High temporal resolution monitoring of multiple pollutant responses in drainage from an intensively managed grassland catchment caused by a summer storm

Granger, S. J.[1], Hawkins, J. M. B.[1], Bol, R.[1], White, S. M.[2], Naden, P.[3], Old, G.[3], Bilotta, G. S.[4], Brazier, R. E.[4], Macleod, C. J. A.[1], and Haygarth, P. M.[5]

[1]*North Wyke Research, Soil and Water Team, North Wyke, Okehampton, Devon, EX20 2SB UK.*

[2]*Natural Resources Department, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK.*

[3]*Centre for Ecology and Hydrology, Wallingford, Oxford, OX10 8BB, UK.*

[4]*School of Geography, Archaeology and Earth Resources, The University of Exeter, Amory Building, Rennes Drive, Exeter, Devon, EX4 4QJ, UK.*

[5]*Centre for Sustainable Water Management, University of Lancaster, Lancaster, LA1 4YQ, UK.*

Abstract

This work presents data on a suite of diffuse pollutants, monitored in a stream draining an intensively managed grassland on a 30 minute time step during a period of intense rainfall to better understand their sources and pathways. Nitrite ($92\mu g\ l^{-1}$), particulate phosphorus ($107\mu g\ l^{-1}$) and soluble phosphorus ($74\mu g\ l^{-1}$), exceeded environmental limits during base flow. Concentrations of nitrate and nitrite were decreased during the storm event, whereas all other pollutants generally increased and exceeded environmental limits where specified, especially when associated with a small subsidiary hydrograph on the rising limb of the main hydrograph. Total pollutants loads, when using a 60 minute sampling frequency, would have lead to significant over and underestimations depending on which 60 minute sample set was used. In the worst case loads of ammonium could have been underestimated by 35% or over estimated by 25%

with errors being associated with loads on the rising limb of the hydrograph and more specifically a small subsidiary hydrograph. This subsidiary hydrograph may have occurred as a result of runoff from the farm hard-standings within the catchment and its associated incidental transfers of pollutants masked the overall grassland pollutant response. To better understand these different source areas and pollutant dynamics there is a need for novel tracing techniques to better understand their relative contribution and pathways.

1. Introduction

With the recent and on-going introduction of legislation and policy aimed at improving aquatic ecology and water quality in river basins (e.g. EU Water Framework Directive), attention is increasingly focused on efforts to decrease inputs of pollutants into surface and groundwaters. In agricultural areas, which represent a large proportion of the land surface in Europe and North America, studies have shown that pollutants are usually derived from diffuse sources spread over large areas. Over 42% of the agricultural land area, or 26% of the total area, of England and Wales is under permanent grassland (source: SEISMIC (Hallet et al., 1995) v.2.0.6. software 2000 dataset). Permanent grassland is usually maintained as such due to the combination of soil type and climate which renders them unsuitable for arable production. Indeed, of the total agricultural land under permanent grassland, approximately 50% occurs on soils with a shallow impermeable substrate (HOST models H-K (Boorman et al., 1995)). This type of heavy soil frequently occurs in western Britain where high levels of rainfall can lead to seasonal water logging where drainage has not been installed or where it is working inefficiently. These systems include the dairy pastures of south-west England which are characterised by high levels of rainfall and sloping land with high stocking densities making them potentially erosive environments (Brazier et al., 2007). These areas also receive high levels of nutrients either through the deposition of animal excreta or through the application of inorganic fertilizers and managed manures (Haygarth et al., 2006). As a result they act as significant sources of diffuse pollution i.e. nitrate (NO_3^-) (Ryden et al., 1984; Haigh and White, 1986; Scholefield et al., 1993), phosphorus (P) and sediment (Heathwaite et al., 1990; Smith et al., 1995b; Hawkins and Scholefield, 1996; Haygarth et al., 1998; Bilotta et al., 2008).

The majority of studies exploring diffuse pollution in permanent grasslands have focused on sources and behaviours of individual pollutants. However, whilst such research provides vital information on the processes and mechanisms associated with these individual pollutants, a more holistic approach is required in order to provide meaningful information for implementing policy and remediation options concerned with the health

of aquatic systems as a whole (e.g.Quinn and Stroud, 2002; Neal et al., 2008). Thus, this study expands to include a suite of potential pollutants including NO_3^-, P and sediment, but also other pollutants which have so far received less attention i.e. nitrite (NO_2^-) and ammonium/ammonia (NH_4^+/NH_3) which are both potentially toxic to aquatic fauna at low concentrations (Lewis and Morris, 1986; Randall and Tsui, 2002). Dissolved forms of inorganic and organic carbon (DIC/DOC) are also recognised to play a significant role in the health of aquatic ecosystems leading to increased biological oxygen demand within water bodies which is potentially detrimental to aquatic fauna (Edwards et al., 2008). Furthermore, hydrochemical catchment studies have typically been based on hourly or sub-hourly measurements of water fluxes and weekly or monthly chemistry samples (Kirchner et al., 2004). Studies which are based on weekly or even lower resolution chemical monitoring may miss base flow variation and also most storm events which can lead to significant miscalculations of pollutant flux (Johnes, 2007). Storm events are often highly significant in terms of pollutant transfer and Pinoke et al. (1996) reported that the majority of P loss from some catchments occurs during the largest three to five storms in a year. Furthermore, knowledge of the dynamics of pollutant delivery during storm events can potentially highlight changing pollutant sources and the mechanisms of delivery which may not be revealed through infrequent sampling. Therefore higher resolution monitoring is vital for defining effective mitigation measures to reduce pollutant loss. Examples of how high temporal resolution series have improved our understanding of hydrochemical processes are given in Scholefield et al., (2005) where hourly monitoring of riverine nutrients revealed marked diurnal patterns occurring during periods of base flow, and Jordan (2005) where ten minute measurements of total P (TP) in a stream draining a small agricultural catchment in Ireland also showed that, although storm events were responsible for major P flushing episodes, cyclical non-storm transfers of TP occurred during base flow.

The aim of this study was to monitor the behaviour of a suite of diffuse pollutants in a stream draining an agricultural grassland system during a storm event at a temporal

resolution sufficient to elucidate variations in the chemographs which will improve our understanding of how pollutants from grassland systems are delivered to surface waters. Specifically, the objectives are to: (1) produce time series of a suite of diffuse pollutants within a stream draining an intensively managed grassland catchment throughout a discrete storm event; (2) interpret observed pollutant concentration with respect to potential sources; (3) monitor the selected pollutants in surface run-off from a grassland field within the larger catchment to understand better the significance of this source; and (4) demonstrate the need for high temporal resolution data to improve flux calculations and provide information on diffuse pollutant dynamics and their controls.

2. Materials and Methods

Study Site

Located in Devon, England, the Den Brook catchment (UK grid ref. SX 67712 99685) is a first-order headwater catchment 48 ha in size (Figure 4.1a and b), characterised by a slowly permeable seasonally waterlogged clay soil of the Hallsworth series (Harrod and Hogan, 2008) (Typic Haplaquept (USDA); stagnogley (UK); HOST 24). The catchment receives high levels of rainfall with an annual average of 1050mm (40yr average), the majority of which typically falls in the winter/spring. However, in recent years it has been observed that heavy rainfall events during the summer months are increasing (Maran et al., 2008). The catchment has a limited amount of field drainage installed, predominantly draining areas close to the stream. With this soil type and the associated wet weather conditions, the hydrological response to rainfall can be very flashy with a large proportion being saturation-excess overland flow. The catchment is predominantly managed as grassland sustaining cattle and sheep and the sward is dominated by perennial ryegrass receiving periodic applications of manure, inorganic fertilizer (N, P and K) and excretal returns during the spring/summer. Within the catchment, there is also a hard-standing area with associated animal housing that is served by a slurry lagoon receiving animal

waste and contaminated run-off. This area is connected to the Den Brook by a large drainage pipe which intermittently discharges farmyard run-off into the stream. The extent of this connection is poorly understood; however, in 2003 the slurry lagoon was rebuilt in an attempt to reduce pollution entering the stream. Waste contained within the lagoon is spread within the catchment area when ground conditions allow, typically during the spring/summer. To the south of the catchment a road drain delivers run-off from the road via a concrete conduit.

