

Excess nitrogen leaching and C/N decline in the Tillingbourne catchment, southern England: INCA process modelling for current and historic time series

P.G. Whitehead⁺, D. J. Lapworth*, R.A. Skeffington⁺ and A. Wade⁺

⁺Aquatic Environments Research Centre, Department of Geography, University of Reading, Whiteknights, Reading, RG6 6AB

*British Geological Survey, Wallingford, OX10 8BB

Abstract

Measurements of nitrate deposition and streamwater chemistry in the Tillingbourne Catchment, in Southern England, made in 1979-1982 and 1999-2001 show a 216% increase in Nitrogen leaching despite a reduction in N inputs. Both the historical and current data sets have been modelled using the Integrated Nitrogen Model in Catchments (INCA). The process based model is shown to reproduce the historical patterns of N release from the catchment. However, modelling the increased leaching of N during recent years required an increase of the mineralization control parameter in the model, suggesting enhanced mineralization rates. Comparing historic and current soils data for C/N ratios shows that there has been a reduction in C/N from 38 to 26 in the humus layer and a reduction from 33 to 26 in the mineral soil horizon. This significant fall in C/N is consistent with the increase in N saturation in the H and Ah horizons of the major catchment soil.

Key words

Acid Deposition, recovery, nitrogen, Carbon-Nitrogen Ratios, Tillingbourne, Catchment studies, nutrient leaching

Introduction

Over the past decade there has been rising concern over nitrogen (N) in the environment. This has been particularly true in relation to upland catchments, where excess nitrogen availability has led to leaching of N from forest and moorland systems (Dise and Wright, 1995). As N deposition levels increase, the short vegetation uptake can be exceeded and excess N leached. This leads to problems in upland waters such as enhanced acidification, as nitrate-nitrogen given that a strong acid anion, or increased eutrophication in stream and lakes driven by increased nutrient levels. Alternatively as forests reach maturity they take up less nitrogen and again excess N may be leached from the forest systems. Another potential mechanism for N release is the impacts of climatic change which could alter rainfall and temperature patterns thereby altering soil moisture, water flows and nitrogen process kinetics, mineralisation and nitrification processes are temperature and soil moisture dependent and climatic change could enhance these process rates (Wright *et al.*, 1998).

The first international protocol to limit N emissions was formulated in 1988 under the auspices of the UNECE and implemented in 1991 in the Sophia Protocol (Hornung and Langan, 1999). Skeffington (this volume) gives a history of N emissions and control strategies since 1988. There has, in fact, been a reduction in N emissions in the UK from 2.59 M tonne of NO₂ in 1980 to 1.75 M tonnes in 1998. Also ammonia emissions have increased slightly from 0.33 M tonne in 1980 to 0.35 M tonne in 1998, but are predicted to fall to 0.26 M tonne by 2010. This should have led to a reduction in N release in catchments but results at the Tillingbourne Catchment in Southern England show a 216% increase in mean nitrate concentration (Hill *et al.*, 2001). This paper addresses the issue of this increased leaching at the Tillingbourne Catchment and makes use of the INCA model (Whitehead *et al.*, 1998, Wade *et al.*, this volume) to evaluate N processes and mass balance in the catchment. Historical and current C/N data are used to evaluate the hypothesis suggested by the INCA modelling study, that mineralisation rates have increased at Tillingbourne.

The Tillingbourne Catchment

The Tillingbourne catchment is situated 7 km south west of Dorking, Surrey, SE England, National Grid Reference TQ 140435 and is in the Thames Valley (Hill *et al.*, 2001) as shown in Figure 1. The catchment is drained by the River Tillingbourne flows first North and then west before joining the River Wey which is a tributary of the River Thames. The catchment consists of a valley cut into the dip slope of the lower Greensand formation, Leith Hill, which is the highest point in South East England. The 'Tillingbourne catchment' refers to the upper part of the catchment draining an area of 93 hectares (Skeffington, 1982).

The catchment has three distinct topographical features; broad, gently sloping interflaves, fairly steep valley sides, with slopes of up to 18°; and a gently sloping valley floor in which the Tillingbourne is situated. The head of the valley rises steeply to the highest

point, Leith Hill (297m a.s.l), the lowest point of the catchment is 172m a.s.l (Skeffington, 1982).

