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<td>Author(s)</td>
<td>Healy, Mark G.</td>
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<td>Publication Date</td>
<td>2013</td>
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<td>Link to publisher's version</td>
<td><a href="http://dx.doi.org/10.3318/BIOE.2013.13">http://dx.doi.org/10.3318/BIOE.2013.13</a></td>
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SPATIAL AND TEMPORAL VARIATIONS OF NUTRIENT LOADS IN OVERLAND FLOW AND SUBSURFACE DRAINAGE FROM A MARGINAL LAND SITE IN SOUTH EAST IRELAND

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Keywords: Grasslands, Nutrient losses, Food Harvest 2020, Sustainable Intensification
ABSTRACT

In Ireland, Food Harvest 2020 focuses on increasing productivity whilst enhancing environmental sustainability of agricultural land. On under-utilised or marginal land, drainage systems may be installed to expand agricultural enterprises. Mixed nutrient losses are inevitable from any drained system, but assessing processes leading to differences in nutrient speciation, fractionation and losses in grasslands between locations or flowpaths is important to achieve sustainability. This study investigates these processes in overland flow and subsurface drains over three rainfall events from four non-grazed plots recently converted from marginal land in the southeast of Ireland. A shallower water table and smaller plot size resulted in greater water and nutrient losses in overland flow per unit of land area. Nutrient losses were less in subsurface drains. Dissolved organic nitrogen dominated, but dissolved inorganic nitrogen was more abundant in the drains. Particulate phosphorus generally dominated in drains, except in plots with a shallow water table where dissolved unreactive phosphorus (DUP) was more abundant. In overland flow, a shallower water table resulted in a switch from dissolved reactive phosphorus (DRP) to DUP. Fertilization strongly increased phosphorus losses in overland flow, with DRP dominating. These results highlight the importance of an integrated assessment of the controls on flow and nutrient losses to design drainage systems in marginal lands.
INTRODUCTION

In Ireland, Food Harvest 2020 (Anon 2010) outlines the future vision for Irish agriculture. It focuses on increasing productivity while enhancing the environmental sustainability of agricultural land. Within this framework, abolition of European Union (EU) dairy milk quota in 2015 (CEC 2008) will allow for the expansion of the dairy sector. Approximately 29% of Irish grasslands have poorly-drained soils (EEA 2009; Fealy et al. 2009). On such marginal land, the water table in floodplains or in areas of a perched aquifer is often shallow (Misstear et al. 2009). These conditions, as well as high rainfall, result in excess water in the soil, which can strongly reduce grass yields, as well as limit access to the fields by grazing animals and machinery during wet periods (Mulqueen 1985; Brereton and Hope-Cawdery 1988; Armstrong and Garwood 1991; Lalor and Schulte 2008). Often in these areas, artificial drainage systems need to be installed to allow sustainable grass production (Galvin 1983). Thus, implementation of designed drainage systems (artificial pipes with drain spacing and depth estimated using soil physical parameters) and renovation or maintenance of existing systems (tile drains and mole drains) on under utilised or marginal land, is likely to increase in the coming years in order to develop new grassland areas for use by the dairy sector. In addition, previously drained land will need modernization.

In agricultural landscapes, nutrients in water can originate directly through fertilizer application or animal excreta, or indirectly due to the effect of poaching of land by cattle on nutrient infiltration and cycling in soils (Richards et al. 2009; Watson and Foy 2001). Enhancing the drainage capacity of poorly-drained soils can increase or decrease losses of these nutrients to the environment (Skaggs et al. 1994). Artificially lowering the water table can also result in bypassing areas of high natural attenuation and further increase nutrient losses (Gold et al. 2001). In turn, increasing nutrient loading to surface water and
groundwater bodies above the natural recycling or retention capacity of these ecosystems can lead to: 1) exceeding drinking water quality standards, as defined by the EU Water Framework directive (EU-WFD; CEC 2000); 2) increasing primary production favouring eutrophication in a surface waterbody (Smith et al. 1999; Watson and Foy 2001; Khan and Ansari 2005; Rivett et al. 2008); and 3) enhancing greenhouse gas emissions from unsaturated and saturated zones (Watson and Foy 2001; Reay et al. 2003; Stark and Richards 2008b).

At present in Ireland, land drainage in agriculture areas is regulated through the European Communities (Environmental Impact Assessment) (Agriculture) Regulations 2011 (CEC 2011). Under this legislation, an Environmental Impact Assessment (EIA) has to be undertaken for works involving more than 15 ha of land or where the farmer feels that drainage may have a significant effect on the environment (DAFF 2011). Nevertheless, this legislative framework does not provide guidelines for the design of subsurface drainage systems in Ireland. Failure in adapting a drainage design to local soil, hydrogeological or climatic conditions can result in enhanced nutrient losses from grassland fields (Skaggs et al. 1994; Gilliam et al. 1999). There is a need to propose guidelines for the design of drainage systems in contrasting natural Irish settings for variable soil, subsoil and aquifer types in different rainfall regimes.

Before such guidelines are developed, a sound understanding of the controlling factors on nutrient losses in surface and subsurface hydrological pathways is needed. Briefly, spatial and temporal variations in surface and subsurface nutrient losses relate to: 1) anthropogenic factors, such as design of drainage systems (Skaggs et al. 1994; Kladivko et al. 2004), timing of fertilizer application (Olness et al. 1980; Hart et al. 2004), excessive fertilization (Jordan et al. 2000; Watson and Foy 2001), or modification of soil properties through the use of
machinery or animal grazing (Watson and Foy 2001); and 2) natural factors, such as variations in event and antecedent hydrometeorological conditions (Heathwaite and Dils 2000; Hart et al. 2004; Haygarth et al. 2004; Kurz et al. 2005; Doody et al. 2006), soil types and microbial activity (Daly et al. 2001; Watson et al. 2007; Stark and Richards 2008a; Ghani et al. 2010), plot size or slope, or depth of the water table. Furthermore, spatial and temporal patterns of total nutrient losses and nutrient bioavailability from surface runoff and subsurface drainage systems can differ strongly (Gilliam et al. 1999). Overall, these differences relate to the total amount of flow generated by these systems for a given rainfall input, and to the contribution of water from different surface and subsurface flow-paths (Haygarth et al. 2005; Ghani et al. 2010), which will differ in terms of intensity of soil-water interactions and/or groundwater inputs.

The objectives of the current study were to investigate the division of nutrient speciation and loads between surface and subsurface drainage over three rainfall events. More specifically, the research assesses to what extent spatial variations of plot size and slope within a similar landscape position, soil characteristics and groundwater patterns impact flow generation, as well as losses and bioavailability of nutrients in overland and subsurface drain flow systems.

In order to address these issues, this paper formulates the following hypotheses:

1-Spatial variation of flow and solutes between plots are smaller than temporal variations for each plot between rainfall events;

2-Nutrient load variability reflects overland and subsurface flow patterns and anthropogenic inputs;
The occurrence and proportions of different species and fractions of P and N are controlled by the contribution of different proportions of water originating from a rainfall event (event water) or stored in the subsurface (pre-event water).

