Monitoring of nitrogen leaching on a dairy farm during four drainage seasons

M. Ryan[1], C. Brophy[2], J. Connolly[2], K. McNamara[3] and O.T. Carton[1]†

[1]*Teagasc, Johnstown Castle Environmental Research Centre, Wexford*
[2]*UCD School of Mathematical Sciences, Environmental and Ecological Modelling Group, University College Dublin, Belfield, Dublin 4*
[3] *Teagasc, Moorepark Research Centre, Fermoy, Co. Cork*

The effect of four commonly used dairy farm management systems (treatments), on nitrogen leaching to 1 m was studied over a 4-year period from October 2001 to April 2005. The treatments were (i) grazed plots receiving dirty water, (ii) 2-cut silage plots receiving slurry, (iii) grazed plots and (iv) 1-cut silage plots receiving slurry. All plots had fertiliser N applied; the soil was free-draining overlying fissured limestone. Mean 4-year N input (kg/ha) was 319 and mean annual stocking density was ~2.38 LU/ha. The annual average and weekly NO_3-N and NH_4-N concentrations in drainage water were analysed for all years, using a repeated measures analysis. For the annual NO_3-N data, there was an interaction between treatment and year ($P < 0.001$). There were significant differences ($P < 0.05$) in NO_3-N concentrations between the treatments in all years except the third. For the NH_4-N data there was no interaction between treatment and year or main effect of treatment but there were differences between years ($P < 0.01$). Mean weekly concentrations were analysed separately for each year. For NO_3-N, in all years but the third, there was an interaction between treatment and week ($P < 0.001$); this occurred with NH_4-N, in all 4 years. Dirty water was significantly higher than grazed-fertiliser only and 1-cut silage in NO_3-N concentrations in 2001–02; in 2002–03, dirty water and 2-cut silage were significantly higher than the other treatments; while in 2004–05, dirty water and grazed-fertiliser only were significantly higher than the other two treatments. The overall 4-year mean NO_3-N and NH_4-N concentrations were 8.2 and 0.297 mg/L, respectively.

Keywords: ammonium-N; leaching; nitrate-N

†Corresponding author: owen.carton@teagasc.ie

Introduction

Grassland farming is the major land use in Ireland and is, due to its permanent ground-cover and long growing season, regarded as relatively benign to the environment. It compares favourably with arable farming with regard to annual N loss. Neill (1989) calculated that the mean N loss from unploughed land was 1.9 kg/ha compared with 75.9 kg/ha from ploughed land and concluded that ploughing agricultural land was the principal factor affecting the concentration of nitrate in rivers. Due to low arable land-use, ground and river water quality in Ireland is generally good (Crawley, 2001; Neill, 2005). However, in the 1990s, some regions had elevated (15 to 50 mg/L) nitrate-N (NO_3-N) in groundwater (Richards *et al.*, 1996), associated primarily with Ballysteen limestone and Ringmoylan shale over sandstone (Richards, 1999). An area underlain by karstified Waulsortian limestone had a public water-supply borehole showing an upward trend since 1990, which occasionally breached the EU drinking water maximum admissible concentration (MAC) of 11.3 mg/L NO_3-N (Cork County Council, 1998). The associated aquifer was recognized by the Geological Survey of Ireland (GSI) to be at risk and was designated R_k/E, i.e., a regionally important karstified aquifer extremely vulnerable to contamination (Bartley, 2003). An associated regional sampling of 54 boreholes in the Fermoy area showed that 28% had NO_3-N concentrations > MAC and 59% were >guide level (GL). It was not clear whether the elevated concentrations were due to diffuse or point sources (Richards, 1999).

Prior to the current study, information on nitrate leaching in Ireland was quite limited. Some previous studies were concerned with the effects of slurry and urine applications on leaching. In these, drainage water was collected at 1 m depth from cut grass in small plots or lysimeters (Sherwood, 1986; Ryan and Fanning, 1996). In related work, leaching from N-fertilised grassland was deduced by combining groundwater recharge rates and downward water flow with the difference between the N concentration in soil cores, extracted with potassium chloride, in autumn and spring (Thorn, 1986; Ryan, Fanning and Noonan, 2001). With regard to dairying, nitrate leaching losses, determined using ceramic cups at 90 cm depth in a moderately well drained loam soil, were compared in plots grazed by dairy cows which received 51 and 408 kg/ha fertiliser N (Sherwood and Ryan, 1990). The mean NO_3-N concentration in the soil water was 2.3 and 4.3 mg/L for the 51 and 408 kg/ha treatments, respectively. The authors suggested that there may have been too few cups (six per block in each of five blocks) to "pick up" the likely variation across grazed paddocks. A similar study (Ryan and Sherwood, 1990) in plots grazed by dairy cows, carried out from January to March on well to moderately well drained loams overlying sandy to clay loam sub-soils, showed that the mean NO_3-N concentration in the soil water at 100 cm depth from applications of zero and 328 kg/ha N was also low, at 0.6 and 2.8 mg/L, for these treatments, respectively.

The latter leaching studies, conducted on grazed fertilised plots, provided no information regarding leaching from dairy farm areas treated with dirty water, slurry and cut for silage. Richards (1999) evaluated sources of nitrate leached to groundwater from grassland on a dairy farm with freely drained soils derived from limestone, shale and sandstone and reported that highest NO_3-N concentrations in drainage water were related to dirty water irrigation. The study described in this report was established to measure

the impact of alternative management practices on NO_3-N leaching on an intensively managed dairy farm in a vulnerable environment.

Material and Methods

Site

Monitoring of NO_3-N in soil water, at 1 m depth, was carried out on Curtin's farm at the Teagasc Dairy Production Centre, Fermoy, County Cork (52°07N, 08°16W) over four winters (2001–02, 2002–03, 2003–04 and 2004–05). This area has a mild moist oceanic climate without extremes in temperature. At Moorepark, 30-year (1961 to 1990) annual rainfall averages 981 mm (Met Éireann, 1996); mean maximum, mean minimum and overall average air temperatures (1961 to 1990) were 13.5, 5.6, 9.5 °C, respectively. Average actual evapotranspiration, as a percentage of annual precipitation, 1961 to 1990, was estimated at 46% (Mills, 2000); average net recharge is 570 mm (Bartley and Johnston, 2006). The soil is freely drained, derived from mixed sandstone-limestone glacial till overlying a karstified limestone bedrock aquifer; soil texture is sandy loam and the soil is 0 to 4.5 m deep with bedrock commonly occurring at 2.0 to 3.0 m below the ground surface (Gibbons, Rodgers and Mulqueen, 2006).

Treatments

Treatment plots: Monitoring was conducted on four grassland treatments within the set of plots dedicated to one herd of dairy cows in a 3-herd genetic merit comparison (Horan *et al.,* 2004). Three replicate plots were selected for monitoring from each treatment. Monitored plots comprised 20.3% of the total experimental area and were representative of those commonly used on intensive dairy farms. The treatment plots were; (Gd) grazed, received fertiliser N and dirty water; (S2) grazed, cut twice for silage, received fertiliser N and cow slurry; (Gf) grazed, received fertiliser N; (S1) grazed, cut once for silage, received fertiliser N and cow slurry.

Soil C and N concentrations: The mean organic C and total N concentrations in Gd, S2, Gf, S1 were 58, 33, 37, 30 and 5.1, 3.4, 3.8, 3.1 g/kg, respectively, with corresponding C/N ratios of 11.4, 9.7, 9.7, 9.7 (Ryan *et al.,* 2006a,b). The laboratory analysis was carried out on 0.5 g air-dried samples using a LECO CN 2000 analyser.

