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**Groundwater: A pathway for terrestrial C and N losses and indirect
greenhouse gas emissions**

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Abstract

Estimating losses of dissolved carbon (C) and nitrogen (N) via groundwater in an agricultural system provides insights into reducing uncertainties in the terrestrial C and N balances. In addition, quantification of dissolved nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) in groundwaters beneath agricultural systems is important for global greenhouse gas (GHG) budgets. Dissolved C (DC: dissolved organic carbon (DOC)+ CO_2 -C+ CH_4 -C) and dissolved nitrogen (DN: NO_3^- -N+ NH_4^+ + NO_2^- -N+ N_2O -N+ N_2) in groundwater were measured in two low permeability ($<0.02 \text{ m d}^{-1}$) and two high permeability ($>0.05 \text{ m d}^{-1}$) aquifers in Ireland. Groundwater in multilevel piezometers was sampled monthly over two years. Mean groundwater discharge to surface water was higher in 2009 (587-836 mm) than in 2010 (326-385 mm). Dissolved C and N delivery to surface water via groundwater caused substantial losses of terrestrial C and N. The extent of delivery was site specific and depended on N input, recharge and aquifer permeability. Mean dissolved N losses ranged from 8-12% of N input in low permeability to 27-38% in high permeability aquifers. The dominant fraction of DN was NO_3^- -N (84-90% of DN) in high permeability aquifers and N_2 (46-77% of DN) in low permeability aquifers. Indirect N_2O emissions via groundwater denitrification accounted for 0.03-0.12% of N input, which was equivalent to 3-11% of total N_2O emissions. Dissolved C loss to surface waters via groundwater was not significant compared to total carbon (TC) content of the topsoil (0.06-0.18% of TC). Site characteristics contributed greatly to the distribution of N between NO_3^- -N and dissolved N gases, N_2O and N_2 . Indirect GHG emissions from groundwater were an important part of farm nutrient budgets, which clearly has implications for national GHG inventories.

Key words: greenhouse gases, indirect N_2O emissions, effective rainfall, dissolved C, dissolved N, groundwater

Introduction

Methane, N₂O and CO₂ are important greenhouse gases (GHG) contributing to global warming (Ferron et al., 2007). More complete knowledge of C and N cycles has become essential because increases in the concentrations of important anthropogenic GHG are changing the earth's climate (Houghton et al., 2001). The Intergovernmental Panel on Climate Change (IPCC) has estimated that agriculture accounts for 10-12% of global anthropogenic GHG emissions, with agricultural land accounting for 50% of CH₄ and 60% of N₂O emissions (Smith et al., 2007). Dissolved gasses in groundwater leaching from top- and subsoils can be a source of GHG emissions to the atmosphere. This source of GHG is usually described as being 'indirect' because as groundwater discharges to surface water, the dissolved GHG are emitted to the atmosphere, thus transferring C and N from terrestrial ecosystems to the atmosphere via the aquatic pathway. Groundwater is a medium where GHG are produced and consumed simultaneously (Minamikawa et al., 2010). Hence, studies of groundwater to atmosphere GHG flux are critical in further developing our understanding of global C and N cycles.

The role of groundwater as a source of indirect GHG emissions is uncertain, partly due to the limitations in the methodologies for quantifying fluxes. Information on dissolved N₂O concentrations in groundwater, and the processes of N₂O production, consumption and transport in groundwater is available from catchment-scale monitoring (Höll et al., 2005; Osaka et al., 2006; von der Heide et al., 2008) but emissions originating from NO₃⁻-N leaching and its associated transformations in groundwater are poorly understood (Clough et al., 2007). Significant NO₃⁻-N reduction in subsoils and groundwater (Jahangir et al., 2012a) indicate that there is a requirement to quantify losses from the soil of dissolved N₂O and N₂ in leachate and the extent to which these are transported in groundwater to aquatic

ecosystems. This information will help estimate the missing piece of N in N balance as well as indirect N₂O emissions via groundwater upon discharge to surface waters.

Current studies have also shown that CO₂ and CH₄ are also emitted via indirect pathways (Minamikawa et al., 2010). Production of CO₂ in soils can lead to super saturation of dissolved CO₂ in groundwater seeps (Johnson et al., 2006) and groundwater has been observed to be an important source of dissolved CO₂ in rivers (Worrall and Lancaster, 2005; Johnson et al., 2006). Dissolved CO₂ in river water is an important source, albeit indirect, of CO₂ emissions to the atmosphere (Minamikawa et al., 2010). Likewise, there can be high CH₄ concentration in groundwater (Gooddy and Darling, 2005) and the concentration gradient between ambient air and a waterbody can cause a substantial release of CH₄ from groundwater to the atmosphere (Sawamoto et al., 2002). In Canada, Cheung et al. (2010) found that a substantial amount of groundwater CH₄ was of biogenic origin via CO₂ reduction. Therefore, C budgets for terrestrial ecosystems are likely to be incomplete and net C sequestration overestimated, if hydrologic exports of CO₂ and other dissolved C fractions are not considered (Cole et al., 2007).

