regarded as entering the model as ^{15}N-enriched N. Simulations were made for plots receiving 0, 48, 96, 144, 192 and 240 kg fertilizer N ha^{-1} yr^{-1} and *c.* 240 kg N ha^{-1} yr^{-1} as farmyard manure (FYM), applied at 35 t ha^{-1} yr^{-1}, from the beginning of the experiment until today, using real weather and crop yields. Atmospheric inputs of N have been increasing since the industrial era (Fig. 1 and Goulding *et al.* (1986)). The preindustrial background deposition was set at 10 kg N ha^{-1} yr^{-1} after Boxman & Roelofs (1988); no
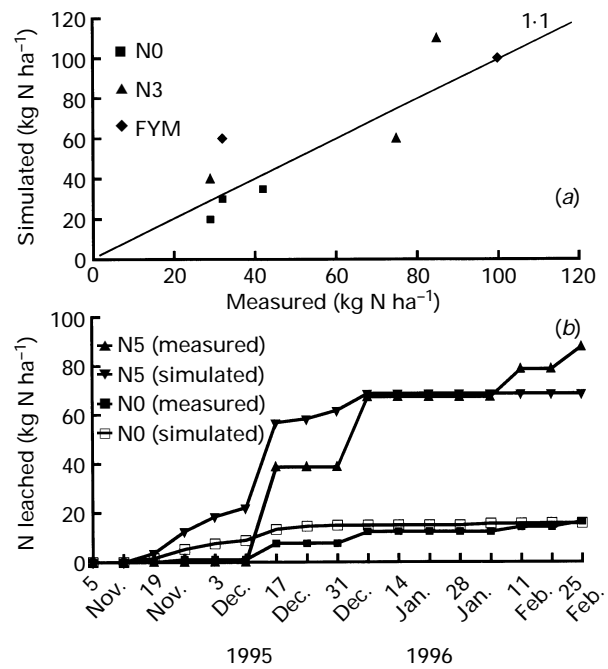
Figure 3. Comparison of simulated and measured data for the Broadbalk Continuous Wheat Experiment, 1995–6 season. (*a*) Mineral nitrogen in the soil (0–75 cm) for plots receiving 0 (N0) and 144 (N3) kg N ha^{-1} yr^{-1} in spring as ammonium nitrate fertilizer, and *c*. 240 kg N ha^{-1} yr^{-1} in farmyard manure (FYM) in autumn; (*b*) Nitrate leached from plots receiving 0 (N0) and 240 (N5) kg N ha^{-1} yr^{-1} as ammonium nitrate fertilizer in spring.

change was made until 1900 and then a gradual increase to a maximum of 45 kg N ha^{-1} yr^{-1} in 1980 calculated, with a constant deposition thereafter; i.e. total deposition approx. paralleled wet deposition (Fig. 1).

The model predicts that, as would be expected, the distribution of the deposited N between the crop, soil organic matter, leaching, denitrification and senescence (ammonia volatilization) varies with the amount of fertilizer applied and the amount of N deposited. After 154 yr of the experiment, of the 40–45 kg N ha^{-1} deposited annually today, about 5 % is leached, 12 % denitrified, 53 % taken off in the crop, and 30 % immobilized in soil organic matter. The leached and denitrified atmospheric N comprise *c*. 10 % and 16 % of the total leaching and denitrification losses, respectively, a significant contribution. As fertilizer N applications increase, more deposited N is lost and immobilized and less used by the crop. Similar modelling for two nitrate-vulnerable zones (data not shown) shows that atmospheric N can comprise up to 40 % of both the nitrate leached and that denitrified, varying greatly with the crop.

To assess how well the model is working, simulated and measured soil mineral N (Fig. 3*a*) and total leaching losses (Fig. 3*b*) were compared for the Broadbalk Experiment for the 1995–6 season. The r^2 value for simulated vs. measured soil mineral N to

75 cm depth was 0·74; graphs of simulated and measured leaching losses show good agreement. The model predictions of the fate of deposited N are therefore likely to be a good indication of reality, indicating a major contribution of atmospheric N to the specific pollution problems of nitrate leaching and increasing nitrous oxide concentrations and the greenhouse effect.