Treatment organic N sources, concentrations and spreading policy: Washing of the cow yard, milking shed and animal pens generated dirty water, which was collected in a concrete settling tank prior to irrigation on Gd plots with a rotary irrigator. The concentration of total N in irrigated dirty water ranged from 20.0 to 823.0 mg/L in the period 29 April, 2002 to 24 July, 2004; irrigation took place on a year-round basis e.g., from April 2002 to July 2004 and one or other of the three plots was irrigated in each month with the exception of September and November 2003. The amounts of N applied per irrigation ranged from 0.5 to 84.7 kg/ha (Ryan *et al.,* 2006b; Ryan, M., unpublished). Slurry was applied in the period 18 March to 16 April, depending on the year, in amounts supplying N ranging from 18.0 to 43.0 kg/ha; total N concentrations in the slurry ranged from 2566 to 4320 mg/kg (Ryan *et al.,* 2006b; Ryan, M., unpublished). The principle in the laboratory analysis for total N in dirty water is that N compounds in alkaline solution are oxidized by persulphate to nitrate. Nitrate is then reduced by copper-hydrazine solution to nitrite. The resultant nitrite reacts with sulphanilimide and N-1-naphthyl ethylenediamine dihydrochloride to form

a red azo dye that was measured at 520 nm on a Burkard continuous flow analyser. The methodology for total N analysis in slurry included digestion of fresh slurry using sulphuric acid and hydrogen peroxide with selenium as catalyst. The principle underlying the analysis is the reaction of ammonia with salicylate and dichloroisocyanurate in alkaline solution. The dichloroisocyanurate decomposes in alkaline solution to release hypochlorite ions, which react with the salicylate to give a substituted indophenol, which was measured at 650 nm on a Burkard continuous flow analyser. Nitroprusside was added as a catalyst.

Grazing management
Twelve of 19 plots, comprising 16.92 ha from January to November 2001 and 16.87 ha from November 2001 onwards, used to carry the dairy herd, managed according to the Moorepark system (Horan *et al.*, 2004), were instrumented for this monitoring study. The 4-year mean N input to the monitored plots was 319 kg/ha; the overall stocking rate was 2.12 cows/ha in the first year and ~2.47 cows/ha in each of the following 3 years. None of the second-cut silage was used for winter-feed in the second or third years, with only one third of it used in the final year. Paddocks were rotationally grazed from spring until October or November. Grazing started in February or March on both sets of silage plots, in April on the Gd plots and in February to May on the Gf plots. First-cut silage was harvested from 22 May to 5 June and second-cut silage was harvested in the week of 21 July.

Sampling and analysis of soil water
The plots were instrumented with ceramic cups; eight cups per plot were inserted at 1 m depth each having a bentonite seal, 150 mm below ground surface, on the flask-connecting tube. Sampling of soil water was carried out by applying suction (50 kPa) to above-ground flasks 1 week prior to sample collection. The samples were stored overnight at 4 °C, acidified with 0.06 mL of concentrated sulphuric acid and transported at 4 °C for analysis, usually within 7 days. Nitrate-N and ammonium-N (NH_4-N) concentrations were determined on a discrete Konelab analyser. The principle behind the chemistry for the determination is that nitrate is reduced to nitrite with copper hydrazine reagent which contains hydrazine sulphate and copper sulphate. Nitrite ions, so produced and those originally present, are determined by diazotisation with sulphanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride. The coloured azo-dye was measured at 540 nm. This reaction measures total oxidised nitrogen (TON). Nitrate was determined by subtracting nitrite from TON. Ammonia reacts with salicylate and dichloroisocyanurate in the presence of sodium nitroprusside to form a blue colour that is proportional to the amount of ammonia present. The colour produced was measured at 660 nm. Sample and standard results are expressed as N. Generally up to 90 samples were analysed in each batch and the following procedures were carried out to check for accuracy of the analyses. The instrument was calibrated every day using manual quality control (QC) samples that contained 30% and 70% of the concentration in the highest standard sample. If either QC sample-type displayed results greater than two standard deviations from the mean, the calibration was rejected and re-checked. If necessary, standard and QC samples were changed or made up again. Routine QC samples, that contained 30% of the concentration in the highest standard, were run as accuracy checks once

per 10 samples. If the QC samples displayed results greater than two standard deviations from the mean, these analyses were rejected and repeated. Persistent QC failure required the instrument to be recalibrated as above. All QC and calibration samples were prepared from separate certified stock solutions.

N inputs

The N inputs for each treatment are shown in Table 1. Weighted (on the basis of plot size) mean N inputs, excluding an annual 9 kg/ha measured wet deposition, were 311, 309, 326 and 331 kg/ha in 2001–02, 2002–03, 2003–04 and 2004–05, respectively. Proportions of 0.85 and 0.25 of the total N applied in dirty water and slurry, respectively, were used to estimate their contribution to total N inputs because of expected losses via ammonia volatilisation.

Fertiliser N formed the largest component of the N input. The difference between the highest and lowest fertiliser N input to the treatments declined from 157 to 68 to 66 to 44 kg/ha in the 4-year period; the difference between the highest and lowest total N input to the treatments declined also from 153 to 95 to 49 kg/ha over the first three years, it was 62 kg/ha in 2004–05. This was in line with the aim of having similar N inputs to the treatments.

Rainfall

Weekly effective rainfall (drainage) was calculated by using a water balance approach. The effective rainfall (ER) was calculated by subtracting the effects of evapotranspiration, determined by the FAO Penman-Monteith method (Allen *et al.,* 1998), and soil moisture deficits, using the Aslyng scale (Aslyng, 1965), from recorded rainfall amounts. The Aslyng scale adjusts effective rainfall to account for soil moisture deficits >30 mm. Due to the free-draining soil and location of the site on a karstic limestone plateau, runoff was deemed to be negligible.

Leaching period loss rates (kg/ha) for each treatment, were calculated for the two N types through multiplying the overall mean concentration (mg/L) by 0.01 times the effective rainfall (mm) with dirty water (mm) added to the effective rainfall for Gd plots. It is assumed that the NO_3-N concentration recorded at the sampling depth represents the concentration in the drainage water. Weighted mean losses (on the basis of plot size) were calculated for the first 3 years.

Data

The raw data for each year consisted of NO_3-N and NH_4-N concentrations (mg/L) in the leachate of 96 individual cups, measured weekly, for 33, 37, 26 consecutive weeks in

Table 1. Mean N inputs (kg/ha) from fertiliser, dirty water (D), slurry (S) in the years 2001–02, 2002–03, 2003–04, 2004–05

Treatment[1]	Year × N source											
	2001–02			2002–03			2003–04			2004–05		
	Fertiliser	DS[2]	Total	Fertiliser	DS[2]	Total	Fertiliser	DS[2]	Total	Fertiliser	DS[2]	Total
Gd	207	36	243	278	31	309	248	95	343	254	106	360
S2	364	28	392	333	27	360	314	22	336	287	41	328
Gf	239	nil	239	265	nil	265	294	nil	294	298	nil	298
S1	323	22	345	266	22	288	298	22	320	298	36	334
Weighted mean			311			309			326			331

[1]Gd = grazed, dirty water, S1 = grazed, cut once for silage, S2 = grazed, cut twice for silage, Gf = grazed-fertiliser only.
[2]Dirty water (treatment Gd) or cow slurry (treatments S1 and S2).

2001–02, 2002–03, 2003–04, respectively and for 24 non-consecutive weeks in 2004–05. There were times when there was insufficient leachate in the collecting vessels to carry out laboratory analyses. For example, in the 4 years, out of 480 sampling occasions (120 dates × 4 treatments) there were only 14 where a water sample was collected from each of the 24 ceramic cups per treatment. Averaged over the 4 years, the number of ceramic cups of the 24 in each treatment, which had no water sample, per sampling date was 9, 9, 10, and 9 for Gd, S2, Gf and S1, respectively. Details of sample numbers collected, per sampling date for the 4 years, are available in Ryan *et al.* (2006) and Ryan M. (unpublished).

Statistical analysis
The analyses consisted of:

1. *Analysis of annual average N concentration in drainage water:* The annual average concentration of the two N types was analysed using a repeated measures analysis over the 4 years. The data consisted of 48 values for each N type (4 treatments × 3 replicates × 4 years). These aggregated data were not normally distributed. A generalised linear mixed model was fitted that assumed a Gamma (positively skewed) distribution and incorporated a log link function (Ryan *et al.,* 2006a).

2. *Analysis of weekly average N concentration in drainage water:* Within each year a repeated measures analysis of the average concentration (over 8 cups) per plot per week, using the procedure described for the annual concentration data, was performed.