Discharge from the catchment was measured using a trapezoidal flume which has been installed since 2001. Stage height, from which discharge is calculated, is measured on 5 minute time-steps by a pressure transducer in a stilling well, 1m upstream of the flume and is recorded by a data logger (Campbell Scientific CR10X). Precipitation is recorded at the catchment outlet by a tipping-bucket rain gauge (Rain-wise Bar Harbor, ME), which records the total number of tips per minute (each tip equivalent to 0.254mm precipitation). Within the catchment, a single field has been defined as a sub-catchment and is also monitored for flow. This field at the west of the catchment (Fig. 1b) represents 12% of the catchment area and slopes at about 5° from its SW to NE corner. The field is bounded on its upslope sides to the south and west by earth banks forming hedges (~1m high) while on its down slope sides only livestock fencing exists. However, on these sides small earth banks (~15cm high) have developed, possibly as a result of the field's recent history; it had been ploughed and used for maize production until 2006, when it was returned to grassland. This field, like the majority of the land within the catchment away from the stream channel, has no field drainage installed, and subsurface flow is considered to be negligible due to the low hydraulic conductivity of the subsoil (<10mm day^{-1}) (Armstrong and Garwood, 1991). Due to the nature of the slope and the presence of surrounding banks, all surface run-off is contained and directed towards the NE corner of the field. In this corner a 'V' notch weir was installed in 2006/07. All surface flow occurring within this field is channelled down to the weir and discharge is calculated from the stage

height measured by a stilling-well and ISCO 6712 auto-sampler, integrated bubbler module (Teledyne Isco Inc, Nebraska, USA).
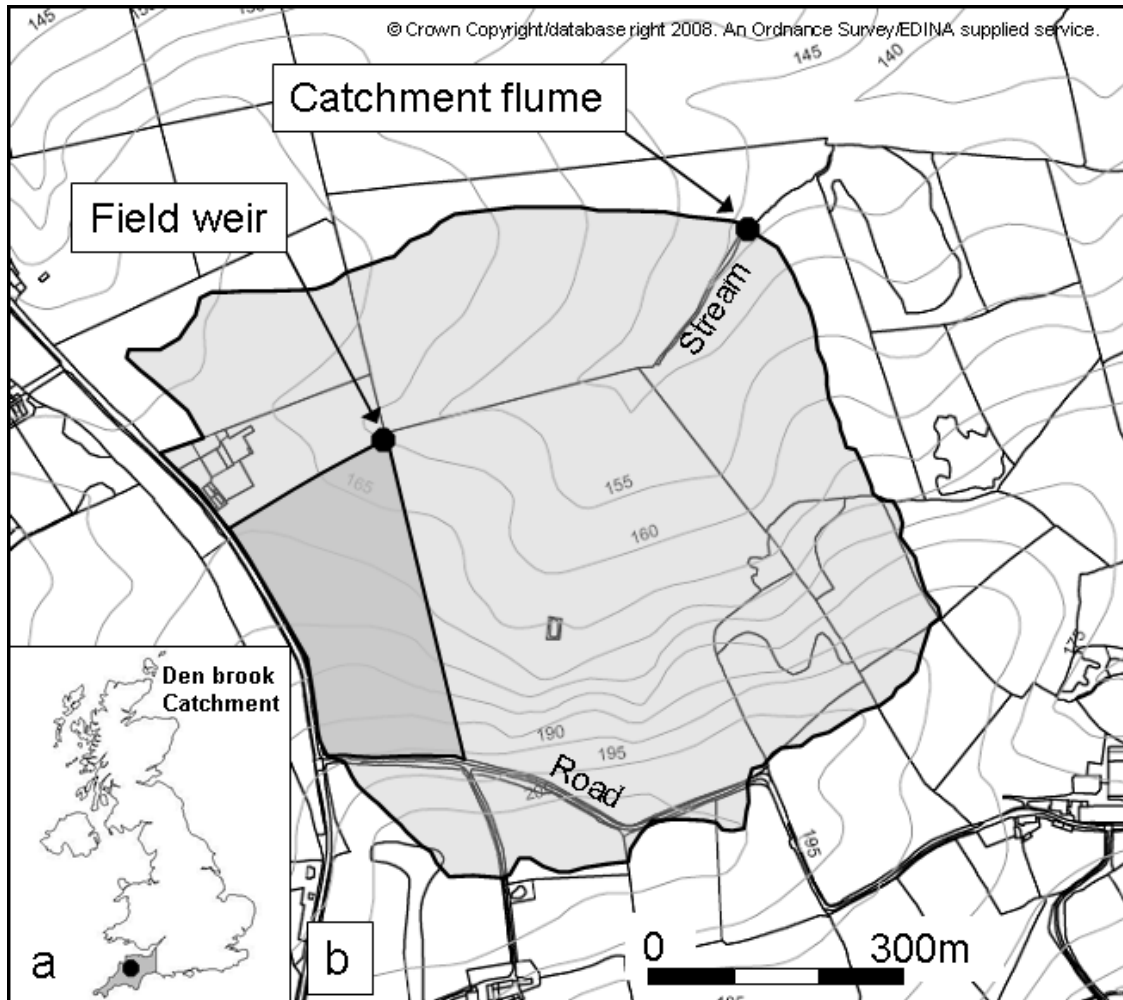

Figure 4.1. Maps showing the location of (a) the Den brook catchment in the south west U.K. and (b) the Den brook catchment and the field sub-catchment along with their associated sampling points.

At the time of the study the regional weather pattern had been highly convective producing large volumes of rainfall in highly localised areas. Monitoring in the catchment was set up in order to capture one such event, ideally with both a base flow and a storm-flow element. On the 2nd June 2008 a large storm event occurred that produced over 13mm of rainfall in 3 hours and at its most intense 8mm falling in 30 minutes.

Sample Collection and Analysis

Samples were collected from both sample points using ISCO automated pump samplers which had depth-integrated inlets, thus samples were taken from throughout the water-column. The auto-samplers were started shortly before a storm event was forecast and programmed to sample on 30 minute time-steps. The internal clocks of the two auto-samplers were synchronised prior to sampling. Samples were collected from the field within 24 hours of the first sample being collected or on the same day as sampling was completed. Samples were immediately refrigerated in the laboratory while still stored in their original plastic ISCO sample bottles and chemical analysis was conducted within a UKAS accredited laboratory. On the same day as the samples were collected subsamples for TP and filtered TP were taken and stored in autoclavable glass digestion bottles, the latter being filtered through a 0.45μm cellulose nitrate filter paper (Whatman) prior to storage. Samples were also analysed for NO_2^--N on the same day as they were collected. Analysis for NH_4^+-N and total oxidised nitrogen (TON) was carried out within 48 hours of sample collection whilst analysis for suspended solids (SS), volatile sediment (VS), DIC and DOC were completed within one month.

The method used to determine TP concentrations was an acid persulfate digestion of the sample using a method adapted from Eisenreich et al.(1975). Phosphate was then determined colourimetrically on a spectrophotometer (Cecil Instruments, Cambridge, UK). Values of filtered TP were subtracted from TP to give values for >0.45μm TP. This fraction has been operationally termed particulate P (PP), while the <0.45μm fraction has been termed soluble P (SP). However, it is recognised that the SP value represents all forms of P

that are <0.45μm, which can include colloids and bacteria as well as 'truly' soluble P. Nitrite-N concentrations were determined colourimetrically, after filtration through a 0.45μm PES filter (Chromacol, Welwyn Garden City, UK), by segmented flow analysis (Bran+Luebbe Autoanalyzer3, Norderstedt, Germany) using the sulphanilamide/naphthylenediamine method (Henricksen and Selmer-Olsen, 1970). Analysis for NH_4^+ and TON was carried out colourimetrically on a continuous flow analyser (CFA; Skalar, Breda, The Netherlands). Ammonium-N was determined through the Indophenol reaction (Searle, 1984). Total oxidised nitrogen was determined after hydrazine sulphate reduction to NO_2^--N and subsequent sulphanilamide/naphthylenediamine analysis (Henricksen and Selmer-Olsen, 1970). The difference between TON and NO_2^--N was considered to be NO_3^--N. Forms of dissolved carbon were determined on samples filtered through a 0.45μm cellulose nitrate filter paper (Watman) using a Formacs[HT] Combustion TOC analyser (Skalar, The Netherlands) through oxidation in a quartz reactor at 950°C containing cobalt oxide, where all forms of carbon are oxidised to carbon dioxide (CO_2). Dissolved inorganic carbon is determined through digestion of the sample in orthophosphoric acid at room temperature to decompose all inorganic carbon forms to CO_2. The CO_2 produced in each case is measured with an infrared detector. Dissolved organic carbon is taken to be the difference between total dissolved carbon (TDC) and DIC. Suspended solids were determined through the vacuum filtration, and a subsequent drying at 105°C, of a known sample volume through a pre-weighed GF/F filter paper (Whatman), with particle size retention of 0.7μm. Filter papers were then heated to 500°C to determine the total residual ash. The difference between SS and total ash is considered to represent VS (UK Standing Committee of Analysts, 1980).

Calculation of Pollutant Loads

The pollutant loads were calculated using linear interpolation of point concentration data followed by multiplication with the corresponding Q data. Loads for the catchment were

calculated from the point at which increased Q occurred through to the end of water sampling 18 hours 25 minutes later. Although at this point both chemistry and Q values had not yet reached base flow levels, values were very low compared to during the event such that further losses were minimal. Loads were calculated using the 30 minute sample dataset and also on a sample set artificially reduced to represent samples collected at 60 minute intervals. Loads for the field sub-catchment were calculated from the time that the first sample was taken until insufficient Q meant no further samples could be collected. Because Q was initiated at 16:05, and the first sample was taken at 16:30, no load can be calculated for the first 25 minutes and therefore loads calculated from the field sub-catchment are underestimated.