Soluble C transport from terrestrial ecosystems accounts for a substantial component of European (Kindler et al., 2011; Ciais et al., 2008; Siemens et al., 2003) and global (Kessler and Harvey, 2001) C balances. The C balance estimates for Europe have high uncertainty; the causes of which are not fully understood (Cernusca et al., 2008). Siemens (2003) argued that the gap between atmospheric and land based estimates of C budgets in Europe could be the result of DC leaching, which decouples the direct exchange of C between atmosphere and biosphere. The importance of the riverine C transport from land to ocean has recently been highlighted by Ciais et al. (2008). In comparison to forest ecosystems, data is limited on DC and dissolved organic nitrogen (DON) losses in grassland and croplands (van Kessel et al., 2009). The objectives of the present research were to (i) quantify losses of dissolved C

and N from terrestrial ecosystems to aquatic ecosystems via groundwater in contrasting landscape settings, and (ii) estimate the contribution of indirect emissions of GHG to the atmosphere.

2 Materials and methods

2.1 Study sites

The investigation was carried out at three vertical zones of groundwater: (i) subsoil, (ii) interface between subsoil and bedrock and (iii) bedrock at four agricultural catchments in Ireland: Johnstown Castle (JC; 53°20'N 6°15'W); Solohead Research Farm (SH; 52°51'N, 08°21'W); Oak Park (OP; 52° 51'N, 6° 54'W) and Dairygold (DG; 50°07'N, 08°16'W). Two sites, JC and SH, have low permeability aquifers (saturated hydraulic conductivity (K_s): 0.001-0.02 m d⁻¹) with low dissolved oxygen (DO; 1-4 mg L⁻¹), electrical conductivity (Eh; <150 mV) and a shallow watertable (WT, 1-2 m below ground level (bgl)). In contrast, the other two sites, OP and DG, have higher permeability aquifers (K_s : 0.05-0.3 m d⁻¹) and had high DO (7-10 mg L⁻¹), Eh (>200 mV) and a deep WT (5-30 m bgl). At JC, the soils are moderate to poorly drained heterogeneous loam and clay loams of varying thickness (Fenton et al., 2009b). At SH, the soils are poorly drained Gleys (90%) and Grey Brown Podzolics (10%) with a clay loam texture overlaying Devonian sandstone at a depth ranging between 5 and 10 m. Drainage is impeded at SH, and this contributes to waterlogged conditions under high rainfall. In contrast the topsoil at OP is a free draining sandy loam over gravely sand subsoils. The soil parent materials were fluvioglacial sands and gravel, which are relatively shallow and very vulnerable to leaching. At DG, the soils are free draining sandy loam (topsoil) and silt loams (subsoil).

2.2 Nitrogen (N) input across sites

An estimation of N inputs across sites is presented in Table 1. The three grassland sites had different stocking densities and N application rates and grassland management, resulting in slightly different farm scale N surpluses and N available to be leached (Table 1). The total N inputs, surplus and leached at the three grasslands are shown in Table 1.

2.3 Monitoring well establishment

Thirty specifically designed multilevel piezometers (0.05 m ID and 2 to 3 m screen length) were installed along groundwater flow paths in order to collect samples at depths (m bgl): 3 to 5 (subsoil), 8 to 10 (subsoil-bedrock interface) and 18 to 30 m (bedrock) at JC, SH and OP. A bentonite cement grout was used as a sealant between the screened piezometer depths. At DG 6 single piezometers were installed in bedrock (30-50 m bgl; 6 m screen section) as no groundwater strike was encountered in the subsoil or subsoil-bedrock interface. The integrity between piezometers installed in each borehole was checked by increasing water level to 1 m above static level and measuring changes in adjacent wells using an electronic DIVER (Eijkelkamp, The Netherland).

2.4 Water balance and effective rainfall estimation

A water balance was used to calculate the effective rainfall (ER), the portion of rainfall that percolates through the rooting zone to recharge groundwater. The modified Penman-Monteith equation (Allen et al., 1998) was used to process the potential evapotranspiration PET (equation 1), subsequently the hybrid model for computing soil moisture deficit (SMD) presented by Schulte et al. (2005) for Irish grasslands (JC, SH and DG) and Premrov (2011) for OP was used to obtain the actual evapotranspiration (AET). Daily weather data were collected from the local weather station situated at close proximity to each site.

$$PET = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma (1 + 0.34u_2)} \quad (1)$$

PET is potential evapotranspiration (mm d⁻¹), R_n is the net radiation at the crop surface (MJ m⁻²d⁻¹), G is soil heat flux density (MJ m⁻²d⁻¹), T is air temperature at 2 m height (°C), u₂ is wind speed at 2 m height (m s⁻¹), e_s and e_a are the saturation and actual vapour pressure (kPa °C⁻¹), γ is the psychrometric constant (kPa °C⁻¹) and Δ is the slope vapour pressure (kPa °C⁻¹). The principal meteorological input factors determining PET are solar radiation, air temperature, air humidity and wind speed. As soil heat flux G beneath the crop reference surface is relatively small, it can be ignored when calculating for day periods. The Food and Agriculture Organization (FAO) guide provides a detailed step-by-step approach for all the computations of the required data (Allen et al., 1998). The SMD was calculated from the cumulative balance of precipitation, evapotranspiration and drainage (Schulte et al., 2005):

$$SMD_t = SMD_{t-1} - P_t + AET_t + Drain_t \quad (2)$$

where SMD_t is SMD at day t (mm), SMD_{t-1} is SMD at day t-1 (mm), P_t is daily precipitation (mm), AET_t is daily actual evapotranspiration (mm), Drain_t is amount of water drained daily by percolation and/or overland flow (mm) with Drain_t = - SMD_{t-1}

AET_t was calculated using equation 3 below.

$$AET_t = PET \frac{SMD_{max} - SMD_{t-1}}{SMD_{max} - SMD_c} \quad (3)$$

when SMD_t > SMD_c with SMD_{max} is maximum SMD (mm), SMD_c is critical SMD (mm).