For both the analyses 1 and 2, repeated responses on each plot were assumed to be a time series with measurements at different time points correlated. Two correlation structures, compound symmetry (CS) and autoregressive (AR), were compared for suitability in each model using the AIC (Akaike information criterion) statistic (Verbeke and Molenberghs, 2000). CS assumes responses within a time series are equally correlated regardless of how far apart they are while AR assumes the further apart the responses within a time series are, the less correlated they are. An unstructured correlation structure (UN) was also tested for suitability in the models in 1; this allows each pair of repeated measurements to have a different unconstrained correlation. The UN structure was not used with analysis 2 as it involved too many correlations for the available data.

Analysis was carried out using the GLIMMIX macro in the SAS/STAT software version 8.2 (Littell *et al.*, 1996). Means predicted from models with a log-link function were back-transformed to give means for presentation on the scale of measurement. To compare pairs of means in *a priori* comparisons a least significant ratio (LSR) was used. At a given time point, if the ratio of the bigger to the smaller mean is larger than the LSR, then the means differ at the significance level at which the LSR was calculated (See Appendix A in Ryan *et al.,* 2006a).

The relationships between rainfall, leachate volume and mean N concentrations were examined as was the relationship between leachate volume and treatment. The annual number of cow-grazing days per ha and N applied (kg/ha) were calculated for each plot. These were included as covariates in the analysis of annual average N concentration in plots.

Results
Rainfall
Monthly rainfall, as recorded at the nearby (3 km) Teagasc Moorepark Research Centre

for 2001 to 2005 and for 1961 to 1990, is shown in Table 2. Rainfall in November, December 2001 was exceptionally low; the months of October, November 2002 were very wet (Table 2). October 2001 to January 2002 and October 2002 to January 2003, had 45 and 43% of the 2001, 2002 annual total, respectively. The years 2001, 2003 had 13 and 10% lower than average rainfall, respectively, whereas 2002 and 2004 had 23 and 5% greater than normal rainfall, respectively.

Average annual recharge, for the years 1961 to 1990, was estimated at 570 mm. Effective rainfall for the leaching period, which ranged October to July, was 440, 539 and 398 mm for 2001–02, 2002–03 and 2003–04, respectively. The fourth year, 2004–05, had a short water-collection period, i.e., October to April, with interrupted sampling (24 sampling weeks in a 26-week period) and had an earlier-than-planned completion date in mid April, which probably resulted in missing end-of-season leaching in May and June, both of which had above-average rainfall.

Analysis of annual average NO_3-N concentration
All effects mentioned in this paragraph were significant (P < 0.05), unless otherwise stated. There was an interaction between treatment and year for the NO_3-N concentration (P < 0.001) and the CS correlation structure was preferred for the yearly

repeated plot measurements. In 2001–02, Gf and S1 had lower mean NO_3-N concentrations than Gd or S2, and S1 was lower than Gf (Figure 1). In 2002–03, Gf and S1 were lower than both Gd and S2. The high NO_3-N concentrations evident in the 2-cut silage (S2, Figure 1) drainage water in 2001–02 and the relatively high concentration in 2002–03, compared to Gf and S1, are difficult to explain. They may have been caused by high applications of slurry (>35 to 55 t/ha) to one of the replicate plots over previous years, which resulted in the mean 4-year water NO_3-N concentration in that plot being 90% higher than that in the other replicates (Ryan *et al.,* 2006b; Ryan, M., unpublished). In 2003–04, there were no significant differences between treatments; and, in 2004–05, S2 was lower than both Gd and Gf. The dirty water treatment (Gd) was consistently high in all years.

The annual weighted mean NO_3-N concentrations for each of the 4 years were 7.8, 4.2, 9.1, 11.7 mg/L, respectively, with an overall 4-year mean NO_3-N concentration of 8.2 mg/L. The drainage water from the grazed-fertiliser-only plots (Gf) showed a dramatic increase in NO_3-N concentration in 2004–05 compared to previous years; the mean value was 10 times the mean in 2002–03. This is probably explained by very high concentrations in the water sampled by two ceramic cups in 2004–05. In the 24 sampling weeks, concentrations in one cup

Table 2. Total monthly rainfall (mm) for 2001 to 2005 and the 30-year (1961 to 1990) mean, at Teagasc Moorepark Research Centre

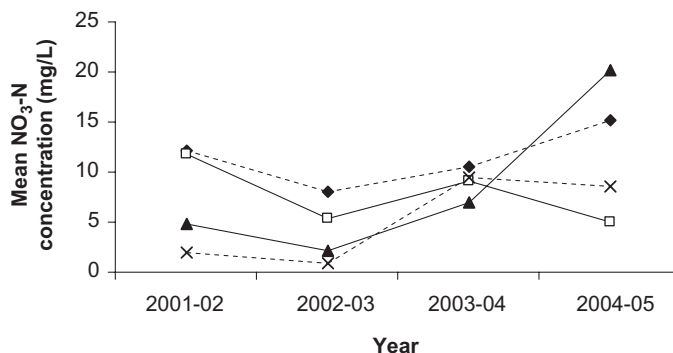| Year	Month												Total
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
2001	76	91	107	73	29	48	47	98	74	120	30	62	855
2002	176	105	54	85	126	78	49	58	21	165	178	107	1202
2003	64	71	61	101	101	105	87	4	41	32	125	91	883
2004	103	57	112	65	43	89	47	171	79	170	27	69	1032
2005	120	35	79	83	75	82	67	-	-	-	-	-	-
30-year mean	117	87	79	59	68	62	55	76	79	100	91	109	981

Figure 1: Mean NO₃-N concentration (mg/L) for each year × treatment combination: Gd (grazed, dirty water ---◆---), S2 (grazed and cut twice for silage ⊟) , Gf (grazed-fertiliser only ▲), and S1 (grazed and cut once for silage ---×---). Differences between treatment means within a year can be assessed using the least significant ratio (LSR = 2.4 at the 5% significance level). Two treatment means differ significantly at the 5% level if the ratio of the larger mean to the smaller one is greater than 2.4.

ranged from 37.4 to 338.3 mg/L (mean 169.0 mg/L) while a second cup ranged from 13.9 to 203.2 mg/L (mean 83.1 mg/L); the annual plot mean (8 cups) was very high at 40.2 mg/L. Concentrations >200 mg/L are very rare and only occurred on one other occasion in one cup in S2 in 2003–04 (Ryan *et al.,* 2006b; Ryan, M., unpublished).

Over the 4 years (Figure 1), the combined application of dirty water and fertiliser to grazed plots (Gd) resulted in relatively high mean NO_3-N concentrations in the drainage water. In 2 years the mean values were >MAC and in the first, third and fourth years the percentage of weekly mean values >MAC were 64, 46 and 83, respectively. S2 and Gf each had one year in which the overall mean concentration was >MAC while S1 did not have a mean concentration >MAC in any year. The 4-year mean NO_3-N concentrations for Gd, S2, Gf, S1 were 11.5, 7.8, 8.5, 5.2 mg/L. An expected outcome of this monitoring was that the NO_3-N concentrations for both silage treatments (S1, S2) would be lower than both grazed treatment (Gd,

Gf) concentrations due to less recycling, and removal of N by grass-harvesting in S1, S2; this only occurred in 2004-05.

Analysis of annual average NH_4-N concentration
For the NH_4-N concentration, the CS correlation structure was preferred for the yearly repeated plot measurements. There was no interaction between treatment and year (P = 0.12) and no evidence for a main effect of treatment, but there were significant (P < 0.01) differences between the years (Figure 2).

Ammonium-N concentration (Figure 2) showed an opposite trend to NO_3-N with the difference between means being minimal in the first and last years. The trend was for concentrations to decline over the four years and overall weighted mean concentrations were 0.336, 0.322, 0.281 and 0.248 mg/L in each year, respectively, with a 4-year overall mean NH_4-N concentration of 0.297 mg/L.