EFFECT OF NITROGEN DEPOSITION ON CROP PLANTS

Annual yields from the long-term experiments at Rothamsted, measured for up to 154 yr, show no detectable effects from the increases in atmospheric N or carbon dioxide concentration (Jenkinson *et al.*, 1994). However, clear and well documented effects of N and soil acidification on the species number and composition of the Park Grass Experiment can be observed. This experiment studies the effects of types and amounts of fertilizers and manures on a hay meadow that was already hundreds of years old when the experiment began in 1856 (Johnston, 1994). Papers by Thurston, Williams & Johnston (1976), Johnston (1994) and Tillman *et al.* (1994) summarize the research, and Figure 4 presents a summary of some of the data reported in these and earlier, less accessible, internal reports; data start from the first detailed sampling in 1862, 6 yr after the beginning of the experiment when some marked changes had already occurred.

On the unfertilized plot, species numbers decreased from *c.* 50–*c.* 35 from 1856 to 1950 while soil pH changed from only 5·8–5·5, solely because of atmospheric deposition. (The number of species found on the unfertilized and sodium nitrate treated plots varies greatly from year to year, as do the species found; approx. 100 species have been identified on Park Grass, but no more than 50 on any one plot in any one year.) It is likely that N deposition was approx. the same as that to the arable land, i.e. 10 kg ha^{-1} yr^{-1} when the Park Grass Experiment began in 1856 increasing to

45 kg N ha^{-1} yr^{-1} today, but it is not possible to separate the effect of the deposited N from that of acidification caused by N, S and protons, H_3O^+. The recent sharp reduction in soil pH to 4·5 on this plot (Blake, Johnston & Goulding, 1994) has not yet had a measurable effect on species numbers but, using the ammonium-treated plot as a guide (see below), we would expect a marked reduction in numbers soon.

Applying N fertilizer as sodium nitrate (which does not acidify the soil) at 48 kg ha^{-1} yr^{-1} or more, led to an immediate disappearance of legumes, and species numbers decreased from *c.* 50–*c.* 35 within a few years. The graphs of species numbers against time for the unfertilized and nitrate-treated plots in Figure 4 are approx. parallel, with about 13 fewer species on the nitrate-treated plot. This suggests that the initial reduction of 13 in species numbers resulted from the nitrate fertilizer, but that the consequent steady decrease has a common cause across the plots – atmospheric deposition.

Applying N as ammonium sulphate, which has strongly acidified the soil from its original pH of 5·8 in water to about 3·5 now, has caused species numbers to decrease from 50 to 30 within 6 yr of the beginning of the experiment, and to one or two acid-tolerant grasses in about 100 yr. Clearly, acidification has an effect additional to that caused by N. After 1880, the graph of species numbers against time for the ammonium-treated plot is approx. parallel to those of the unfertilized and nitrate-treated plots, but with 16 fewer species than the nitrate-treated plot (Fig. 4), attributable to the acidifying effects of the ammonium-N. The value of liming to ameliorate acidification is shown by the recovery in species numbers to *c.* 15 on the sub-section of the ammonium treated plot which has been limed regularly since 1903. Extrapolating the species number : time curve for the ammonium-N/limed section suggests that numbers will return to those on the nitrate-treated plot, indicating that the effects of acidification can be overcome by liming.