At the southern end of the catchment the Tillingbourne is ephemeral, comprising mostly of soil and surface runoff. At the northern end of the catchment the river is perennial and is comprised mostly of water from groundwater sources. The catchment averages about 900mm rainfall annually and this is well distributed throughout the year, the driest months being March and April. Mean daily temperatures in January range from 0-6°C, and those in July range from 11-2°C. The wind direction is predominantly South-westerly. Anthropogenic pollution comes from three main sources; N and NE London (35km), Southampton (80km), and there are some sources locally within a 50km radius including Dorking, Horsham and Guildford.

The geology of the area, as shown in Figure 2, has been described by Gallois (1965). The entire catchment is contained within the Lower Greensand formation. The oldest stratum of the catchment is the Atherfield Clay, which outcrops at the valley bottom but is continuous under the whole catchment. It is between 10 and 20 m thick and consists of shales and mudstones which weather to form silty clays, and provides an impervious base to the catchment. This is overlain by the Hythe Beds, consisting of porous, non-calcareous sandstones with some beds of chert providing resistance to weathering. Both formations dip 3° in the northerly direction, are of marine origin, and were laid down in Cretaceous times.

Figure 3 shows a typical profile of four of the different soil types with their different horizons. The soils of the catchment were surveyed by the Soil Survey of England and Wales (Moffat and Jarvis, 1984), and classified according to the National Soil Survey scheme (Avery, 1980). Five soil types were identified (A-E), based on sixty-nine one meter-deep auger borings and four profile pits, as shown in Figure 4. The 5 soils consist of:

(A)- Coarse loamy humo-ferric podsol (deep phase): These soils are the most extensive, covering approximately 50% of the survey area on all valley slopes up to 18°. Soil A exhibits a usual podsol sequence of horizons; dark brown organic enriched topsoil (Ah) over an ashy grey horizon (Ea) over organic and sesquioxide enriched horizons (Bh and Bs). For this project only the top horizon (Ah) and humus horizon (H) were sampled as these are the most relevant to N enrichment and saturation. What distinguishes this soil from soil B is that the soil depth is usually greater than 60 cm. The soil is acid and free draining, base saturation and weathering rates are low.

(B)- Coarse loamy humo-ferric podsol (shallow phase): These are located in the gently sloping interfluves, covering, approximately 34% of the survey area. Soils classified in this section are similar to soil type A, but are shallower and have cherty sandstone slabs within the Hythe Beds at a depth of 30-60 cm. Horizon definition is poorer and in place the horizon (Ea) may be absent.

(C)- Fine and coarse loamy typical argillic gley and argillic humic gley soils: These are located in the valley bottom and in small areas around flux sites at the head of the Tillingbourne, covering approximately 9% of the survey area. These soils are affected by the high groundwater in the valley bottom and changes in water level. Most are stoneless and consist of coarse loamy upper layers (Eg) over grey and ochreous mottled fine loamy subsoil. Thin humos and peaty topsoil's are common and may be as deep as 10 cm; these have developed as the soil is saturated over long periods in the year. Below the topsoil structural development is weak and Atherfield Clay occurs at a depth of over 100 cm. Base saturation is in general higher than in soils A and B, especially in the lower horizons due to the presence of exchangeable cations.

(D)- Coarse loamy gleyic argillic brown earths: These soils are located in a small area towards the bottom of the valley, and cover approximately 1% of the catchment. It is a transitional zone between soils A and C and is thus difficult to distinguish clearly, but the dominant soil is characterised by yellowish brown slightly stony coarse loamy material in which a clay-rich subsoil horizon with mottled colours (like that of soil C) is found.

(E)- Raw peat soils: These cover 6% of the surveyed area and are located in a basin at the northerly end of the catchment. The depth of the peat varies, but is about 50 cm deep, overlies a silty clay loam drift, and is permanently saturated. The peat is acidic, pH<4.5, but has a high base saturation and could be classified as eutrophic or mesotrophic. Sulphate reduction is known to occur in this soil.

Forest vegetation covers about 89% of the catchment and is a mix of coniferous and deciduous forest. The main tree species are Scots pine (*Pinus sylvestris*), Oak (*Quercus robur*) and birch (*Betula pendula*), and has been classified as oak-birch heath with sub-spontaneous pinewoods (Tansley, 1953). Pine dominates the interfluves, while oak and birch dominate the valley bottom. Alder (*Alnus glutinosa*) dominates the peat area. Other tree species include beech and Norway spruce. The trees date from about 1920, calculated from ring counts, this indicates that most large trees were felled during the first world war, 1914-18, and has had important implications for the historic N processes within the catchment. Ground vegetation is dominated by bracken (*Pteridium aquilinum*) present in all locations except in a beech plantation, and in the peat soil where mosses and grass species dominate. Vegetation cover has changed little in the last 20 years, except to mature, and there has been limited management of the bracken (rolling) since 1995 with some success.