The ER was calculated by subtracting daily AET from daily rainfall (P) and assuming no

overland flow. The SMD on the day one for each year (1 January 2009 and 1 January 2010) was set to zero and ED was estimated for each subsequent day.

2.5 Groundwater sampling

Groundwater sampling was carried out monthly between February 2009 and January 2011 using a bladder pump (Geotech Environmental Equipment, Inc., USA) following United States Environmental Protection Agency (USEPA) Region I Low Stress Purging and Sampling Procedures (USEPA, July 30, 1996). Triplicate samples were collected slowly (100 ml min^{-1}), to prevent degassing, from a Teflon pump outlet tube (ID 0.006 m). Samples for dissolved N_2O , CO_2 and CH_4 , were collected in 160 ml serum bottles after overflowing the sample tube by approximately 150 ml excess water and then sealed immediately with butyl rubber septa and aluminium crimp caps (WHEATON, USA). Samples for dissolved N_2 were collected in a 12 ml exetainer (Labco Wycombe Ltd., UK) by slowly overflowing the sample tube with approximately 10 ml excess water and then immediately sealing the tube using double septum (butyl rubber + Teflon) stoppers. Dissolved gas samples were stored under water in a cool box. Samples for geochemical analysis were kept in a cool box, transported to the laboratory and stored at 4°C . All samples were analysed within one week of sampling.

2.6 Analysis of dissolved N_2O , N_2 , CO_2 and CH_4

To determine the dissolved N_2O , CO_2 and CH_4 , samples were degassed (Lemon, 1981) using high purity *He* (BOC, Linde Group, Germany) (*He*: water 1:3; v/v) at 21°C . The headspace volume was augmented to 40 ml by an additional injection of 40 ml of *He* and simultaneous replacement of 40 ml water using a plastic syringe. Samples were mechanically shaken for 5 min at 400 rpm and left to stand for 30 min. Headspace gas sub

samples were collected in 15 ml exetainers (Labco Wycombe Ltd., UK) with an additional injection of 15 ml *He* using a PVC syringe. The N₂O, CO₂ and CH₄ were analysed by gas chromatography (CP-3800, Varian, Inc. Switzerland) equipped with electron capture (N₂O), thermal conductivity (CO₂) and flame ionization (CH₄) detection using Ar as the carrier gas for N₂O and N₂ for CO₂ and CH₄. The exetainer samples for N₂ were analysed in a high precision membrane inlet mass spectrometer (MIMS) (Kana et al., 1994).

2.7 Dissolved N₂O, denitrified N₂, CO₂ and CH₄ estimation

The N₂O, CO₂ and CH₄ concentrations in water samples were estimated using the Henry's law constant, the concentrations of the gas in the headspace, the bottle volume and the temperature of the water. The partial pressures of N₂O, CO₂ and CH₄ in the equilibrated headspace and water were calculated using gas solubilities from Weiss and Price (1984) for N₂O, Weiss (1974) for CO₂ and Wilhelm et al. (1977) for CH₄ at the recharge temperature as measured at the interface between the unsaturated zone (USZ) and groundwater surface. Denitrified N₂, termed excess N₂ (Heaton and Vogel, 1981), was estimated using equations provided by Weymann et al. (2008).

2.8 Geochemistry

Soil samples were collected from three randomly selected soil profiles, which were excavated to a depth of 1.6 m bgl at each site. Soil samples were stored immediately after collection in a cold room at 4°C. Soil TC and total nitrogen (TN) were determined on dry (oven dried at 105°C for 24 h) bulk soil samples using combustion analysis (Leco CNS 2000 analyzer; Leco Corporation, USA). Groundwater non-metallic ions, total oxidised N (TON) consisting of NO₃⁻ and nitrite (NO₂⁻), ammonium (NH₄⁺), and chloride (Cl⁻) were analyzed colorimetrically using an Aquakem 600 Discrete Analyser (Aquakem 600A,

01621 Vantaa, Finland). DOC was analysed using a Total Organic Carbon Analyser (TOC-V cph/cpn; Shimadzu Corporation, Kyoto, Japan) and TN was analysed using the persulfate method (Askew and Smith, 2005). Prior to groundwater sampling each month WT depth was measured using an electronic dip meter.

2.9 Estimation of dissolved C and N losses via groundwater

Dissolved C and N discharged from groundwater to surface water was estimated using the water balance approach (Misstear et al., 2008; Misstear et al., 2009), with the following assumptions: (i) dissolved N₂O, CO₂ and CH₄ concentrations over time were in equilibrium by simultaneous production and reduction processes; (ii) the ER was equal to the volume of groundwater recharge assuming that overland and lateral flow were minimal (Fitzsimons and Misstear, 2006) and (iii) volume of water discharging from groundwater to surface water was approximately equal to recharge i.e., the ER, because the position of the WT at the beginning (1 October) and at the end (30 September) of a hydrological year remains approximately the same; and the change in groundwater storage was almost zero (Fitzsimons and Misstear, 2006). The quantity of C and N lost was estimated using equation 4 below.

$$\text{C or N loss (kg ha}^{-1}\text{)} = \frac{\text{Volume of water discharged (L)} \times \text{concentration of C or N (mg L}^{-1}\text{)}}{1000000} \quad (4)$$

2.10 Statistical analysis

Analysis was performed using the General Analysis of Variance (GenStat, Version 13, VSN International Ltd., UK). As most of the variables showed an approximately lognormal distribution, log transformations were used with appropriate re-scaling so that residual checks indicated that the assumptions of the analyses were not violated. For each dissolved gas, the effects of location and time were examined along with their interactions using

repeated measures analysis. Where significant differences were found, Tukey Kramer HSD multiple comparison test were used to distinguish differences between individual locations. Differences between the two study years (2009 and 2010) were tested using a paired t test. Treatment effects were considered statistically significant at $p < 0.05$.