3. Results

Hydrological Response

Figure 4.2 shows the rainfall measured close to the catchment outlet and the hydrographs generated from both the catchment outlet (Figure 4.2a) and the monitored field (Figure 4.2b) within the catchment. These hydrographs present discharge (Q) as uncertain hydrographs (Q_{max} and Q_{min}) through a technique developed by (Krueger et al., 2008) based on estimates of the errors associated with the calibration technique (Bilotta et al., 2008). A centre Q line has been plotted through this uncertainty interval to give a clearer visual indication of the nature of the flow response. The values of Q cited, or parameters related to Q, are the centre value with the uncertainty interval. The uncertainty interval is presented in parentheses following this value i.e. Q (Q_{min}-Q_{max}).

A 2.5 hour period of base flow (about 1.9l s^{-1}) was monitored before the onset of increased Q at the catchment outlet which occurred at 14:25, 20 minutes after the onset of rainfall and after 5.6mm had fallen on the catchment. Peak Q reached 61l s^{-1} (52-70) at 17:10, 2 hours 45 minutes after the onset of increased Q and after 14mm of rain had fallen on the catchment which accounted for 96% of the rainfall received over the study

period; once rainfall had stopped, Q began to recede. On the rising limb of the hydrograph a small subsidiary peak occurred at 15:05, 40 minutes after the onset of increased Q. Here the peak Q was 19l s^{-1} (14-24) before receding to 16 l s^{-1} (11-20) over a 20 minute period, Q subsequently increased to its maximum value. Surface flow generated from the field sub-catchment was initiated at 16:05, 2 hours after the onset of rainfall – some 1 hour 40 minutes later than the catchment outlet. The maximum Q was 3.4l s^{-1} (2.9-4.0) and occurred at 17:00, 55 minutes after the initial generation of flow and roughly coincidental with the peak discharge at the catchment outlet. Surface flow then decreased until its cessation at 03:35 the following morning. The subsidiary hydrograph peak that appears on the rising limb of the main catchment hydrograph preceded the onset of the field sub-catchment hydrograph.

If it is assumed that the rainfall measured at the catchment outlet represents the rainfall over the whole catchment then the total volume of water deposited was 6748m^3. The base flow over the 3 hours immediately prior to the storm event was 6.9m^3 hr^{-1} (1.8-12) and the volume of water leaving the catchment from the point at which Q increased after the onset of rainfall until sampling ceased was 1260m^3 (949-1572). The volume of water from the catchment outlet less base flow is therefore calculated to be 1132m^3 (915-1349) and gives a runoff coefficient of 17% (14-20). Again, assuming even rainfall across the catchment, the total water deposited on the field sub-catchment was 796m^3. The volume of water that left the field via surface flow was 23m^3 (16-29) giving a runoff coefficient of 2.9% (2.1-3.7).

Chemical Variation

The data obtained for the chemical response in drainage derived from the catchment as a whole are presented in Table 4.1, while Figure 4.3 shows the chemographs of the variation in concentration presented alongside Q from the catchment outlet (Figure 4.3a) and field outlet (Figure 4.3b). Base flow concentrations are presented as a mean and two standard errors in parentheses.
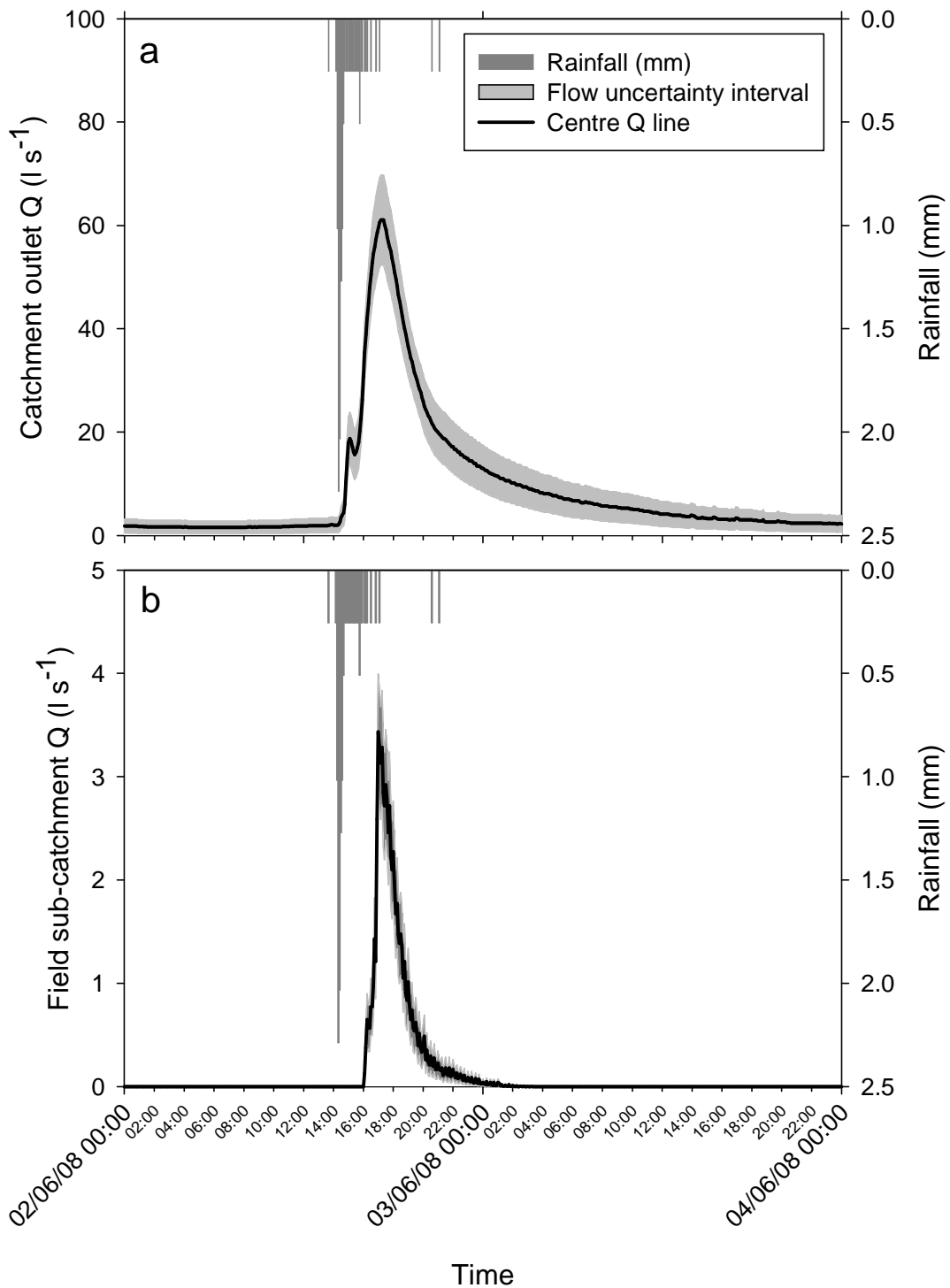
Figure 4.2. Rainfall and 'uncertain' hydrographs generated at (a) the catchment outlet and (b) the field sub-catchment in response to an intense rainfall. The bold line indicates the centre of the uncertainty envelope.

Nitrate/Nitrite

The concentration of NO_3^--N in the stream base flow before the storm event averaged 2.0 ($\pm$ 0.03)mg l^{-1}. As Q rapidly increased, so NO_3^--N concentrations rapidly decreased such that within 35 minutes of the onset of increased Q, NO_3^--N concentrations were below analytical quantification (<0.18mg N l^{-1}). Concentrations of NO_3^--N only became analytically detectable again at 17:30, after Q had peaked and continued to rise throughout the duration of the falling limb of the hydrograph. Concentrations measured from the field sub-catchment were all below quantifiable levels (<0.18mg l^{-1}).

Concentrations of NO_2^--N in the catchment base flow averaged 92 ($\pm$ 5)μg l^{-1} and followed a similar trend to that of the NO_3^--N chemograph with concentrations falling rapidly (to about 8μg l^{-1}) with the onset of increased Q and gradually increasing as Q decreased. However, unlike NO_3^--N concentrations of NO_2^--N remained initially low once Q had peaked and did not start to increase for about 3 hours. One anomaly exists in the data, which corresponds to the peak Q, whereby a value close to pre-storm concentrations occurs.

Concentrations of NO_2^--N in the surface flow from the field sub-catchment ranged between 2 and 6μg l^{-1} and did not appear to show any temporal variation during the period of flow from the field weir.

Ammonium

Ammonium-N concentrations in the catchment base flow were largely below levels which could be quantified analytically (<0.26mg l^{-1}). Concentrations of NH_4^+-N remained low throughout the majority of the storm and unlike NO_3^--N and NO_2^--N did not show any temporal variation over the rising and falling limbs of the hydrograph. However, two sample points were substantially higher in concentration than the rest of the storm. These concentrations of 14.3 and 2.87mg l^{-1} corresponded to the occurrence of the subsidiary peak on the rising limb of the main hydrograph. The duration of the spike in NH_4^+-N concentrations lasted for 90 minutes before concentrations fell back below levels which

were analytically quantifiable. In contrast, concentrations of NH_4^+-N measured in surface flow from the field sub-catchment were always below analytical quantification (<0.26mg N l^{-1}).

