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Catchment land use effects on fluxes and concentrations of organic and inorganic nitrogen in streams

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Abstract

We present annual downstream fluxes and spatial variation in concentrations of dissolved inorganic nitrogen (NH_4^+ and NO_3^-) and dissolved organic nitrogen (DON) in two adjacent Scottish catchments with contrasting land use (agricultural grassland vs. semi-natural moorland). Inter- and intra-catchment variation in N species and the relation to spatial differences in agricultural land use were studied by determining catchment N input through agricultural activities at the field scale and atmospheric inputs at a 25 m grid resolution. The average agricultural N input of 52 kg N ha^{-1} yr^{-1} to the grassland catchment was more than four times higher than the input of 12 kg N ha^{-1} yr^{-1} to the moorland catchment, supplemented by 12.3 and 8.2 kg N ha^{-1} yr^{-1} through atmospheric deposition, respectively. The grassland catchment was associated with an annual downstream total dissolved nitrogen (TDN) flux of 14.4 kg N ha^{-1} yr^{-1}, which was 66% higher than the flux of 8.7 kg ha^{-1} yr^{-1} from the moorland catchment. This difference was largely due to the NO_3^- flux being one order of magnitude higher in the grassland catchment. Dissolved organic N fluxes were similar for the two catchments (7.0 kg ha^{-1} yr^{-1}) with DON contributing 49% to the TDN flux in the grassland compared with 81% in the moorland catchment. The results highlight the importance of diffuse agricultural N inputs to stream NO_3^- concentrations and the importance of quantifying all the major aquatic N species for developing a better understanding of N transformations and transport in the atmosphere-soil-water system.

Keywords: nitrogen, organic nitrogen, stream export, catchment flux, land use

Highlights

- Local farm inventory provided field specific N input to catchments
- Streamwater chemistry is sensitive to landscape scale variation in N input
- Agricultural N input determined streamwater NO_3^- concentrations
- DON contributes significantly to fluvial N export in grazed grassland catchments

1 Introduction

Human actions at the landscape scale impact the ecological state of stream ecosystems, particularly through land use change (Allan, 2004; Likens and Bormann, 1974). Over the last few centuries, land use change has taken place on a global scale increasing the area of different types of agricultural land (Goldewijk, 2001). One of the most significant changes in agricultural systems is the increase in nitrogen (N)

inputs caused by application of mineral and organic fertiliser as well as organic manures associated with grazing livestock (Nieder and Benbi, 2010; Wade et al., 2005). However, significant uncertainties remain about the influence of land use on N export to the aquatic system at the catchment scale, due to the complexity of N dynamics in terrestrial systems (Alvarez-Cobelas et al., 2008).

In aquatic ecosystems, N enrichment at the catchment scale can have significant impact on water quality and is well known to be linked to eutrophication (e.g. Grizzetti et al., 2011). The main forms of reactive, i.e. biologically available, N dissolved in streamwater are ammonium (NH_4^+), nitrate (NO_3^-) and dissolved organic nitrogen (DON). However, most studies on catchment N export have focused on single N species, particularly on NO_3^- as this was understood to be the dominant form of N leaching from agricultural systems (Alvarez-Cobelas et al., 2008; Van Kessel et al., 2009). Generally, high soil organic matter content is considered to result in high concentrations and fluxes of streamwater dissolved organic carbon (DOC) and N compounds (e.g. Aitkenhead et al., 1999; Neff et al., 2003). A number of studies on the organic N fraction in streamwater have been conducted in forested systems associated with organic soils (e.g. Campbell et al., 2000; Perakis and Hedin, 2002). In recent years the importance of organic N as a significant form of streamwater N not only in semi-natural but also in agricultural areas has become apparent (e.g. Murphy et al., 2000; Scott et al., 2007), although the behaviour and origin of DON in streamwater is not fully understood (Durand et al., 2011). Catchment studies therefore need to take into account all forms of streamwater N, including organic forms, to gain better understanding of controls on N export.

In this study, we investigated two Scottish catchments with contrasting land use, one dominated by grazed grassland, the other dominated by semi-natural moorland. Annual downstream fluxes of NH_4^+, NO_3^- and DON were established by sampling at the gauged catchment outlets at both fortnightly and hourly intervals; the latter during selected high flow events during 2008. A detailed landscape inventory provided data

on spatial N input to the catchments by agricultural activities. The relationship between agricultural land use N input and spatial variability of concentrations within the catchments was studied by conducting synoptic intensive samplings throughout the year. This study aimed to quantify the relationship between land use and streamwater N concentrations with particular emphasis on understanding the speciation of the aqueous N forms.

2 Site and methods

2.1 Study area

The Black Burn and Lead Burn catchments are located approximately 20 km south of Edinburgh in southern Scotland. They are subcatchments of the North Esk River and the streams flow in a northeast direction. The Black Burn catchment covers an area of 6.2 km^2, has an average slope of 1.7° and an average altitude of 270 m (range 218 - 303 m) (Figure 1). The upper part of this catchment has been studied previously in terms of its hydrochemistry with particular emphasis on carbon concentrations and fluxes (Billett et al., 2004; Dinsmore and Billett, 2008; Dinsmore et al., 2010). The main soil types of the Black Burn catchment are (Scottish Soil Survey terms in brackets) histosol (peat) (67%), with lesser amounts of cambisols (brown forest soils) (16%) and humic gleysol (peaty gleys) (10%). Semi-natural moorland accounts for 63% of the land cover, a further 12% is used for peat extraction, 10% is rough grass and 2% woodland. Only 11% of the Black Burn catchment is improved grassland and there is no arable land. Two thirds of the semi-natural moorland are grazed by sheep at a very low stocking density (<1 sheep ha^{-1}) and the remaining third is a protected Site of Special Scientific Interest (SSSI) with no grazing.

The Lead Burn catchment covers an area of 8.9 km^2, has an average slope of 3.1° and average altitude of 280 m (range 241 - 368 m) (Figure 1). Approximately half of the catchment consists of cambisols (brown forest soils) (48%), associated

with gleysols (noncalcareous gleys) (21%) and histosols (peat) (21%). The main land cover types are improved grassland (59%), rough grassland (10%), woodland (14%), moorland (5%), shrubs (3%), peat extraction (2%) and arable land (2%). The agricultural land is grazed by beef cattle and sheep (stocking density: <1 beef cattle ha^{-1} and 10 sheep ha^{-1}). There are also six poultry houses with over ¼ million laying hens. The poultry farming operations are largely disconnected from the catchment hydrology, as feeds are imported and manure exported by road. However, ammonia emissions from the poultry houses contribute to significant atmospheric N inputs to both catchments (Vogt et al., 2013a; Vogt et al., 2013b).

INSERT FIGURE 1

Both catchments lie to the south of the Southern Upland Boundary Fault in an area where the underlying parent materials are dominated by sandstone, containing thin bands of limestone, mudstone, coal and clay (Billett et al., 2004). Southern Scotland has a temperate and oceanic climate. In 2008, the catchments received an annual rainfall of 1208 mm (M. Coyle, pers. com. 2009), measured at Auchencorth Moss field site located within the Black Burn catchment. The air temperature varied from -8.3°C to 25.4°C with an annual average of 7.6°C.

2.2 Discharge measurements

Discharge was measured continuously in both streams using Level Troll® (In-Situ Inc.) pressure transducers, located at the catchment outlets. Measurements were made at 1 Hz with 15 minute averaging. In-stream pressure was corrected for atmospheric pressure and stage height data were established by a linear regression between pressure data and gauge height readings (for both streams: $r^2 = 0.99$, $n = 17$). Continuous discharge was then calculated using a curvilinear regression

between stage height data and a series of dilution gauging measurements (Black Burn: $r^2 = 0.98$, n = 14; Lead Burn: $r^2 = 0.92$, n = 15).

2.3 Streamwater sampling

During 2008, both streams were sampled using three approaches: (a) Fortnightly samples were collected at the outlet of each of the two study catchments to estimate annual downstream fluxes, (b) Automatic water samplers (Teledyne Isco) were installed at the catchment outlets to collect hourly streamwater samples during several high flow events (4 Oct, 7 Oct, 9-11 Oct, 12/13 Dec 2008) for improving annual flux calculations and (c) Streamwater chemistry was sampled spatially during synoptic intensive samplings at stable low flow conditions on consecutive days for both streams on 22/23 July, 25/26 September and 9/10 December 2008. The aim of the latter approach was to capture the spatial variability in the concentrations of N species across the two catchments (and possible links to sources) by sampling the main streams and their tributaries (36 samples from Black Burn and 46 from Lead Burn).

All water samples were collected in prewashed and dried bottles (either 1 L PP or 125 ml PE (Nalgene)), filtered on the same day in the laboratory and frozen prior to analysis.

2.4 Chemical determination of NH_4^+, NO_3^-, TDN and DOC

All water samples were filtered through 0.45 µm syringe filters (Minisart® NML, Sartorius Stedim Biotech). The syringe filters were pre-flushed with sample water. Each sample was stored in two 24 ml PE bottles (Kartell) and two 2 ml glass vials (Chromacol) and frozen at -18°C until analysis. Ammonium (NH_4^+) and nitrate (NO_3^-) were determined using a dual channel continuous-flow colourimetric analyser (ChemLab Instruments Ltd). Total dissolved nitrogen (TDN) was determined using an 8060-M HPLC-CLND (Antek Instruments Inc.), which catalytically oxidises nitrogen

and detects the resulting nitric oxide (NO) with chemiluminescence (Gonzalez Benitez et al., 2010). The detection limit for TDN was 0.01 mg L^{-1}. As dissolved organic nitrogen (DON) in water samples cannot be quantified directly (Gonzalez Benitez et al., 2009), it was calculated as the difference between TDN and dissolved inorganic nitrogen (NH_4^+-N + NO_3^--N). Dissolved organic carbon (DOC) was determined by ultra-violet oxidation and subsequent infra-red detection with a LABTOC® analyser (Pollution Process Monitoring Ltd). The detection limit for DOC was 0.1 mg L^{-1}.