3. Results

3.1 Total and daily rainfall

Rainfall varied considerably between sites and years. Annual rainfall distribution was similar at each of the sites. At all sites, the total amount of rainfall was higher ($p < 0.01$) in 2009, by approximately 35%, compared with 2010 (Table 2). This created a marked contrast in USZ water contents and its delivery to WT between the two years. In general, the JC and SH sites were wetter than the OP and DG sites (Table 2). Rainfall was well above average in 2009 (130-140%) and below average (87-90%) in 2010 across sites. The highest total rainfall was recorded during October to December and the lowest during July to September in each year at all sites (Figure 1 to 4).

3.2 Total and daily effective rainfall (ER)

Both the PET and AET were approximately the same at each site within each year. However, ER differed between sites, highest at JC and lowest at OP (Table 2). The ER as a percentage of rainfall was higher in 2009 (46-60%) than in 2010 (32-46%). The highest ER was observed during October to December and the lowest during July to September at all sites (Figure 1 to 4). Moreover, due to the higher rainfall amounts, the period of ER at lower permeability JC and SH was longer than at the higher permeability OP and DG (Table 2).

3.3 Watertable (WT) fluctuations

Watertable fluctuations followed rainfall and ER trends over time (Figure 1 to 4, presented as electronic supplemental materials). The shallowest WT depths observed were 0.6, 0.7, 2.0 and 24.7 m bgl, measured during October to December at JC, SH, OP and DG, respectively, whereas the deepest depths were 2.5, 1.4, 5.5 and 30.5 m bgl, respectively, measured during July to September. Therefore, the annual WT fluctuation ranges were 1.9, 0.7, 3.5 and 5.3 m, respectively. The WT depths were shallowest in subsoil and deepest in bedrock at all sites except DG where the saturated zone began in the bedrock. Mean WT depth was deeper ($p < 0.05$) at the high permeability sites (OP and DG) than at the low permeability sites (JC and SH). Mean WT depth over the two years ranged from 1.7 m bgl in subsoil to 2.8 m bgl in bedrock at JC; 1.0 m bgl in subsoil to 2.1 m bgl in bedrock at SH; 3.0 m bgl in subsoil to 5.4 m bgl in bedrock at OP and was 29 m bgl at DG.

3.4 Soil physico-chemical conditions

Soil TC content to 1.6 m depth was lower ($p < 0.05$) at OP than the other sites (Table 3). The TC differed ($p < 0.001$) with soil depth and was highest in the A horizon and lowest in the C horizon. It was interesting to note that TC at >0.30 m bgl at OP increased abruptly and at this depth was higher than all other sites, whereas in the topsoil it was lower than at the other sites. This may be due to the presence of interbedded clay lenses, limestone gravel and sand in subsoils at OP. OP had significantly higher soil inorganic C, which accounted for approximately 24% of TC, whereas at the other sites soil inorganic C was low accounting for $<2\%$ of TC. The TN content was lower ($p < 0.001$) at OP (arable) than at the grassland sites. TN content at each site significantly decreased ($p < 0.001$) with depth, with the highest TN in the A horizon and lowest in the C horizon.

3.5 Dissolved N_2O , CO_2 and CH_4 concentrations in groundwater

The N_2O -N concentrations in groundwater differed ($p<0.001$) between sites (Figure 5a); lowest at SH and highest at DG. Groundwater N_2O -N concentrations were higher ($p<0.01$) in February and March than all other sampling times of each year (Figure 6a). Mean coefficients of variation (CV) between sampling times were 83, 91, 82 and 70%, whereas mean within site CV were 87, 99, 85 and 82%. Dissolved CO_2 -C varied significantly between sites. There were higher ($p<0.001$) CO_2 -C concentrations at the three grassland sites than at OP (Figure 5.b). In general, CO_2 -C concentrations in groundwater were consistently higher, in the period July to September, than at other times of the year (Figure 6b). Elevated CH_4 -C in groundwater was observed at all sites but frequency of occurrence and magnitude differed between sites. Groundwater CH_4 -C concentrations were higher in the low permeability (Figure 5c). Temporal changes in CH_4 -C concentrations were even higher than the CO_2 -C production, the highest concentrations were observed August to October and lowest observed in the period December to February (Figure 6c).