MATERIALS AND METHODS

FIELD SITE

This study was conducted between January and April 2009 on a 4.2-ha study area, divided into six un-grazed grassland plots within the same landscape position, located on a beef farm at the Teagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford, SE Ireland (52° 17' 36" N, 6° 31' 6" W). The soil and subsoil onsite originates from heterogeneous glacial parent material, which is underlain by Pre-Cambrian greywacke, schist and massive schistose quartzites that have been subjected to low grade metamorphism (Fenton et al. 2009). Four plots (1, 2, 3 and 4) were used in the study (Fig. 1). Plot areas and slope, and soil texture and nutrient concentrations are presented in Tables 1 and 2. The design of the site ensures no runoff from adjacent (1.5-m-deep drains) or up-gradient (3-m-deep drains) sites can enter the isolated plots. Overland flow was collected in a surface drain at a low point within each plot and transported off site to a v-notch weir setup (Fig. 1). The site had a subsurface herring bone drainage system at 1 m bgl (tapping into higher permeability subsoil) made of corrugated pipes (15 cm, inner diameter) fitted with a gravel pack (washed and less than 20 mm in size), with drain spacing of 10 m and connected to another set of v-notch weirs (outflow of the drainage network). This allowed for the monitoring and sampling of subsurface drain flow. Flow through the v-notch weirs (for both runoff and drain flow) was measured using a calibrated pressure transducer (Sigma, Hach Company, USA). Three
shallow piezometers (4.5-m-depth, screen interval 1 m at end of casing) were drilled to below lowest water strike within each plot (Fig. 1), each fitted with a mini-diver (Schlumberger Water Services, Delft, Netherlands) to record variations of water level at 15-min-intervals.

**AGRONOMIC MANAGEMENT**

Plots received fertilizer inputs of nitrogen (N) fertilizer (applied twice a year) and phosphorus (P) and potassium (K) (applied once a year). For the period of study, P and K were applied on the 21st and 22nd March 2009 at a rate of 37 Kg ha\(^{-1}\) P and 74 Kg ha\(^{-1}\) K, respectively, while N fertilizer application in the form of urea was applied to all plots at a rate of 118 Kg ha\(^{-1}\) N on the 23rd March 2009. The plots were re-seeded at establishment in 2001 and left ungrazed until the experiment stated. All plots were sown with mid-season yielding variety of Lolium perenne. Subject to soil conditions, plots were cut three times a year for silage (last week in May, last week in July and last week in September/first week in October). After the study period, a second application of N, in the form of calcium ammonium nitrate (101.8 kg ha\(^{-1}\) N), was applied after the first cut. Plots received no other inputs.

**CLIMATE AND SOIL MOISTURE DEFICIT**

The study area has a cool maritime climate, with mean annual precipitation 1002 mm, effective rainfall ranging 400 to 500 mm, and mean annual air temperature of 9.6°C (Ryan and Fanning 1996). Daily weather data were recorded at the Johnstown Castle Weather Station and were used to estimate soil moisture deficit (SMD) for moderately-drained soil using the Hybrid model (Schulte *et al.* 2005).

**WATER SAMPLING AND ANALYSIS**

Water samples from v-notch weirs were taken on a flow-weighed basis using a 900 Max Portable auto-sampler (Sigma, Hach, USA). Filtered (0.45 µm membrane) and non-filtered
water samples (20 ml) were analysed using a Thermo Konelab 20 analyser (Technical Lab Services, Ontario, Canada). Total dissolved nitrogen (TDN) consists of dissolved inorganic nitrogen (DIN, sum of nitrate (NO$_3$-N), nitrite (NO$_2$-N), ammonia (NH$_3$-N) and ammonium (NH$_4$-N)) and dissolved organic nitrogen (DON = TDN-DIN). Total P consists of particulate P (PP) and total dissolved P (TDP), with TDP being the sum of dissolved reactive P (DRP) and dissolved unreactive P (DUP).

**GEOPHYSICAL SURVEY AND SOIL ANALYSIS**

Several 2D resistivity profiles (to a depth of 50 m) and electromagnetic surveys (to a depth of 5 m) were used to develop a conceptual model of the site, to ascertain soil/subsoil material and bedrock type and quantify depth to bedrock on site (Fig. 1). Soil samples were taken from the top, middle, bottom of each plot, and soil texture was obtained using particle size distribution techniques using the sieving and pipette method (BS 1796; BSI 1989) (Table 1). Plot soil nutrient status (Table 2) was determined on soil samples (0-0.3m) at the top, middle and bottom segments of each plot and were analysed using Morgan’s extractant (Morgan 1941) for soil test P, K$^+$ and magnesium Mg$^{2+}$ (Table 2). Total Nitrogen was analysed after KCl extraction on a TN analyser (TNM-1, Shimadzu Corporation, Kyoto, Japan). According to previous soil analysis (unpublished Johnstown Castle soil and land use summary report), Carbon (C) /N ratios at the sites are between 8.3 and 11.4.

**RAINFALL EVENT DELINEATION AND CHARACTERIZATION**

Three events, the two first in Winter (Event 1 and 2, starting on the 11$^{th}$ January and 24$^{th}$ January 2009, respectively) and the second in Spring (Event 3, starting on the 24$^{th}$ April 2009) were used in this study. These events were chosen to represent contrasting pre-event and event rainfall and SMD patterns (Figs 2 and 3) and to discuss incidental losses of
nutrients following a fertilizer application. Event 1 was the first significant event occurring after a dry period (peak of 12.9 mm of SMD immediately before the event), while Event 2 occurred during a wet period (peak of -7.0 mm of SMD immediately before the event). Event 3 occurred in intermediate weather conditions (SMD ranging from -4.7 to 10.6 mm before the event), at 36 days after fertilizer application. Absence of rainfall for more than 12 h was used to separate one rainfall event from the other (Kurz et al. 2005). The slopes of cumulative overland and drain flow were computed at hourly intervals. According to Vidon and Cuadra (2010), the start of a flow event can be delineated when a “perceptible rise in discharge” occurs. Accordingly, in the present study, the start of an overland or subsurface drain flow event occurred when the slope of the cumulative flow exceeded the maximum slope observed for the 12 h preceding the rainfall event. Similarly, the end of the flow event occurred when the slope of the cumulative flow reached smaller value than the maximum observed before the event.

Runoff coefficients in overland and subsurface drain flow were defined as the ratio of total runoff and rainfall depth (both in mm) for the event (Macrae et al. 2010). Loads of dissolved and particulate N and P species and fractions for a time interval were calculated by multiplying the mean concentration of the species and fractions by the corresponding flow occurring during the interval (Kurz et al. 2005). Total loads for single flow events were computed by adding the loads from each sampling interval occurring during the event.

RESULTS

PRE-EVENT AND EVENT HYDROMETEOROLOGICAL CONDITIONS
Total precipitation was the greatest for Event 3 and the smallest for Event 2 (29.3 and 12.3 mm, respectively, Fig. 2a), while rainfall intensity was the greatest for Event 3 and the smallest for Event 1 (1.5 and 0.5 mm hr\(^{-1}\), respectively, Fig. 2a). Maximum rainfall intensities were more comparable between events, with a minimum value observed for Event 2 and a maximum for Event 1 (3.6 and 6.8 mm hr\(^{-1}\), respectively). Pre-event cumulative rainfall (Fig. 2b) was the lowest for Event 1 (0.1 mm in the pre-event 14 days, and 30.4 mm in the 30 pre-event days) and the highest for Event 2 (up to 92.5 mm in the 30 pre-event days), while Event 3 had intermediate values. This resulted in generally 1) shallower groundwater depths before Event 2 (Fig. 2c) and larger depths before Events 1 and 2), a sharp decrease from positive to negative SMD at the start of Event 1 and 3, and fluctuating negative SMD between Event 1 and 2 (Fig. 3).