2.5 Flux calculation

Fluxes of NH_4^+-N, NO_3^--N, DON and DOC in kg ha^{-1} yr^{-1} were calculated according to 'Method 5' of Walling and Webb (1985). This method is recommended when continuous discharge and non-continuous concentration data are available (e.g. Dawson et al., 2002; Hope et al., 1997). 'Method 5' is described by equation (1), where K is the conversion factor for scaling up to annual fluxes (i.e. number of seconds in one year), Q_r is the mean annual discharge [L s^{-1}] and C_F is the flow-weighted mean concentration [mg L^{-1}].

$$Flux = K \cdot Q_r \cdot C_F \tag{1}$$

C_F is calculated according to equation (2), where C_i are concentration values [mg L^{-1}] associated with Q_i [L s^{-1}], the discharge values at the time.

$$C_F = \sum_{i=1}^{n} \left(C_i \cdot Q_i \right) / \sum_{i=1}^{n} Q_i \tag{2}$$

The subsequent downstream flux in mg yr^{-1} was converted to kg ha^{-1} yr^{-1} and the percentage contribution of the inorganic and organic fraction to the overall N flux determined.

Approximate standard errors of the flux estimates were calculated using equation (3) (see Hope et al., 1997 for details), where F is the total annual discharge [L yr^{-1}]

and v*ar(C_F)* [mg L^{-1}] the variance of C_F. The approximate standard error (SE) in mg yr^{-1} was converted to the same unit as the downstream flux.

$$SE = F \cdot \sqrt{var\left(C_F\right)} \quad (3)$$

The variance of C_F is calculated according to equation (4), where Q_n [L s^{-1}] is the sum of all individual Q_i values.

$$var\left(C_F\right) = \left[\sum_{i=1}^{n}\left(C_i - C_F\right)^2 \cdot Q_i / Q_n\right] \cdot \sum_{i=1}^{n}\left(Q_i^2 / Q_n^2\right) \quad (4)$$

2.6 Soil, land use and topography data

All spatial data were processed with the geographical information system ArcGIS (ESRI). The digital soil map was acquired from the James Hutton Institute under license (MI/2008/296). Land use data for 2008 were obtained through a local farm and field inventory carried out by CEH and SRUC staff (Dragosits et al., 2011). Inventory data include information on each livestock house (e.g. type of livestock, animal numbers, and manure management) and management for each field (e.g. grazing intensity, fertiliser and manure applications). From these data, nitrogen inputs were calculated for every field within the catchments (see Section 2.7). Surface topography data at a resolution of 5 m from a Digital Terrain Model (DTM) (Intermap Technologies Inc., 2010) were used to derive subcatchments in ArcGIS for the sample locations chosen for the intensive spatial sampling along the main streams. This resulted in 8 and 10 subcatchments for Black Burn (ranging in size from 2.6 to 6.2 km²) and Lead Burn (ranging in size from 4.1 to 8.9 km²), respectively.

2.7 Land use and atmospheric nitrogen input

For each field within the catchments, the N input was calculated from grazing livestock, manure and fertiliser applications during 2008 from the detailed farm and field inventory and from modelled atmospheric deposition. It is noted that there are several different budget approaches to calculating N input into a system, e.g. a field,

a farm or a catchment, summarised in de Vries et al. (2011). In this work the N input "soil budget" approach is used (see Vogt et al. 2013a for further detail). N applied to the soil system which can potentially leach into water is accounted for. Uncertainty classes were assigned to N inputs depending on the accuracy of the data source using a similar classification scheme as in Kros et al. (2012). Nitrogen input from grazing livestock was estimated using grazing records and daily N excretion data from the UK ammonia inventory (Table 1). The uncertainty of N input through grazing livestock excreta is estimated to be high (± 50%) as the N content of the grazed grass is not known. Nitrogen input from manure applications were calculated by assigning a typical N content to different manure types as specified by the farmer according to Defra guidelines (2010) (Table 2). Thus, N input from manure applications is estimated to carry a moderate (± 30%) uncertainty. Nitrogen input from fertiliser applications is considered accurate (± 10%), as this value is known by individual farmers. Nitrogen inputs estimated from grazing livestock, manure and fertiliser applications were summed for each field and the total input per (sub) catchment was calculated.

INSERT TABLES 1 AND 2

Atmospheric N deposition was estimated by Vogt et al. (2013b), by combining the different N deposition components: (a) Dry deposition of ammonia (NH_3) resulting from farming activities in a 6 km x 6 km landscape surrounding the catchments was calculated at a 25 m grid resolution using the LADD model (Theobald et al., 2012), and (b) Contributions of imported wet deposition of reduced nitrogen (NH_x) as well as wet and dry deposition of oxidised N compounds (NO_y) from UK and European sources were derived using the UK FRAME model at a 1 km resolution (Dore et al., 2007). Nitrogen inputs from the above sources to each catchment are summarised in Table 3. Neither catchment was found to include any significant area of legume

cultivation and the input of N by biological nitrogen fixation was assumed to be negligible. The overall uncertainty in N inputs were calculated using the same method as in Vogt et al (2013a) and was ~23% for both catchments.

INSERT TABLE 3

2.8 Statistical analysis

Fortnightly streamwater concentrations were tested if to differ significantly between the streams by Whitney-Mann *U* test (Table 5). This non-parametric test compares the medians of two data sample sets (e.g. Currell and Dowman 2009). The Spearman rank correlation ρ was used to assess if different chemical species measured fortnightly in streamwater were correlated, i.e. if any chemical species co-vary (Table 6). A regression analysis was carried out using the coefficient of determination r^2 to test if streamwater concentrations are dependent on variations in discharge (Table 7). This approach calculates the magnitude of the effect of the explanatory variable on the dependent variable and produces a linear model to describe the relationship. Discharge data were transformed to logarithmic scale and concentrations were calculated from streamwater samples collected fortnightly and during high flow events. A regression analysis was also carried out between streamwater concentrations and land surface N input (Table 10). For this, annual mean streamwater concentrations at the outlet of each subcatchment (see Section 2.6) and N input to the subcatchment land surface area were used. Subcatchment N input was calculated from grazing livestock excreta, manure and fertiliser applications plus atmospheric deposition (see Section 2.5). All statistical tests were performed with a two-tailed significance level of 5% ($p = 0.05$).

3 Results

3.1 Stream discharge

Mean discharge, measured continuously in 2008 and averaged over 15 minute intervals, was 140 L s^{-1} for Black Burn and 225 L s^{-1} for Lead Burn (Table 4). The difference was largely due to catchment size as the mean specific (area-weighted) discharges were 23 L s^{-1} km^{-2} for Black Burn and 25 L s^{-1} km^{-2} for Lead Burn. Discharge was highly variable in both streams (Figure 2) with the percentage of the standard deviation to mean discharge being 204% for Black Burn and 132% for Lead Burn. High discharge events make an important contribution to the overall discharge. In 2008, the highest 10% of the data (90^{th} percentile) contributed 53% to the total discharge in Black Burn and 40% in Lead Burn.

INSERT TABLE 4

INSERT FIGURE 2

3.2 Fortnightly streamwater concentrations

Time series of fortnightly NH_4^+-N, NO_3^--N, DON and DOC concentrations during 2008 are shown in Figure 3 and basic statistical analysis in Table 5. Median concentrations were tested to see if significant differences existed between the streams by Whitney-Mann *U* test at a two-tailed 95% significance level (p = 0.05). Annual median NH_4^+-N concentrations were not significantly different between the two streams. However, the streams differed in their NH_4^+-N contribution to TDN (16% in Black Burn and 6% in Lead Burn). Concentrations of NH_4^+-N during winter months were greater in Black Burn compared with Lead Burn (Figure 3).

Median streamwater NO_3^--N concentrations were significantly lower (Table 5) in Black Burn (0.12 mg L^{-1}) compared with Lead Burn (1.46 mg L^{-1}). Hence, in Lead

Burn NO_3^--N accounted for most of the TDN (64%), and made a much larger contribution to the total N concentration than in Black Burn (13%).

Dissolved organic N concentrations were not significantly different between the two streams. However, Figure 3 shows clear differences in DON behaviour between the streams with large changes in concentration in Lead Burn, particularly during the first half of the year. The contribution of DON to TDN was much lower in Lead Burn (31%) compared with Black Burn (72%). Dissolved organic C concentrations were not significantly different between the two streams and followed a similar temporal pattern throughout the year with the highest concentrations in the late summer (Figure 3). Ratios of DOC:DON differed significantly between the streams. From fortnightly samples, the median DOC:DON ratio was 37 at Black Burn and 26 at Lead Burn, with the variation in DOC:DON ratios much larger in Lead Burn compared with Black Burn.

INSERT FIGURE 3

INSERT TABLE 5

Significant correlations between chemical species are shown in Table 6. For Black Burn, a significant positive correlation between DOC and DON concentrations was observed. However, no such relationship existed for Lead Burn. In both streams, NO_3^--N and DOC concentrations were negatively correlated.

INSERT TABLE 6

3.3 Measurements at high flows

As fluxes associated with high flow events can make a significant contribution to annual fluxes, one aim of our study was to conduct high frequency measurements

during several (four) high flow events (Figure 4). Those measurements, while rarely capturing the complete storm event, were used to establish concentration-discharge relationships and improve annual downstream flux estimates (see Section 3.4). A regression analysis was carried out to test relationships between discharge and streamwater concentrations of samples collected fortnightly and during high flow events (Table 7). Scatter plots between streamwater concentrations and log discharge showed that in both streams, discharge was negatively related to NO_3^--N and positively related to DOC concentration (Figure 5). However, while Black Burn discharge was also positively related with DON concentration, no such relationship was observed for Lead Burn.