Suspended and Volatile Solids

Concentrations of SS in base flow from the catchment outlet averaged 9 (± 0.5)mg l^{-1} of which VS comprised 43%. During the storm event, concentrations of SS and VS rose to maximum concentrations of 925 and 387mg l^{-1} respectively. These maxima both occurred on the subsidiary hydrograph peak. A small secondary peak in SS concentrations was observed after the initial spike in concentrations; however, a corresponding secondary peak in VS concentrations was not apparent. Concentrations of both SS and VS declined throughout the remainder of the rising limb of the main hydrograph such that at peak Q, concentrations of SS and VS were already reduced to 103 and 25mg l^{-1} respectively. Concentrations of both SS and VS continue to decline over the duration of the falling limb.

With the onset of increased Q, despite concentrations of both SS and VS increasing, the relative contribution of VS fell from a base flow value of 43% to 18%, and although this increased back to 42% on the subsidiary hydrograph, levels decreased immediately after to ~ 25% throughout the remainder of the rising limb. Throughout the duration of the falling limb, although both SS and VS concentrations decreased, the relative contribution of VS began to increase reaching pre-storm levels before the study had been concluded.

Concentrations of SS and VS measured in the field sub-catchment Q did not appear to show any temporal variation and averaged 15.3 (± 0.6) and 8.2 (± 0.6)mg l^{-1} respectively. The relative contribution of VS was larger than that observed at any point from the catchment outlet, averaging 54% of the SS.

Table 4.1. Summary of the water quality data measured at the catchment and field sub-catchment outlets. Data presented as a range and also as a mean ± two standard errors in the case of catchment base flow.

Sample point	Flow type	NO_3^--N (mg l^{-1})	NO_2^--N (µg l^{-1})	NH_4^+-N (mg l^{-1})	PP (µg l^{-1})	SP (µg l^{-1})	SS (mg l^{-1})	VS (mg l^{-1})	DIC (mg l^{-1})	DOC (mg l^{-1})
Catchment	Base flow	2.0 - 2.1 (2.04 ± 0.03)	85 – 99 (92 ± 5)	<0.26[a] - 0.27 (0.22 ± 0.02)	97 – 127 (107 ± 9)	61 – 83 (74 ± 6)	8 – 10 (9 ± 0.5)	3 – 5 (3.8 ± 0.5)	11 – 11 (11 ± 0.1)	7.5 – 9.6 (8.7 ± 0.6)
	Storm flow	<0.18[a] – 1.9	8 - 105	<0.26[a] - 14.3	205 - 5947	90 - 5870	20 - 925	9 - 387	10 - 58	9 - 248
Field sub-catchment	Storm flow	<0.18[a]	2 - 6	<0.26[a]	140 - 222	197 - 263	13 – 17	5 - 10	11 - 17	23 - 29

[a]Concentration data was lower than analytical quantification limits.

Phosphorus

Concentrations of PP and SP in base flow from the catchment outlet were comparable, with mean values of 107 ($\pm$ 9) and 74 ($\pm$ 6)μg P l^{-1} respectively. During the storm event, concentrations of PP and SP remained broadly similar to one another, reaching maximum concentrations of 5947 and 5870μg P l^{-1} respectively. These maxima were both reached on the subsidiary peak. However, while PP increased dramatically with the onset of increased Q, increases in SP appeared to be slightly delayed. Concentrations of PP rapidly reduce after their maximum to 1957μg P l^{-1} over the next 30 minutes, coinciding with the trough between the subsidiary hydrograph and the remainder of the rising limb. It then continued to decrease at a slower rate throughout the remainder of the rising limb of the main hydrograph. Similarly concentrations of SP also decreased on the rising limb of the hydrograph after their initial peak, although the reduction in concentrations was more rapid than that of PP. Although PP and SP both continued to decrease generally over the duration of the hydrograph falling limb, both appear to have small increases in concentration occurring over a 1-2 hour period with the apparent increase in SP occurring shortly after peak Q.

In base flow, the relative contribution of PP to TP was ~ 60%. However, with the onset of increased Q, due to the lag in the increase in SP concentrations, this rose to 88%. On the subsidiary hydrograph peak, where both PP and SP maximum concentrations occurred, the relative contributions of PP and SP were equal, while over the remainder of the main rising limb PP tended to be the more dominant fraction. However, after peak Q occurred, SP initially became the more dominant fraction, coinciding with the secondary SP concentration peak, before pre-storm levels of contribution were achieved.

Concentrations of PP and SP in surface flow from the field were far smaller than those in the stream during the storm event at 177 ($\pm$ 7) and 216 ($\pm$ 11)mg P l^{-1} respectively. While concentrations of SP appeared to show no variation over time, concentrations of PP

appeared to decline slightly over the period from ~ 200 to 160mg P l^{-1}. This trend leads to a slight decline in the contribution of PP to TP over the period from ~ 50% to 45%.

Carbon

Concentrations of DIC and DOC in the catchment base flow were comparable at 11 (± 0.1) and 8.7 (± 0.6)mg l^{-1} respectively. Although neither DIC nor DOC concentrations were affected immediately by the onset of increased Q, both DIC and DOC rapidly increased in concentration in association with the subsidiary hydrograph peak (58 and 248mg l^{-1} respectively) before concentrations decreased throughout the rest of the main hydrograph rising limb (12 and 36mg l^{-1} respectively). Concentrations of DOC rose slightly after peak Q had been reached (43mg l^{-1}) before declining gradually thereafter to 21mg l^{-1} some 14 hours later. Concentrations of DIC however, rose gradually after peak Q had been reached from 12 to 16mg l^{-1} at the cessation of sampling. The relative contribution of DOC to TDC increased with the onset of increased Q and was at its maximum at the peak Q of the subsidiary hydrograph (81%). After this DOC comprised 75% of the TDC throughout the remainder of the hydrograph rising limb and, due to the contrary tends in DIC and DOC concentrations over the falling limb, the proportion of DOC reduced from 76 to 58%. Concentrations of DIC and DOC measured in the surface flow from the field sub-catchment both increased over time. Concentrations of DIC increased from 11 to 17mg l^{-1}, while DOC concentrations increased from 23 to 29mg l^{-1} however these concentrations were less than those observed at the catchment outlet during the storm.

4. Discussion

Catchment Base Flow

Concentrations of chemical parameters in base flow (Table 1) have been assessed in terms of documented acceptable limits and the data reported from a long term study using weekly grab samples from this sample site (Jarvie et al., 2008). Concentrations of NH_4^+-N

and SS were within the range of values previously reported from this catchment and well below levels specified by the EU (0.78 and 25mg l^{-1} for respectively) (European Economic Community, 1978) The concentration of NO_3^--N was also well below the 11.3mg l^{-1} level set out by the European Union for identifying waters designated as 'nitrate vulnerable zones' (NVZ's) (European Economic Community, 1991) and comparable to those reported in this catchment for this time of year and those reported in a nearby river system draining land of equivalent soil type and management (Scholefield et al., 2005). While NO_3^--N is typically perceived to be the species of N with most environmental relevance within grassland systems it would appear that NO_2^--N may be more environmentally significant. While NO_2^--N may only account for a small proportion of the total inorganic N present (~ 4%), it is highly toxic to aquatic fauna and the concentrations measured were an order of magnitude higher than European acceptable limits (European Economic Community, 1978). The concentrations measured were larger than those reported in this catchment previously and those reported elsewhere in river water (Scholefield et al., 2005) but consistent with reports from Northern Ireland that have shown that concentrations of NO_2^--N within certain river systems draining grassland catchment can be large and frequently in the range of 100 to 150µg l^{-1} (Smith et al., 1995a).