EFFECT OF NITROGEN DEPOSITION ON SOIL PROCESSES

Our research has shown acidification resulting from atmospheric deposition, including N, under woodland as well as grassland. Soil pH has decreased from 7 to 4 or less in 110 yr, mobilizing aluminium and toxic metals (Johnston, Goulding & Poulton, 1986; Blake *et al.*, 1994; Sverdrup *et al.*, 1995). Recent research on trace gas fluxes and N-cycling processes has shown clear evidence of major effects of deposited N, aside from those of acidification, on microbiologically-mediated soil processes: deposited N is saturating woodland ecosystems, greatly increasing nitrous oxide emissions, reducing methane oxidation rates, and altering the balance of
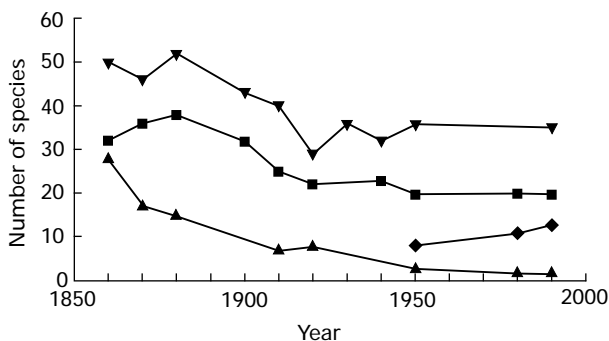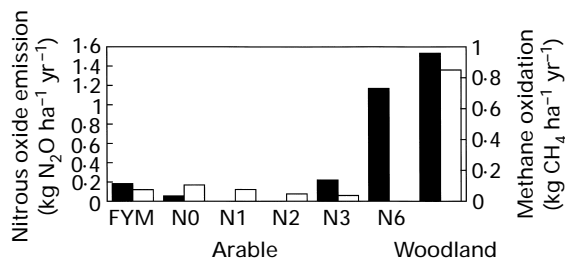

Figure 4. Changes through time in the number of species on plots of the Park Grass Experiment. ▼, no fertilizer; ■, sodium nitrate; ▲, ammonium sulphate, no lime; ◆, ammonium sulphate with lime.

Figure 5. Nitrous oxide emission (■) and methane oxidation (□) rates (kg N_2O or CH_4 ha^{-1} yr^{-1}) on selected plots of the Broadbalk Experiment: N0, N1, N2, N3, N6 and FYM receive 0, 48, 96, 144, 288, and *c.* 240 kg N ha^{-1} yr^{-1}, respectively.

Table 3. *Mean nitrous oxide emission (kg N_2O ha^{-1} yr^{-1}) from arable land (Broadbalk, Plot 3, unfertilized), grassland (Park Grass Plot 3, unfertilized), and deciduous woodland (Knott Wood)*

	Arable	Grass	Woodland
Emission	0·05	0·04	0·73
SE	0·07	0·10	1·38

Measurements made monthly for 1 yr using eight replicate soil cores per treatment.

nitrification and mineralization/immobilization, as described below.

Trace gas fluxes in N-saturated systems

Detailed research into the microbial basis of methane oxidation during the past 5 yr (e.g. Goulding *et al.* (1995); Willison, Goulding & Powlson (1995*a*)) has shown that N affects the oxidation of methane by soils (Fig. 5). Applications of fertilizer of 48 and 96 kg N ha^{-1} yr^{-1} for 150 yr have reduced the ability of soil from the Broadbalk Experiment to oxidize methane by *c.* 28% and 55%, respectively, over that of unfertilized arable soil (Fig. 5 and Willison *et al.* (1995*b*)). This represents an approximate reduction in methane oxidation rates of 10% for every 17 kg N ha^{-1} yr^{-1} applied. Although this is only for arable land, and the fertilizer application is super-imposed on atmospheric deposition, one can use these data to estimate the effect of atmospheric N on the UK methane sink. Taking a current mean deposition of 25 kg N ha^{-1} yr^{-1} for the whole of the UK would cause an overall decrease in the rate of oxidation of methane of 15%. Willison *et al.* (1995*a*) calculated the current UK methane sink at 22·7 kt CH_4 yr^{-1}. If this is 15% less than it could be it represents a decrease in sink strength of 4 kt CH_4 yr^{-1}. This reduction is small compared with an 80% reduction in oxidation rate caused merely by cultivating soil (Arable N0 vs. Woodland, Fig. 5; Goulding *et al.* (1995)), and UK methane production rates of 3530 kt yr^{-1} (Houghton, Callander & Varney, 1992), but it does show the importance of atmospheric N deposition on one important soil microbial process.