Hydrochemical change at Tillingbourne

A study of the influence of precipitation acidity on stream acidity was carried out between 1977 and 1982 as part of the Central Electricity Generating Board's (CEGB) programme to assess the effects of acid precipitation from fossil fuel combustion on soils and freshwater. This research was initiated after claims that acid S precipitation was causing damage to aquatic ecosystems in Scandinavia (Oden and Ahl, 1972). Many process-based studies were carried out at the Tillingbourne catchment during this period

including; wet deposition (rainfall), dry deposition (throughfall), vegetation effects, soil processes, and hydrological processes. The results of these studies were published in a series of documents produced by the CEEB, and journal publications, largely under the authorships of R.A. Skeffington (e.g. 1981, 1982, 1985) and K.A. Brown (e.g. 1982). Emissions of acidifying pollutants have declined across Europe as a result of tight emission standards being imposed since the early 1980s. In the UK, SO₂ emissions declined by 67% between 1977 and 1997, and NO₂ emissions by 26% over the same time period. However the increase in road transport offset the decline in NO₂ emissions until 1992 (Hill, *et. al.*, 2001, Skeffington this volume). The recent decline in S and N emissions have given the opportunity to investigate the recovery and effects of S and N deposition on catchment processes.

The CEEB studies were followed by an investigation carried out by the Aquatic Environments Research Centre (AERC) between 1998 and 2001, to determine the recovery from acidification in the Tillingbourne catchment, (Hill *et. al.*, 2001). In 1998 the catchment was re-instrumented in order to measure the same parameters as the historic period. Measurements of the key catchment processes included; bulk precipitation, throughfall, and stream chemistry, to determine the changes in these fluxes over the last 20 years. A comparison between the fluxes of various substances has shown some important results across the whole catchment. Tables 1 and 2 show changes in these key measurements in the last 20 years.

Table 1: Mean Volume-Weighted Concentrations in Rain and Throughfall 1979-82 and 1999-2000

	pH	H ⁺	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Cl ⁻
Rain 79-82	4.16	70.1	4.04	0.51	0.53	3.31
Rain 99-00	4.67	21.6	1.59	0.32	0.33	2.46
Throughfall 79-82	2.84	1446	72.7	0.88	1.10	34.2
Throughfall 99-00	4.51	30.8	8.44	1.52	1.80	13.1

Units are µeq L⁻¹ for H⁺, mg L⁻¹ for SO₄²⁻, and Cl⁻, and mg N L⁻¹ for NO₃⁻ and NH₄⁺

Table 2: Changes in Mean Streamwater and Groundwater Concentrations, 1979-82 and 1999-2000.

Substance	Streamwater			Groundwater		
	1979-82	1999-2000	% change	1979-82	1999-2000	% change
NH ₄ -N	0.02	0.01	-50	0.013	0.002	-86
NO ₃ -N	0.21	0.67	+216	0.15	0.89	+496
pH	4.12	4.42		5.36	5.72	
SO ₄ ²⁻	17.96	16.53	-8	19.3	26.0	+25
Cl ⁻	13.3	14.9	+12	14.1	22.2	+57

All values in mg L⁻¹

Changes in Bulk Precipitation and Throughfall

It can be seen from Table 1 that since the historical study there has been an improvement in precipitation quality, with a significant reduction in acidic inputs. Sulphate has declined by 69%, nitrate and ammonium by 37% and hydrogen by 69%. The high degree of change in chloride is due to the large variability of the sea-borne aerosols. It can be seen that these changes in precipitation are closely linked to the changes in emission levels for the UK, described above. Changes in throughfall can only be regarded as qualitative at present as the changes in instrumentation and the effects of individual trees chosen have introduced significant changes. Marine sulphate in throughfall is considered a good surrogate for dry deposition (Hill *et. al.*, 2000), and it can be seen that the reduction rate of dry deposition has been greater than that in wet deposition. It can also be seen that the concentration of ammonium and nitrate in throughfall behaves in a similar way, since both have been increased significantly with respect to the historical study. In the historical data the N flux was less in throughfall than rainfall, whereas the reverse was true in the recent study. This suggests that foliar N uptake has decreased, and to a greater extent than the decrease in N precipitation. This could indicate that the availability of N in the soil mass has increased and that the soil has shifted from a N-limited status towards N saturation..