Concentrations of PP and SP in base flow were also large, but within previously reported ranges, with mean values of 107 (± 9) and 74 (± 6)µg P l^{-1} respectively. These concentrations can be considered large as the Organization for Economic Cooperation and Development suggests that eutrophication problems can be triggered by TP concentrations of 35 to 100µg l^{-1} (OECD, 1982) while the EU cite threshold values of 65 and 130µg P l^{-1} for salmonid and cyprinid waters respectively (European Economic Community, 1978). Interestingly, TP was evenly apportioned between PP and SP which was an unexpected finding as it is generally considered that P losses from grassland are dominated by SP, especially during periods of base flow (Sharpley and Rekolainen, 1997; House and Warwick, 1998). However, there is growing discussion on this subject (Bilotta et al., 2007, Brazier et al., 2007).
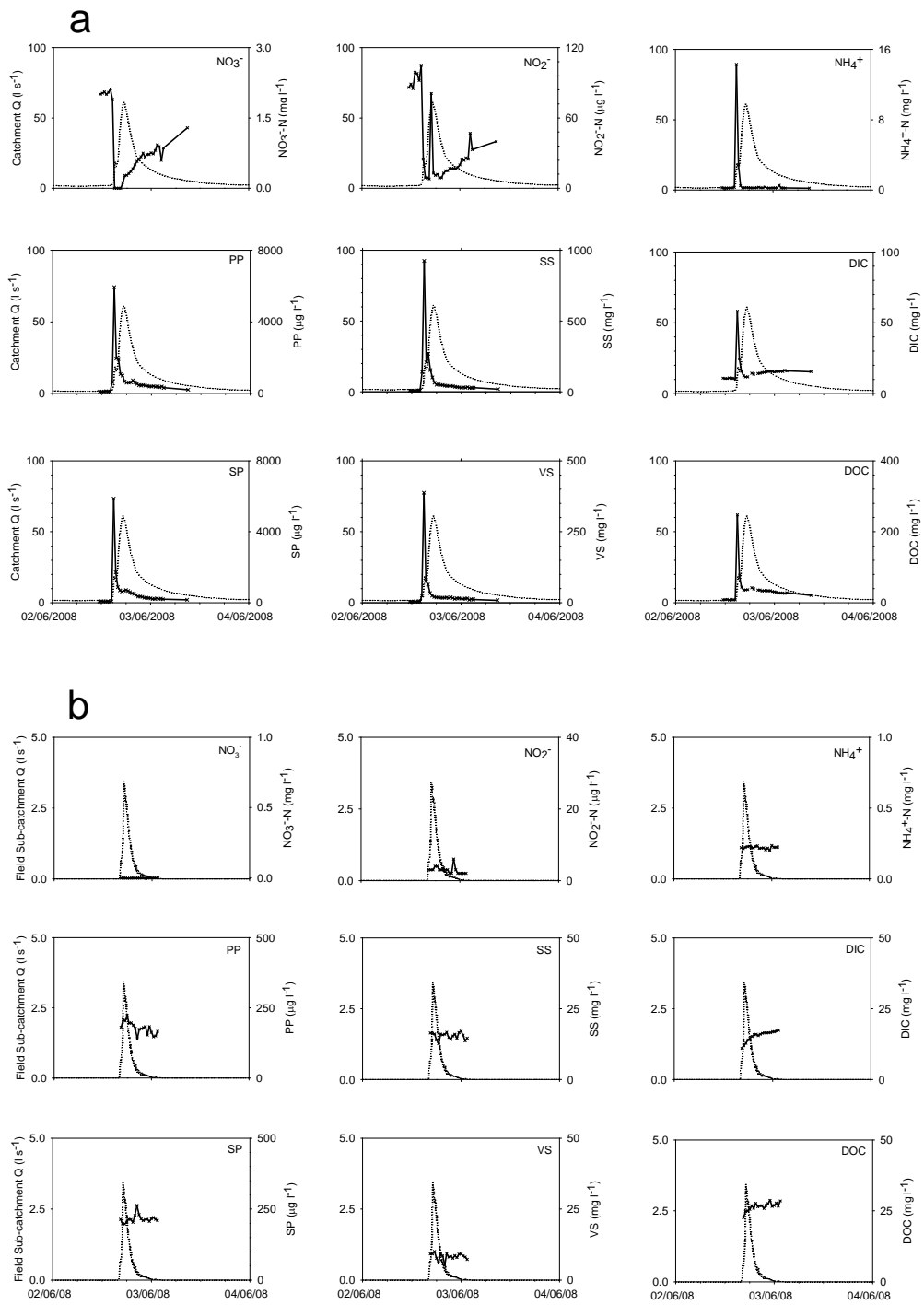
Figure 4.3. Chemographs of the diffuse pollutant temporal dynamics at (a) the catchment outlet and (b) the field sub-catchment. Discharge is plotted as only the centre line of the uncertainty envelope for visual clarity.

19

There is little information in the literature about the evolution of DIC and DOC from intensively managed grasslands due generally to the perception that such systems yield little carbon. In general the DOC concentrations of 'uncoloured' streams range between 2 and 10mg l^{-1} while concentrations in 'organically coloured' streams may range from 3 and 50mg l^{-1} (Malcolm, 1993). The values measured in this study support these previous findings and those reported previously within this catchment for DOC.

Hydrological Response

Both hydrographs demonstrate the rapid, flashy response of the catchment to rainfall, especially at the intensity experienced, due to the heavy clay nature of the soil type.

Discharge from the catchment outlet started to increase rapidly 20 minutes after the onset of an intense period of rainfall and increased from 2 (0.6-3.6) to 61 (52-70)l s^{-1} over a 2 hour 45 minute period. Discharge from the field sub-catchment was initiated 2 hours after the onset of rainfall with the lag time representing the period needed for the field to wet-up sufficiently to generate surface and subsurface flow. Both catchment and sub-catchment peak Q occur almost simultaneously indicating that most of the catchment Q is derived from the grassland area that makes up the majority of the catchment with the delayed response time between the onset of increased Q from the catchment and from the field sub-catchment representing a period of wetting-up and in-field storage. The higher runoff coefficient of the catchment compared to the field sub-catchment probably reflects the contribution of near-channel areas as well as the contribution of other pathways such as field drainage and preferential flow pathways. The subsidiary peak present on the main catchment hydrograph rising limb responded sufficiently quickly, and was short-lived enough, for a recession limb to have started to occur before the rest of the catchment response led to the remainder of the rising limb of the main hydrograph. The presence of a greatly increased NH_4^+-N concentration points to the fact that the subsidiary hydrograph represents the contribution of the hard standing area within the catchment, which is dominated by the presence of animal manures. The results suggest that the

impermeable surface of the hard standings offered a near immediate run-off response initiated by the period of intense rainfall, channelled through a concrete pipe, with a similarly rapid fall in Q once rainfall had ceased. The remainder of the catchment exhibited a more buffered response, which allowed the individual hydrological signal from the hard standing to be observed. With an area of $4744m^2$, the volume of water deposited on the hard standings would have been $66m^3$. The volume of water represented by the subsidiary hydrograph peak, less base flow, is calculated to be $35m^3$ (26-45) giving a runoff coefficient of 53% (40-67). This value may underestimate the true runoff coefficient of the hard standings as it is not possible to resolve the full extent of the subsidiary hydrograph falling limb.

Catchment Chemographs

Concentrations of NO_3^--N responded negatively with Q producing a characteristic chemograph whereby soil microbial NO_3^--N is diluted by rainwater. This response in NO_3^--N concentrations has been reported elsewhere (Webb and Walling, 1985; Armstrong et al., 1999; Gächter et al., 2004) and is typical of systems where rainwater moves quickly over or through the soil thus having only limited opportunities for the diffusion of NO_3^--N from soil water to storm event water. The storm water in effect dilutes the base flow NO_3^--N leading to a rapid decrease in concentration. While it has been shown that a seasonal effect can be observed in NO_3^--N evolution chemographs, with increased concentrations occurring with increased Q during the summer, in cases where intense rainfall occurs a dilution effect is still expected (Webb and Walling, 1985). If the NO_3^--N in the drainage was sourced from fertilizer N applications, then the opposite effect might be expect to occur with an increase in NO_3^--N concentrations associated with increased Q as storm runoff washes material off the soil and into the stream. This type of transfer has been previously studied in relation to P losses (Haygarth and Jarvis, 1999; Preedy et al., 2001; Withers et al., 2003) and has been termed 'incidental' transfer and while there is no specific definition of incidental losses they have been described as "direct losses from fertilizers or

manures soon after application to land perhaps when coincident with a rainstorm" (Haygarth and Jarvis, 1999). In practical terms incidental mobilisation describes the unpredictable losses of source materials that are initially separate to the soil.

Nitrite-N produced a similar chemograph to that of NO_3^--N and, although no other chemographs of NO_2^--N concentrations during a storm event at this resolution could be found, it would seem likely they would be similar to NO_3^--N chemographs. This is because NO_2^-, like NO_3^-, is a highly soluble anion, formed within the soil system and held within the soil water and is therefore subject to the same mobilisation and transport processes as NO_3^-. The one data anomaly, which corresponds to the peak Q, cannot be explained but is probably erroneous and therefore should be ignored. As with NO_2^--N, the literature provides little information on the chemographs of NH_4^+-N concentrations from grassland catchments at high temporal resolution and is a determinand generally ignored. However it might be predicted that concentrations would be very low and unaffected by Q. Although the NH_4^+ cation is soluble, that which is formed through the mineralisation of soil organic matter, or enters the soil system from the excreta of grazing animals, will be retained by the negatively charged clay-humus particles within the soil before being rapidly nitrified to NO_3^-. Therefore, the leaching and drain flow losses of NH_4^+-N would tend to be small (Watson et al., 2000; Hatch et al., 2004). This is the case at the catchment outlet, with concentrations of NH_4^+-N below analytical quantification (<0.26mg l^{-1}) throughout the majority of the storm and unchanged from base flow levels. However, the concentration of NH_4^+-N shows a spike co-incident with the subsidiary hydrograph and exceeds levels permitted by the European Union for water supporting freshwater fish (0.78mg l^{-1}) (European Economic Community, 1978). As was the case with the NO_2^--N concentrations, this spike in concentration could be anomalous, however this is not believed to be the case for three reasons; i) it is not a single datum point, but consists of two elevated data points, ii) the two samples were visually different to the other storm event samples, being dark in colour, and had a noxious smell and iii) the timing of the concentration spike coincided with the subsidiary hydrograph. The occurrence of the

concentration spike with the subsidiary hydrograph is characteristic of an incidental loss and a recent review by Hatch et al. (2004) has highlighted the importance of such losses of NH_4^+-N on water quality. Ammonium-N entering ditches and drains from the uncontained run-off from farmsteads, the leachate from field heaps of solid manure, and summer storms washing manure and fertilizer from the field surface are all highlighted as significant routes of transfer.