**OVERLAND AND SUBSURFACE DRAIN FLOW PATTERNS**

*Flow variations across plots*

Overland total flow values (Fig. 4a) and runoff coefficients (Fig. 4c) for the three events increased from Plot 2 to Plot 4 (Plot 2 < Plot 1 < Plot 3 < Plot 4, up to 2.5 times more flow for Plot 4 than for Plot 2). Subsurface drain total flow patterns (Fig. 4b) were less consistent (e.g. flow in Plot 4 was higher than in Plot 1 and 2 for Events 2 and 3, but smaller than for Plot 1 for Event 1). Nevertheless, runoff coefficients for subsurface drain flow (Fig. 4d) were generally ordered in a similar way than total flow values.

For all three events, there was between 2.1 to 6.9 more total flow measured in overland flow than in the subsurface drains. For Event 1 and 2, Plot 1 had the smallest ratios of overland and subsurface drain flow (down to 2.1), while Plot 4 had the biggest (up to 4.9); in contrast, Plot 1 had a greater ratio than Plot 4 for Event 3 (6.9 and 6.3, respectively).
Flow variations across events

In general, total overland flow (Fig. 4a) was slightly smaller for Event 2 than for Event 1 and increased greatly for Event 3 (up to 2.8 times more flow for Plot 1 for Event 3 than for Event 1). Runoff coefficients in overland flow (Fig. 4c) had different patterns. They were minimal for Event 1 and maximal for Event 2, except for Plot 1, where a small increase was observed between Events 2 and 3; differences in runoff coefficients between Plots 1 and 2, and Plots 3 and 4 were also more variable, with maximum differences observed for Event 2 (coefficient 2.5 times higher for Plot 4 than for Plot 2).

As in overland flow (Fig. 4a), subsurface drain total flows (Fig. 4b) decreased from Event 1 to Event 2 for Plots 1 and 2 (up to 2.1 times less for Plot 2). For these two plots, even if the flows increased for Event 3, they remained lower than for Event 1. A reverse pattern was observed for Plot 4: an increase was observed between Events 1 and 2 (1.5 times more flow), and a subsequent decrease between Events 2 and 3 (1.4 times less flow). Runoff coefficients in subsurface drain flow (Fig. 4d) had similar patterns than total flow for Plot 4 (Fig. 4b), but they were reversed for Plots 1 and 2.

For Plots 1 and 2, ratios of overland and subsurface drain total flow increased from Event 1 to Event 3 (up to 3.3 times greater for Plot 1). In contrast, for Plot 4, they decreased from Event 1 to Event 2 (1.6 times less), and increased from Event 2 to Event 3 (2.1 times more).

GROUNDWATER CHEMISTRY

The concentrations of PP, TDP, NH$_4$-N and NO$_3$-N for selected piezometers sampled on the 5$^{th}$ March 2009 are presented in Table 3. Particulate phosphorus concentrations were all below detection limits, while TDP concentrations were similar at Plots 2, 3 and 4 (overall range of 0.008 to 0.020 mg L$^{-1}$) and below detection limits at Plot 1. There were no spatial
concentration trends within the plots. Ammonium concentrations were similar across plots (overall range of 0.054 to 0.071 mg L$^{-1}$). Average NO$_3$-N concentrations were lower and displayed more variations in Plots 1 and 2 than in Plots 3 and 4 (average of 4.7 and 8.7 mg L$^{-1}$, respectively).

**NUTRIENT PATTERNS**

**Total P and TDN variations**

Flow-weighted mean concentrations of TP and TDN for all plots and events are presented in Table 4, and the corresponding total loads (in g ha$^{-1}$) in Figs 5a to 5f. For the events before fertilization (Events 1 and 2), flow-weighted mean concentrations of TP and TDN in overland flow increased from Plot 1 to Plot 3 and 4 (up to 1.6 times more TP and TDN). Plot 2 had the highest concentrations for Event 1, and intermediary concentrations between those of Plot 1 and 3 for Event 2. Similarly, total loads of TP and TDN in overland flow increased from Plot 1 to Plot 4, but to a greater extent than flow-weighted mean concentrations (up to 3.3 times more TP and 2.9 times more TDN for Plot 4 than for Plot 1, Fig. 5a to 5d). For the event after fertilization (Event 3), Plot 2 had the highest flow-weighted mean concentrations of TP and TDN. Otherwise, there were no clear spatial trends in flow-weighted mean concentrations across plots for this event. Both TP and TDN loads were slightly smaller for Plot 2 than for Plot 1 (Fig. 5e to 5f), but still greater for Plots 3 and 4 (1.5 more TP and 1.4 more TDN for Plot 4 than for Plot 2).

In overland flow, Event 3 had the highest flow-weighted mean concentrations of TP and the highest loads of TP and TDN (up to 183.2 and 144.4 g ha$^{-1}$, respectively, Fig. 5e to 5f). Similarly, Event 2 had the lowest flow-weighted mean concentrations of TP and the lowest loads of TP and TDN (down to 2 and 31.2 g ha$^{-1}$, respectively, Fig. 5c to 5d). Increases in
total loads of TP in overland flow for Event 3 (16.1 to 30.4 times more loads for Event 3 than for Event 1) were much higher than for TDN (1.3 to 3.1 times more loads for Event 3 than for Event 1).

In subsurface drains, flow-weighted mean concentrations of TP and TDN were more variable between plots than in overland flow. Total dissolved nitrogen loads increased from Plot 2 to Plot 4 for Event 1 (Fig. 5b), and from Plot 1 to Plot 4 for Event 2 (Fig. 5d). Total phosphorus loads behaved similarly for Event 2 between Plots 1 and 4 (Fig. 5c), but they decreased from Plot 1 to Plot 3 for Event 1 (Fig. 5a).

In contrast to overland flow patterns, ranges of flow-weighted mean concentrations and total loads of TP and TDN in subsurface drains between events were very comparable (total loads of 0.5 to 4.7 g ha\(^{-1}\) and 6.2 to 61.9 g ha\(^{-1}\) for TP and TDN, respectively, across all plots and events). For the same plots, flow-weighted mean concentrations of TP and TDN were generally smaller for Event 2, while they were more similar for Events 1 and 3. There were few variations in loads of TP and TDN between events at the same plots, except for Plot 1, where they were maximum for Event 2 (6.4 and 9.7 times more P and N at Event 2 than Event 1, respectively) and minimum for Event 1.

**Phosphorus and N speciation and fractionation patterns**

For the events before fertilization, dissolved reactive phosphorus was the most abundant P fraction in overland flow for Plots 1 and 2 for Event 1 (49.9 and 53.1% of TP loads, respectively, Fig. 5a) and for Plot 2 for Event 2 (39.2% of the TP loads, Fig. 5c), and in much greater proportions in all plots for Event 3 (from 78.8 to 83.3% of TP loads, Fig. 5e). In contrast, Plots 3 and 4 had DUP as the dominant P fraction in overland flow for Events 1 and 2 (up to 41.8 and 55.9% of TP loads for Events 1 and 2, respectively, Fig. 5a and 5c). In
contrast, PP was the most abundant fraction in subsurface drain flow for Plots 1 and 2 (up to 80.6% of TP loads) for Events 1 and 2. This was also the case for Plot 4-Event 1 (Fig. 5a); otherwise Plots 3 and 4 had DUP as the dominant P fraction in subsurface drains (up to 89.2% of total P).