INSERT FIGURES 4AND 5

INSERT TABLE 7

3.4 Catchment chemical fluxes

Annual downstream fluxes of NH_4^+-N, NO_3^--N, DON and DOC for 2008 were calculated using both the data from routine fortnightly sampling as well as from high frequency sampling during high flow events (Table 8). The contribution of NH_4^+-N, NO_3^--N, DON to the catchment TDN flux of both streams is illustrated in Figure 6.

The Lead Burn TDN flux (14.4 kg ha^{-1} yr^{-1}) is 66% higher than the TDN flux for Black Burn (8.7 kg ha^{-1} yr^{-1}). This difference is mainly due to the NO_3^--N flux in Lead Burn being about 10 times higher than in Black Burn. The relative contributions of the different N components to the total flux therefore vary considerably. In Black Burn, DON makes up the largest proportion (81%), followed by NH_4^+-N (12%) and NO_3^--N (8%). In contrast, DON (49%) and NO_3^--N (47%) make a similar contribution to the total flux in Lead Burn. The NH_4^+-N flux, although relatively small, is 60% higher in

Black Burn compared with Lead Burn. Annual DOC fluxes were also higher in Black Burn.

INSERT TABLE 8

INSERT FIGURE 6

3.5 Spatial variability of concentrations

Thirty-six sampling locations within the Black Burn catchment and 46 sampling locations within the Lead Burn catchment were sampled at stable low flow conditions on three separate occasions (summer, autumn, winter 2008). From these values, an annual mean concentration for each sample location was calculated (Figure 7). Table 9 shows the mean, median and range of the annual mean concentrations for both catchments.

In relative terms, the greatest spatial variability within each catchment was shown by the inorganic N fraction. In the Black Burn, the standard deviation relative to the mean was 108% for NH_4^+-N and 112% for NO_3^--N; for Lead Burn, it was 95% and 66%, respectively. The dissolved organic fraction was more variable in Lead Burn with standard deviations of 41% for both DON and DOC, compared with 28% and 26% in Black Burn. Spatial differences in streamwater concentrations between the streams were tested using the Whitney-Mann *U* test ($p = 0.05$). Ammonium concentrations were not significantly different between the two catchments, although NO_3^--N, DON and DOC varied significantly. The clearest differences were for NO_3^--N concentrations with Lead Burn characterised by >16 times higher mean concentration than Black Burn. Means of spatial DON and DOC concentrations were greater in Black Burn than in Lead Burn.

INSERT TABLE 9

INSERT FIGURE 7

3.6 Relationships between spatial concentrations and nitrogen input

Nitrogen inputs to land through agricultural activities, such as grazing livestock and fertiliser applications, were calculated for both main catchments and their individual subcatchments at field scale. Based on the drainage pattern, the Black Burn catchment (6.2 km²) was divided into 8 subcatchments and the Lead Burn catchment (8.9 km²) into 10 subcatchments. A regression analysis was carried out between subcatchment N input (land use plus atmospheric deposition) and streamwater concentrations at the outlet of each subcatchment (Table 10, Figure 8). As the residence time for N in the catchment is not known, the underlying assumption of the regression analysis is that N inputs remain similar from year to year and hence the variations in N inputs are reflected in the aquatic N chemistry.

Both streams showed significant negative relationships between NH_4^+-N concentrations and N input and significant positive relationships between NO_3^--N concentrations and N input. Thus, the higher the N input from land use and atmospheric deposition, the lower the streamwater NH_4^+-N concentrations and the higher NO_3^--N concentrations. For DON concentrations, no relationship was observed in either catchment.

The main catchment N input from agricultural activities was more than four times higher in Lead Burn (51.9 kg N ha^{-1} yr^{-1}) compared with Black Burn (12.1 kg N ha^{-1} yr^{-1}) and the land use was in general more homogeneous across the Black Burn sub-catchments compared to the Lead Burn (see details in Vogt et al 2013a). Direct inputs from grazing livestock contributed the majority of those inputs in both catchments. In the Black Burn catchment, 73% of the agricultural N input was derived from grazing livestock, and organic and mineral fertiliser contributed 17% and 10% respectively. The annual N input to each catchment is summarised in Figure 9 both in

terms of totals and per unit area of the subcatchment. In the Lead Burn catchment, grazing livestock contributed 51%, organic fertiliser 31% and mineral fertiliser 18%. The majority of the N input was observed in three of the subcatchments: L1, L3 and L10. However when normalised to per-area input, there were fairly similar loadings across all the subcatchments, and in general these were significantly higher than for all the Black Burn subcatchments. The high NH_4^+ concentrations observed at the outlet of L1 may reflect a rapid run-off of NH_4^+ from surface deposition. The Black Burn N input into the subcatchments is in general lower than for the Lead Burn. The two highest N inputs per m^2 were B7 and B8, and these subcatchments had the highest grazing density of all the catchment. The higher N input did not lead to a significantly higher stream concentration in the N species measured (Figure 8). The N input through atmospheric deposition was modelled to be smaller in the Black Burn (8.2 kg N ha^{-1} yr^{-1}) compared with the Lead Burn catchment (12.3 kg N ha^{-1} yr^{-1}). The reasons for this difference are primarily due to higher levels of dry deposition of NH_x from local sources in the Lead Burn catchment (Vogt et al., 2013a).The local sources mean that the atmospheric input to the 25 m^2 areas which are aggregated up to fields from atmospheric N deposition are highly variable: from 0.2 to > 100 kg N ha^{-1} yr^{-1}(mean: 6.4 kg N ha^{-1} yr^{-1}).

INSERT TABLE 10

INSERT FIGURE 8

INSERT FIGURE 9

4 Discussion

4.1 Stream discharge

The stream discharge graphs for both streams are shown in Figure 2. The hydrological parameters measured for the Black Burn are very similar to that

measured over a five year period (in which 2008 was included, Dinsmore et al. 2013). It can be seen that for calculating annual catchment fluxes, it is important to incorporate high discharge events in the estimation of nutrient fluxes (e.g. Bowes et al., 2009; Vidon et al., 2009). Both streams show a rapid response to precipitation with a short rainfall-runoff response (this work and for the Black Burn see Dinsmore and Billett 2008). It can be seen that the Black Burn is a slightly more hydrologically "flashy" stream compared with Lead Burn, with consistently lower base flow levels, though the response times are similar. Though the response of specific subcatchments and tributaries were not characterised under all conditions, by studying the discharge of both streams for the full year, the hydrological nature of the two streams is well characterised.

4.2 Concentrations and sources of NH_4^+

Ammonium concentrations in both the Black Burn and Lead Burn were relatively low compared with concentrations of other forms of N. However, NH_4^+ concentrations were higher than in 28 semi-natural streams in upland Scotland studied by Chapman et al. (2001), who reported an annual mean concentration of 0.03 mg NH_4^+-N L^{-1} compared with 0.15 and 0.13 mg L^{-1} for the Black Burn and Lead Burn, respectively. Chapman et al. (2001) also found that NH_4^+ concentrations were constant through the seasons and accounted for 5% of TDN. A similar pattern was observed in Lead Burn, although in Black Burn NH_4^+ concentrations showed a tendency to be higher during winter months. The annual contribution of NH_4^+-N to TDN was also much higher (16%) in Black Burn. The dominance of histosols in the Black Burn catchment is likely to have a significant effect on streamwater NH_4^+ concentrations. Previous studies have found that waterlogged peat catchments associated with anaerobic conditions inhibit the oxidation of NH_4^+ to NO_3^- allowing NH_4^+ deposited from the atmosphere to transfer into ground and surface waters (Cresser et al., 2004; Evans et al., 2000). The atmospheric N deposition to the Black Burn catchment has been

estimated by Vogt et al. (2013a) to be 8.2 kg ha^{-1} yr^{-1}, 60% of which was NH_x deposition. The elevated N input to subcatchment B2 compared to B1 and B3-B6 may reflect the footprint of the atmospheric N deposition as B2 is more closely located to the major atmospheric point sources in the landscape.

The influence of wet peaty soils on streamwater NH_4^+ concentrations is a likely explanation for the seasonal differences in Black Burn and the differences between Black Burn and Lead Burn as the nitrification rates will be very much reduced in the acid, wet conditions. These findings are consistent with a negative relationship between streamwater NH_4^+ concentrations and N input (Figure 8), suggesting that the main source of NH_4^+ in streamwater are the wetter peaty soils which receive less agricultural N input. Specifically, the wet peaty soils with low N input are acidic and nitrification is likely to be inhibited. As the N load increases, the acidic nature is reduced and nitrification converting ammonium across to nitrate occurs more readily. Furthermore, short lived concentration increases at the beginning of the sampled high flow events (not shown) suggest that the source of NH_4^+ in streamwater could be very shallow and located close to the stream. Our results may thus indicate that catchments with wet peaty soils in areas subject to atmospheric N pollution are vulnerable to NH_4^+ leaching into streamwaters, especially in the winter when soil temperatures are low and water tables high which is consistent with conclusions of Daniels et al. (2012).

4.3 Concentration and sources of NO_3^-

Annual mean streamwater NO_3^--N concentrations of Black Burn (0.12 mg L^{-1}) were similar to those observed in other comparable studies (Edwards et al. 2000; Halliday et al. 2013). For example, Betton et al. (1991) collected information from >700 sites in Britain and found that mean annual NO_3^--N concentrations in Scotland were <1 mg L^{-1}, and Chapman et al. (2001) found that a group of 28 Scottish upland (nutrient-poor) catchments had a mean annual NO_3^--N concentration of 0.39 mg L^{-1},

accounting for 50% of the TDN. Likewise, Black et al. (1993) found NO_3^--N concentrations to be <1 mg L^{-1} in seven upland moorland catchments in northeast Scotland. Black et al. (1993) also observed the highest NO_3^- concentrations during the winter months when low temperatures and wet soils result in low biological NO_3^- uptake. Similarly, Black Burn had the highest NO_3^- concentrations during January and February.