As with the NH_4^+-N, all the other pollutants in this study have concentration spikes associated with the subsidiary hydrograph. However, while it may be reasonable to assume that all NH_4^+-N was sourced from the hard standing area within the catchment, such a conclusion cannot be made about PP, SP, SS, VS, DIC and DOC. These potential pollutants taken individually or as a suite may very well characterise the response expected when animal manures enter a water body, however unlike NH_4^+-N their presence in the catchment is not restricted to one specific area. The rapid run-off from the hard standings could have mobilised these pollutants from other source areas such as exposed soil along the line of connectivity between the hard standings and the stream or from the stream channel itself. Despite this, it seems very likely that there was a contribution from manure material sourced from the hard standings in the stream associated with the subsidiary hydrograph peak.

The contribution of pollutant losses associated with the hydrological response of the hard standings masks the contribution of the grassland on the rising limb of the main hydrograph and it is not possible to resolve the two contributing areas without some form of tracing experiment. However, there is an indication of a second smaller peak in concentration in some of the chemographs (Fig 4.3a. SP, SS and DOC). The concentrations of SP indicate the presence of a second peak which corresponds to the main hydrograph peak and appears to represent a more subtle Q-related SP contribution. Concentrations of SS exceed the 25mg I^{-1} limit set by the European Union for rivers supporting fresh water fish (European Economic Community, 1978) throughout the majority of the hydrograph and also appear to have a second, more sharply defined, peak after the main spike

although PP concentrations do not exhibit a corresponding secondary peak, perhaps indicating that the second SS peak has a high proportion of P deficient sediment within it. While a second smaller peak in DOC concentration, also associated with the main hydrograph peak, is also suggested by the data the same cannot be said of DIC; the concentration of which continued to rise throughout the storm event. The nature of the response of carbon and other pollutants from the multiple source areas within the catchment is clearly complex. To understand better the relative contribution of these areas and pathways requires further investigation and highlights a role for tracers to improve understanding of diffuse pollution from agriculture (Granger et al., 2007).

Field sub-catchment Chemographs

Chemographs of chemistry plotted against Q from the field sub-catchment give the reader some idea of the nature of the response generated from an agricultural grassland. However, it should be noted that the field studied was managed differently to the rest of the catchment, in that livestock were excluded and there was a good herbage cover crop in place at the time of the rainfall event.

In general, pollutant concentrations did not vary over the period of flow generation with the exceptions being PP, DIC and DOC. The response was not surprising for NO_3^--N, NO_2^--N and NH_4^+-N as these exist within the soil profile contained in soil water, and not on the soil surface, therefore limiting potential interactions with surface run-off. Furthermore, given that the field had no animals or amendments for over a month prior to the storm event, it would seem unlikely that these forms of N would be present in surface flow in the form of an incidental transfer. Similarly, SP may be considered to be a constituent of soil water and not readily accessible to surface flows. However it is possible that some proportion of PP transported by surface flows may move into solution leading to an apparent SP response (House et al., 1998). Particulate P appeared to decrease slightly with decreasing Q. This is in keeping with the literature which indicates that PP concentrations require the hydraulic energy of rainfall and surface run-off to mobilise

sediment and its associated P. In contrast, SS did not appear to decrease over time. While this might not be surprising given the management of the field at the time, it might also be expected that PP should also demonstrate no relationship with Q, although there is considerable uncertainty in the link between PP and SS (Krueger et al., 2008). The reason for this disparity is unclear but it might be that the analytical resolution of SS concentrations at these low levels was unable to reveal any underlying relationships with Q. Apart from PP, dissolved carbon was the only other determinand to show any temporal variation. There is little evidence in the literature reporting grassland DOC concentrations. However, a study investigating DOC losses from grazed grasslands under different managements found that concentrations in flow from undrained plots decreased over the winter period and were larger in plots which had received inorganic N (11-47mg l^{-1}) when compared with plots which had received none (7-31mg l^{-1}). Concentrations of DOC from drained plots which had received the same fertilizer N management did not show a decrease with time and were similar in concentration, however, peaks in DOC concentration coincided with periods of high rainfall (McTiernan et al., 2001). Concentrations of DOC measured in surface run-off from the grassland were in broad agreement with those reported in this study.

Pollutant Loads

Table 4.2 contains the calculation of pollutant load from the catchment outlet based on the 30 minute sample frequency undertaken within the study and also the calculated loads based on two artificially depleted 60 minute sample set with samples removed on the hour and half hour respectively. Despite the relatively short duration of the event, the two 60 minute pollutant loads showed considerable variation when compared with the 30 minute sample set. Loads calculated from 60 minute sample set (I) were generally under-estimated with the greatest underestimation associated with NH_4^+-N (-35%) with DIC flux under-estimated the least (-4%). The total load of NO_3^--N was found to be unaffected, being over-estimated by 1%, while NO_2^--N was overestimated by 12%. A more detailed

breakdown of the total load during different periods of the drainage event is presented in Figure 4.4. Estimates of load from the catchment outlet were made for each pollutant exported during; i) the subsidiary hydrograph up to the end of its receding limb, ii) the remainder of main hydrograph rising limb, and iii) the main hydrograph falling limb. The change in sampling resolution typically has little effect on the calculation of load on the falling limb of the hydrograph, ranging from +9.9% for NO_2^--N to -4.1% for NO_3^--N, with most pollutant fluxes being over estimated by no more than 3%. The main deviation in load between 30 and 60 minute sample data (I) occurs on the rising limb, and more specifically the subsidiary hydrograph. Over this period loads were over estimated for NO_2^--N (57%) and NO_3^--N (206%) and underestimated for all other pollutants. The degree of underestimation ranged from just -58% for DIC up to -82% for NH_4^+-N.

Conversely, loads calculated using the 60 minute sample set (II) was generally under-estimated. Again, the greatest error occurred associated with NH_4^+-N (25%) while the total load of NO_3^--N was unaffected and NO_2^--N was underestimated by 3%. Again, the falling limb of the hydrograph accounted for little of this error (1.8% to -4.2% for SS and NO_2^--N respectively) with the rising limb dominant however errors associated with the subsidiary hydrograph was not solely responsible. Over estimations with the 60 minute sample set (II) were more evenly apportioned between the subsidiary hydrograph and the main hydrograph rising limb for SS, VS, PP, SP, DIC and DOC, while the main rising limb accounted for a 75% overestimation for NH_4^+-N.

5. Conclusions

It is clear from the data presented in this paper that catchments dominated by intensively managed grassland systems have the potential to be a significant source of a range of diffuse pollutants. Within the study catchment base flow concentrations of P (both as PP and SP) and NO_2^--N were found to be environmentally significant while during storm flow

Table 4.2 Loads calculated for the field sub-catchment and the catchment based on 30 minute sample frequency and uncertain hydrographs. Loads for the catchment have also been calculated based on artificially depleted 60 minute sample sets with data removed on the hour (I) and half hour (II) and compared to 30 minute loads.

			PP	SP	NO_3^--N	NO_2^--N	NH_4^+-N	SS	VS	DIC	DOC
Field sub-catchment	30 minute	Total storm load	3.2 – 5.6 g	3.3 – 5.8 g	0	52 – 91 mg	3.6 – 6.2 g	0.2 – 0.4 kg	0.1 – 0.2 kg	0.2 – 0.4 kg	0.4 – 0.7 kg
Catchment	30 minute	Total storm load	0.8 – 1.2 kg	0.6 – 1.0 kg	0.4 – 0.8 kg	[a]15 – 28 g	0.6 – 1.0 kg	86 – 137 kg	28 – 47 kg	14 – 24 kg	39 – 63 kg
	60 minute (I)	Total storm load	0.7 – 1.0 kg	0.6 – 0.8 kg	0.4 – 0.8 kg	16 – 32 g	0.4 – 0.6 kg	70 – 107 kg	22 – 36 kg	14 – 23 kg	36 – 57 kg
		% difference from 30 minute loads	-14	-13	0.6	12	-35	-21	-23	-3.7	-9.0
	60 minute (II)	Total storm load	0.9 – 1.4 kg	0.7 – 1.1 kg	0.4 – 0.8 kg	[a]14 – 27 g	0.7 – 1.3 kg	99 – 161 kg	33 – 56 kg	15 – 25 kg	40 – 67 kg
		% difference from 30 minute loads	12	9	0.1	-3	25	16	18	3	6