Dissolved organic nitrogen was the most abundant fraction of N in both overland and subsurface drain flow (up to 99.6% of total N for Plot 1-Event 2, Fig. 5d), except for Plot 6-Event 2. The relative abundance of DIN was nevertheless generally greater in subsurface drain flow. For Events 1 and 2, this trend was more marked for Plots 3 and 4 (overall range of 25.8 to 58.2% of total N as DIN in subsurface drain flow, and only 1.3 to 3.5% in overland flow, Fig. 5b and 5d) than for Plots 1 and 2 (overall range of 6.6 to 26.2% of total N as DIN in subsurface drain flow, and 0.4 to 3.3% in overland flow). For Event 3, subsurface drain flow at Plots 1 and 4 had a relative abundance of DIN of 38.5 and 32.5% of total N as DIN, respectively (Fig. 5f).

The relative proportions of NH$_4^+$ and NO$_3^-$ in DIN are presented in Figures 6a to 6c. In overland flow, NH$_4^+$ was the only N species detected in samples for Event 1 for all plots, for Event 2 for Plots 2 and 3, and for Event 3 for Plot 2. Nitrate was also the less abundant fraction of DIN in overland flow for Plots 1 and 3-Event 3, while it was more abundant than NH$_4^+$ for only two occasions (Plot 1-Event 2 and Plot 4-Event 3). In contrast, NO$_3^-$ appeared to be the dominant fraction in all samples of subsurface drain flow, except for Plot 2-Event 1 and Plot 3-Event 3 (43.3% and 31.7% of total DIN as NO$_3^-$, Fig. 6a and 6c). In general, the relative abundance of NO$_3^-$ was greater for Plots 3 and 4 than for Plots 1 and 2.

**DISCUSSION**
This section evaluates the hypothesis that spatial variations of flow patterns between plots for the same event are smaller than temporal variations for each plot between events.

**Overland Flow**

Total flow and runoff coefficients values followed a consistent ordering in overland flow across plots for all events (Plot 2 < Plot 1 < Plot 3 < Plot 4, Fig. 4a and 4c). This pattern links to spatial differences in physical controls on runoff generation. In particular, the overall increase in runoff coefficients from Plot 2 to Plot 4 (up to 2.5 times for Event 2) can be in part linked to a decrease in surface area of up to 47% from Plots 1 and 2 to Plots 3 and 4 (Table 1). This scale dependency of runoff coefficients has been observed in numerous studies, as reviewed by Wainwright and Parsons (2002), Cerdan *et al.* (2004) or Norbiato *et al.* (2009). Joel *et al.* (2002) found that over eight rainfall events, experimental plots with a surface area of 50 m$^2$ had surface runoff coefficients of 40% less than plots with a surface area of 0.25 m$^2$. When looking at a wider range of scales over a 5-year period in predominantly arable land in Normandy (France), Cerdan *et al.* (2004) found that 450 m$^2$ plots had mean runoff coefficients 10 and 30 times greater than larger catchments of 90 and 1100 ha, respectively. In the present study, differences in size – and slope length – of the different plots were smaller than in the above studies. This suggests that the effect of plot size can only explain a part of the increase in runoff coefficients from Plots 1 and 2 to Plots 3 and 4.

Runoff coefficients also tend to increase with increasing slope (Scherrer and Naef 2003; Alaoui *et al.* 2011). Even if Plots 3 and 4 were of similar size (4080 and 4070 m$^2$, respectively, Table 1), the slightly greater slope in Plot 4 than in Plot 3 (5.4 and 4.2%,...
respectively) may be responsible for the increase in overland flow runoff coefficient. Runoff coefficients also tend to increase with decreasing soil permeability. The influence of permeability was shown at the catchment scale in northern Italy by Norbiato et al. (2009) and in a study of preferential flow in forest and grassland sites in Switzerland by Alaoui et al. (2011). In the present study, soil texture based on soil sampling to depths of 0.1 and 0.3 m was very similar between plots (Table 1), but geophysical surveys, which include subsoils, showed some differences (Fig. 1). Plots 3 and 4 had sandy, gravelly clay and less silt clay horizons than Plots 1 and 2. These patterns may have influenced the difference in runoff coefficients between these two groups of plots, but they were probably not sufficient to counterbalance the effect of other parameters, such as plot size. Nevertheless, when comparing Plots 1 and 2, the greater proportion of silt-clay horizons in Plot 2 may explain the higher overland runoff coefficients observed in Plot 2 than in Plot 1.

In addition to these differences in plot size and sediment characteristics, a shallower water table in Plots 3 and 4 than in Plots 1 and 2 (Fig. 2c) also possibly implies that a greater amount of rainfall was required in these latter plots to reach saturation of the soils, further enhancing the effect of plot size on runoff generation. As pointed out by Doody et al. (2010), infiltration excess overland flow can dominate over saturation excess overland flow in poorly-drained soils in Irish grasslands, in particular in areas of high soil water repellency. In the present study, the respective importance of both processes was difficult to assess, as no field measurements where available to compare the volumetric soil moisture to the soil field capacity. As all plots had a very similar soil texture, it is therefore likely that they had very similar infiltration capacity. Nevertheless, saturation excess overland flow would probably occur more often where the water table is shallower i.e. in Plots 3 and 4 (water table depth
often shallower than 0.5 m for the period of study), as well as towards the bottom of the slopes.

Overland flow runoff coefficients (Fig. 4c) were at a maximum for Event 2 for all plots except Plot 1, and were at a minimum for Event 1. Event and pre-event - or antecedent - hydrologic conditions need to be accounted for in the discussion of these patterns. An increase in total rainfall or rainfall intensity, as well as wetter antecedent conditions, have been shown to increase surface runoff coefficients (Norbiato et al. 2009; Macrae et al. 2010; Vidon and Cuadra 2010; Vidon and Cuadra 2011). Accordingly, an increase in rainfall intensity and total rainfall between Events 1 and 3, as well as wetter pre-event conditions, as indicated by higher pre-event cumulative precipitation and a shallower water table in the majority of wells, can explain the increase in runoff coefficients between Events 1 and 3. In contrast, the high increase in runoff coefficients from Event 1 to Event 2 is not related to an increase in event precipitation, but rather to much wetter antecedent conditions for Event 2 than for other events.

**Subsurface drain flow**

Subsurface drains generated less flow than surface flow systems (Fig. 4b). They also lacked a consistent ordering of total flow and runoff coefficients observed across plots in overland flow. There were nevertheless clear differences in flow behaviour between plots for each event. Vidon and Cuadra (2010) also observed large variations (often > 50%) of flow generation between two nearby tile drains of the same design installed within a similar soil type. In the present study, the design of the drainage system was identical for all plots. Therefore, differences in drain flow patterns could not be related to factors related to drainage design criterion (Kladivko et al. 2004), but rather to the inherent soil and subsoil
heterogeneity of the plots, which impact the hydrological connectivity between the surface
and the subsurface drains.