Annual mean NO_3^--N concentrations of Lead Burn (1.53 mg L^{-1}) were higher than those found in the above mentioned studies, however at the low end of some studies on agriculturally impacted streams, with concentrations closer to 10 mg L^{-1} (e.g. Wohlfart et al. 2012, Bartoli et al. 2012). Streamwater NO_3^- concentrations were significantly positively related to subcatchment N inputs, which were primarily associated with greater agricultural land use (Table 10, Figure 8). This input of N from subcatchments with agricultural activity has been previously reported (Edwards *et al.* 2000), and highlights the importance of a high degree of spatial coverage in streamwater sampling in order to identify sources of input. Furthermore, NO_3^- concentrations were negatively correlated with discharge. This dilution of streamwater NO_3^- during storm events has been observed in other agricultural systems (Durand et al., 2011), although increasing concentrations with increasing discharge have also been observed (e.g. Van Herpe and Troch, 2000). Hence, it is generally considered that NO_3^- reacts inconsistently to changes in discharge which leads to complex hysteresis patterns (e.g. Oeurng et al., 2010). This is probably due to different NO_3^- concentrations in different water sources contributing to the streamwater and to variation in their contribution during storm events (Durand and Torres, 1996). Porewaters of well-drained soils and associated shallow groundwater generally exhibit high NO_3^- concentrations, while rainwater, porewater of wet soils and deep groundwater are usually less concentrated (Durand et al., 2011). Depending on the water pathways in the catchment, one or other of these stores may

be the predominant source during storm events, causing either dilution or concentration.

4.4 Concentrations and sources of dissolved organic N and C

Dissolved organic N concentrations of both streams in this study were relatively high with annual means of 0.67 mg L^{-1} in Black Burn and 0.74 mg L^{-1} in Lead Burn, compared with those reported in the literature. Chapman et al. (2001) report a range of annual DON concentrations in 28 Scottish catchments of 0 to 0.87 mg L^{-1}. On average, DON concentrations reported by Chapman et al. (2001) were 0.18 mg L^{-1} and accounted for 40% of TDN. Lower DON concentrations were reported by Willett et al. (2004). They analysed 102 streams in Wales and found DON concentrations ranging from 0.03 to 0.22 mg L^{-1} with a mean of 0.09 mg L^{-1}. The contribution of DON to TDN varied from 4 to 85% with a mean of 39%. Adamson et al. (1998) found slightly higher DON concentrations of 0.37 mg L^{-1} (79% of TDN) in a peat dominated catchment in England. Although the concentrations found in our study were much higher than the reported means, they lie within the range that Chapman et al. (2001) found for Scottish semi-natural upland sites. Contributions of DON to TDN vary greatly in the literature with peat dominated catchments usually showing a larger contribution of organic N compared with NO_3^--N.

Annual mean DOC spatial and outflow concentrations of 31.1 ±7.9 and 23.9 ±10.2 mg L^{-1} for Black Burn are in good agreement with the five year average catchment outflow concentration of 28.4 ±1.7 mg L^{-1} reported in Dinsmore et al. (2013). Positive relationships between DON/DOC and discharge were found in the Black Burn, indicating that storm events lead to an increase in streamwater DOC concentrations through flushing of soil water DOC into the stream from near-surface horizons and the riparian soils (e.g. Boyer et al., 1997; Morel et al., 2009; Scott et al., 1998). A similar positive relationship between DOC and discharge was also found by Dinsmore et al. (2010) in the upper part of the Black Burn catchment. Furthermore,

DON and DOC concentrations in Black Burn were positively correlated which indicates that they are likely to originate from the same source (Bernal et al., 2005). The overall DOC:DON ratio of the Black Burn streamwater of 34:1 (derived from the ratio of annual downstream fluxes) was close to the C:N ratio of peat (Aitkenhead and McDowell, 2000).

Lead Burn DON and DOC concentrations appeared to follow different temporal patterns (Figure 3), with large changes in the DOC:DON ratio indicating changes in the dominant source (e.g. Hagedorn et al., 2000). High DOC:DON ratios are usually connected to terrestrial sources (e.g. Mattsson et al., 2009) and lower ratios to in-stream sources (Chapman et al., 2001). Highest concentrations of DON in the Lead Burn were observed in the summer months, which is consistent with its formation as a result of in stream biotic processes (Edwards et al. 2000). In addition, organic fertiliser or sewage catchment inputs may reduce the C:N ratio (Helliwell et al., 2001). Thus, Lead Burn streamwater DON appears to have multiple significant sources of DON with contributions of organic-rich soil porewater causing high streamwater C:N ratios and agricultural activities causing leaching of organic matter with low C:N ratios, probably linked to animal excretion.

4.5 Catchment fluxes

Annual TDN fluxes of 8.7 kg N ha^{-1} yr^{-1} and 14.4 kg N ha^{-1} yr^{-1} for Black Burn and Lead Burn, respectively, were in the range of total N flux values (< 2 to > 40 kg N ha^{-1} yr^{-1}) reported for European catchments (Billen et al., 2011). The present study sites were characterised by a relatively large fraction of DON, with NO_3^- not significantly exceeding the threshold of 1.5 mg N L^{-1} for high potential threat to ecosystems, as estimated by Grizzetti et al. (2011). Nevertheless, the larger catchment N fluxes at Lead Burn compared with Black Burn were associated with a predominantly agricultural catchment, as evidenced by the high loading for all the subcatchments (Figure 9). The 66% higher annual TDN flux of the agricultural Lead Burn catchment

compared with the peat dominated Black Burn catchment was entirely due to the higher NO_3^- flux, which was positively related to the magnitude of N inputs (Figure 8). In both catchments, DON accounted for the largest contribution to the TDN flux with 81% in Black Burn and 49% in Lead Burn. In European streams, DON has been observed to contribute between 11% and 100% to TDN (Durand et al., 2011). Dissolved organic nitrogen fluxes of 7.0 kg N ha^{-1} yr^{-1} in both studied streams were relatively high compared with fluxes reported in a Welsh moorland catchment of 3.1 kg N ha^{-1} yr^{-1} (Reynolds and Edwards, 1995) and fluxes of 5.7, 6.0 and 6.5 kg N ha^{-1} yr^{-1} in three English peat dominated catchments (Adamson et al., 1998).

Although the absolute catchment flux of Lead Burn was higher than that of Black Burn, the percentage of N input through agricultural activities and atmospheric deposition which was exported downstream was much higher in Black Burn compared with Lead Burn. In Lead Burn, 22% of the N input of 64.2 kg N ha^{-1} yr^{-1} were lost downstream, while in Black Burn, 43% of the N input of 20.3 kg N ha^{-1} yr^{-1} were lost, i.e. the peat dominated catchment “leaks” much more of its N input. This finding is consistent with the negative N balances found for the Black Burn catchment when compiling overall N budgets (Drewer et al., 2010; Vogt et al., 2013a). Annual Black Burn catchment DOC fluxes of the of 235 kg ha^{-1} yr^{-1} are in line with fluxes of 186 and 322 kg ha^{-1} yr^{-1} in 2007 and 2008 respectively, measured by Dinsmore et al. (2010) at a site further upstream, representative of the peat-rich part of the catchment.

In both study catchments, a high proportion of the total annual discharge was delivered during high flow events. Hence, it is important to include event sampling to accurately quantify annual nutrient exports from the catchments. In this study, high frequency concentration data were collected during four high flow events. Thus, a large number of high flow events during 2008 were not sampled which may have an effect on the calculated flux.

5 Conclusions

The effect of agricultural land use on streamwater concentrations and fluxes of NH_4^+, NO_3^- and DON was evident from both the inter- and intra-catchment variability. The use of detailed farm inventory data to establish high resolution, subcatchment N input was a key component of this analysis and to our knowledge this is the first time that such a comprehensive catchment N balance has been achieved at this level of detail. The overall agricultural N input to the grassland dominated Lead Burn catchment of 51.9 kg N ha^{-1} yr^{-1} was about four times higher than the input to the moorland dominated Black Burn catchment of 12.1 kg N ha^{-1} yr^{-1}. These inputs were larger than the corresponding inputs from atmospheric deposition at 12.3 kg N ha^{-1} yr^{-1} and 8.2 kg N ha^{-1} yr^{-1}, respectively. A more detailed future study of the specific N inputs (atmospheric, manure, fertiliser) may be possible at subcatchment level and used to hypothesise about the drivers of the stream chemistry, however that was beyond the scope of the current study. The ecosystem and hydrological pathways would require further study.

The annual downstream TDN flux of the Lead Burn catchment of 14.4 kg ha^{-1} yr^{-1} was 66% higher than the Black Burn flux of 8.7 kg ha^{-1} yr^{-1}. This was due to the different NO_3^- fluxes of 6.8 kg ha^{-1} yr^{-1} and 0.7 kg ha^{-1} yr^{-1}, respectively. Thus, despite the relatively high DON flux of 7.0 kg ha^{-1} yr^{-1} in both catchments, the contribution of DON to the TDN flux was 49% in Lead Burn and 81% in Black Burn. However, the downstream flux of Black Burn represents a much higher percentage (43%) of N input than in Lead Burn (22%), which means the Black Burn catchment looses more of its N input.