[a]Excluding anomalous high data point occurring at 17:00
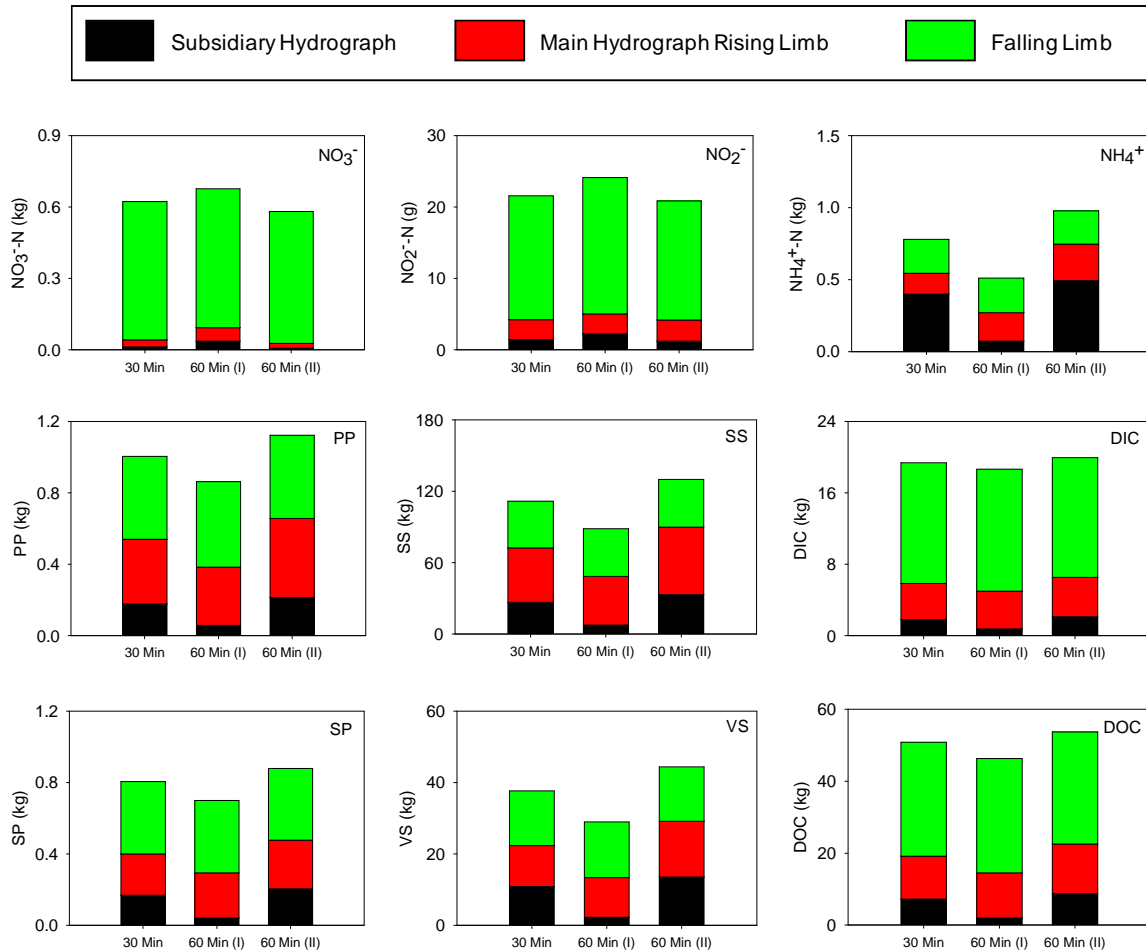
Figure 4.4. Total loads of each pollutant exported from the catchment and the contribution of different phases of the hydrograph calculated on the 30 minute data set and two artificially depopulated 60 minute data sets with data removed on the hour (I) and on the half hour (II). Loads were calculated using the middle Q value of the uncertain range.

marked pollutant concentration/discharge dynamics were observed and concentrations of P remained high and SS concentrations also rose above environmentally significant levels concentrations rose. Both NO_3^--N and NO_2^--N concentrations were observed to decrease in a manner that was typical of rainwater dilution indicating that both were derived from within the soil. Other pollutants, both particulate and soluble, were observed to increase with increased discharge. A subsidiary hydrograph which occurred on the main hydrograph rising limb appeared to be a response to rapid run-off from farm building and hard standings within the catchment. This conclusion was reached due to a significant increase in NH_4^+-N concentrations which occurred in association with the subsidiary hydrograph peak. While a

marked spike in other pollutant concentrations also occurred at this point on the hydrograph, the same conclusion could not be reached as to their source. This is because these pollutants could have been sourced elsewhere in the catchment in addition to the hard standings and merely mobilised by the increased discharge. However, the delayed hydrological response of the field sub-catchment relative to the catchment outlet would indicate that the catchment was still in the process of wetting up while the spike in pollutants was occurring at the catchment outlet. This would suggest that the spike in pollutant concentrations could only have been sourced from the hard standings, from within the stream channel, or from areas proximal to the stream channel.

Concentrations of pollutants in the surface flow from the field sub-catchment were lower than those observed at the catchment outlet and did not show the same degree of temporal variation with the exception of DIC and DOC the concentration of which increased over time. The clearly complex nature of the pollutant/discharge dynamics of this relatively small first order stream catchment highlights the need to understand better the role of different source areas and pathways in pollutant delivery to water bodies.

Within this study, the 30 minute sampling strategy adopted was only just sufficient to capture the significant incidental pollution event associated with the subsidiary hydrograph. An hourly sampling strategy may not have captured the concentration dynamics associated with this small subsidiary hydrological event. Calculated pollutant loads were also severely affected by a reduction in sample frequency such that in the worse case loads of NH_4^+-N could have been underestimated by 35% or over estimated by 25% depending on when hourly samples were collected. Typically loads calculated on the falling limb of the hydrograph were not greatly affected with most errors occurring on the rising limb and more specifically on the subsidiary hydrograph which was associated with an incidental transfer of pollutants.

While the findings presented in this paper are useful they are limited to one small catchment and one storm event. To better understand multi-pollutant dynamics there is a need to monitor more storms of different magnitudes and during different seasons, and on different catchments with contrasting soil types and land uses. This short study also highlights the need to understand better the source areas and pathways from which potential pollutants become entrained. These may be better understood through the use of

novel tracing techniques to discriminate between the different source areas, and to highlight the pathways by which pollutants are transported.

Acknowledgements

References

ARMSTRONG, A. C. & GARWOOD, E. A. 1991. Hydrological consequences of artificial drainage of grassland. *Hydrological Processes.,* 5**,** 157-174.

ARMSTRONG, A. C., LEEDS-HARRISON, P. B., HARRIS, G. L. & CATT, J. A. 1999. Measurement of solute fluxes in macroporous soils: techniques, problems and precision. *Soil Use and Management.,* 15**,** 240-246.

BILOTTA, G. S., BRAZIER, R. E. & HAYGARTH, P. M. 2007. Processes affecting transfer of sediment and colliods, with associated phosphorus, from intensively farmed grasslands: erosion. *Hydrological Processes.,* 21**,** 135-139.

BILOTTA, G. S., BRAZIER, R. E., HAYGARTH, P. M., MACLEOD, C. J. A., BUTLER, P., GRANGER, S., KRUEGER, T., FREER, J. & QUINTON, J. 2008. Rethinking the contribution of drained and undrained grasslands to sediment-related water quality problems. *Journal of Environmental Quality.,* 37**,** 906-914.

BOORMAN, D. B., HOLLIS, J. M. & LILLY, A. 1995. Hydrology of soil types: a hydrologically based classification of the soils of the United Kingdom. Wallingford, Oxfordshire: Institute of Hydrology report No.126.

BRAZIER, R. E., BILOTTA, G. S. & HAYGARTH, P. M. 2007. A perspective on the role of lowland, agricultural grasslands incontributing to erosion and water quality problems in the UK. *Earth Surface Processes and Landforms.,* 32**,** 964-967.

EDWARDS, A. C., KAY, D., MCDONALD, A. T., FRANCIS, C., WATKINS, J., WILKINSON, J. R. & WYER, M. D. 2008. Farmyards, an overlooked source for highly contaminated runoff. *Journal of Environmental Management.,* 87**,** 551-559.

EISENREICH, S. J., BANNERMAN, R. T. & ARMSTRONG, D. E. 1975. A simplified phosphorus analysis technique. *Environmental Research Letters.,* 9**,** 43-53.

EUROPEAN ECONOMIC COMMUNITY 1978. Council directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life (78/659/EEC). *Official Journal of the European Commiunties.,* 21**,** 1-10.

EUROPEAN ECONOMIC COMMUNITY 1991. Council directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). *Official Journal of the European Commiunties.,* L375**,** 1-8.

GÄCHTER, R., STEINGRUBER, S. M., REINHARDT, M. & WEHRLI, B. 2004. Nutrient transfer from soil to surface waters: differences between nitrate and phosphate. *Aquatic Sciences.,* 66**,** 117-122.

GRANGER, S. J., BOL, R., BULTER, P. J., HAYGARTH, P. M., NADEN, P., OLD, G., OWENS, P. N. & SMITH, B. P. G. 2007. Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: tracing sediment and organic matter. *Hydrological Processes.,* 21**,** 417-422.

HAIGH, R. A. & WHITE, R. E. 1986. Nitrate leaching from a small, underdrained, grassland, clay catchment. *Soil Use and Management.,* 2**,** 65-70.