The freshwater quality standard required for *Salmonid* fish is 0.778 mg/L NH_4-N (Anon., 1988). Expert opinion
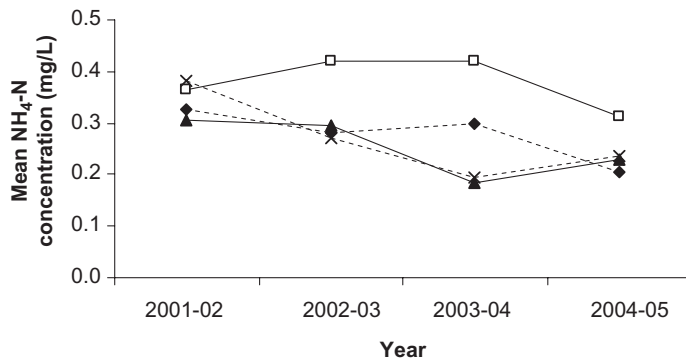
Figure 2: Mean NH₄-N concentration (mg/L) for each year × treatment combination: Gd (grazed, dirty water ---◆---), S2 (grazed and cut twice for silage ⊟), Gf (grazed-fertiliser only ▲), and S1 (grazed and cut once for silage ---×---). The LSR at the 5% significance level is 2.0.

considers that this standard may be too lenient (M. Neill, personal communication) and that the EU water quality guide level concentrations of 0.156 and 0.031 mg/L NH_4-N, for *Cyprinid* and *Salmonid*, are more appropriate.

The number of concentrations <GL for both fish types, for each treatment and year, is shown in Table 3. Clearly

the majority of the water samples collected and analysed were in breach of the *Salmonid* GL; the number of samples <GL for *Cyprinid* fish was very low being proportionally in the range 0 to 0.064.

Annual loss of N

The mean annual loss of NO_3-N in drainage water, from the combined four treat-

Table 3. The number of drainage water samples with NH_4-N concentrations <EU guide level (GL) for *Salmonid* and *Cyprinid* fish, by year and treatment

Year	Treatment[1]	No. of samples <GL for		Total number of samples
		Salmonid	*Cyprinid*	
2001–02	Gd	0	3	384
2001–02	S2	0	5	384
2001–02	Gf	0	6	336
2001–02	S1	0	5	312
2002–03	Gd	0	13	390
2002–03	S2	0	7	364
2002–03	Gf	4	20	312
2002–03	S1	2	19	364
2003–04	Gd	0	11	444
2003–04	S2	0	0	518
2003–04	Gf	1	19	407
2003–04	S1	2	16	555
2004–05	Gd	0	7	561
2004–05	S2	0	2	495
2004–05	Gf	0	10	594
2004–05	S1	0	7	660

[1]Gd = grazed, dirty water, S1 = grazed, cut once for silage, S2 = grazed, cut twice for silage, Gf = grazed-fertiliser only.

ments for the first 3 years, based on effective rainfall, was 34.8, 22.6, 36.2 kg/ha, equivalent to 11.2, 7.3 and 11.1% of total N input (Table 1) respectively; the mean annual loss, as NH_4-N, for those years was 1.6, 1.8, 1.1 kg/ha, equal to 0.5, 0.6 and 0.3% of total N input, respectively.

Analysis of weekly average N concentration NO_3-N: The AR correlation structure was preferred between weekly repeated plot measurements for each of the models for each of the four years. In 2001–02 there was an interaction between treatment and week ($P < 0.001$) (Figure 3a). S1 had the lowest NO_3-N concentration at most times during the year and was significantly lower than Gd in 29 of the 33 weeks. S1 was significantly lower than S2 in 28 weeks but was only significantly lower than Gf in 14 of the weeks. Treatment peak concentrations were 24.7, 22.0, 11.1, 4.8 mg/L for Gd, S2, Gf, S1, respectively.

In 2002–03, there was an interaction between treatment and week ($P < 0.001$). Similar to 2001–02, S1 had the lowest mean NO_3-N concentration in most weeks (Figure 3b). It was significantly lower than Gd, S2 and Gf in 32, 32 and 20 of the 37 weeks, respectively. Treatment peak concentrations were 20.3, 26.9, 5.0, 3.5 mg/L for Gd, S2, Gf, S1, respectively.

In 2003–04, interaction between treatment and week was not significant ($P = 0.086$). The trends observed in the first 2 years were not repeated (Figure 3c). Treatment peak concentrations were 20.7, 17.4, 12.2, 31.9 mg/L for Gd, S2, Gf, S1, respectively.

In 2004–05, there was an interaction between week and treatment ($P < 0.001$). Gf was high at the beginning of the year and was significantly higher than Gd, S2 and S1 for 4, 12 and 6 of the

first 12 weeks, respectively (Figure 3d). During the second 12 weeks, Gf declined to the level of the other treatments and Gd emerged as the highest treatment, with S2 the lowest. S2 was significantly lower than Gd in 8 of the last 12 weeks. Treatment peak concentrations (mg/L) were 35.2, 7.1, 72.2, 16.0, for Gd, S2, Gf, S1, respectively.

NH_4-N: While no trends were observed in the analysis of the annual NH_4-N concentration, each year was still analysed separately. The correlation structures preferred between weekly repeated plot measurements for each of the 4 years was CS, AR, CS and CS, respectively. In all years there was an interaction between treatment and week ($P < 0.01$, $P < 0.001$, $P < 0.01$, $P < 0.01$ for successive years, respectively). In 2001–02 the interaction between treatment and week was associated with differences in a small number of weeks (Figure 4a). There were treatment effects in 6 of the weeks during the year but these effects were not consistent; e.g., NH_4-N concentration for S1 was lower than all other treatments at week 2 but was higher than all other treatments at week 26. In 2002–03, the only trend observed was that S2 was significantly higher than S1 in 10 of the 37 weeks (Figure 4b). In 2003–04, S2 was significantly higher than Gf and S1 in 9 and 8 of the 26 weeks, respectively (Figure 4c). In 2004–05, no trends were observed (Figure 4d).