Instead, variations in drain flow patterns across plots for different events highlight some
similarities with overland flow behaviour. For Event 2, wetter pre-event hydrological
conditions, in particular, appeared to result in the greatest runoff coefficients (Fig. 4d), with
the greatest increase for Plot 4 and the lowest for Plot 2. This pattern was probably related to
spatial variations in water table depth across plots, with groundwater inputs to the subsurface
drains being more important in wetter periods in areas of shallower water table (Plot 4) than
in areas of deeper water table (Plots 1 and 2). Similarly, the small increase in subsurface
runoff coefficient between Events 1 and 3 for Plot 4 may be related to increased inputs in
both pre-event and event water, as indicated by both wetter pre-event conditions and higher
precipitation for the event (total precipitation and rainfall intensity, Fig. 2a). In contrast to
what the hypothesis suggested, spatial differences in overland and subsurface drain flow
patterns can be greater between plots than between events for the same plots. Overland flow
patterns were nevertheless clearly different between Plots 1 and 2, and Plots 3 and 4; indeed,
if these two pairs of plots are considered separately, their flow patterns confirm our
hypothesis.

**CONTROLS ON SPATIAL AND TEMPORAL VARIATIONS IN TDN AND TP LOADS**

This section evaluates the hypothesis that TDN and TP load variability is inherited from
overland and subsurface flow patterns and anthropogenic inputs.

*Overland flow*
In overland flow, variations of loads of TP and TDN across plots appeared to follow the same ordering than that of total flow and runoff coefficients for Event 3 (Plot 2<Plot 1<Plot 3<Plot 4, Fig. 4a, 5e and 5f), while for the other events, values were smaller for Plot 1 than for Plot 2. Furthermore, increases in loads of TP and TDN between plots were similar to the increase in total flow generation. For example, in Event 2, 2.1 times more flow was generated for Plot 3 than for Plot 1, resulting in a 3.3 and 2.3 times increase in loads of TP and TDN, respectively. For the same plots during Event 3, 1.2 times more flow resulted in a similar increase in loads of TP and TDN. Kurz et al. (2005) showed in a similar setting that P losses would increase in overland flow with increasing soil test P concentration in soils. This confirmed the findings of other studies (Sharpley 1995; Smith et al. 1995; Heckrath et al. 1995; Hesketh and Brookes 2000; Hart et al. 2004; Watson et al. 2007). Similarly, high N losses in surface runoff often occur as incidental losses under standard or excessive fertilizer applications (Cuttle and Scholefield 1995; Scholefield and Stone 1995). The present study considered soils with very similar Morgan’s P concentrations (arithmetic mean of 2.8 to 3.9 mg L⁻¹, low P-index, Table 2) compared to a range of 4 to 17 mg L⁻¹ in Kurz et al. (2005), as well as identical fertilizer applications across plots. The lack of strong variability in P and N availability in soils, or through fertilizer application across plots, explains the general absence of large differences in TP and TDN flow-weighted mean concentrations in overland flow. The increase in flow-weighted mean TP concentrations from Plot 1 to Plot 4, possibly related to the contribution of water with higher TP concentrations at Plots 3 and 4, contributes to the overall increase in TP loads across plots. Nevertheless, the absence of such patterns for TDN, and the good correlations between flow and total load variations suggest that spatial variations in nutrient losses in overland flow are primarily controlled by differences in flow generation across plots.
Variations in TP and TDN loads between Event 1 and 2 in Plot 3 were proportional to those of flow generation i.e. 1.2 times more flow for this plot between these two events resulted in 1.4 greater P but similar N losses (Fig. 4a, and Fig. 6a to 6d). Nevertheless, the higher TP and TDN flow-weighted mean concentrations for Event 1 than for Event 2 for Plot 2 (Table 4) resulted in 2.5 times more TP loads for Event 1 than for Event 2, and up to 1.7 times more TDN loads, for similar volumes of water (Fig. 4a, and Fig. 5a to 5d). The strong increase in TP losses for Event 3 relates to the application of fertilizer on the 20th and 21st March 2009 (i.e. 36 days before the start of the event). This pattern relates to a change from small critical P losses in a low P-index context to high incidental losses resulting from the occurrence of rainfall events after the spreading of fertilizers (Haygarth et al. 1999). Increases in TP of 16.1 to 30.4 times greater than for Event 1 are within the range shown by other studies (see Hart et al. (2004) for a review). For example, TP losses for native grassland watersheds in Oklahoma (USA) increased 10 to 25 times after application rates of 75 kg P ha\(^{-1}\) of ammonium phosphate fertilizer (Olness et al. 1980; Hart et al. 2004). In contrast to this, Kurz et al. (2005) reported no obvious increase in DRP levels in overland flow 44 days after the application of P fertilizer in mid-March; they attributed this result to a “time lag” effect, as rainfall only occurred 44 days after the fertilizer application. Ideally, advice on the timing of fertilizer spreading should account for variations in rainfall patterns occurring over similar periods; nevertheless, present weather forecast capabilities do not allow to do so. In the present study, N fertilizers were applied two to three days after P fertilizer. The small increase in TDN losses in overland flow at Event 3 reflects an increase in flow generation for this event (up to 2.8 times greater flow, for up to 3.1 times greater TDN losses). This pattern suggests that the time lag between fertilizer application and Event 3 was enough to mobilize excess N, either by biological processing or through losses along surface and subsurface flowpaths.
Subsurface drain flow

As in overland flow, differences in loads of TP and TDN between plots in subsurface drain flow often followed the flow generation sequence for the same event, whereas differences between events were more variable (Fig. 4b and 5). Furthermore, Event 3 was not characterised by a large increase in TP loads as in overland flow (Fig. 5e and 5f). Indeed, for this event, loads of TP and TDN in subsurface drain flow were similar to those observed for Event 1. This pattern suggests that soil-water interactions, as well as losses of nutrients in overland flow, were sufficient to significantly buffer the effect of P fertilisation on incidental losses, or that transit times of P towards the subsurface drains are longer than the period between the application of fertilizers and Event 3.

Overland flow versus subsurface drain flow

Loads of TP and TDN in subsurface drain flow were, in general, significantly smaller than those in overland flow (2.3 to 123.1 times higher TP loads, and 2.6 to 5.0 times higher TDN loads in overland flow), except for Plot 1-Event 1 (1.1 and 1.6 times less TP and TDN loads, respectively, in overland flow than in subsurface drain flow, Fig. 5). Haygarth et al. (1998) related higher mean concentrations of TP in the shallowest horizons of the soil to a greater soil test P. Indeed, P is often considered to be retained in the shallow subsurface. In the present study, the smaller loads of TP and TDN in the subsurface drainage system could be attributed to a combination of such processes, and to the fact that smaller amounts of water were generated by the subsurface drainage system. For example, in Event 1, ratios of loads of TP between overland and subsurface drainage flow were larger than ratios of overland versus subsurface drainage flow for all Plots except Plot 1 (up to 17.5 times less P in subsurface drainage flow for 6.5 times less flow for Plot 3), while there was an overall decrease in TP flow-weighted mean concentrations between overland and subsurface drainage flow. This
suggests that the reduction in TP loads in the subsurface drainage system comparatively to the surface system is potentially a result of: 1) P retention in the shallow soil, 2) dilution with water from subsurface flowpaths less concentrated in TP and 3) smaller amount of flow in the subsurface drains. In contrast, for the same event, ratios of loads of TDN between overland and subsurface drainage flow were slightly smaller than ratios of overland and subsurface drainage flow, except for Plot 2, while TDN flow-weighted mean concentrations were often higher in the subsurface drainage system. This specific pattern suggests losses of N from the subsurface flowpaths to the subsurface drains.