Intensive spatial sampling of streamwater chemistry gave further insight into the effect of land use on streamwater concentrations. Streamwater NO_3^- was significantly positively related to N input from agricultural land use and atmospheric deposition within each catchment and, NH_4^+ significantly negatively related to N input. This was

linked to the wet peat-rich areas of the catchments soils, which receive less agricultural N input and inhibit (due to anaerobic conditions), the oxidation of NH_4^+ to NO_3^-. Sources of DON and DOC differ between the catchments: In Black Burn, DON and DOC mainly originated from peat runoff, indicated by positive relationships with discharge and the similarity between the streamwater DOC:DON ratio and the peat C:N ratio. The sources of Lead Burn DON and DOC change frequently as streamwater DOC:DON ratios were highly variable. Potential sources of Lead Burn DON and DOC may be high C:N soil porewater and low C:N organic matter leached from agricultural sources, in particular from manure applications and grazing livestock excreta. The additional agricultural sources of DON in the Lead Burn catchment are likely to be the cause of the similarly high DON flux as in the Black Burn catchment, while at the same time the Lead Burn DOC flux remains much lower. Our data therefore show that streamwater chemistry is sensitive to landscape scale variability of N input and that the organic N fraction is a significant component of fluvial N export. These issues should receive much more attention in future studies on the analysis of specific sources and processes within agricultural areas, particularly in grazed areas. While the impact of high N inputs on streamwater N chemistry and fluxes is clearly evident from this study, the residual effects of high N loadings on the aquatic system are one of the key aspects to understanding the long term effects of reducing N usage on the environment.

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Tables

Table 1: Values of total N excreted per grazing animal used for calculating land use nitrogen input to catchments (Misselbrook et al. 2009).

Livestock category	Total N excreted [kg N animal^{-1} yr^{-1}]
Adult sheep (upland)	9.9
Lambs (< 1 year, upland)	0.7
Beef cows & heifers	79.0
Beef cattle 1-2 years	56.0
Calves (< 1 year)	38.0
Horses	50.0
Young horses & ponies (est. as ½ horse)	25.0

Table 2: Typical N content of different manure types used for calculating land use nitrogen input to catchments (Defra, 2010).

Manure type	N content [kg N t^{-1}]
Cattle/sheep/goat farm yard manure (FYM)	6.0
Cattle slurry	2.6
Solid poultry manure	19.0

Table 3: Nitrogen input (kg N ha^{-1} yr^{-1}) to the Black Burn and the Lead Burn catchment

Type of nitrogen input	Black Burn	Lead Burn
Grazing livestock excreta	8.8	26.3
Manure applications	2.1	16.3
Fertiliser applications	1.2	9.3
Atmospheric deposition	8.2	12.3

Table 4: Discharge characteristics during 2008 for Black Burn and Lead Burn. Discharge values are presented in L s^{-1} and L s^{-1} km^{-2}.

	Black Burn		Lead Burn	
	[L s^{-1}]	[L s^{-1} km^{-2}]	[L s^{-1}]	[L s^{-1} km^{-2}]
Mean	140	23	225	25
Median	56	9	141	16
Standard deviation	285	46	296	33
Range	7 - 5469	1 - 881	30 - 3012	3 - 337

Table 5: Statistics of annual streamwater concentrations for Black Burn and Lead Burn from fortnightly sampling in 2008.

	NH_4^+-N [mg L^{-1}]	NO_3^--N [mg L^{-1}]	DON [mg L^{-1}]	DOC [mg L^{-1}]	DOC:DON
Black Burn					
Mean	0.15	0.12	0.67	23.9	39
Median	0.13	0.12	0.63	21.2	37
Standard deviation	0.06	0.11	0.29	10.2	7
Range	0.06-0.26	0.00-0.45	0.29-1.44	11.8-52.5	27-58
% of TDN	15.7	12.8	71.5	-	-
Lead Burn					
Mean	0.13	1.53	0.74	19.1	33
Median	0.12	1.46	0.67	18.4	26
Standard deviation	0.04	0.58	0.52	6.5	22
Range	0.07-0.27	0.56-3.26	0.00-1.94	7.8-37.7	9-91
% of TDN	5.6	63.7	30.7	-	-

Table 6: Spearman rank correlation coefficient ρ of significant correlations (p = 0.05, two-tailed) between concentrations of different chemical species.

	Black Burn	Lead Burn
NO_3^--N - NH_4^+-N	0.86	ns
NO_3^--N - DOC	-0.51	-0.58
NO_3^--N - DON	ns	-0.56
DON - DOC	0.85	ns

ns = not significant

Table 7: Coefficients of determination r^2 calculated between log discharge and streamwater concentrations of both streams.

	Black Burn	Lead Burn
NH_4^+-N	0.02	0.00
NO_3^-N	0.04* (-)	0.25* (-)
DON	0.15* (+)	0.01
DOC	0.13* (+)	0.25* (+)

* regression slope significant (p = 0.05, two-tailed), (-) = negative slope, (+) = positive slope

Table 8: Annual downstream fluxes of Black Burn and Lead Burn for 2008 (± SE)

	Black Burn [kg ha^{-1} yr^{-1}]	Lead Burn [kg ha^{-1} yr^{-1}]
NH_4^+-N	1.01 (± 0.098)	0.63 (± 0.057)
NO_3^-N	0.66 (± 0.062)	6.76 (± 0.342)
DON	7.02 (± 0.200)	7.02 (± 0.221)
DOC	235.3* (± 7.33)	184.5* (± 6.35)

* 10 kg C ha^{-1} yr^{-1} is equivalent to 1 g C m^{-2} yr^{-1}

Table 9: Spatial variability of annual mean concentrations* [mg L^{-1}] within the catchments (SD = standard deviation).

	Black Burn	Lead Burn
NH_4^+-N		
Mean	0.17	0.20
Median	0.11	0.14
SD	0.18	0.19
Range	0.07-0.97	0.07-0.84
NO_3^-N		
Mean	0.08	1.32
Median	0.05	1.30
SD	0.09	0.87
Range	0.01-0.39	0.02-4.77
DON		
Mean	0.92	0.73
Median	0.84	0.66
SD	0.26	0.30
Range	0.59-1.71	0.13-1.93
DOC		
Mean	31.1	18.7
Median	28.0	15.7
SD	7.9	7.7
Range	17.3-53.9	7.9-51.2

* For each sampling location, annual means were calculated from sampling in July, September and December 2008 (n = 3).

Table 10: Coefficients of determination r^2 calculated for N input through land use and atmospheric deposition and concentrations of subcatchments in Black Burn and Lead Burn.**

	Black Burn	Lead Burn
NH_4^+-N	0.92*(-)	0.77*(-)
NO_3^--N	0.67*(+)	0.61*(+)
DON	0.38	0.14
DOC	0.78*(-)	0.16

* regression slope significant (p = 0.05, two-tailed), (-) = negative slope, (+) = positive slope

** one sample from one Lead Burn subcatchment taken in July was left out as with a very high NH_4^+ concentration (2.2 mg L^{-1}) and a very low NO_3^- concentration (0.03 mg L^{-1}) it is likely to represent a local anomaly rather than the subcatchment characteristics.

Figure 2

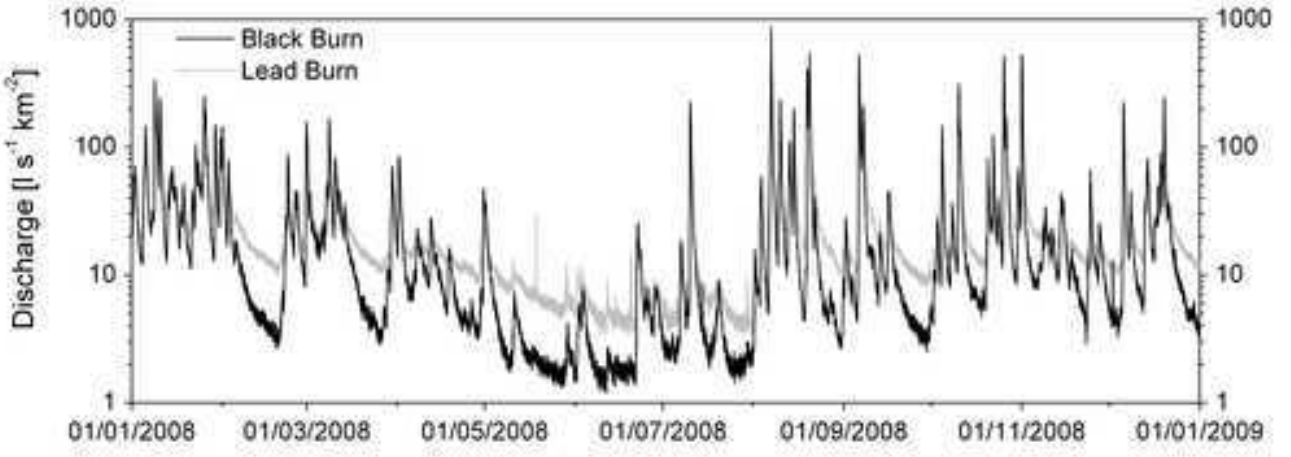

Black Burn
Lead Burn
Discharge [l s-1 km-2]
1000
100
10
1
01/01/2008
01/03/2008
01/05/2008
01/07/2008
01/09/2008
01/11/2008
01/01/2009