N concentration relationships
No relationship was found between N concentration and weekly rainfall, cow grazing days or total N applied within each treatment. N concentration and leachate volume were negatively related over time but not within plots or across plots. There was no effect of treatment on the leachate volume (Ryan *et al.,* 2006a).
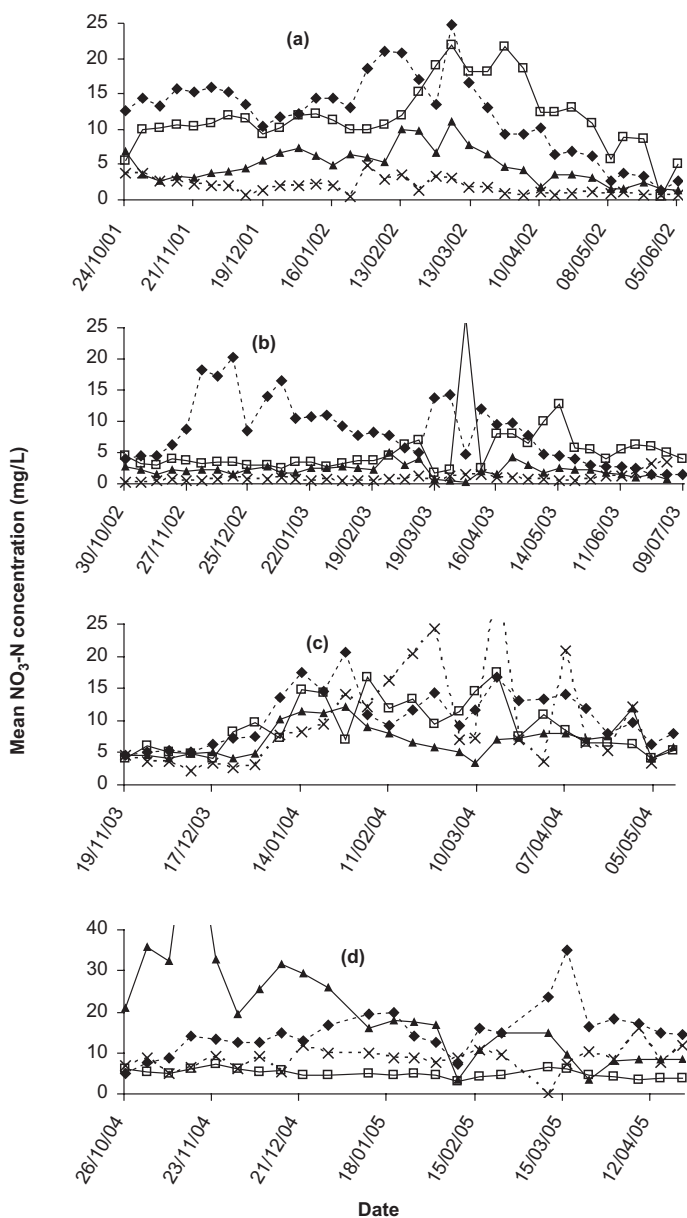
Figure 3: Mean NO₃-N concentration (mg/L) by week for each year (a) 2001–02; (b) 2002–03; (c) 2003–04; and, (d) 2004–05 for each treatment: Gd (grazed, dirty water --- ♦ ---), S2 (grazed and cut twice for silage ⊞), Gf (grazed-fertiliser only ▲), and S1 (grazed and cut once for silage ---✕---). The LSR at the 5% significance level for each year are (a) 2.3; (b) 3.3; (c) 2.;8 and, (d) 3.2.
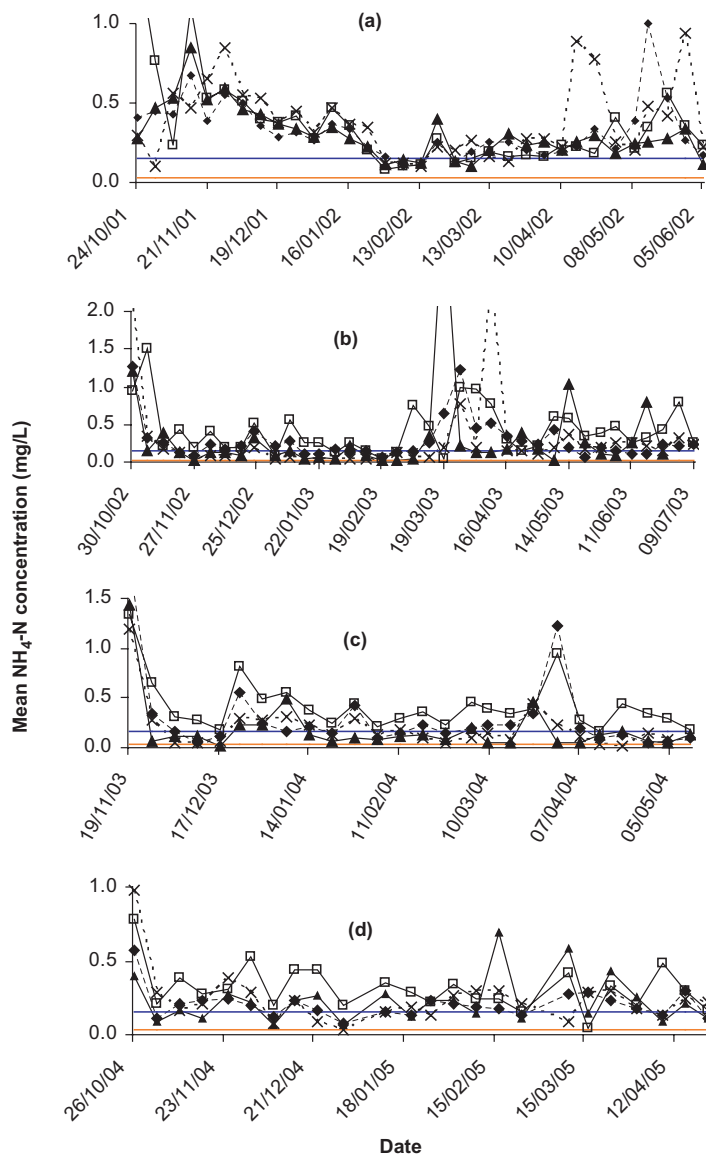
Figure 4: Mean NH$_4$-N concentration (mg/L) by week for each year (a) 2001–02; (b) 2002–03; (c) 2003–04; and, (d) 2004–05 for each treatment: Gd (grazed, dirty water ---◆---), S2 (grazed and cut twice for silage ⊟), Gf (grazed-fertiliser only ▲—), and S1 (grazed and cut once for silage ---✕---). Also shown are the EC Salmonid (-) and EC Cyprinid (-) guide levels. The LSR at the 5% significance level for each year are (a) 2.6; (b) 3.9; (c) 4.2; and, (d) 3.3.

Discussion

A common feature of nitrate leaching studies is the variation seen in mean NO_3-N concentration from one year to the next (Figure 1). This results primarily from physical and chemical factors affecting soil N, e.g., soil moisture percolation volumes and rates, N uptake, recycling and mineralisation-immobilisation of N in the soil. In the current study, comparing the first year with the last, the most notable change was an increase of 15.3 mg/L in the mean NO_3-N concentration in the Gf water samples in 2004–05 (Figure 1), which may have been partly related to increased fertiliser N input in 2004–05 (Table 1). As recorded by O'Connell, Humphreys and Watson (2004), at two sites, soil mineral-N concentration in urine patches increases with increasing fertiliser N input to grazed pasture. These authors recorded high soil mineral-N concentrations (334 and 410 kg/ha) below the effective rooting zone (0 to 20 cm) and in the entire soil profile (0 to 80 cm) in urine-patch areas compared to areas without urine patches (29 and 57 kg/ha), where 220 kg/ha fertiliser N had been applied up to June. The amount applied up to June on the Gf plots in 2004–05 was comparable (231 kg/ha) (Ryan, M., unpublished) and although not measured, may also have resulted in high mineral-N concentrations in the urine patches. In grazed pasture the N loading rate on an individual urine patch is equivalent to about 1000 kg/ha (Silva *et al.*, 1999). Even with half that load, Richards *et al.* (2004) recorded December NO_3-N concentrations of 105 and 130 mg/L in drainage water from a free-draining soil, which received urine N (486 kg/ha) in August and September, respectively. Ledgard *et al.* (1996) attribute very high NO_3-N concentrations in soil water to the effect of localised recycling of urine N at these high rates while Cuttle, Scurlock

and Davies (2001) have shown that large accumulations of urine-N are lost from the soil profile before the start of the following growing season.

In addition to the N load added via dirty water irrigation, which was about 20% of the total N applied, enhanced N mineralisation may have contributed to the N available for leaching in the Gd plots. Relatively high mean mineral N concentrations (5.1 g/kg) in the soil of those plots together with a favourable mean C/N ratio (11.4), should favour higher mineralisation of soil organic N compared to the other treatments. Also, since drying and wetting of soil is an important process in soil organic matter decomposition and nutrient cycling (Mikha, Rice and Milliken, 2005), this could increase N mineralisation. Zaman, Di and Cameron (1999) and Zaman *et al.* (1999) have shown that, under field conditions, irrigation of dairy shed effluent (solid faecal organic material mixed with urine and water) significantly increased gross N mineralisation rate. More recent work by Hawke and Summers (2003) has shown how 6 years of farm dairy effluent irrigation has improved fertility in the topsoil. Effluent application led to significant increases in the concentrations of total N and C in the upper part of the soil profile; organic matter concentration increased by about 30%. It was considered likely that effluent application had resulted in increases in microbial biomass C and N, which consequently increased gross N mineralisation rates. Of interest with regard to the Gd results is the fact that, in a related study, ungrazed small plots were used for a series of soil investigations on Curtin's farm. Gibbons *et al.* (2006) reported little effect on NO_3-N concentrations, at 0.9 m deep, from dirty water applications of 10 mm in November and May while applications of 25 mm in

November, higher than those recorded in Gd, resulted in a maximum concentration of 18.3 mg/L NO_3-N in early March of the following year. The latter is lower than maxima recorded in Gd (20.3 to 35.2 mg/L) due probably to the non-application of fertiliser N to the soil investigation plots, the absence of recycled N and lower N mineralisation rates.