**PHOSPHORUS FRACTIONATION AND N SPECIATION**

This section tests the hypothesis that the occurrence and proportions of different species and fractions of P and N are controlled by the contribution of different proportions of water originating from a rainfall event (event water) or stored in the subsurface (pre-event water).

**Phosphorus fractions**

The predominance of dissolved forms of P in overland flow possibly reflects particle retention by the vegetation and limited erosion in the absence of livestock (Haygarth *et al.* 1997; Hart *et al.* 2004; Heathwaite and Dils 2000). McDowell and Sharpley (2002) observed through rainfall experiments that PP increased with increasing distance along the slope in un-manured grass plots. In the present study, differences in plot size – and slope length – did not seem to impact on the relative proportion of PP in overland flow. The predominance of DRP in overland flow for Plots 2 and 1-Event 1 and for Plot 2-Event 2 (Fig. 5a and c) reflects the result of previous studies (Haygarth *et al.* 1997; Heathwaite and Dils 2000; Hart *et al.* 2004). The higher contribution of pre-event water for Plots 3 and 4 is probably responsible for the fact that DUP was the major fraction of P released at these locations for the first two events.
Indeed, processing of P by plants and soil biota, as well as higher adsorption of DRP in soils, cause increases in organic forms of P in pre-event water (Haygarth et al. 1998; Reynolds and Davies 2001; Gburek et al. 2005). Dissolved reactive phosphorus was nevertheless the most abundant P fraction in overland flow for all plots for Event 3 (Fig. 5e). This pattern probably relates to the application of mineral P fertilizers 36 days before the event (Hart et al. 2004), which effectively overrides differences in the respective contribution of pre-event and event water across plots or events. As in overland flow, the predominance of DUP in subsurface drainage flow at Plots 3 and 4 is probably linked to the predominance of pre-event water. In contrast, in Plots 1 and 2, where the water table is deeper, the predominance of PP can be indicative of the development of preferential flow along macropores, in areas of finer soil texture than those found in Plots 3 and 4 (Heathwaite and Dils 2000; Kramers et al. 2009, 2012).

**Nitrogen species**

As in few previous studies, DON was generally the predominant form of N in overland and subsurface drain flow for all events. Streeter et al. (2003) also found that DON amounted to over 90% of TN in soil water and surface water (lake water, as well as lake inflow and outflow) in upland semi-managed grassland in Cambria (UK). Similarly, Willett et al. (2004) found that DON represented from 40% to over 85% of the total nitrogen pool in streams and lakes in Wales (UK), in areas predominantly covered by grazed grasslands and forests. A similar predominance of DON over inorganic forms of N was observed in soil water under pasture (Ghani et al. 2010) or un-grazed grassland (Dijkstra et al. 2007; van Kessel et al. 2009). In the present study, this pattern probably relates to the use of Urea as N fertilizer in Spring, to the uptake of DIN inputs through fertilization by grass species as well as to high rates of organic matter decomposition in the soil (Stark and Richards 2008a; van Kessel et al.
Several studies and reviews show the need to better assess the importance of DON losses to groundwater and surface water systems (Seitzinger and Sanders 1997; Pellerin et al. 2006; Willett et al. 2004; van Kessel et al. 2009). These works especially highlight that the bioavailability of DON in aquatic ecosystems - and its contribution to eutrophication - and the overall function of DON in the N cycle should be more accounted for.

The shift from NH\textsubscript{4}\textsuperscript{+} dominated water in overland flow to NO\textsubscript{3}\textsuperscript{-} dominated water in subsurface drain flow (Fig. 6), and the greater loads of DIN in the subsurface drain flow further indicate the impact of soil microbial activity (i.e. nitrification; Stark and Richards 2008a) on the chemical transformation of N in the subsurface. Here again, a shallower water table for Plots 3 and 4 probably relates to higher inputs of NO\textsubscript{3} in the subsurface drainage system than for Plots 1 and 2. Higher concentrations of NO\textsubscript{3}-N than NH\textsubscript{4}+N in groundwater, as well as higher NO\textsubscript{3}-N concentrations at Plots 3 and 4 than at Plots 1 and 2, confirm this process. In contrast, higher NH\textsubscript{4}+ concentrations in Plots 1 and 2 possibly relate to quick transfer of NH\textsubscript{4}+ in macropores (Kramers et al. 2009); the absence of an increase in P in the subsurface drains for Event 3 nevertheless suggest that this pathway is of small importance. Alternatively, limited nitrification in areas of higher than optimal soil water content (Grundmann et al. 1995) could explain this pattern.

**MANAGEMENT IMPLICATIONS**

This study highlights the necessity to adopt a common holistic and interdisciplinary framework, which seeks to identify the controlling factors for water and solute losses in both surface and subsurface environments in Irish marginal lands. Due to the mixed nature of nutrient losses (i.e. both P and N losses) in surface and subsurface drainage, any end-of-pipe solution to ameliorate discharges must consider both nutrient types. In addition, buffer strip areas positioned at the bottom of slopes can decrease such losses, providing the subsurface...
drainage system does not extend into these areas and the outflow still exists further down-gradient.

**Plot size**

In this study, the size of the plots – and the correlated slope length – appears to relate to the volume of water generated by unit of land area (i.e. in mm) and total loads of P and N (in g ha\(^{-1}\)) in overland flow. As pointed out above, it was difficult to quantify the importance of these controls with respect to others such as watertable depth. It is nevertheless likely that in this kind of setting, significantly increasing field size will result in a decrease of nutrient losses in overland flow. In contrast, the decrease in flow volume and nutrient loads with increasing field size were not compensated by correlated increases in subsurface drain flow. This suggests that other pathways such as evapotranspiration, losses to groundwater, or retention in the soil, are enough to compensate for the difference. In Ireland, the mean size of permanent pastures not classified as commonage is 5.5 ha (standard deviation of 12.2 ha). A median size of grassland fields of 3 ha was determined by excluding extreme outliers (CEC 2001). In areas where the natural attenuation capacity of nutrients in subsurface flowpaths is enough to accommodate increasing nutrient loads, increasing field size could be considered as a measure to limit nutrient losses to a connected waterbody.