Changes in Stream and Groundwater Chemistry

The stream data, Table 2, shows an increase in pH across the catchment, presumably as a result of decreased acid loading. Ammonium concentrations have apparently declined by 50%, but are so close to detection limits as to make comparisons uncertain. Sulphate concentrations have decreased by only 8% but nitrate concentrations have increased by 216%. Groundwater data differ somewhat from the stream data (Table 2) but nitrate concentrations have increased even further, by almost 500%. Neither the present concentration of nitrate in the groundwater and the streamwater are high enough to cause alarm since the drinking water limit for nitrate is 11.3 mgNl⁻¹. However the rate at which they have increased is of concern particularly as the soil appears to be leaching N into the stream.

Historic and current soil nitrogen status and C/N ratios

Soil N status has been shown to have a significant relationship to the degree of N leaching that occurs from the soil mass in European forest ecosystems (Gundersen, 1991; Wilson and Emmett, 1999). Forest floor organic horizon C/N ratios have been shown to be a useful indicator of ecosystem N status (Dise *et. al.*, 1998). It has been shown through work carried out as part of the NITrogen EXperiments (NITREX) programme that the greater the N status within the soil mass, the greater the potential for leaching for any given input above 10 kgNha⁻¹y⁻¹. Table 3 shows the relationship between soil C/N ratios, throughfall and N leaching risk. This model categorises throughfall as low, intermediate, high and very high, and leaching risk is considered as a sliding scale related to both N input and C/N ratio which is also categorised as low, intermediate or high. In Table 3 confidence intervals on estimated nitrate leaching increase with levels above 30

kgNha⁻¹y⁻¹ and is a reflection of the high degree of variability in the data used. The % N content has also been shown to be an indicator of nitrification, the microbial conversion of ammonium to nitrate, which appears to control nitrate leaching also (Wilson and Emmett, 1999). A threshold for nitrification between 1.2 and 1.5 %N has been found for a number European and American forest soils, soils with a N content above this threshold have been shown to leach N, see Figure 5.

Table 3: The Relationship Between Soil C/N Ratio, Throughfall and N Leaching

C/N Ratio	Throughfall N Category (KgNha ⁻¹ y ⁻¹)			
	Low (<10)	Intermediate (10-20)	High (20-30)	V.High (>30)
35	(0-5) L	(0-7) L	(0-1) L	(0-32) H
30	(0-5) L	(0-9) L	(1-9) L	(0-38) H
25	(0-5) L	(0-12) I	(11-18) I	(0-46) H
20	(0-5) L	(2-15) I	(20-28) H	(6-57) H
15	(0-5) L	(4-18) I	(28-37) H	(12-70) H

95% confidence intervals (C-I) on predicted nitrate leaching (kg N ha⁻¹y⁻¹) from data of 33 conifer forest ecosystems in Europe, as a function of throughfall N input and organic horizon C/N ratio. Letters next to each C.I. are leaching risk assessments based on the upper limit of the confidence interval: **L**ow risk-upper limit of C.I < 10kg N ha⁻¹y⁻¹; **I**ntermediate risk < 20kg N ha⁻¹y⁻¹ (from Dise, *et. al.*, 1998).

Table 4 Historical Soil C/N Ratio at the Tillingbourne Catchment

Horizon	Total N (mg/g dw)	LOI 450°C (g/100g dw)	C (mg/g dw)	C/N ratio
Humus	12.050 ± 0.345	80.20 ± 0.71	465.2	38.76
Soil 0-9 cm	1.092 ± 0.05	6.22 ± 0.13	36.08	32.81

Historical Total N, LOI, Total C and CN ratio for humus and 0-9 cm soil in deep phase humo-ferric podsol, all values on a dry weight basis, source (Brown, 1982).