HALLET, S. H., THANIGASALAM, P. & HOLLIS, J. M. 1995. SEISMIC: a desktop information system for assessing the fate and behaviour of pesticides in the environment. *Computers and Electronics in Agriculture.,* 13**,** 227-242.

HARROD, T. R. & HOGAN, D. V. 2008. The soils of North Wyke and Rowden. Unpublished report to North Wyke Research, revised edition of original report by T.R. Harrod,

Soil Survey of England and Wales (1981). North Wyke Research, Okehampton, Devon.

HATCH, D. J., CHADWICK, D. R., SMITH, K. A. & CHAMBERS, B. J. Year. Ammonium-N losses from agriculture. *In:* LEWIS, D. & GAIRNS, L., eds. Proceedings of the SAC and SEPA Biennial Conference., 2004 Edinburgh, 24-25 March 2004., 165-173.

HAWKINS, J. M. B. & SCHOLEFIELD, D. 1996. Molybdate-reactive phosphorus losses in surface and drainage waters from permanent grassland. *Journal of Environmental Quality.,* 25**,** 727-732.

HAYGARTH, P. M., BILOTTA, G. S., BOL, R., BRAZIER, R. E., BUTLER, P. J., FREER, J., GIMBERT, L. J., GRANGER, S. J., KRUEGER, T., MACLEOD, C. J. A., NADEN, P., OLD, G., QUINTON, J. N., SMITH, B. & WORSFOLD, P. 2006. Processes affecting transfer of sediment and colloids, with

associated phosphorus, from intensively farmed grasslands: an overview of key issues. *Hydrological Processes.,* 20**,** 4407-4413.

HAYGARTH, P. M., HEPWORTH, L. & JARVIS, S. C. 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed land. *European Journal of Soil Science.,* 49**,** 65-72.

HAYGARTH, P. M. & JARVIS, S. C. 1999. Transfer of phosphorus from agricultural soils. *Advances in Agronomy.,* 66**,** 195-249.

HEATHWAITE, A. L., BURT, T. P. & TRUDGILL, S. T. 1990. The effect of land use on nitrogen, phosphorus and suspended sediment delivery to streams in a small catchment in southwest England. *In:* THORNES, J. B. (ed.) *Vegetation and Erosion.*: John Wiley & Sons Ltd.

HENRICKSEN, A. & SELMER-OLSEN, A. R. 1970. Automatic methods for determining nitrate and nitrite in water and soil extract. *Analyst.,* 95**,** 514-518.

HOUSE, W. A., JICKELLS, T. D., EDWARDS, A. C., PRASKA, K. E. & DENISON, F. H. 1998. Reactions of phosphorus with sediments in fresh and marine waters. *Soil Use and Management.,* 14S**,** 139-146.

HOUSE, W. A. & WARWICK, M. S. 1998. Hysteresis of the solute concentration/dischagre relationship in rivers during storms. *Water Research.,* 32**,** 2279-2290.

JARVIE, H. P., HAYGARTH, P. M., NEAL, C., BUTLER, P., SMITH, B., NADEN, P. S., JOYNES, A., NEAL, M., WICKHAM, H. D., ARMSTRONG, L., HARMAN, S. & PALMER-FELGATE, E. J. 2008. Stream water chemistry and quality along an uplnad-lowland rural land-use continuum, south west England. *Journal of Hydrology.,* 350**,** 215-231.

JOHNES, P. J. 2007. Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. *Journal of Hydrology.,* 332**,** 241-258.

JORDAN, P., ARNSCHEIDT, J., MCGROGAN, H. & MCCORMICK, S. 2005. High-resolution phosphorus transfers at the catchment scale: the hidden importance of non-storm transfers. *Hydrology and Earth System Sciences.,* 9**,** 685-691.

KIRCHNER, J. W., FENG, X., NEAL, C. & ROBSON, A. J. 2004. The fine structure of water-quality dynamics: the (high frequency) wave of the future. *Hydrological Processes.,* 18**,** 1353-1359.

KRUEGER, T., QUINTON, J. N., FREER, J., MACLEOD, C. J. A., BILOTTA, G. S., BRAZIER, R. E., BUTLER, P. & HAYGARTH, P. M. 2008. Uncertainties in data and models to describe event dynamics of agricultural sediment and phosphorus transfer. *Journal of Environmental Quality.*

LEWIS, W. M. & MORRIS, D. P. 1986. Toxicity of nitrite to fish: a review. *Transactions of the American Fisheries Society.,* 115**,** 183-195.

MALCOLM, R. L. 1993. Concentration and composition of dissolved organic carbon in soils, streams, and groundwaters. *In:* BECH, A. J., JONES, K. C., HAYES, M. H. B. & MINGELGRIN, U. (eds.) *Organic substances in soil and water: natural constituents and their influences on contaminant behaviour.* Cambridge: Royal Society of Chemistry.

MARAN, D., OSBORN, T. J. & GILLET, N. P. 2008. United Kingdom daily precipitation intensity: improved early data, error estimates and an update from 2000 to 2006. *International Journal of Climatology.,* 28**,** 833-842.

MCTIERNAN, K. B., JARVIS, S. C., SCHOLEFIELD, D. & HAYES, M. H. B. 2001. Dissolved organic carbon losses from grazed grassland under different management regines. *Water Research.,* 35**,** 2565-2569.

NEAL, C., JARVIE, H. P., LOVE, A., NEAL, M., WICKHAM, H. & HARMAN, S. 2008. Water quality along a river continuum subject to point and diffuse sources. *Journal of Hydrology.,* 350**,** 154-165.

OECD 1982. *Eutrophication of Waters: Monitoring, Assessment and Control.,* Paris, Organisation for Economic Co-operation and Development.

PINOKE, H. B., GBUREK, W. J., SHARPLEY, A. N. & SCHNABEL, R. R. 1996. Flow and nutrient export patterns for an agricultural hill-land watershed. *Water Resources Research.,* 32**,** 1795-1804.

PREEDY, N., MCTIERNAN, K., MATTHEWS, R., HEATHWAITE, L. & HAYGARTH, P. 2001. Rapid incidental phosphorus transfers from grassland. *Journal of Environmental Quality.,* 30**,** 2105-2112.

QUINN, J. M. & STROUD, M. J. 2002. Water quality and sediment and nutrient export from New Zealand hill-land catchments of contrasting land use. *New Zealand Journal of Marine and Freshwater Research.,* 36**,** 409-429.

RANDALL, D. J. & TSUI, T. K. N. 2002. Ammonia toxicity in fish. *Marine Pollution Bulletin.,* 45**,** 17-23.

RYDEN, J. C., BALL, P. R. & GARWOOD, E. A. 1984. Nitrate leaching from grassland. *Nature.,* 311**,** 50-53.

SCHOLEFIELD, D., LE GOFF, T., BRAVEN, J., EBDON, L., LONG, T. & BUTLER, M. 2005. Concerted diurnal patterns in riverine nutrient concentrations and physical conditions. *Science of the Total Environment.,* 344**,** 201-210.

SCHOLEFIELD, D., TYSON, K. C., GARWOOD, E. A., ARMSTRONG, A. C., HAWKINS, J. & STONE, A. C. 1993. Nitrate leaching from grazed lysimeters: effects of fertilizer input, field drainage, age of sward and patterns of weather. *Journal of Soil Science.,* 44**,** 601-613.

SEARLE, P. L. 1984. The Berthelot or Indophenol reaction and its use in the analytical chemistry of nitrogen. *Analyst.,* 109**,** 549-568.

SHARPLEY, A. N. & REKOLAINEN, S. 1997. Phosphorus in agriculture and its envoronmental implications. *In:* TUNNEY, H., CARTON, O. T., BROOKES, P. C. & JOHNSON, A. E. (eds.) *Phosphorus Loss from Soil to Water.*: CAB International, Oxon, U.K.

SMITH, R. V., FOY, R. H., LENNOX, S. D., JORDAN, C., BURNS, L. C., COOPER, J. E. & STEVENS, R. J. 1995a. Occurrence of nitrite in the Lough Neagh river system. *Journal of Environmental Quality,* 24**,** 952-959.

SMITH, R. V., LENNOX, S. D., JORDAN, C., FOY, R. H. & MCHALE, E. 1995b. Increase in soluble phosphorus transported in drainflow from a grassland catchment in response to soil phosphorus accumulation. *Soil Use and Management.,* 11**,** 204-209.

UK STANDING COMMITTEE OF ANALYSTS 1980. *Suspended, settleable and total dissolved solids in waters and effluents,* London, HMSO.

WATSON, C. J., JORDAN, C., LENNOX, S. D., SMITH, R. V. & STEEN, R. W. J. 2000. Inorganic nitrogen in drainage water from grazed grassland in Northern Ireland. *Journal of Environmental Quality.,* 29**,** 225-232.

WEBB, B. W. & WALLING, D. E. 1985. Nitrate behaviour in streamflow from a grassland catchment in Devon, U.K. *Water Research.,* 19**,** 1005-1016.

WITHERS, P. J. A., ULEN, B., STAMM, C. & BECHMENN, M. 2003. Incidental phosphorus losses - are they significant and can they be predicted? *Journal of Plant Nutrition and Soil Science.,* 166**,** 459-468.