**Water table depth**

Generally, fields with similar soil characteristics will generate more overland flow where the water table is shallow when compared with areas where more rainfall is needed to reach full saturation (Doody *et al.* 2010). In the present study, this mechanism, in conjunction with the increase in plot size, was probably responsible for the increase in the volume of water and in the total loads of P and N generated in overland flow from Plots 1 and 2 (deeper water table)
to Plots 3 and 4 (shallower water table). Subsurface drain flow also increased more at Plots 3 and 4, further enhancing nutrient losses. In addition, for events preceding the application of fertilizer, a shallower water table depth across plots related to: 1) an increase in the proportions of DUP over DRP in overland flow, and those of DUP over PP in subsurface drain flow; 2) an increase in the proportions of DIN relatively to DON in subsurface drain flow; and 3) a decrease in the proportions of NH$_4^+$ relatively to NO$_3^-$ in subsurface drain flow. Dissolved inorganic forms of P and N (i.e. DRP and DIN) are said to be more bioavailable than organic (i.e. DON and the majority of DUP) or particulate fractions (i.e. PP) (Seitzinger and Sanders 1997; Reynolds and Davies 2001; Willett et al. 2004). Similarly, NH$_3$ is highly toxic to aquatic ecosystems (Camargo and Alonso 2006), whereas in the current water legislation in Ireland, NO$_3^-$ is mostly considered to be a limiting nutrient in coastal waters and a contaminant in drinking water. Implementing subsurface drainage may enhance crop growth and nutrient uptake and thereby decrease nutrient loads. Nevertheless, in many circumstances, artificially lowering the water table could result in decreasing total loads of N and P lost from surface pathways, but increasing the nutrient bioavailability in quick flow (e.g. increasing the proportions of inorganic forms of nitrogen) through the subsurface drainage system. In order to address this issue, technologies such as permeable reactive barriers or constructed wetlands (Brix et al. 2012; Healy et al. 2012), which aim at remediating mixed contaminant sources could be implemented. Similar studies should be undertaken to evaluate the impact on nutrient losses of installing mole or gravel mole drains to enhance the infiltration capacity of soils (Galvin 1983). In the 1970s and 1980s, the priority was to drain land without an environmental framework. As drainage implementation is now being re-visited to provide environmentally sustainable
CONCLUSION

This study investigated the controls on flow generation and P and N losses and fractionation/speciation in surface and subsurface drainage for three rainfall events in four un-grazed grassland plots in Ireland. Spatial differences in runoff coefficients and in the total amount of water by unit area (in mm) generated by the overland flow systems mainly linked to 1) the size of the plots (an increase in size linked with a decrease in flow) and 2) water table depth (shallow water table linked with an increase in flow). Temporally, both event and pre-event hydrometeorological conditions were the main controls. In contrast, controls on spatial differences in flow generation in the subsurface drainage systems were more difficult to assess. Overall, these controls imposed greater spatial differences in overland and subsurface drainage patterns between all plots than temporal variations between events for the same plot. In turn, an increase in overland and subsurface drain flow induced higher TP and TDN total losses. Subsurface drain flow generated smaller loads of TDN and TP than overland flow. Before the application of fertilizer, the proportions of different P fractions and N species reflected the influence of pre-event water to overland and subsurface drain flow. Even if DON was generally the dominant form in both systems, the proportion of DIN was higher in the subsurface drains, especially in areas of shallower water table. Nitrate also dominated over NH$_4^+$ in the subsurface drain flow, but not in overland flow. Similarly, DUP was the dominant P fraction in subsurface drain flow where the water table was shallow, while PP was the most important fraction elsewhere. In overland flow, a shallower water table implied a switch from DRP to DUP-dominated water. The application of fertilizer treatments further increased P and N losses and influenced the speciation.
resulted in a strong increase in TP concentrations in overland flow, and a dominance of DRP in all plots. Both P and N total losses and speciation/fractionation will affect the nutrient bioavailability in aquatic ecosystems. This study highlights the importance of an integrated assessment of the controls of flow and solute patterns in both surface and subsurface flow systems when aiming at identifying the impact of grassland management on nutrient losses in water. Further research is needed to test whether the implementation of design criteria specific to local soil and groundwater conditions can further reduce P and N losses from grasslands.
ACKNOWLEDGEMENTS

This research was financially supported under the National Development Plan, through the Research Stimulus Fund, administered by the Department of Agriculture, Food and Marine (RSF 07 525). We also wish to thank Atul Haria, Sean Kenny, John Murphy, Alan Cuddihy, Denis Brennan, Linda Maloney Finn, Maria Radford and Eddy McDonald for their help on the field, in the laboratory and in data-processing.
REFERENCES


BSI. 1989 Test sieving. Methods using test sieves of woven wire cloth and perforated metal plate.


Table 1 - Plot area, slope and soil texture. Clay Loam (CL), Sandy Silt Loam (SSL), Sandy Clay Loam (SCL), Sandy Loam (SL).

<table>
<thead>
<tr>
<th>Plot Number</th>
<th>Area (m²)</th>
<th>Slope (%)</th>
<th>Soil Texture (0-10 cm)</th>
<th>Soil Texture (0-30cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7780</td>
<td>3.9</td>
<td>CL/CL/CL</td>
<td>CL/CL/SSL</td>
</tr>
<tr>
<td>2</td>
<td>7470</td>
<td>4.1</td>
<td>CL/SSL/CL</td>
<td>CL/SL/CL</td>
</tr>
<tr>
<td>3</td>
<td>4080</td>
<td>4.2</td>
<td>CL/SSL/SL</td>
<td>CL/SSL/SCL</td>
</tr>
<tr>
<td>4</td>
<td>4070</td>
<td>5.4</td>
<td>CL/CL/CL</td>
<td>CL/SSL/SSL</td>
</tr>
</tbody>
</table>
Table 2-Mean soil nutrient concentrations (mg L\textsuperscript{-1}) and standard deviation (mg L\textsuperscript{-1}, in brackets) of TN, P, K and Mg at all plots from 0-30 cm depth soil samples

<table>
<thead>
<tr>
<th>Plot</th>
<th>TN</th>
<th>P*</th>
<th>K*</th>
<th>Mg*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.3 (0.9)</td>
<td>2.8 (0.8)</td>
<td>107.3 (69.7)</td>
<td>183.3 (36.4)</td>
</tr>
<tr>
<td>2</td>
<td>2.5 (0.6)</td>
<td>3.7 (0.5)</td>
<td>77.4 (30.3)</td>
<td>235.2 (18.1)</td>
</tr>
<tr>
<td>3</td>
<td>2.5 (0.7)</td>
<td>3.9 (1.7)</td>
<td>66.6 (12.5)</td>
<td>167.7 (32.1)</td>
</tr>
<tr>
<td>4</td>
<td>1.9 (0.4)</td>
<td>3.4 (0.9)</td>
<td>56.0 (15.8)</td>
<td>158.9 (45.4)</td>
</tr>
</tbody>
</table>

*Morgan’s soil nutrient concentration
Table 3-Groundwater nutrient concentrations (mg L$^{-1}$) of PP, TDP, NH$_4$-N and NO$_3$-N for selected piezometers sampled on the 5$^{th}$ March 2009.

<table>
<thead>
<tr>
<th>Piezometer</th>
<th>PP</th>
<th>TDP</th>
<th>NH$_4$-N</th>
<th>NO$_3$-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>bdl</td>
<td>bdl</td>
<td>0.065</td>
<td>10.417</td>
</tr>
<tr>
<td>B</td>
<td>bdl</td>
<td>bdl</td>
<td>0.068</td>
<td>0.863</td>
</tr>
<tr>
<td>D</td>
<td>bdl</td>
<td>0.020</td>
<td>0.064</td>
<td>0.840</td>
</tr>
<tr>
<td>E</td>
<td>bdl</td>
<td>0.012</td>
<td>0.060</td>
<td>6.424</td>
</tr>
<tr>
<td>F</td>
<td>bdl</td>
<td>0.010</td>
<td>0.054</td>
<td>9.848</td>
</tr>
<tr>
<td>G</td>
<td>bdl</td>
<td>0.012</td>
<td>0.051</td>
<td>9.420</td>
</tr>
<tr>
<td>H</td>
<td>bdl</td>
<td>0.008</td>
<td>0.059</td>
<td>8.123</td>
</tr>
<tr>
<td>I</td>
<td>bdl</td>
<td>0.009</td>
<td>0.071</td>
<td>5.680</td>
</tr>
<tr>
<td>J</td>
<td>bdl</td>
<td>0.009</td>
<td>0.060</td>
<td>8.670</td>
</tr>
<tr>
<td>K</td>
<td>bdl</td>
<td>0.008</td>
<td>0.065</td>
<td>10.270</td>
</tr>
</tbody>
</table>

bdl refers to concentrations below detection limits.
Table 4-Flow-weighted mean nutrient concentrations (mg L\(^{-1}\)) for all plots (1-, 2-, 3- and 4-) in overland flow (OF) and subsurface drain flow (DF) for the three events (Event 1/Event 2/Event 3). bdl refers to concentrations below detection limits and n.a. to samples not analyzed.