The relatively high mean NO_3-N concentration in the drainage water from the S2 treatment in 2001–02 may have been related to high applications of slurry N to part of the plot area prior to the commencement of the experiment. It has been noted that slurry treatment provides an input of substrate for soil micro-organisms and tends to increase activities of enzymes involved in N cycling (Bol *et al.*, 2003) with implications for N release from organic matter. Also, it has been estimated that 20-year application of slurry increases annual mineralisation of N from soil organic matter by 45 to 70 kg/ha (Whitmore and Schroeder, 1996) quoted by Barkle *et al.* (2000).

Farmers and scientists acknowledge the need to improve recovery of applied N in farming systems; sustainability in agriculture requires it (Culleton, Tunney and Coulter, 1994). EU directives impose pressure on agriculture to make more efficient use of N since <20% of N inputs return as usable products to consumers. Highly stocked dairy farms accrue N surpluses annually. In Ireland, Mounsey *et al.* (1998) reported a mean annual surplus of 304 kg/ha N (range 198 to 409 kg/ha) for dairy farms stocked at >2.0 LU/ha. Aarts, Habekotte and van Keulen (2000), in the Netherlands, compared the N balance of a prototype dairy farm of low inputs with an intensive commercial farm and showed that the annual N surplus decreased from 487 to 166 kg/ha with careful N management. The proportion of applied N lost to the environment is an important component of these balance studies. Hence, the interest in calculating the N mass lost per hectare, through leaching, in this study. The average proportion of the applied N lost through leaching was similar to UK findings. Jarvis *et al.* (1989) evaluated the effects of the level of N input, climate and soil physical characteristics on the extent of nitrate accumulation in the soil after grazing pasture with cattle and the subsequent loss through either denitrification or leaching. The experiment was carried out at four sites in the UK on loam, silty clay loam and clay soils with annual rainfall in the range 620 to 1,100 mm. At rates of 450 kg/ha N or less, the average amount, either present in the soil profile and available for loss, or lost in leachate from four soils, represented 10.5% of that applied. Much higher loss rates were recorded at high N inputs, e.g., at 750 to 800 kg/ha N applied, the soil NO_3-N content or losses were equivalent to 37% of that applied. The 3-year mean losses from the Gf treatment (8%) are lower than the 8-year mean (13%), reported for grazed plots that received similar fertiliser N (298 kg/ha) in Northern Ireland (Watson *et al.*, 1998). The Northern Ireland study had drains installed to capture all subsoil drainage flow and may have provided a more representative sample of downward moving water at 1 m than the ceramic cups at Curtin's farm since preliminary evidence for preferential flow was noted in that soil (Bartley and Johnston, 2006). Preferential flow could mean that ceramic cup samplers are by-passed by some of the downward flowing water as it moves in quick-flow paths such as root channels, burrows or structural voids.

Denitrification may have been responsible for the lower losses recorded in 2002–03. From October to December 2002, rainfall at Moorepark was higher

than in the first and third years (450 *versus* 212, 248 mm). There were 15 days with >10 mm in those months in 2002–03 compared with 6 days in the first and third years. This extra wetting of the warm soil (11.3, 9.3, 7.2 °C mean maxima at 0.3 m in October to December) with daily air maxima of 9.7 to 19.5 °C in October, 8.2 to 16.7 °C in November, 4.1 to 12.8 °C in December 2002 (Met Éireann, 2002), could have induced relatively high denitrification rates in the soils. A soil temperature of >5 °C is usually required for significant denitrification to occur (Aulakh, Rennie and Paul, 1983). It is expected that highest rates would have occurred in the dirty water plots (Gd) due to their higher soil C and N concentrations. Though not measured, moisture levels in this treatment would probably have been higher than in the others due to the extra liquid load added by irrigation. Hyde *et al.* (2006), in a denitrification study carried out on N-treated grazed plots, demonstrated significant correlations between total soil mineral N content and nitrous oxide (N_2O) emission. Highest emissions occurred following rainfall and its consequent effects on soil moisture status in association with fertiliser N application and grazing. Various models relating emissions to N treatment, soil N concentration, time after N application, soil moisture status and treatment covariate interactions were investigated. Predicted N_2O emission levels at various soil NO_3-N concentrations, soil moisture levels and days after N application showed a positive effect of gravimetric soil moisture content on N_2O emissions at fertiliser N inputs of 0, 225 and 390 kg/ha. Folorunso and Rolston (1984) have conclusively shown that the soil parameters mentioned as well as organic C concentration, are primary factors affecting N_2O losses from soil. Clough *et al.* (1999) have shown that the

mutual presence of a suitable C form and nitrate substrates in the subsoil can stimulate denitrification activity.

The free draining acid brown earth (Soil no. 13, Gardiner and Radford, 1980), which dominates Curtin's farm, comprises 1.69% of the land area of the Republic of Ireland to which the results have direct application. However, it is thought that soils with similar vulnerability may extend to about 4.6% of the country. It is very unlikely that similar leaching studies will be undertaken on different soils throughout the country and, consequently, it may be worthwhile to use a model to make N-loss predictions. The model, NCYCLE_IRL (del Prado *et al.,* 2006), is one of the first efforts to integrate all of the available data on N cycling in Irish grasslands. It calculates annual N transformations, fluxes and losses for cut and grazed grassland and makes predictions of concentrations. For example, the model predicts a mean NO_3-N concentration of 15.7 mg/L for the mean stocking rate (2.38 LU/ha) used in this experiment compared with a recorded mean of 8.5 mg/L for Gf. The mean predicted by the model for silage cut areas in the south of Ireland is 5.3 mg/L with a peak of 43.3 mg/L compared with mean and peak concentrations, for S1, of 5.2 and 31.9 mg/L, respectively. For poorly drained clay loam soils the prediction is close (3.0 mg/L) to the measured NO_3-N concentrations (2.45 mg/L) when stocked at 2.5 cows/ha and fertilised with 350 kg/ha N (Darmody, 2004).

In conjunction with fortnightly determination of soil mineral-N levels, the model can be used to assess the amount of fertiliser N to apply in order to maintain NO_3-N concentrations in drainage water below MAC. Substantial reductions in N surpluses have been achieved in the UK using this tactical N application combined with slurry injection and early housing

of cattle compared to conventional mineral N application and broadcast slurry (Laws *et al.,* 2000). Slurry application via the 'trailing shoe' together with low-cost outwintering pads may make adaptation of this approach to reduce N surpluses of interest in Ireland where receiving waters are at risk of nitrate pollution.

Nitrate leaching is greatly influenced by the supply of fertiliser N, drainage status, sward age and weather patterns (Scholefield *et al.,* 1993). The variation in peak and annual NO_3-N concentrations seen in this experiment, poses a question as to how many years sampling are required to obtain reliable monitoring data, which could be used to predict long-term treatment effects. This observation is supported by the large change in the NO_3-N concentration recorded in the grazed-fertiliser only treatment (Gf) in 2004–05 compared to other years (Figure 1) and similar large changes in peak concentrations for the remaining treatments in years 3 and 4 (Figure 3). Watson *et al.* (2000) reported a mean NO_3-N concentration of 8.5 mg/L for grazed, drained plots in Northern Ireland that received 300 kg/ha fertiliser N, which is identical to the mean recorded for the Gf plots which received a mean fertiliser N input of 274 kg/ha. The Northern Ireland authors noted that the annual mean NO_3-N concentration usually did not exceed the European Community MAC for drinking water below an annual fertiliser N application rate of 300 kg/ha. Where 300 kg/ha N was applied this was true for 7 of the 9 experimental years and also occurred in the current study in 3 of the 4 years, where 274 kg/ha N was applied to grazed-fertiliser-only plots (Gf). However, it is disquieting to note that the mean NO_3-N concentration in the fourth year, at 20.2 mg/L ($1.8 \times$ MAC), was much higher than in preceding years, pointing to the need for a longer period of study, perhaps on the time-scale used in Northern Ireland.

The low compliance of the NH_4-N concentrations to the *Salmonid* GL in all years and to the *Cyprinid* GL (Table 3), to a lesser extent, is similar to results obtained in the Northern Ireland study. There, the annual flow-weighted mean NH_4-N concentrations were well above the EC GL for *Salmonid* waters (0.031 mg/L) for all plots, which received fertiliser N input in the range 100 to 500 kg/ha and exceeded those for *Cyprinid* waters (0.156 mg/L) in some years. It must be remembered that N concentrations measured at 1 m deep may not exactly reflect those in surface or ground waters due to N transformations and so the results should be seen as indicative.