3.6 Quantity of dissolved N delivered to the surface waters

Groundwater TN includes NH_4^+ , TON and DON. The weighted mean value of TN estimated to be delivered from groundwater to the surface water was higher at OP and DG than at JC and SH in both years (Table 4). The highest calculated groundwater TN load was at DG (106 and 52 kg ha^{-1} , respectively, in 2009 and 2010) and lowest at SH (8 and 2 kg ha^{-1} , respectively). At all sites, significantly lower TN loads were discharged from groundwater to surface water in 2010 compared with 2009. The distribution of NO_3^- -N loads over the sampling times in a year were similar between sites and between the hydrological years, and it comprised the majority of TN (Table 4). To estimate catchment scale N delivery from groundwater to surface water, there was an additional opportunity to include dissolved N_2O and N_2 gas into the total N loss. Dissolved N_2O and N_2 losses were estimated based on the

data available from Jahangir et al. (2012b). Therefore, the total DN (kg N ha^{-1}), including the $\text{N}_2\text{O-N}$ and N_2 was 54 and 24 at JC; 24 and 10 at SH; 73 and 40 at OP; and 109 and 54 at DG in 2009 and 2010, respectively. The mean DN loads over these two years accounted for 12, 8, 38, and 27% of the N input at each site. Most of the DN at OP and DG was NO_3^- N, which accounted for 81% (2010) to 91% (2009) at OP and 89% (2010) to 92% (2009) at DG. Mean indirect $\text{N}_2\text{O-N}$ emissions via groundwater ranged from 0.15 and 0.01 kg N ha^{-1} at SH to 0.34 and 0.15 kg N ha^{-1} at DG during 2009 and 2010 (Table 4). The $\text{N}_2\text{O-N}$ lost (% N input) via groundwater was lowest at SH (0.07 and 0.01% of N input in 2009 and 2010) and highest at OP (0.17 and 0.07% of N input in 2009 and 2010) (Table 4). Over the two years, the mean N_2O emission as a percentage of DN delivered to surface waters ranged from 0.29% at OP to 0.42% at JC (Table 4).

3.7 Amount of dissolved C delivered to the surface waters

A substantial quantity of C was lost as DOC in both years at JC and SH. Losses at OP and DG were lower ($p < 0.05$) than at JC and SH (Table 5). Groundwater was found to be an important pathway of terrestrial C losses as DC (sum of DOC, $\text{CO}_2\text{-C}$ and $\text{CH}_4\text{-C}$). The quantities of DC discharged ranged from 143-344 kg ha^{-1} at JC; 78-266 kg ha^{-1} at SH; 30-89 kg ha^{-1} at OP and 116-217 kg ha^{-1} at DG during each year. The dissolved groundwater $\text{CO}_2\text{-C}$ losses equated to as high as 0.22% of the topsoil TC content at JC in 2009 (Table 5).

4. Discussion

4.1 Rainfall and effective rainfall during the study

The annual average rainfall during the study period at all sites was higher than the annual average of the preceding ten years (1999-2008); rainfall was 30-40% higher in 2009 and 10-15% lower in 2010. Therefore, it appeared that in 2010 dissolved N, including NO_3^- -N,

leached from the soil and subsoils to groundwater appeared to be low. This is because the hydraulic loadings (i.e. period as well as volume of drainage) that carry N from soils to groundwater were lower in 2010 than 2009. Despite the contrasting annual rainfall during this study, mean rainfall was within the range of mean Irish rainfall (800-1400 mm) (Daly, 1995).

4.2 Watertable (WT) response to effective rainfall (ER)

The response of WT to rainfall depends on the amount of rainfall and the evaporative demand plus the SMD. The ER in 2009 and 2010 contrasted between sites, reflecting the total rainfall. However, ER was consistently higher in 2009 than the mean Irish ER (350-553 mm yr⁻¹) over the last couple of years which was opposite in 2010. During July to September evaporation exceeded rainfall resulting in WT depth increasing. Changes in WT reflected ER temporal patterns similar to that reported by Bartley and Johnston (2006). In the current study there was a general recession period for ER during March to September in each year at all sites. This resulted in the WT depth steadily decreasing during this 7 month period. GWT level increased almost instantaneously when the ER reoccurred. Similar to our study, Daly (1995) noted that there is a defined recharge period in Ireland from mid-October to mid-March and thereafter, a general recession period of up to 7 months occurs. During this dry period there is substantially lower risk of nutrient leaching to groundwater. The depth of USZ, as delineated by the depth of WT, and the annual fluctuations in WT were lower at JC and SH than at OP and DG reflecting the lower aquifer permeability at JC and SH than at OP and DG. Annual fluctuations of WT depth ranged from 0.7 m at SH to 5.3 m at DG and increased with increasing permeability of the aquifer, being the highest at DG (Ks: 0.26 m d⁻¹) and lowest at SH (Ks: 0.02 m d⁻¹). Fitzsimons and Misstear (2006) noted that annual WT fluctuations in Ireland are approximately 5 m, which is comparable to

what was observed in the current study sites. Previous research at the JC observed that mean WT depth in subsoil was 2.2 m bgl (Fenton et al., 2009a). Where WT depths are similar at the start and end of ER, then ER can be used to estimate the amount of groundwater that is discharged to the receptors during a hydrological year. Fenton et al. (2009a) suggested that all of the ER reached the WT as the rainfall intensity is generally lower than the soil infiltration capacity in the same study sites. In addition, runoff losses and lateral flows of rainfall can be assumed to be zero in the agricultural catchments in Ireland (Bartley, 2003; Fitzsimons and Misstear, 2006). Therefore, the total amount of ER at each site can be considered as the amount of groundwater recharged and then discharged to surface waters because the change in groundwater storage in Irish aquifers is zero (Fitzsimons and Misstear, 2006). The period of ER is very important for agricultural management practices as it represents the period for nutrient transport to groundwater.