<table>
<thead>
<tr>
<th>Plot</th>
<th>TP</th>
<th>PP</th>
<th>DRP</th>
<th>DUP</th>
<th>TDN</th>
<th>DON</th>
<th>DIN</th>
<th>NH(_4)-N</th>
<th>NO(_3)-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-</td>
<td>0.096/0.061</td>
<td>0.024/0.02</td>
<td>0.048/0.01</td>
<td>0.025/0.01</td>
<td>0.861/0.88</td>
<td>0.833/0.88</td>
<td>0.027/0.00</td>
<td>0.027/0.00</td>
<td>bdl/bdl/</td>
</tr>
<tr>
<td>OF</td>
<td>1.381</td>
<td>8/0.227</td>
<td>5/1.088</td>
<td>9/0.066</td>
<td>5/1.268</td>
<td>2/1.183</td>
<td>4/0.084</td>
<td>1/0.050</td>
<td>.035</td>
</tr>
<tr>
<td>2-</td>
<td>0.218/0.077</td>
<td>0.060/0.01</td>
<td>0.096/0.03</td>
<td>0.062/0.02</td>
<td>1.492/0.94</td>
<td>1.443/0.90</td>
<td>0.049/0.03</td>
<td>0.049/0.03</td>
<td>bdl/bdl/</td>
</tr>
<tr>
<td>OF</td>
<td>1.586</td>
<td>9/0.127</td>
<td>0/1.289</td>
<td>7/0.170</td>
<td>4/1.351</td>
<td>9/1.310</td>
<td>5/0.042</td>
<td>5/0.042</td>
<td>bdl</td>
</tr>
<tr>
<td>3-</td>
<td>0.114/0.095</td>
<td>0.022/0.03</td>
<td>0.045/0.01</td>
<td>0.048/0.05</td>
<td>0.876/1.00</td>
<td>0.845/0.98</td>
<td>0.031/0.01</td>
<td>0.031/0.01</td>
<td>bdl/bdl/</td>
</tr>
<tr>
<td>OF</td>
<td>1.237</td>
<td>1/0.105</td>
<td>1/1.002</td>
<td>3/0.129</td>
<td>0/1.145</td>
<td>7/1.088</td>
<td>3/0.057</td>
<td>5/0.039</td>
<td>0.018</td>
</tr>
<tr>
<td>4-</td>
<td>0.123/bdl/</td>
<td>0.035/n.a./</td>
<td>0.042/n.a./</td>
<td>0.046/n.a./</td>
<td>1.365/n.a./</td>
<td>1.332/n.a./</td>
<td>0.033/n.a./</td>
<td>0.033/n.a./</td>
<td>bdl/n.a./</td>
</tr>
<tr>
<td>OF</td>
<td>1.380</td>
<td>0.096</td>
<td>1.128</td>
<td>0.156</td>
<td>1.067</td>
<td>1.060</td>
<td>0.007</td>
<td>0.001</td>
<td>0.006</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plot</th>
<th>TP</th>
<th>PP</th>
<th>DRP</th>
<th>DUP</th>
<th>TDN</th>
<th>DON</th>
<th>DIN</th>
<th>NH(_4)-N</th>
<th>NO(_3)-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-</td>
<td>0.233/0.065</td>
<td>0.188/0.05</td>
<td>0.008/0.00</td>
<td>0.037/0.01</td>
<td>2.956/0.55</td>
<td>2.555/0.50</td>
<td>0.401/0.04</td>
<td>0.085/0.00</td>
<td>0.315/0.04</td>
</tr>
<tr>
<td>DF</td>
<td>0.217</td>
<td>2/0.150</td>
<td>1/0.008</td>
<td>2/0.059</td>
<td>1/2.138</td>
<td>6/1.315</td>
<td>5/0.822</td>
<td>5/0.773</td>
<td>0/0.049</td>
</tr>
<tr>
<td>2-</td>
<td>0.098/0.082</td>
<td>0.070/0.05</td>
<td>0.010/0.00</td>
<td>0.018/0.01</td>
<td>0.786/0.86</td>
<td>0.734/0.63</td>
<td>0.052/0.23</td>
<td>0.029/0.04</td>
<td>0.022/0.18</td>
</tr>
<tr>
<td>DF</td>
<td>n.a.</td>
<td>8/n.a.</td>
<td>6/n.a.</td>
<td>8/n.a.</td>
<td>8/n.a.</td>
<td>6/n.a.</td>
<td>1/n.a.</td>
<td>8/n.a.</td>
<td>4/n.a.</td>
</tr>
<tr>
<td>3-</td>
<td>0.042/n.a./</td>
<td>0.004/n.a./</td>
<td>0.002/n.a./</td>
<td>0.036/n.a./</td>
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Fig. 1-(a) Map of the study area, (b) interpreted resistivity profiles.
Fig. 2-Event precipitation characteristics (a) total precipitation (Bulk P), maximum precipitation (Max P) and rainfall intensity (R Int), (b) pre-event cumulative precipitation for 7 days (7DP), 14 days (14DP) and 30 days (30DP) preceding the event, (c) water table depth at the start of the event for selected piezometers (see Fig. 1 for position on the plots).
Fig. 3-(a) Precipitation and (b) soil moisture deficit (SMD) computed from the model by Schulte et al., (2005). Vertical dashed lines indicate start of the three rainfall events and vertical plain lines dates of fertilization and grass cut events.
Fig. 4 - Overland and subsurface drain flow patterns per event and plot. (a) ; (b) Total subsurface drain flow; (c) Runoff coefficient for overland flow (ratio of total overland flow and total precipitation per event); (d) Runoff coefficient for drain flow (ratio of total subsurface drain flow and total precipitation per event).
Fig. 5—Total loads of P per plot in overland flow (OF) and drain flow (DF) for Event 1 (a), Event 2 (c) and Event 3 (e) and the relative contribution of particulate phosphorus (PP), dissolved unreactive phosphorus (DUP) and dissolved reactive phosphorus (DRP). Total loads of N per plot in overland flow (OF) and drain flow (DF) for Event 1 (b), Event 2 (d) and Event 3 (f) and the relative contribution of dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN).
Fig. 6 - Total loads of DIN expressed as N per plot in overland flow (OF) and subsurface drain flow (DF) for Event 1 (a), Event 2 (b) and Event 3 (c) and the relative contribution of ammonium (NH$_4^+$) and nitrate (NO$_3^-$).