Soil C and N content at the Tillingbourne catchment were determined as part of the CEGB soil process studies on nitrogen transformations in bracken ecosystems (Brown, 1982) overlying the deep phase humo-ferric podsol. These were determined using old methodologies of Loss On Ignition (LOI) for C, and Kjeldahl digestion for N. Table 4 shows the humus and soil C and N values, and their associated standard deviation based on at least two samples. From these values the C/N ratios can be calculated. The resulting C/N ratios were 38.76 for the humus and 32.81 for the underlying soil horizon, the historical throughfall was 11.3 kg ha⁻¹y⁻¹ (Hill, *et. al.*, 2001). Using the model shown in Table 3 it can be seen that the throughfall category was intermediate and there was a low risk of N leaching from the soil mass. This assessment of the historical N status of the Tillingbourne catchment is in agreement with the historical stream and throughfall data already discussed, suggesting that the system was N limited.

In order to determine the current soil nitrogen status and C/N Ratio, Lapworth (2001) conducted a field programme of soil sampling at Tillingbourne with laboratory analysis of these samples for carbon and nitrogen. Table 5 shows the present and historical C and N information and ratios for both the humus and mineral soil horizons. Following a detailed statistical analysis by Lapworth (2001), it is suggested that there has been a reduction in C/N ratio from 38.76 to 25.86 for the humus soil horizon and a fall from 32.81 to 26.42 for the mineral soil horizon.

Table 5 Historic and Present C, N and C/N ratios for the humus (H) and mineral (Ah) soil horizons

	Historic			Present		
	%C	%N	C/N	%C	%N	C/N
Means for Humus (H)	46.52	1.20	38.76	44.12	1.73	25.86
Means for Mineral Soil (Ah)	3.61	0.11	32.81	5.06	0.21	26.42

All analysis used historical methodologies for analysis. Soil C/N ratios by Kjeldahl Digestion and LOI. All results are presented on a dry weight basis.

This reduction in C/N has resulted in a shift in soil N status from N limited to moderately N saturated. Applying the model in Table 3 once again, throughfall N deposition was $19.6 \text{ kgNha}^{-1}\text{yr}^{-1}$ and the C/N ratio about 25, bringing the risk of N leaching from “low” to “intermediate”. Historically the humus horizon had a higher C/N ratio whilst at present there is no significant difference between C/N ratios in the two horizons.

Modelling nitrogen processes at Tillingbourne

The historical and current catchment study data at Tillingbourne provide excellent data sets for process-based modelling studies. The INCA model has been used to investigate N transformation and dynamic response of the catchment.

The INCA model has been designed to investigate the fate and distribution of nitrogen in the aquatic and terrestrial environment (Whitehead, *et. al.*, 1998). The model simulates flow, nitrate-nitrogen and ammonium-nitrogen and tracks the flow paths operating in both the land phase and riverine phase. The model is dynamic in that the day-to-day variations in flow and nitrogen can be investigated following a change in input conditions such as atmospheric deposition/sewage discharges or fertilizer addition. The model can also be used to investigate a change in land use (e.g. moorland to forest or pasture to arable). Dilution, natural decay and biochemical transformation processes are included in the model as well as the interactions with plant biomass such as nitrogen uptake by vegetation. The model has been updated recently (Wade *et. al.*, this volume) to include mass balance checks and enhanced graphics so that the model is easy to use, fast and has

excellent output graphics. The menu system allows the user to specify the semi-distributed nature of a river basin or catchment, to alter reach lengths, rate coefficients, land use, velocity-flow relationships and to vary input nitrogen deposition loads.

INCA provides the following outputs:

- daily time series of flows, nitrate-nitrogen and ammonium-nitrogen concentrations at selected sites along the river,
- profiles of flow or nitrogen along the river at selected times;
- cumulative frequency distributions of flow and nitrogen at selected sites;
- table of statistics for all sites;
- daily and annual nitrogen loads for all land uses and all processes.

The hydrological model as shown in Figures 7 and 8 provides information on the flow moving through the soil zone, the groundwater zone and the river system. Simultaneously, whilst solving the flow equations, it is necessary to solve the mass balance equations for both nitrate-nitrogen and ammonium-nitrogen in both the soil and groundwater zones. The key processes that require modelling in the soil zone, as shown in Figure 7 are plant uptake for $\text{NH}_4\text{-N}$ and NO_3 , ammonia nitrification, denitrification, ammonia mineralisation, ammonia immobilisation and N fixation. All of these processes will vary from land use to land use and a generalised set of equations is required for which parameter sets can be derived for different land uses. The land phase model must also account for all the inputs affecting each land use including dry and wet deposition of $\text{NH}_4\text{-N}$ and NO_3N and fertiliser addition for both $\text{NH}_4\text{-N}$ (e.g. as ammonium nitrate). Also, temperature and soil moisture will control certain processes so that, for example, nitrification reaction kinetics are temperature dependent and denitrification and mineralisation are both temperature and soil moisture dependent.