4.3 N delivery from groundwater to surface water

Dissolved N concentrations in groundwater at the beginning and at the end of each hydrological year were approximately the same (data not shown). Therefore it can be assumed that DN losses from groundwater to surface water are equivalent to the DN leached from soil and subsoils to the groundwater. The results of DN losses are comparable with past studies reported on European grasslands. Scholefield et al. (1993) measured losses of 38.5-133.8 kg N ha⁻¹ with a fertilizer application rate of 200-400 kg N ha⁻¹ but losses varied with N input rates and weather patterns. Walmsley (2009) measured drainage DN at OP in 2007 (approximately 0.5 m bgl) of 36 kg N ha⁻¹ in a reduced tillage system to 114 kg N ha⁻¹ in a conventional tillage system. At the same site, Hooker et al. (2008) reported NO₃⁻-N loads leached in the USZ of 70 to 94 kg N ha⁻¹ with no winter cover crop or 16 to 67 kg N

403 ha^{-1} when a cover crop was present. The results of both studies are in agreement with the
 404 present estimation of 73 kg N ha^{-1} in 2009 and 40 kg N ha^{-1} in 2010 at OP.

405 Dissolved N losses also vary with soil type and aquifer permeability. At the low
 406 permeability (K_s : $0.02\text{-}0.03 \text{ m d}^{-1}$) sites mean DN losses observed ranged from 17 to 38 kg
 407 N ha^{-1} with N input rates of 213 to 300 kg N ha^{-1} , whereas at the high permeability (K_s :
 408 $0.07\text{-}0.26 \text{ m d}^{-1}$) sites mean DN losses ranged from 57 to 82 kg N ha^{-1} with N input rates of
 409 150 to 297 kg N ha^{-1} . Discharges of DN from groundwater to the surface water were
 410 equivalent to 27-38% of N input in the higher permeability aquifers (OP and DG) and 8-
 411 13% of N input in the low permeability aquifer (JC and SH). Fenton et al. (2009a) also
 412 observed a strong relationship between aquifer permeability and groundwater NO_3^- -N
 413 distribution and they hypothesised that denitrification lowered groundwater NO_3^- -N
 414 concentrations at lower permeability sites.

415 Although NO_3^- -N formed the major part of DN at the high permeability sites (mean 86 and
 416 91% at OP and DG, respectively) this was not the case at the lower permeability sites (mean
 417 61 and 28% at JC and SH, respectively). However, the results from the high permeability
 418 sites are comparable with Walmsley (2009) who measured 72-92% of dissolved N losses as
 419 NO_3^- -N in arable land, and with those of Vanni et al. (2001) who estimated NO_3^- -N as 70-
 420 87% of DN in three catchments adjacent to intensively cultivated ($>90\%$ cropland) land.

421 The importance of measuring N_2 as a component of DN to estimate farm scale N balance as
 422 well as N leaching to groundwater has been highlighted in the current study on the lower
 423 permeability sites.

424 Interestingly at JC and SH, mean groundwater N_2 over the two years was approximately 46
 425 and 77% of DN. This highlights the need, particularly on lower permeability sites, to
 426 include indirect N_2 emissions in farm scale N balance studies to improve balance estimates
 427 and reduce uncertainty. On the higher permeability sites, mean groundwater excess N_2

accounted for only 8 and 4% of DN at OP and DG, respectively. Unfortunately, despite the extensive research on farm scale N balances, there is little data available on the estimation of N₂ emissions from soil or groundwater available in the literature. The estimated N₂ emissions in groundwater in our study are an underestimate of total terrestrial N₂ emissions due to the potential for direct USZ N₂ emissions. Previous research has highlighted that subsoil denitrification results in nearly complete reduction of NO₃⁻-N to N₂ (Jahangir et al., 2012) and this gas may exchange with the atmosphere prior to entering groundwater. Thus both unsaturated and saturated zone N₂ emissions should be included in farm scale N balances.

Indirect N₂O emissions from groundwater discharge to a surface waterbody are an important source of atmospheric N₂O emissions. Indirect N₂O emissions (% N₂O-N over N input) results in this study are in line with the results of Reay et al. (2005) who measured the indirect N₂O emissions of 0.09% at farm-scale and of 0.035% at catchment-scale in UK. The percentage of dissolved NO₃⁻-N lost as N₂O-N at JC, OP and DG (0.68, 0.34 and 0.33%, respectively) were also in line with Reay et al. (2009) who reported a mean value of 0.3%. The exception was at SH, where a higher value of 1.63% was observed, which is attributable to the low groundwater NO₃⁻-N concentrations at SH. Nonetheless, indirect N₂O emissions via groundwater were higher than the IPCC default value of 0.25% (N₂O as a percentage of leached NO₃⁻-N).

When N₂O emissions are expressed as a percentage of the total DN lost, the values were 0.42, 0.40, 0.29 and 0.30% at JC, SH, OP and DG, respectively. DN included other species of N (N₂O and N₂) resulting from reduction from NO₃⁻-N through denitrification. Moreover, in situ production of N₂O and N₂ in groundwater (Jahangir et al., 2011a) indicates that NO₃⁻-N is not a conservative ion in groundwater, rather it undergoes a microbial reduction in favourable environments. Therefore, it should be more appropriate to consider total DN in

groundwater to estimate the indirect N₂O emissions than the approach that considers NO₃⁻-N only. This argument has also been proposed by Weymann et al. (2008) who measured dissolved N₂O-N and N₂ at four different sand and gravel aquifers in Germany. Contributions of indirect N₂O emissions to the total emissions (direct via surface soil and indirect via groundwater) were approximately 5, 3, 11 and 6% (estimated based on the IPCC default 1% of N input for surface emissions). These results are approximately in line with the global average figure of 3-5%, being suggested by Crutzen et al. (2008) for poorly permeability sites (JC and SH); total emissions were considerably higher on the high permeability sites (OP and DG).