Figure 3

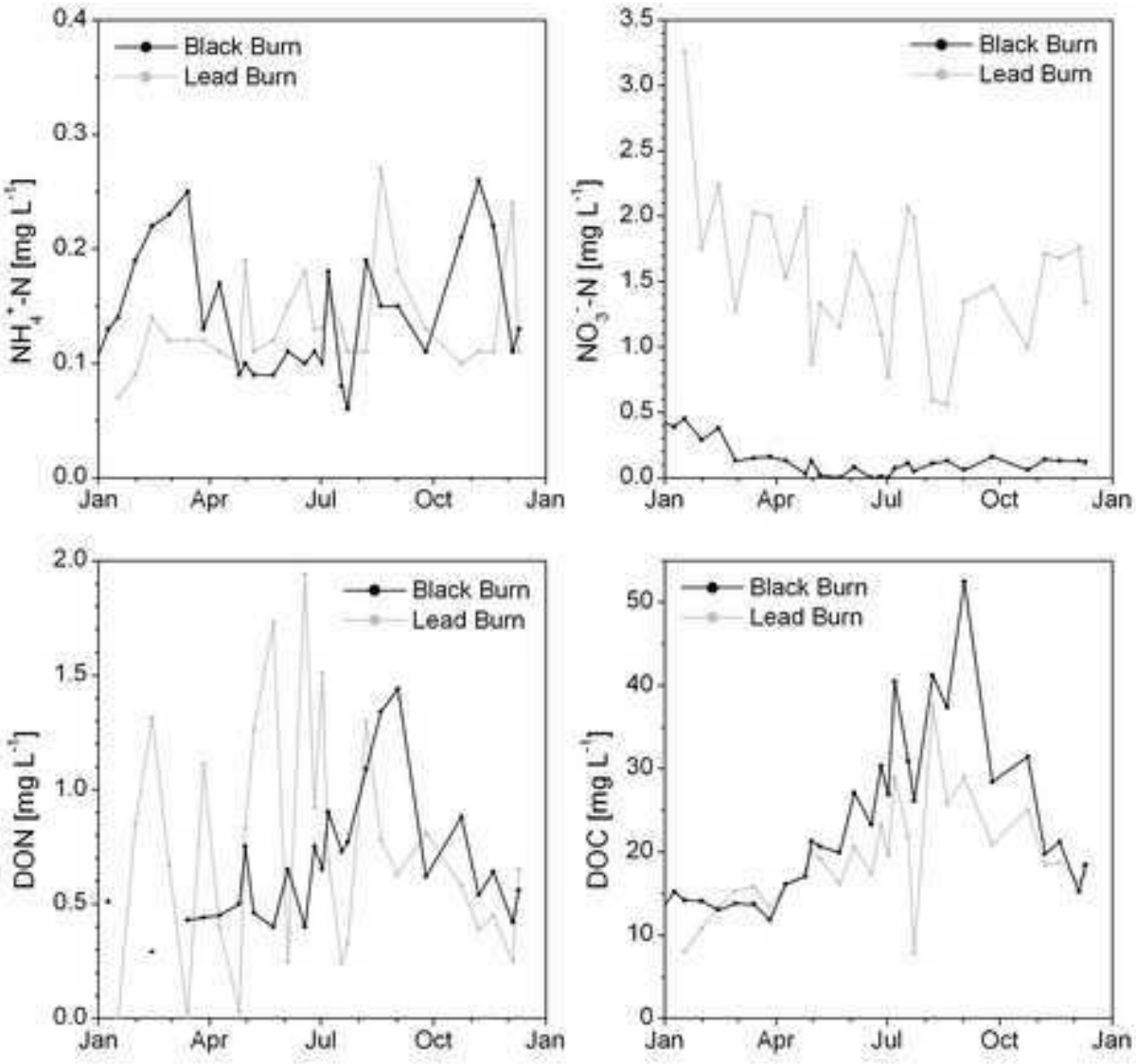

Black Burn
Lead Burn
NH_4^+-N [mg L^{-1}]
NO_3^--N [mg L^{-1}]
DON [mg L^{-1}]
DOC [mg L^{-1}]
Jan
Apr
Jul
Oct
Jan

Figure 4

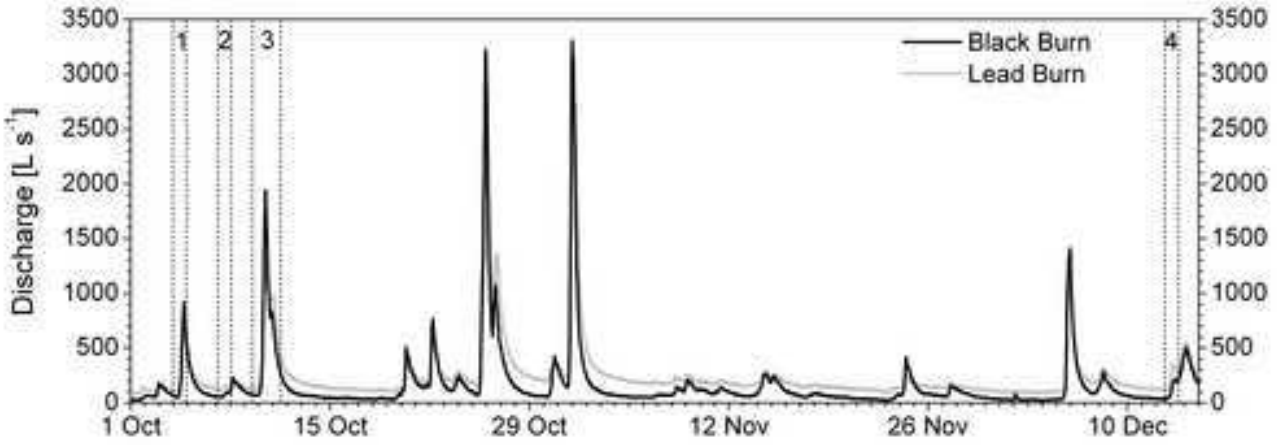

Discharge [L s-1]
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
Black Burn
Lead Burn
1 Oct
15 Oct
29 Oct
12 Nov
26 Nov
10 Dec

Figure 5

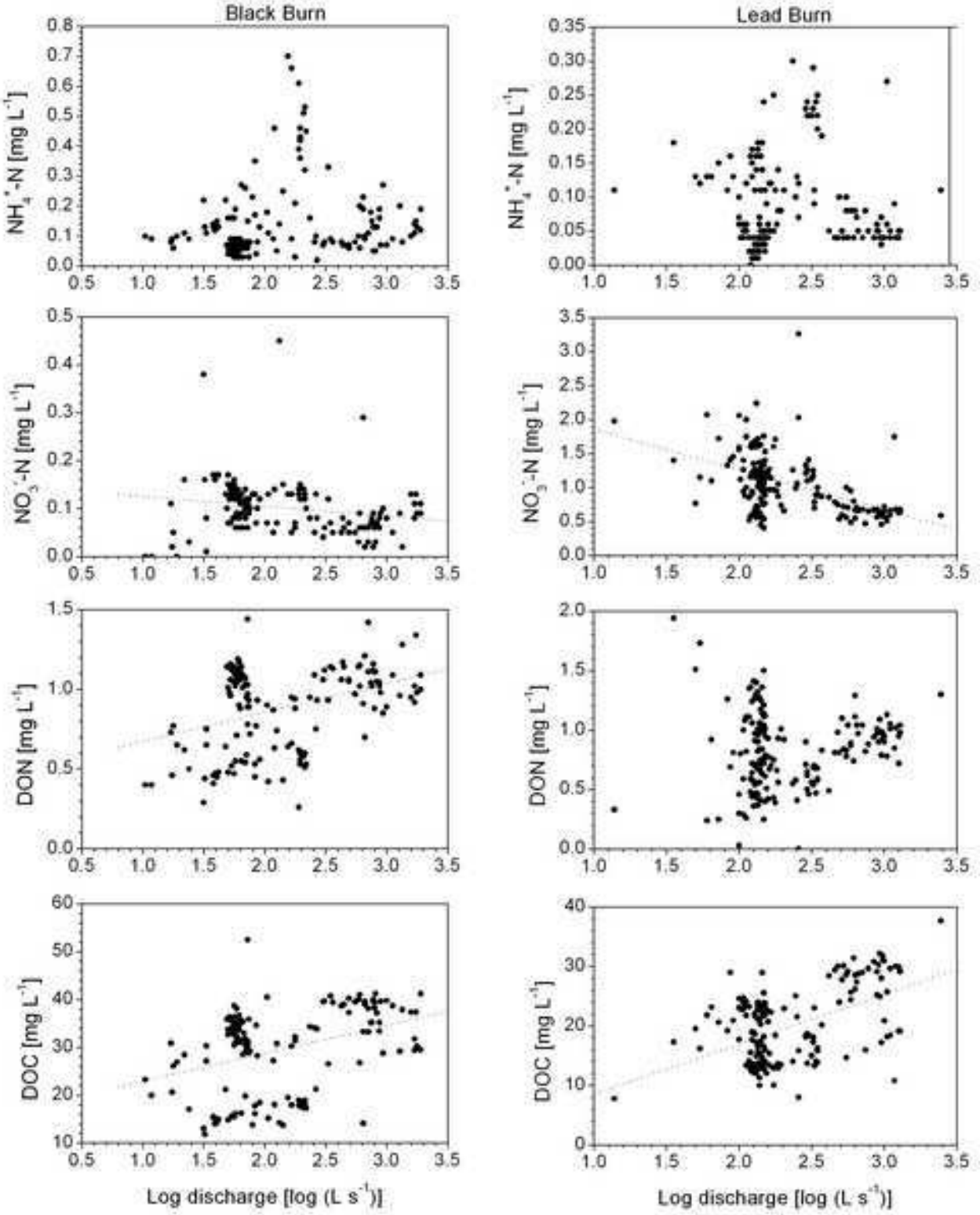

Black Burn
Lead Burn
NH_4^+-N [mg L^{-1}]
NO_3^--N [mg L^{-1}]
DON [mg L^{-1}]
DOC [mg L^{-1}]
Log discharge [log (L s^{-1})]