In the groundwater zone it is assumed that no biochemical reactions occur and that there is mass balance for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. Details of the INCA model are given elsewhere (Whitehead *et al.*, 1998, Wade *et al.*, this volume). In this section of the report we focus on the application of the model to the historical and current data sets from the Tillingbourne.

Calibration of INCA to Historical and Current Data

INCA has been applied to the Tillingbourne assuming the catchment is 100% forest with an area of 0.93 km^2 , a reach length of 800m and a base flow index (BFI) of 0.66. The BFI describes the proportion of water moving through the groundwater system and at Tillingbourne we estimate this to be approximately 66%. In other words two thirds of the water moves through the deeper flow paths and one third moves in the near surface soil zone. INCA has been set up for both the historical data set (1978-1982) and the current data set (1997-2000). The INCA application shows some fascinating results with an excellent simulation of historical N data, as shown in Figure 9. This simulated and observed nitrate shows a significant seasonal pattern of behaviour with peak nitrogen in the winter months and low levels in the summer. The ammonia data shows a similar

pattern but levels are generally low and close to levels of detection. There is a reasonable fit to the discharge data but some further work is required to improve the hydrological response of the model. The daily driving variables for the INCA model are the hydrologically effective rainfall, the temperature and the soil moisture deficit and these are shown in Figure 10. Again the seasonal pattern of behaviour is clear with dry soils, higher temperatures and low rainfall in summer months. These seasonal patterns of behaviour have a large effect on nitrogen response. Mineralization of N occurs in summer as temperature rises, but the available N is not flushed from the catchment until the wetter conditions prevail in autumn or winter months. Figure 11 shows a statistical summary of the historical model simulation data and indicates a highly skewed N distribution which reflects the low N in summer months. The table of statistics reveals a mean nitrate-N concentration of 0.15 mg l^{-1} and a 95 percentile level of 0.439 mg l^{-1} .

The INCA model has also been applied to the current data set (1997-2000) and Figures 12, 13 and 14 show the results for the present day application. In order to obtain a good fit to the Nitrate-N observed data it was necessary to alter the process parameter controlling mineralization in the model. Changing this parameter from 0.4 kg N/Ha/day to 0.6 kg N/Ha/day enabled the model to simulate the current data observation as shown in Figure 12.

Figure 13 shows that the present day simulated concentrations are 0.24 mg l^{-1} compared to the 0.15 mg l^{-1} for the historical level. The 95 percentile levels have risen from 0.44 mg l^{-1} to 0.72 mg l^{-1} . The model results suggest strongly that an enhanced mineralization process is responsible for this increase in N leaching.

Discussion and Conclusions

Both the soil chemical analysis of C/N ratios and the modelling results suggest a change in the N status and N behaviour of the Tillingbourne Catchment over the last twenty years. The ability of an ecosystem to retain N is closely related to its internal N status. Some components of the N status are easy to measure, for example foliage N concentration and the forest floor, with the forest floor C/N ratio is especially closely related to nitrate leaching (Tietema *et. al.*, 1997; Gundersen *et. al.*, 1998a). In the historical study the soil A was found to be N limited and it had a low risk of N leaching given the historical N deposition. This assessment seems to be true as there was little evidence of N leaching from the soil mass either as ammonium or nitrate in the historical period. However, in the last 20 years the soil mass in the catchment has acted as a net sink for N deposition and this has caused a significant shift in N status of the soil.

Nitrogen Leaching

The saturation of the soil mass with N is characterised by a persistent leaching of N from the soil mass resulting in a sharp signal in the stream water, or elevated levels in groundwater. As the C/N ratio of these upper horizons have been shown to be closely related to nitrate leaching in the NITREX programme and studies in the USA it is not unreasonable to say that the recent nitrate signal in the Tillingbourne could be due to the

fact that the soil mass is experiencing N breakthrough. Indeed the mean C/N ratio and %N in the forest floor both indicate that there is strong likelihood of N leaching. Using the present throughfall flux of $19.6 \text{ kgNha}^{-1}\text{y}^{-1}$ and the mean C/N ratio for site A of 25 there is an intermediate risk of nitrate leaching from the soil mass.