4.4 Dissolved C losses from groundwater to the surface waters

Dissolved OC concentrations in groundwater at these study sites were low (4-20 kg C ha⁻¹). However, the amount of dissolved C loss as CO₂-C was substantial comprising 0.05-0.22% of top soil TC content. Higher groundwater CO₂-C concentrations were observed at the JC, SH and DG than OP which are likely to reflect the higher organic C inputs through organic matter recycling by grazing animals via direct deposition of dung, manure and soiled water irrigation. In addition, the highest groundwater CO₂-C concentrations were observed at JC which might reflect the bedrock geology of interbedded shales, which are believed to be a source of C (Schultz et al., 1980). Groundwater CH₄-C concentrations were generally low with detectable loads on the low permeability sites but these are negligible when compared with the TC content of soil (<0.001% of TC).

4.5 Soil type and land use impacts on C and N losses

Site characteristics had an important role in the partitioning of reactive N losses from the four study sites. Soil type and aquifer permeability were significantly related to NO₃⁻

leaching, N_2 and N_2O emissions. Indirect N_2O emissions were greater on the higher permeability sites resulting from nitrification and/or incomplete denitrification in groundwater with higher DO availability. This agrees with Rivett et al. (2008) who suggested that groundwater denitrification rates were limited primarily by oxygen concentration and electron donor concentration and availability. On the high permeability sites (OP and DG) groundwater DO concentrations were higher and electron donor concentrations (DOC) were lower than observed on the low permeability sites. In contrast, N fractionation on the low permeability sites suggested that groundwater denitrification was more complete resulting in lower N_2O -N and NO_3^- -N emissions and higher N_2 emissions. Groundwater CH_4 -C occurrence was similar to N_2 , higher on the low permeability sites than the high permeability sites, reflecting the reducing groundwater conditions on these sites. Direct N_2O emissions are also highly dependent on site characteristics, in particular water filled pore space (WFPS) and nitrogen inputs. Sites with higher WFPS have a higher total denitrification potential. Jahangir et al. (2012) observed high total denitrification in subsoil. The combination of a more complete denitrification (N_2) and a longer USZ residence time, due to lower permeability, result in higher rates of total denitrification to N_2 . Denitrification rates vary depending on soil type. Rafique et al. (2011) found that direct N_2O emissions were significantly higher from the DG site compared to SH which were attributed to N_2O from nitrification under higher oxygen availability. They also suggested that denitrification was more complete, higher proportion of N_2 , on the gley soils with higher WFPS due to greater anaerobic conditions. Over all our study observed significantly higher DN emissions in high permeability sites and this balance was dominated by NO_3^- -N. Future research should aim to improve agricultural C and N balances by coupling direct and indirect GHG emissions to reduce global GHG uncertainties.

The effect of land-use is more difficult to disaggregate in this study as there was only a single arable site. There were no significant differences in the groundwater $\text{N}_2\text{O-N}$, N_2 or NO_3^- -N concentrations observed on the high permeability grassland and arable sites. Interestingly, land use did have an effect on indirect CO_2 emissions and DC emissions were significantly higher under grassland than tillage. Grassland soils have been shown to have higher carbon leaching losses compared to arable (Kindler et al., 2011; Walmsley, 2011). The low mean groundwater CH_4 concentrations in our study are negligible in carbon balance terms and are in agreement with Kindler et al. (2011). The coupling of higher carbon loss to groundwater under grassland agriculture with low oxygen aquifers is likely to enhance groundwater denitrification.

5. Conclusions

The WT depth showed a clear response to ER, being shallowest during October to December and deepest during July to September. Groundwater discharge to surface water resulted in substantial loads of C and N being lost from the terrestrial agricultural ecosystems. However, the extent of these losses depended on the land use, hydrology and drainage conditions. Aquifer permeability was critical in determining groundwater NO_3^- -N occurrence, which was highest at high permeability sites and lowest at low permeability sites. Groundwater DOC export to the surface water was low in comparison with topsoil C content due to C retention and consumption during recharge and groundwater transport. Groundwater CO_2 -C export was an important part of the farm C balance accounting for loads up to $314 \text{ kg C ha}^{-1}\text{y}^{-1}$. Methane occurrence in groundwater from the terrestrial agricultural ecosystem was episodic, with low emissions. Mean indirect N_2O emissions via groundwater denitrification accounted for approximately 0.03 to 0.12% of farm N input, which seems to be an important component of atmospheric N_2O emissions. Indirect

greenhouse gas emissions from groundwater are an important part of farm and national scale budgets. Site characteristics contribute greatly to the fractionation of N between NO_3^- -N and dissolved N gases, N_2O -N and N_2 .