Figure 6

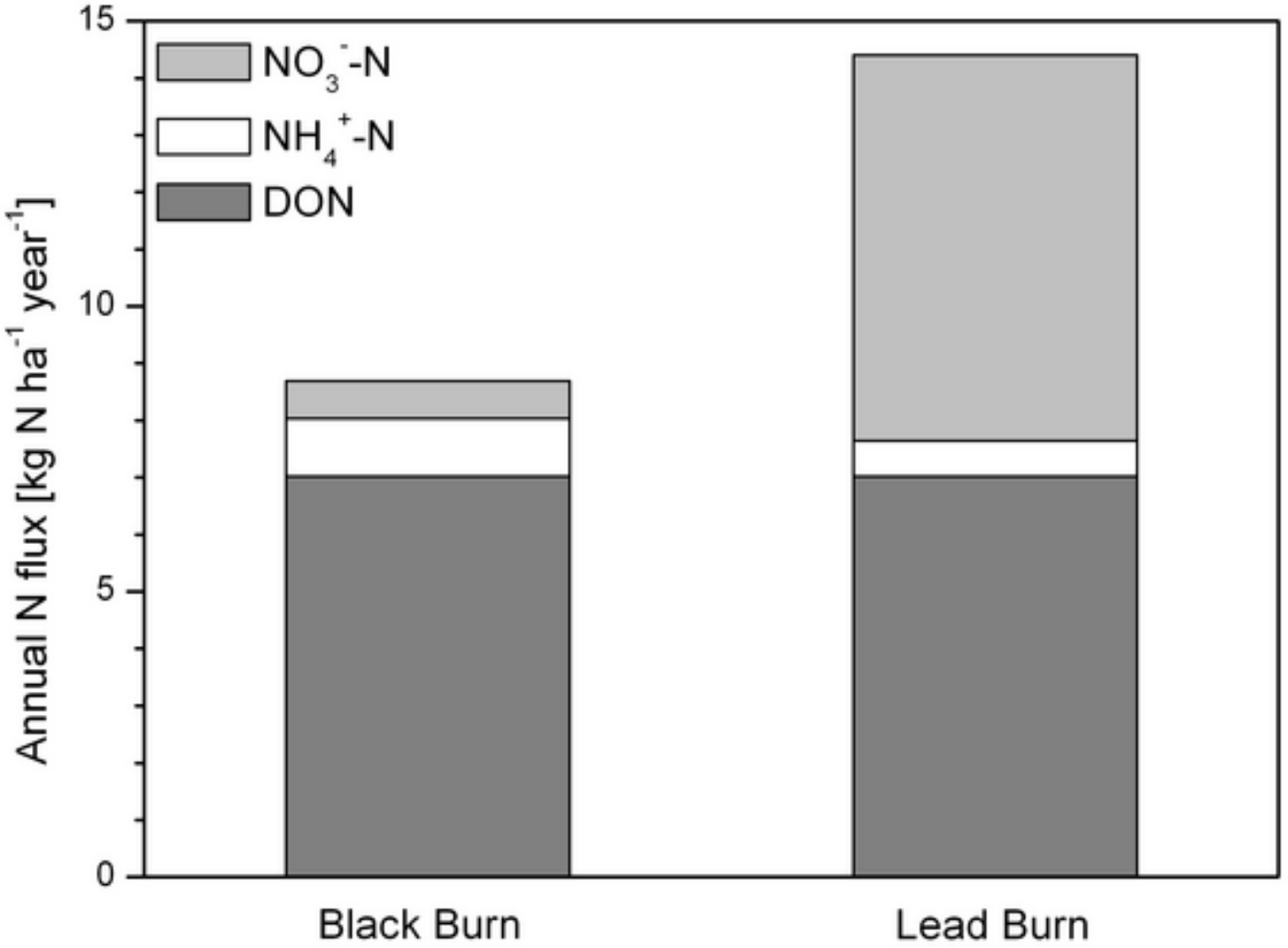

15
10
5
0
Annual N flux [kg N ha-1 year-1]
NO3--N
NH4+-N
DON
Black Burn
Lead Burn

Figure 8

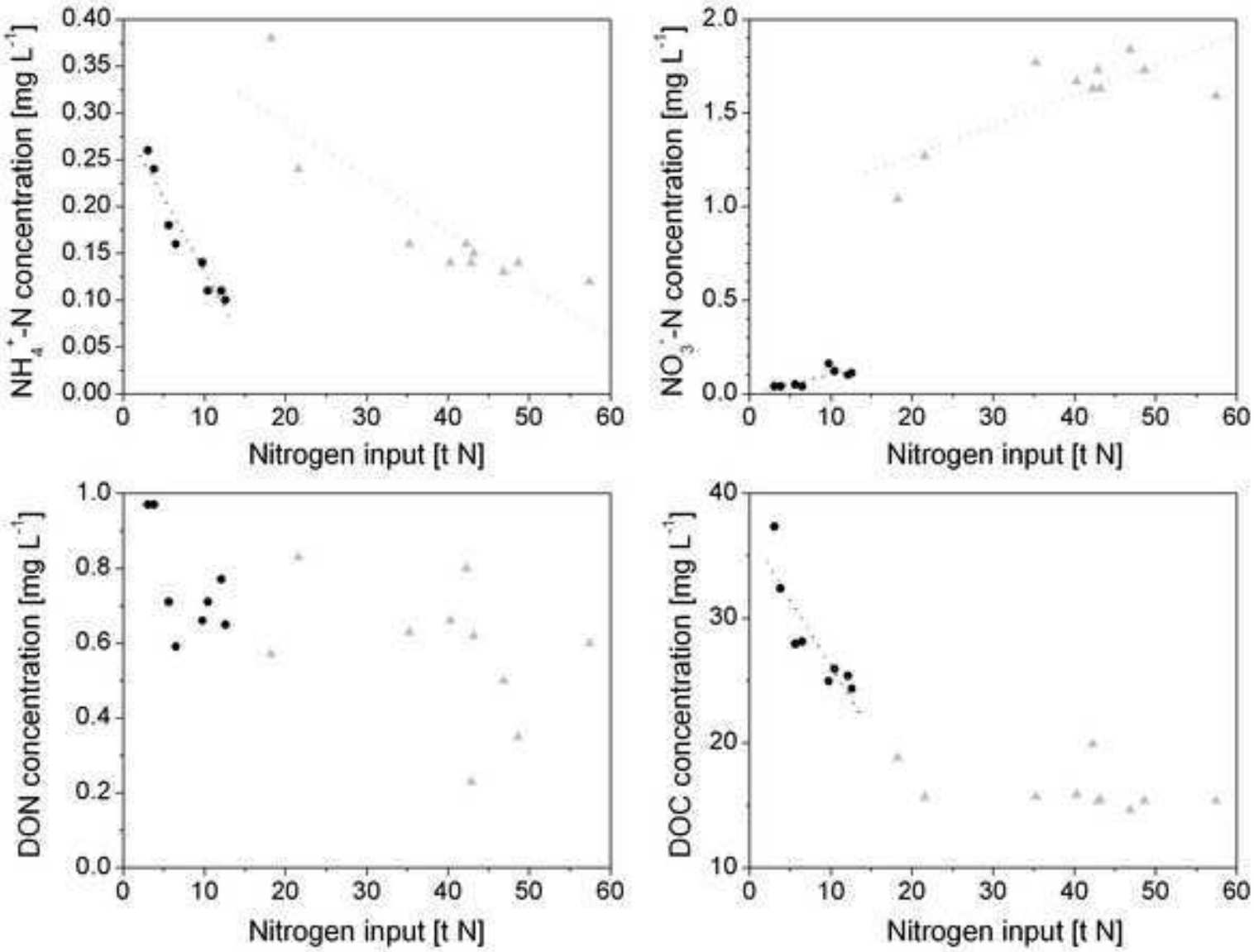

NH4+-N concentration [mg L-1]
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
10
20
30
40
50
60
Nitrogen input [t N]
NO3--N concentration [mg L-1]
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
Nitrogen input [t N]
DON concentration [mg L-1]
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Nitrogen input [t N]
DOC concentration [mg L-1]
40
30
20
10
0
10
20
30
40
50
60
Nitrogen input [t N]