N retention is possibly limited in the Tillingbourne catchment due to hydrological factors. The soils are thin for much of the catchment and this will limit the residence time of water borne N in the soil. However this does not seem to have affected the retention of N to a great extent. Thin soils may, however, partly account for the nitrate signal in the groundwater since nitrate could be rapidly transported to the underlying bedrock.

N saturation comes about because of a reduced demand for N within an ecosystem; internal sources of N through mineralisation and fixation, and external sources of deposition, exceed the demand of the biotic and abiotic processes. It occurs through a series of changes in critical ecosystem processes and is thus gradual. Systems with inputs of $15.20 \text{ kgNha}^{-1}\text{y}^{-1}$ have been shown to have a variety of responses with some increasing N immobilisation as a result and others increasing nitrification (Emmett *et. al.*, 1998). The balance between these two processes will to some extent be governed by the N status of the soil. In a soil of low N status immobilisation will be great as micro-organisms involved will not be able to satisfy their need for N and nitrification and leaching of N will be insignificant as a result. As the system becomes increasingly saturated, N availability will increase and thus microbial immobilisation would be reduced, resulting in a greater potential for nitrification, mineralisation and nitrate leaching. In the INCA modelling study this has been simulated by increasing the mineralisation rate which leads to an increased nitrification rate. The fact that the current data can only be simulated by such a model parameter change is further evidence that this is the primary process change occurring.

Future Nitrogen Processes Within the Catchment

This study seems to indicate that N deposition has had a significant affect in changing the N status of the Tillingbourne in the last 20 years from being N limited to moderately N saturated. Saturation within the Tillingbourne catchment is an ongoing process, thus given sustained conditions the soil might become more saturated with time. At present the ecosystem is not fully saturated, the increased saturation has only amplified the existing seasonal trends by a factor of about 3, and it would be possible for saturation to progress further to a situation where the seasonal trends are lost altogether. Conversely, the saturation of the soil mass could have reached a maximum level for the overall input into the catchment. If this was the case the seasonal trends would not be emphasised further, and would potentially recover at some point in the future in response to depositional changes.

We suggest that the recent emission standards and the development of catalytic converters and the change from coal to gas power stations have had a great influence on the speed, timing, and extent of the saturation process at the Tillingbourne catchment, and

will continue to do so in the future. What will happen at the Tillingbourne catchment will be governed by future internal and external N catchment processes. Continual monitoring of the stream water for nitrate is crucial as this signal is by far the fastest responding indicator to the process of N enrichment in the short term. The response of soil C/N ratios is much slower by comparison and is more applicable to studies investigating long-term changes in N status. The leaching of NH_4^+ also has a slow response time and this should be monitored, since if saturation was to proceed it might be an important signal in the Tillingbourne in the future.

Soil temperature increases are said to have the affect of increasing mineralisation rates which would in turn lead to the loss of N and C from the soil mass. This investigation cannot account for this happening, but it would seem to be an insignificant process at the Tillingbourne site as there has been an increase in net soil N, and no decrease in soil C. With accelerated global warming in the last few decades this could become a significant factor in the loss of N from the soil mass. Increases in CO_2 could increase the primary production of forest ecosystems further, and this would provide an additional sink for N as well as C and thus could elevate the process of N enrichment in the future, conversely, mineralisation rates could increase and this would lead to increased mineralisation of C and N. These processes are likely to be important factors that could affect N processes in forest ecosystems in the future.

Acknowledgements

The authors are grateful to the DTI and the EU for funding this research project and to the National Trust and Wotton Estate for permission to undertake the research at the Tillingbourne Catchment.

References:

- Avery, B.W. 1980. *Soil Classification for England and Wales*. Soil survey of England and Wales, Rothamsted, UK.
- Brown, K.A. 1982. Studies on nitrogen transformations in an acidic soil-braken ecosystem in the Tillingbourne Catchment. *CERL Report*. RD/L/2212/N81. 20 pp.
- Dise, N.B., and Wright, R.F. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management*, **71**, 153-161.
- Dise, N.B., Matzner, E., Forstus, M. 1998. Evaluation of organic horizon C/N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environmental Pollution*, **102**, 453-456.
- Emmett, B.A., Stevens, P.A., Reynolds, B. 1995. Factors influencing nitrogen saturation in Sitka spruce stands in Wales. *Water Air and Soil Pollution*, **85**, 1629-1634.
- Emmett, B.A., Reynolds, B., Silgram, M., Sparks, T.H., Woods, C. 1998. The consequences of chronic nitrogen additions on N cycling and soil water chemistry in a Sitka spruce stand, North Wales. *Forest Ecology and Management*, **101**, 165-175.
- Gallois, R.W. 1965. *British regional geology: the Wealden district*. HMSO, London, 4th Edition.
- Gundersen, P. 1991. Nitrogen deposition and the forest nitrogen cycle: Role of denitrification. *Forest Ecology and Management*, **44**, 15-28.
- Gundersen, P., Callesen, I., De Vries, W. 1998a. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution*, **102**, 403-407.
- Gundersen, P., Emmett, B.A., Koيناas, O.J., Koopmans, C.J., Tietema, A. 1998b. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *Forest Ecology and Management*, **101**, 37-55.
- Hill, T.J., Skeffington, R.A., Whitehead, P.G. 2000. The Tillingbourne acidification study: recovery of low critical load areas in southern England. *Final report for National power plc*. 76 pp.
- Hill, T.J., Skeffington, R.A., Whitehead, P.G. 2001. Recovery from acidification in the Tillingbourne catchment, southern England: catchment description and preliminary results. *The Science of the Total Environment*. In press.
- Hornung, M., Langan, S.J. 1999. N deposition: source and responses. In: Langan, S.J (Ed). *The impact of nitrogen deposition on natural and semi-natural ecosystems*. Volume 3 of Series on Environmental Pollution, Kluwer Academic Publishers. pp. 1-15.

Lapworth, D.J., 2001, Long-term Soil Nitrogen Enrichment at Leith Hill, South East England. Masters Dissertation, University of Reading.

Moffat, A.J., Jarvis, M.G. 1984. *Soils of the Tillingbourne Valley, Wotton, Surrey*. Proceedings of the Croydon Natural History Society, **17**, 177-181.

Oden, S., Ahl, T. 1972. Air pollution across national boundaries- the impact on the environment of sulphur in air and precipitation. Sweden's case study for the UN, Royal Ministry of Foreign Affairs and Royal Ministry of Agriculture, Stockholm.

Skeffington, R.A. 1981. Tillingbourne catchment interim report, *CERL Report*, TPRD/L/2083/N81. 28 pp.

Skeffington, R.A. 1982. A description of the Tillingbourne catchment. *CERL Report*, TPRD/L/2278/N82. 12 pp.

Skeffington, R.A. 1985. Effects of acid deposition and natural soil acidification processes on soil: some studies in the Tillingbourne catchment, Leith Hill, Surrey. *Seesoil*, **2**, 18-34.

Skeffington, R.A., this issue. European nitrogen policies and nitrate in rivers

Tansley, A.G. 1953. *The British Isles and their vegetation*. Cambridge University Press. Cambridge.

Tietema, A., Beier, C., De Visser, P.H.B., Emmett, B.A., Gundersen, P., Kjonaas, O.J., Koopmans, C.J. 1997. Nitrate leaching in coniferous forest ecosystems: the European fieldscale manipulation experiments NITREX (nitrogen saturation experiments) and EXMAN (experimental manipulations of forest ecosystems). *Global Biogeochemical Cycles*, **11**, 617-626.

Wade, A et al, ., Whitehead, P.G. The INCA Model, this Volume

Whitehead, P.G., Wilson, E.J. & Butterfield, D. 1998 A semi-distributed integrated nitrogen model for multiple source assessment in catchments (INCA) Part I – model structure and process equations. *The Science of the Total Environment*, **210/211**, 547-558.

Whitehead, P.G., Wilson, E.J., Butterfield, D. & Seed, K. 1998 A semi-distributed integrated nitrogen model for multiple source assessment in catchments (INCA): Part II – Application to large river basins in South Wales and Eastern England. *The Science of the Total Environment*, **210/211**, 559-583.

Wilson, E.J., & Emmett, B.A. 1999. Factors influencing nitrogen saturation in forest ecosystems: advances in our understanding since the mid 1980s. In: Langan, S.J., (Ed).

The impact of nitrogen deposition on natural and semi-natural ecosystems, (pp123-152).
Volume 3 of Series on Environmental Pollution. Kluwer Academic Publishers.

Wright, R.F., Beier, C., Cosby, B.J. 1998. Effects of nitrogen deposition and climate change on nitrogen runoff at Norwegian boreal forest catchments: the MERLIN model applied to Risdalsheia (RAIN and CLIMEX projects). *Hydrology and Earth System Science*, **2**(4), 399-414.