All of the leaching data must be seen in the context that the soil was selected on the basis of its high vulnerability to nitrate leaching and while the 4-year overall mean NO_3-N concentration at 1 m depth, was <MAC, mean concentrations for two treatments in the first and final years and many of the weekly concentrations in each year were >MAC. MAC, the EU limit for potable water is the most lenient of several standards. The eutrophication criterion for tidal freshwaters is appreciably lower at 2.6 mg/L while the EPA has set 5.6 mg/L NO_3-N as the interim guideline value for the protection of groundwater (Bartley and Johnston, 2006). An important characteristic of the soil (and geological formation) under investigation is the ability to respond to change in management. In a control treatment, monitored by Gibbons *et al.* (2006), the NO_3-N concentration in the soil pore water declined from an initial value of 19 mg/L to <10 mg/L over a period of 5 weeks in November–December 2001, remaining low thereafter. Bartley and Johnston (2006) demonstrated a rapid response of groundwater hydrochemistry

to hydrological and agronomic loadings in the hydrogeologically vulnerable conditions at Curtin's farm. The significance of this rapidly responding hydrogeological system to dairy farming is that all improvements in management should result in an observable improvement in groundwater quality.

To ensure a valid comparison of herd performance it was desirable that DM intake at grazing would not be limiting. This was achieved by not being parsimonius with N inputs. Considering that silage was exported from the farm in 3 of the 4 study years, it would appear that there is room for a reduction in N input to the silage area while still carrying the stocking rate of the second, third and fourth years (~2.47 cows/ha). Less fertiliser N should be applied to the dirty water plots. In 2 of the 4 years, mean N input to the dirty water treatment (Gd) was greater than overall mean N input. Lower N fertiliser inputs could lessen losses directly, due to a lower N load on plots and indirectly, perhaps, through decreased N concentration in the herbage. Leaching may be lessened, through improved N efficiency, whereby the benefit of soil organic N is maximised. Lower loading of Gd areas with dirty water is also an achievable target.

The study did not include monitoring of leached dissolved organic N (DON) now recognized as important in the N cycle. It has a role in phytoplankton nutrition, cell biology and ecology (Anita, Harrison and Oliveira, 1991), was seen as a cog in the N cycle by Chapin (1995) and may still, largely by not being measured, be a missing piece of the N cycle. DON can be readily leached from soil (Siemens and Kaupenjohann, 2002) and a positive relationship ($P < 0.001$) exists between the amount of DON in solution and the amount of NO_3 and

NH_4 in solution in grassland (Christou *et al.*, 2005). Future studies should include measurement of DON and dissolved organic matter assays since the latter are important for short-term dynamics of the microbial biomass and gross N fluxes (Cookson *et al.*, 2005). DON can contribute significantly to plant and microbial activity in freshwater and marine environments. It represents a significant portion of soil total dissolved N in agricultural land-use systems (Christou *et al.,* 2005) and there may be significant loss of DON in surface runoff (Jarvis, 1993).

References

Anon. 1988. *European Communities (Quality of Salmonid Waters) Regulations*, 1988 [Online] available from <http://www.irishstatutebook.ie/ZZSI293Y1988.html>, 8 pages.

Aarts, H.F.M., Habekotte, B. and van Keulen, H. 2000. Nitrogen (N) management in the 'De Marke' dairy farming system. *Nutrient Cycling in Agroecosystems* **56:** 231–240.

Allen, R.G., Pereira, L.S., Raes, D. and Smith, M. 1998. "Crop evapotranspiration guidelines for computing crop water requirements". FAO Irrigation and Drainage paper 56, 227 pages.

Anita, N.J., Harrison, P.J. and Oliveira, L. 1991. The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. *Phycologia* **30:** 1–89.

Aslyng, H.C. 1965. Evaporation, evapotranspiration and water balance investigations at Copenhagen 1955–64. *Acta Agriculturae Scandinavaca* **XV:** 284–300.

Aulakh, M.S., Rennie, D.A. and Paul, E.A. 1983. Field studies on gaseous nitrogen losses from soils under continuous wheat versus a wheat-fallow rotation. *Plant and Soil* **75:** 15–27.

Barkle, G.F., Stenger, R., Singleton, P.L. and Painter, D.J. 2000. Effect of regular irrigation with dairy farm effluent on soil organic matter and soil microbial biomass. *Australian Journal of Soil Research* **38:** 1087–1097.

Bartley, P. 2003. Nitrate responses in groundwater under grassland dairy agriculture. Unpublished *PhD Thesis*, University of Dublin, Trinity College, 376 pages.

Bartley, P. and Johnston, P. 2006. "Eutrophication from Agriculture Sources. Nitrate Leaching – Groundwater (2000-L S 2.3.1.3)", Final Report. EPA, Wexford, Ireland, 89 pages.

Bol, R., Kandeler, E., Amelung, W., Glaser, B., Marx, M.C., Preedy, N. and Lorenz, K. 2003. Short-term effects of dairy slurry amendment on carbon sequestration and enzyme activities in a temperate grassland. *Soil Biology and Biochemistry* **35:** 1411–1421.

Chapin, F.S. 1995. New cog in the nitrogen-cycle. *Nature* **377:** 199–200.

Christou, M., Avramides, E.J., Roberts, J.P. and Jones, D.L. 2005. Dissolved organic nitrogen in contrasting agricultural ecosystems. *Soil Biology and Biochemistry* **37:** 1560–1563.

Clough, T.J., Jarvis, S.C., Dixon, E.R., Stevens, R.J., Laughlin, R.J. and Hatch, D.J. 1999. Carbon induced subsoil denitrification of ^{15}N-labelled nitrate in 1 m deep soil columns. *Soil Biology and Biochemistry* **31:** 31–41.

Cookson, W.R., Abaye, D.A., Marschner, P., Murphy, D.V., Stockdale, E.A. and Goulding, K.W.T. 2005. The contribution of soil organic matter fractions to carbon and nitrogen mineralization and microbial community size and structure. *Soil Biology and Biochemistry* **37:** 1726–1737.

Cork County Council. 1998. Report on nitrate levels in Co. Cork water supplies. Internal Report from Cork County Council Environment Department, Inniscarra, Co. Cork to the Department of the Environment and Local Government, 19 pages.

Crawley, P. 2001. "Rural Environmental Indicators". Environmental Protection Agency, PO Box 3000, Johnstown Castle Estate, County Wexford, Ireland, 49 pages.

Culleton, N., Tunney, H. and Coulter, B. 1994. Sustainability in Irish agriculture. *Irish Geography* **27:** 36–47.

Cuttle, S.P., Scurlock, R.V. and Davies, B.M.S. 2001. Comparison of fertilizer strategies for reducing nitrate leaching from grazed grassland, with particular reference to the contribution from urine patches. *Journal of Agricultural Science, Cambridge* **136:** 221–230.

Darmody, P. 2004. "Losses of nitrogen by leaching from grazed dairy pastures". *M Phil Thesis,* Queen's University, Belfast, 158 pages.

del Prado, A., Brown, L., Schulte, R., Ryan, M. and Scholefield, D. 2006. Principles of development of a mass balance N cycle model for temperate grasslands: an Irish case study. *Nutrient Cycling in Agroecosystems* **74:** 115–131.

Folorunso, O.A. and Rolston, D.E. 1984. Spatial variability of field-measured denitrification gas fluxes. *Soil Science Society of America Journal* **48:** 1214–1219.

Gardiner, M.J. and Radford, T. 1980. "Soil Associations of Ireland and their Land Use Potential". National Soil Survey of Ireland. An Foras Talúntais, Dublin, 142 pages.

Gibbons, P., Rodgers, M. and Mulqueen, J. 2006. "Eutrophication from Agriculture Sources. Nitrate Leaching - Soil Investigation (2000- LS - 2.3.1.2.)" Final Report, EPA, Wexford, Ireland, 128 pages.