Figure 9

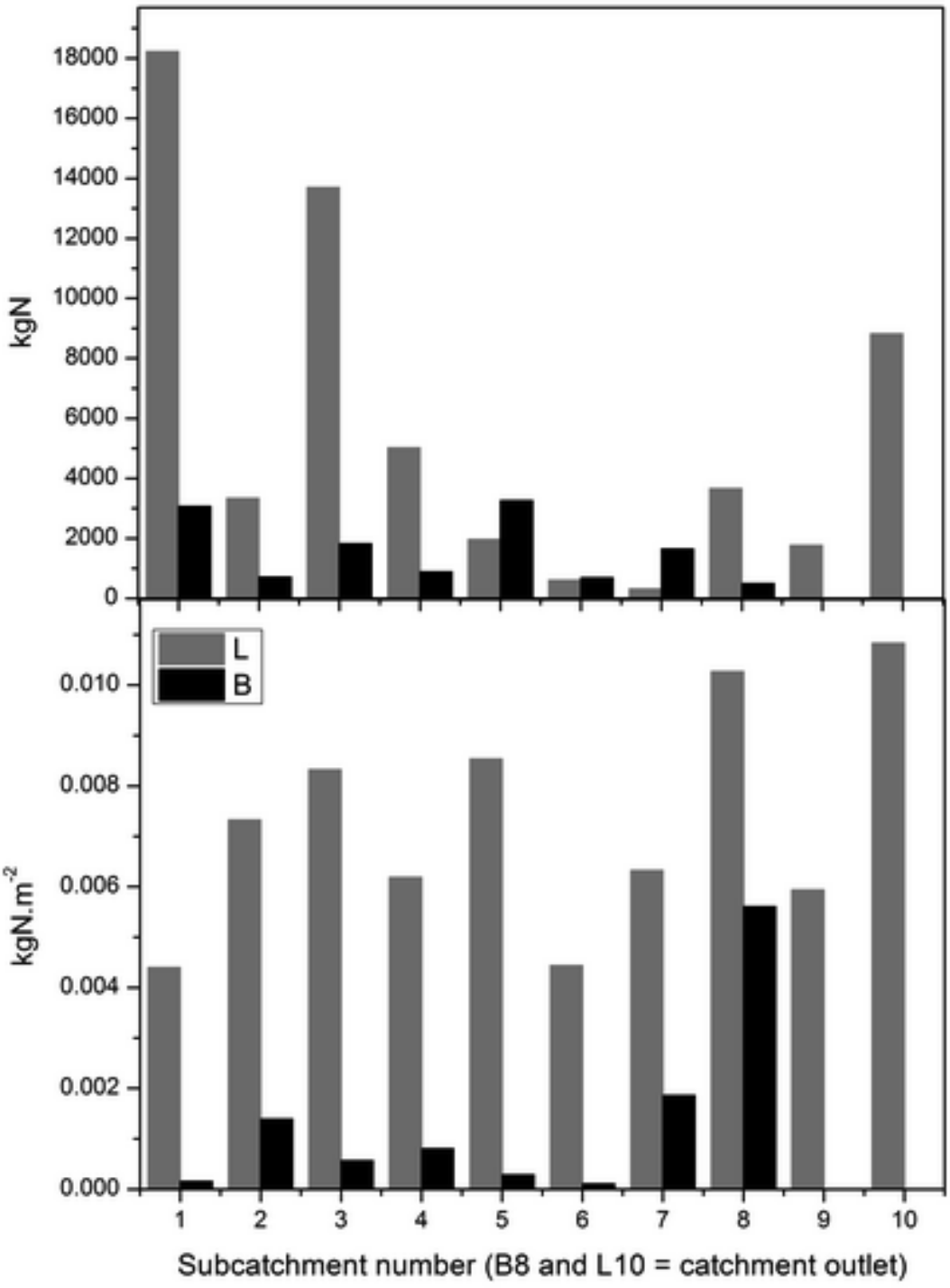
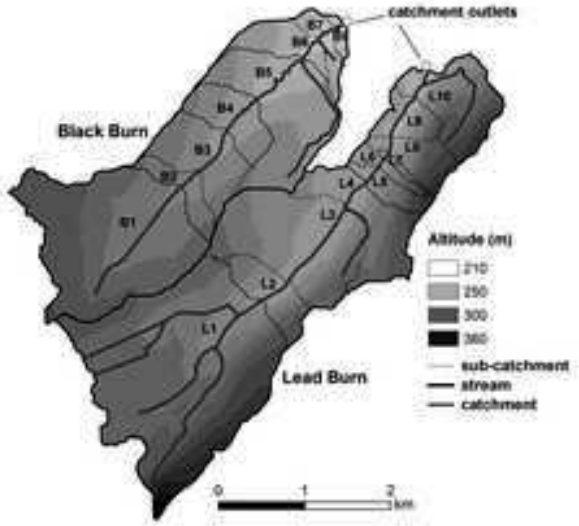
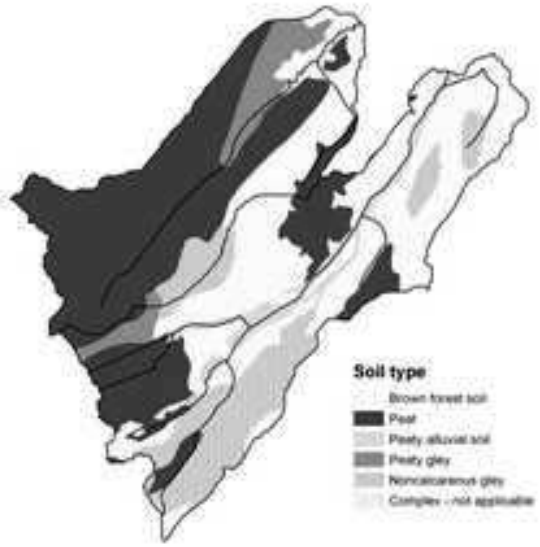

kgN
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
L
B
kgN.m-2
0.010
0.008
0.006
0.004
0.002
0.000
1
2
3
4
5
6
7
8
9
10
Subcatchment number (B8 and L10 = catchment outlet)

Figure 1abc


catchment outlets
Black Burn
Lead Burn
B7
B6
B5
B4
B3
B2
B1
L10
L9
L8
L7
L6
L5
L4
L3
L2
L1
Altitude (m)
210
250
300
360
sub-catchment
stream
catchment
0
1
2
km


Soil type
Brown forest soil
Peat
Peaty alluvial soil
Peaty gley
Noncalcareous gley
Complex - not applicable

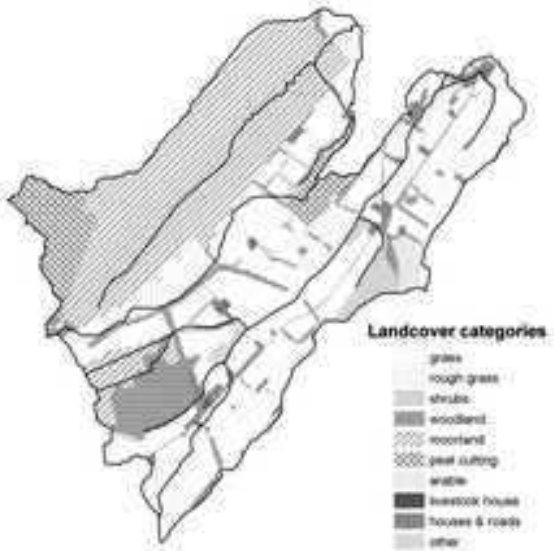

Landcover categories
grass
rough grass
shrubs
woodland
moorland
peat cutting
arable
livestock house
houses & roads
other

Figure 7abcd

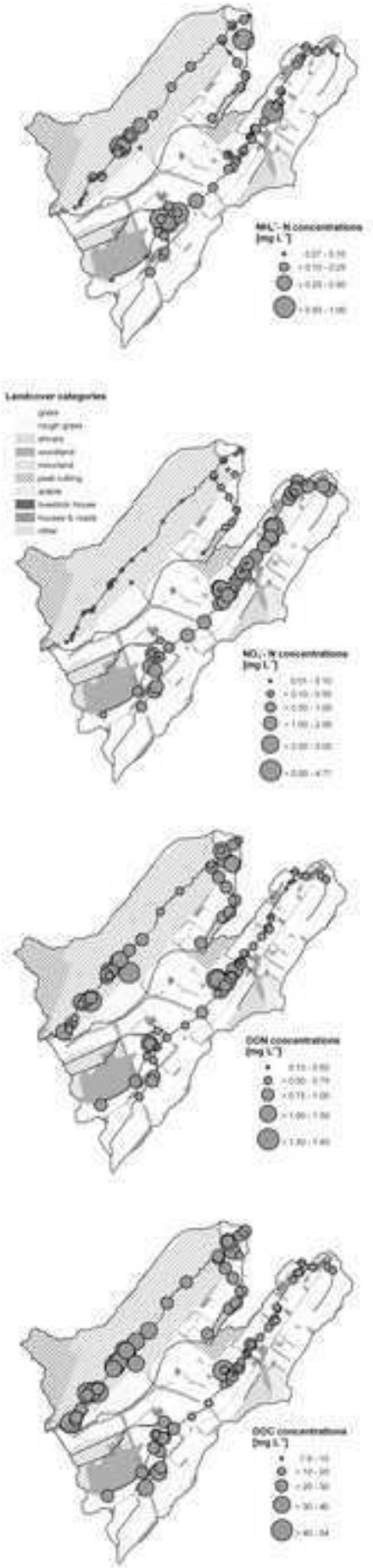


FIGURE CAPTIONS

Figure 1: Maps of (a) topography[1] and subcatchment outlines (b) soil[1,2] and (c) land cover[1] of the Black Burn and the Lead Burn catchment. Streamwater samplings and discharge measurements were carried out at the catchment outlets. Not all tributaries of the main streams are shown.

[1] © Digital terrain data from Intermap Technologies Inc. 2010, used in the derivation of catchment boundaries, together with other information

[2] © The James Hutton Institute 2011 (license MI/2008/296). Soil types are based on the Scottish Soil Survey, the equivalent FAO names are: brown forest soil = cambisol, peat = histosol, peaty alluvial soil = humic fluvisol, peaty gley = humic gleysol, noncalcareous gley = gleysol (FAO/UNESCO, 1974)

Figure 2: Specific discharges (log axis) in 2008 in Black Burn (black) and Lead Burn (grey).

Figure 3: Concentration time series of NH_4^+-N (top left), NO_3^--N (top right), DON (bottom left), DOC (bottom right) in Black Burn (black) and Lead Burn (grey) from fortnightly samples in 2008.

Figure 4: Continuous discharge data from October to December 2008. Periods of high frequency samplings 1, 2, 3 and 4 are indicated by dotted lines.

Figure 5: Scatter plots of streamwater concentrations and log discharge of Black Burn (left) and Lead Burn (right). Regression analysis and significance are summarised in Table 6.

Figure 6: Composition of the annual catchment TDN flux in Black Burn (left) and Lead Burn (right).

Figure 7: Annual mean concentrations throughout both catchments of a) NH_4^+-N, b) NO_3^--N, c) DON and d) DOC.

Figure 8: Scatter plots of N input and concentrations of subcatchments in Black Burn (black) and Lead Burn (grey). Fitted linear regressions are indicated by dotted lines.

Figure 9: Subcatchment N input. Upper panel: total N input for 2008; Lower panel: N input per unit area of subcatchment. Grey bars = Lead Burn (L) subcatchments, black bars = Black Burn (B) subcatchments. (Note: see Figure 1a for outline of subcatchment areas)