Figure 5 shows that there is still a rapid oxidation of methane under Rothamsted woodland, despite deposited N. There are no direct measurements of N deposition to Knott Wood or Broadbalk Wilderness, but N deposition to a forest has been measured at 2·5–3 times that to surrounding pasture land (Beier & Gundersen, 1989). As a first approximation one might therefore estimate N deposition to woodland in the Rothamsted area at *c.* 100 kg ha^{-1} yr^{-1}. There is, of course, no woodland that is not receiving

nitrogenous componds via the atmosphere and so no comparative method for measuring the effect of this N on methane oxidation rates. However, assuming the same magnitude of effect of N on the woodland as the arable land, and a mean deposition of N to UK woodland of 50 kg ha^{-1} yr^{-1}, i.e. twice that to grassland and arable land, then methane oxidation rates under woodland have been reduced by N deposition by at least 30%.

As well as reducing methane oxidation rates, deposited N greatly increases fluxes of nitrous oxide. Broadbalk Wilderness is a small area of woodland at the western end of the Broadbalk experiment and immediately downwind of the farm buildings which house cattle in winter (Johnston *et al.*, 1986). It emits *c.* 1·5 kg N_2O ha^{-1} yr^{-1} (Fig. 5). Another, rather larger area of woodland, Knott Wood, is several hundred years old, part-coppiced, unfertilized and upwind of the farm buildings. Mean annual nitrous oxide emission rates from it are *c.* 0·73 kg ha^{-1} yr^{-1} (Table 3). These contrast with modest annual nitrous oxide emission rates of 0·04 and 0·05 kg N_2O ha^{-1} yr^{-1} from unfertilized grass and arable land on Park Grass and Broadbalk, respectively, where the harvested plants are able to utilize the deposited N very efficiently (Fig. 5; Table 3). For arable plots on the Broadbalk Experiment receiving 48–288 kg N ha^{-1} yr^{-1}, emissions increase approx. linearly from 0·04 to 1·4 kg N_2O ha^{-1} yr^{-1} with N fertilizer applied (Fig. 5; Harrison *et al.*, 1995; Yamulki *et al.*, 1995); large emissions are measured only from plots receiving N in excess of crop requirements, optimum N-fertilizer require-ments being 150–180 kg N ha^{-1} yr^{-1} on Broadbalk. Rates of emission of nitrous oxide from the woodland compare with those from the arable land receiving excess N (> 200 kg ha^{-1} yr^{-1}), indicating that the woodland is N-saturated. Can N deposition explain these large but different emission rates from the two areas of woodland?

Beier & Gundersen (1989) measured deposition rates of N to the edge (0–15 m) of a forest to be 2–2·5 times that in the centre. Broadbalk Wilderness is at most 30 m wide. Using Beier & Gundersen's factors, deposition to Knott Wood and Broadbalk Wil-derness is *c.* 100 and 200 kg N ha^{-1} yr^{-1}, respectively. This is *c.* 90 and 190 kg N ha^{-1} yr^{-1} in excess of the

Table 4. *Gross mineralization, net mineralization and gross nitrification and nitrate content for soil under deciduous woodland* (*Knott Wood*) *at Rothamsted, measured using* ^{15}N *pool dilution*

Process/ pool	Flux or amount
Gross mineralization (mg N kg^{-1} soil d^{-1})	2·46
Net mineralization (mg N kg^{-1} soil d^{-1})	0·71
Gross nitrification (mg N kg^{-1} soil d^{-1})	1·03
Inorganic nitrate pool (mg N kg^{-1} soil)	30·24
Gross nitrification (mg N kg^{-1} soil d^{-1})/ gross immobilization (mg N kg^{-1} soil d^{-1})	0·55

requirements of the trees, which need only 8–12 kg N ha^{-1} yr^{-1} (Jenkinson, 1971; Pearson & Stewart, 1993). There is, therefore, a large excess of N and likely N-saturated soils under both areas of woodland, but with twice the excess on Broadbalk Wilderness. Very approximately, every 10 kg N ha^{-1} yr^{-1} in excess of demand generates 0·07 kg N$_2$O ha^{-1} yr^{-1}.