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Table 1 Annual N balance at four experimental sites: JC (Johnstown Castle), SH (Solohead), OP (Oak Park) and DG (Dairy Gold) between 2009 and 2010

		N input‡	N output‡	N surplus‡	N leached‡
Site	Land use	(kg N ha ⁻¹)			
JC	Grassland	312	69	243	106
SH	Grassland	213	76	137	47
OP	Arable land	150	75	75	70
DG	Grassland	298	35	263	148

‡Total N input included fertilizer N, concentrates, atmospheric deposition and biological N₂-N fixation (BNF). Total output included milk and meat. Total surplus was calculated by subtracting total output from total input (Scholefield et al., 1991). Total N to be leached was calculated considering N losses via volatilization (NH₃ emission) and denitrification in soil surface (Ryan et al., 2011).

Table 2 Annual rainfall, potential evapotranspiration (PET), actual evapotranspiration (AET) and effective rainfall (ER) data at four experimental sites: JC (Johnstown Castle), SH (Solohead), OP (Oak Park) and DG (Dairy Gold) between 2009 and 2010

Hydrologic events	JC		SH		OP		DG	
	2009	2010	2009	2010	2009	2010	2009	2010
‡P (mm)	1452	947	1403	879	1167	759	1293	869
‡PET (mm)	632	633	681	686	713	718	694	700
‡AET (mm)	615	562	643	553	630	518	620	543
‡ER (mm)	836	385	759	326	537	241	673	326
No. of days ER occurred	211	168	200	45	83	43	105	50
Portion of P as ER (%)	57	41	54	41	46	32	52	38

‡P: precipitation, PET: potential evapotranspiration, AET: actual evapotranspiration and ER: effective rainfall

727 Table 3 Mean (n = 3) soil profile TN and TC concentrations (t ha⁻¹) at four experimental
728 sites: JC (Johnstown Castle), SH (Solohead), OP (Oak Park) and DG (Dairygold) at the
729 beginning of the experiment

Sites		JC		SH		OP		DG	
Horizon	Depth (m bgl))	TN	TC	TN	TC	TN	TC	TN	TC
A	0-0.2	14.4±1.5	150.6±18	21.4±6	194±59	8.7±2	110±25	19.3±2	194±18
B	0.2-0.6	3.3±0.7	31.9±7	6.8±2	59.8±15	1.6±1	68±24	4.7±1	46±9
C	0.6-1.6	2.0±0.4	16.8±3	1.9±1	58.3±11	0.7±0	77±29	1.2±0	24±15

Table 4 Total N, NO₃⁻-N and DN effluxes from groundwater to the receptors at four experimental sites: JC (Johnstown Castle), SH (Solohead), OP (Oak Park) and DG (Dairy Gold) during 2009-2010

	JC		SH		OP		DG	
	2009	2010	2009	2010	2009	2010	2009	2010
Groundwater N fraction (kg N ha ⁻¹)								
TN *	34	15	8	2	69	36	106	52
NO ₃ ⁻	33	13	7	2	66	32	100	47
DON¶	1.4	1.4	1.7	0.3	2.9	4.3	5.3	5.4
N ₂ O-N	0.28	0.06	0.15	0.01	0.25	0.10	0.34	0.15
Denitrified N ₂ -N	18	9	15	8	4	3	3	2
DN*	52	24	24	10	73	40	109	54
Groundwater N fraction (%)								
DN/N input	17.5	8.0	11.3	5.0	48.9	26.5	36.6	18.1
N ₂ O-N emission †	0.09	0.02	0.06	0.01	0.17	0.07	0.10	0.04
N ₂ O-N emission‡	0.56	0.28	0.69	0.13	0.36	0.22	0.33	0.27
N ₂ O-N emission**	0.003	0.001	0.001	0.001	0.003	0.002	0.003	0.001

*TN sum of NH₄⁺+NO₃⁻-N+DON

¶DON dissolved organic nitrogen

*DN sum of NH₄⁺+TON+DON+ N₂O-N+denitrified N₂-N

†calculated from annual N₂O-N delivered to receptors divided by TN input load

‡calculated from annual N₂O-N delivered to receptors divided by DN delivered to receptors

**calculated from annual N₂O-N delivered to receptors divided by TN content in top soil

740 Table 5 Annual dissolved C (DOC; CO₂ and CH₄) effluxes from groundwater to the
 741 receptors at four experimental sites: JC (Johnstown Castle), SH (Solohead), OP (Oak Park)
 742 and DG (Dairy Gold) during 2009-2010

Groundwater C fractions	JC		SH		OP		DG	
	2009	2010	2009	2010	2009	2010	2009	2010
DOC (kg ha ⁻¹)	28	12	12	5	6	2	7	3
CO ₂ (kg C ha ⁻¹)	314	130	254	73	83	28	210	113
CH ₄ (kg C ha ⁻¹)	1.73	1.07	0.09	0.14	0.04	0.01	0.01	0.01
CO ₂ lost (%)*	0.22	0.13	0.10	0.06	0.07	0.05	0.14	0.08
CH ₄ lost (%)*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

743 *calculated from weighted mean of dissolved CO₂-C and CH₄-C divided by TC in topsoil

744 *Figure 5* (a) N₂O, (b) CO₂ and (c) CH₄ concentrations in groundwater at four experimental
745 sites: Johnstown Castle (JC), Solohead (SH), Oak Park (OP) and Dairygold (DG)
746 in 2009 and 2010 (mean $\pm$ SE, n=24)

747 *Figure 6* (a) mean dissolved N₂O-N, (b) CO₂-C (c) CH₄-C concentrations over time at four
748 sites: Johnstown Castle (JC, n=15), Solohead (SH, n=9), Oak Park (OP, n=6) and
749 Dairygold (DG, n=6) (mean $\pm$ SE)