Hawke, R.M. and Summers, S.A. 2003. Land application of farm dairy effluent: results from a case study, Wairarapa, New Zealand. *New Zealand Journal of Agricultural Research* **46:** 339–346.

Horan, B., Mee, J.F., Rath, M., O'Connor, P. and Dillon, P. 2004. The effect of strain of Holstein-Friesian cow and feeding system on reproductive performance in seasonal-calving milk production systems. *Animal Science* **79:** 453–467.

Hyde, B.P., Hawkins, M.J., Fanning, A.F., Noonan, D., Ryan, M., O'Toole, P. and Carton, O.T. 2006. Nitrous oxide emissions from a fertilized and grazed grassland in the south east of Ireland. *Nutrient Cycling in Agroecosystems* **75:** 187–200.

Jarvis, S.C. 1993. Nitrogen cycling and losses from dairy farms. *Soil Use and Management* **9**: 99–105.

Jarvis, S.C., Barraclough, D., Unwin, R.J. and Royle, S.M. 1989. Nitrate leaching from grazed grassland and after straw incorporation in arable soils. In: "Management Systems to Reduce Impact of Nitrates" (ed. J.C. Germon), Elsevier Applied Science, pages 110–125.

Laws, J.A., Pain, B.F., Jarvis, S.C. and Scholefield, D. 2000. Comparison of grassland management systems for beef cattle using self-contained farmlets: effects of contrasting nitrogen inputs and management strategies on nitrogen budgets, and herbage and animal production. *Agriculture, Ecosystems and Environment* **80:** 243–254.

Ledgard, S.F., Clark, D.A., Sprosen, M.S., Brier, G.J. and Nemaia, E.K.K. 1996. Nitrogen losses from grazed dairy pasture, as affected by nitrogen fertiliser application. *Proceedings of the New Zealand Grassland Association* **57**: 21–25.

Littell, R.C., Milliken, G.A., Walter, W.S., Wolfinger, R.D. 1996. SAS System for Mixed Models. SAS Institute Inc., Cary, NC, USA, pages 423–460.

Met Éireann. 1996. Monthly and annual averages of rainfall in Ireland 1961-1990. Climatological Note 10.

Met Éireann. 2002. Monthly Return of Daily Observations from Climatological Station(s), Moorepark, County Cork. Form 8109.

Mills, G. 2000. Modelling the water budget of Ireland – evapotranspiration and soil moisture. *Irish Geography* **33**: 99–116.

Mikha, M.M., Rice, C.W. and Milliken, G.A. 2005. Carbon and nitrogen mineralization as affected by drying and wetting cycles. *Soil Biology & Biochemistry* **37**: 339–347.

Mounsey, J., Sheehy, J., Carton, O.T. and O'Toole, P. 1998. "Nutrient management planning on Irish dairy farms". End of Project Report ARMIS 4347, Teagasc, Wexford, 22 pages.

Neill, M. 1989. Nitrate concentrations in river waters in the south-east of Ireland and their relationship with agricultural practice. *Water Research* **23**: 1339–1355.

Neill, M. 2005. "River Water Quality in South-East Ireland, 2004". Environmental Protection Agency, Regional Water Laboratory, Kilkenny, Ireland.

O'Connell, K., Humphreys, J. and Watson, C.J. 2004. "Quantification of nitrogen sources for grassland". *Winter Scientific Meeting, The Fertiliser Association of Ireland*, pages 15–28.

Richards, K., Coxon, C., Ryan, M., Daly, D. and Kiely, J. 1996. Quantification of nitrate leaching to groundwater. *Irish Journal of Agricultural and Food Research* **35**: 67 (Abstract).

Richards, K. 1999. Sources of nitrate leached to groundwater in grasslands of Fermoy, Co. Cork. Unpublished *PhD Thesis,* Trinity College, Dublin, 290 pages.

Richards, K., Sills, P., Hooker, K. and Coxon, C. 2004. "Nutrient export and cycling from an efficient farming system". Research Report, Teagasc, Johnstown Castle Research Centre, pages 24–26.

Ryan, M. and Fanning, A. 1996. Effect of fertiliser N and slurry on nitrate leaching-lysimeter studies on five soils. *Irish Geography* **29**: 126–136.

Ryan, M., Fanning, A. and Noonan, D. 2001. "Monitoring of potential N losses from dairy and organic farming systems". End of Project Report ARMIS 4482, Teagasc, Wexford, 24 pages.

Ryan, M., McNamara, K., Carton, O.T., Brophy, C., Connolly, J. and Houtsma, E. 2006a. Eutrophication from Agriculture Sources. "Nitrate leaching – Farm Scale (2000-LS- 2.3.1.1)" Section 1 of 3. Final Report*,* EPA, Wexford, Ireland, 54 pages.

Ryan, M., McNamara, K., Carton, O.T., Brophy, C., Connolly, J. and Houtsma, E. 2006b. Eutrophication from Agriculture Sources. "Nitrate leaching – Farm Scale (2000-LS- 2.3.1.1)" Section 2 of 3. Final Report*,* EPA, Wexford, Ireland, 90 pages

Ryan, M. and Sherwood, M. 1990. Nitrogen movement in grazed pasture soils. Proceedings of European Grassland Federation, Banska Bystrica, pages 39–43.

Scholefield., D., Tyson, K.C., Garwood, E.A., Armstrong, A.C., Hawkins, J. and Stone, A.C. 1993. Nitrate leaching from grazed grassland lysimeters: effects of fertilizer input, field drainage, age of sward and patterns of weather. *Journal of Soil Science* **44**: 601–613.

Sherwood, M. 1986. Nitrate leaching following application of slurry and urine to field plots. In: "Efficient Land use of Sludge and Manure" (ed. A. Dam Kofoed, J.H. Williams, P. L'Hermite), Elsevier Applied Science, London, pages 150–157.

Sherwood, M. and Ryan, M. 1990. Nitrate leaching under pastures. In: "Nitrates-Agriculture-Eau" (ed. R. Calvet), INRA, Paris, pages 323–333.

Siemens, J. and Kaupenjohann, M. 2002. Contribution of dissolved organic nitrogen to N leaching from four German agricultural soils. *Journal of Plant Nutrition and Soil Science* **165**: 675–681.

Silva, R.G., Cameron, K.C., Di, H.J. and Hendry, T. 1999. A lysimeter study of the impact of cow urine, dairy shed effluent and nitrogen fertiliser on nitrate leaching. *Australian Journal of Soil Research* **37**: 357–369.

Thorn, R.H. 1986. Factors affecting the leaching of nitrate to groundwater in the Republic of Ireland. *Irish Geography* **19**: 23–32.

Verbeke, G. and Molenberghs, G. 2000. Linear mixed models for longitudinal data. Springer Series in Statistics. Springer-Verlag New York, Inc., pages 74–76, 97–101.

Watson, C.J., Jordan, C., Lennox, S.D., Smith, R.V. and Steen, R.W.J. 2000. Inorganic Nitrogen in Drainage Water from Grazed Grassland in Northern Ireland. *Journal of Environmental Quality* **29**: 225–232.

Watson, C.J., Stevens, R.J., Steen, R.W.J., Jordan, C. and Lennox, S.D. 1998. "Minimizing nitrogen losses from grazed grassland". *Annual Report*

1997–1998, Agricultural Research Institute of Northern Ireland, pages 49–61.

Whitmore, A.P. and Schroeder, J.J. 1996. Modelling the change in soil organic C and N and the mineralization of N from soil in response to applications of slurry manure. *Plant and Soil* **184:** 185–194.

Zaman, M., Di, H.J. and Cameron, K.C. 1999. A field study of gross rates of N mineralization and nitrification and their relationships to microbial biomass and enzyme activities in soils treated with dairy effluent and ammonium fertilizer. *Soil Use and Management* **15:** 188–194.

Zaman, M., Di, H.J., Cameron, K.C. and Frampton, C.M. 1999. Gross nitrogen mineralization and nitrification rates and their relationships to enzyme activities and the soil microbial biomass in soils treated with dairy shed effluent and ammonium fertilizer at different water potentials. *Biology and Fertility of Soils* **29:** 178–186.