Nitrification in N-saturated systems

Current research into N-cycling processes has involved the development of new techniques using ^{15}N-pool dilution. These are mainly for use in agricultural systems, for understanding and predicting N availability from mineralization and its contribution to nitrate leaching, denitrification and nitrous oxide emissions. However, the techniques have also been applied to semi-natural systems such as unfertilized grassland and woodland in order to develop quantitative indices of N saturation (Aber, 1992). Isotopic ^{15}N pool dilution experiments were conducted using the method developed by Barraclough & Puri (1995). Fresh soil was labelled with ($^{15}NH_4$)$_2$SO$_4$ or K^{15}NO$_3$ and extracted with 2 M KCl after 0, 1, 2, 3 and 7 d. Ammonium and nitrate concentrations were measured and ^{15}N:^{14}N ratios of the ammonium and nitrate molecules determined by mass spectrometry. Gross rates of mineralization, immobilization and nitrification were obtained from these measurements using the formula of Barraclough (1991).

The soil under Knott Wood has a large nitrate pool relative to the measured rates of mineralization and nitrification (Table 4). Other data (not shown) indicate that the ammonium pool has a longer residence time than those in soil under arable and grass. Woodland soils are usually highly conservative of N; it is unusual for so much nitrate to be available. The gross nitrification:gross immobilization index (Aber, 1992) of 0·55 (Table 4) also suggests that this soil is not conserving N, and that the nitrate pool is building up from inefficient recycling and outside sources.

Table 5 shows the results of similar measurements of nitrate-N, total mineral-N and the ratio of gross nitrification:gross immobilization pre- and post-cultivation of arable and ley-arable land at Woburn Experimental Farm. Following cultivation, there is no indication from the content of nitrate or total mineral N in the soil that excess nitrate is present, unlike the woodland (Table 4); the excess would have been rapidly leached on this sandy (10 % clay) soil. However, a ratio of gross nitrification to gross immobilization of > 1 indicates the over-production of nitrate, an inefficient cycling of N, and a nitrate-saturated system, as would be expected after ploughing out a grass ley.

CONCLUSIONS

Nitrogen deposition to winter cereals at Rothamsted is *c.* 45 kg N ha^{-1} yr^{-1}; deposition to woodland is likely to be 100 kg N ha^{-1} yr^{-1} or more. This N is making a significant contribution to environmental pollution especially under the woodland, being emitted back to the environment as nitrate and nitrous oxide. Above-ground effects on arable land are minimal, but atmospheric deposition has ensured that the unfertilized plot on the Broadbalk Experiment receives enough N to maintain a yield of 1–2 t wheat ha^{-1} yr^{-1}. (Total N in the soil of this plot

Table 5. *Nitrate and mineral N* (*nitrate-N* + *ammonium-N*), *and nitrification and immobilization measured by* ^{15}N *pool dilution on the Ley-arable experiment at Woburn Experimental Farm*

Treatment	Nitrate-N (mg N kg^{-1} soil)	Mineral N (mg N kg^{-1} soil)	Gross nitrification (mg N kg^{-1} soil d^{-1})/ gross immobilization (mg N kg^{-1} soil d^{-1})
Pre-cultivation			
Continuous arable	3·91	6·54	0·17
Grass ley	0·32	3·03	0·10
Post-cultivation			
Continuous arable	4·89	7·67	0·52
Grass ley	2·38	5·06	2·24

has been in equilibrium for > 100 yr (Glendining *et al.*, 1996) so the net input of N cannot have come from soil reserves.) Such an amount of 'free' N would greatly benefit organic and other low input farming systems, but will significantly change semi-natural habitats. For example, atmospheric N has had no measurable effect on the yield of the hay from the Park Grass Experiment but it has reduced species numbers, with an approx. equal effect through eutrophication and acidification; liming can offset the latter but not the former. There are also clear effects of deposited N on soil processes. The present deposition is sufficient to reduce methane oxidation and greatly increase nitrous oxide production through its inhibition of methane-oxidizing organisms and stimulation of nitrifiers. Woodland systems in the Rothamsted area are N-saturated, as shown by rapid nitrification rates and large nitrous oxide emissions comparable to arable land receiving 200 kg N ha^{-1} yr^{-1} or more. The ratio of gross nitrification:gross immobilization suggested by Aber (1992) would seem to be a useful index of N saturation.

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