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ORIGINAL PAPER

# Upscaling understanding of nitrogen dynamics associated with overland flow in a semi-arid environment

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**Abstract** An experiment was designed to further the empirical understanding of the effects of scale on fluxes of water and dissolved nitrogen from hillslopes in semi-arid shrubland. It was hypothesised that the behaviour of dissolved nitrogen is related to the scale of the contributing hillslope/catchment area and dynamics of the overland flow as has been demonstrated to be the case for soil erosion (Parsons et al. 2006). Data from four hillslope scales (ca. 21–300 $m^2$) and one subcatchment (ca. 1,500 $m^2$), collected over two monsoon seasons, support this hypothesis and demonstrate that the key controls of average dissolved nitrogen yields are flow discharge and plot scale. The slope of the best-fit line describing the relationship between flow discharge and total dissolved nitrogen (TDN) yields descreases with increasing scale, from 0.0183 at 21.01 $m^2$, 0.0092 at 56.84 $m^2$, 0.0059 at 115.94 $m^2$, 0.0024 at 302.19 $m^2$ to 0.0004 at 1,500 $m^2$. An implication of these findings is that care must be taken when upscaling results describing nutrient behaviour from small, plot experiments, as this behaviour appears to be scale dependent. For example, average yields of TDN in overland flow increase to a maximum with increasing plot area until an area of 50 $m^2$ is reached, and decline with increasing plot size thereafter. Thus, studies that rely upon fixed plot scales may misrepresent catchment- or landscape-scale fluxes as they do not describe the changing relationship between overland flow and nutrient fluxes with increasing spatial scale. Further investigations into intra-event behaviour illustrate that nitrogen losses from natural rainfall/runoff events are supply limited as over the course of the events monitored, decreasing concentrations illustrate a pattern of nutrient exhaustion. When events are compared at the same sites through the monsoon season, however, the anticipated seasonal exhaustion effect is not present. This work provides an empirical basis to upscale the understanding of dissolved nitrogen behaviour from small hillslope plots to catchment scales in degraded semi-arid environments.

**Keywords** Nitrogen · Nitrogen yields · Overland flow · Soil erosion · Scale

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## Introduction

Understanding the movement of water, sediment and nutrients within a landscape is critical in order to address the effects of land degradation, which include erosion (Frederickson et al. 1998; Wainwright et al. 2000), nutrient depletion (Schlesinger et al. 1999) and the consequent pollution of waterways (Brazier 2004). In semi-arid areas, which are often subject to high levels of land degradation, rates of sediment and nutrient movement are highest where shrub species dominate (Parsons et al. 1996; Schlesinger et al. 1999, 2000; Wainwright and Thornes 2003; Wainwright 2004; Boardman et al. 2003). In US south-west, over the past 150 years, a shift in dominance of shrub species over grass species has occurred, resulting in severe erosion and potentially high-nutrient losses (Buffington and Herbel 1965; Conley et al. 1992; Frederickson et al. 1998; Parsons et al. 2003; Schlesinger et al. 1990). Understanding the implications of this shift is therefore of fundamental importance if the currently unsustainable levels of land degradation and nutrient depletion in such environments are to be arrested (Frederickson et al. 1998; Peters 2002). Furthermore, as semi-arid areas occupy some 17% of the global land area and are home to 1/6th of the global population (UNEP 1992) the extrapolation of this understanding will provide a much needed insight into degradation of drylands throughout the world.

Although some effort has been made to understand the distribution of nutrients within semi-arid soils (see Schlesinger et al. 1996; E. N. Müller 2004, unpublished data; Müller et al. in press) and the redistribution of nutrients in overland flow from different vegetation types (for example, Pardini et al. 2003; Parsons et al. 2003, submitted; Schlesinger et al. 1999, 2000), very little work has addressed the dynamics of nutrient fluxes at both different spatial and temporal scales under natural rainfall events within areas dominated by shrub species. Although Schlesinger et al. (2000) report findings from natural rainfall events, data are limited to one spatial scale and are presented as event totals and annual yields. Consequently, the issue of scale in understanding nutrient behaviour has been poorly addressed, particularly so for spatial scale (though see Meixner and Fenn 2004 for a catchment scale budgetting approach). Furthermore, as the understanding of nutrient behaviour is currently-based upon small-scale experiments (see aforementioned papers and Wainwright et al. 2000 for examples), but is required at larger scales to meet the needs of recent legislation (Dressing et al. 2003), there is a fundamental requirement to improve understanding at a wider range of spatial and temporal scales. This paper builds upon recent work reported by Parsons et al. (2004, 2006) who establish the link between hillslope scale and erosion rates in semi-arid environments, and it postulates that a similar relationship may be found between hillslope scale and nutrient dynamics. Herein we describe the behaviour of dissolved nutrients, primarily nitrogen, as dissolved phosphorus concentrations in runoff have been shown to be negligible in such semi-arid environments (Schlesinger et al. 1999).

It has been shown that as hillslope length increases and runoff coefficients decrease sediment yield from interrill areas initially increases (up until ~7 m downslope) and then decreases (Parsons et al. 2004; Parsons and Wainwright 2005) as the travel distance of particles and decrease in runoff coefficients controls rates of erosion. Consequently, spatial scaling of erosion is partly due to spatial scaling of runoff (Parsons et al. 2006; Wainwright and Parsons 2002; Yair and Kossovsky 2002; Yair and Raz-Yassif 2004). Thus, it is an objective of this paper to test whether such spatial scaling behaviour is also true of nitrogen that is transported by the same flow as it is hypothesised that the increase in scale and decreases in runoff coefficients (promoting retention of water, sediment and nutrients within the landscape) that control erosion should also control nitrogen yields. This objective is tested via interpretation of field data collected during 14 natural rainfall events over two monsoon seasons in the semi-arid south west of the USA.

Additionally, the behaviour of nitrogen entrained and transported by overland flow is described at a range of temporal scales in order to improve understanding of the intra- and inter-event dynamics of water and nitrogen yields from semi-arid hillslopes. It is hypothesised that a decline in nutrient concentrations will be evident both during events (Schlesinger et al. 1999) as exhaustion of nitrogen supply occurs and through monsoon seasons (Schlesinger et al. 2000) as vegetation cover increases effecting a reduction in the mobilisation of nitrogen from the soil.

## Methods

The study was undertaken at a field site within the Lucky Hills catchment, which is part of the Walnut Gulch Experimental Watershed, southern Arizona, USA (Canfield and Goodrich 2003; Renard et al. 1993). It is a highly eroded landscape that is strongly connected to the neighbouring San Pedro River system and riparian zone (Kepner et al. 2004) with consequently serious implications for the off-site impacts of sediment and nutrients delivered from the hillslopes within the catchment area (Ritchie et al. 2005). Vegetation cover is predominantly woody shrubs dominated by *Larrea tridentata* and *Acacia constricta* (Weltz et al. 1994) that have invaded the grassland community over the past 100–150 years (Renard et al. 1993). Soil types are Lucky Hills-McNeal sandy loams (Ustochreptic Calciorthids), which typically contain large proportions of rock fragments and have developed a distinct stone pavement across much of the catchment (Parsons and Abrahams 1992; Wainwright et al. 1999) resulting in increased runoff rates and high levels of erosion throughout the catchment (Ritchie et al. 2005). Rainfall events are monsoonal; high intensity and short duration, the majority of which fall between July and September, with mean annual rainfall of 356 mm (Nichols et al. 2002).

Within the field site, pairs of plots were constructed to monitor soil erosion at four locations (Parsons et al. 2006). In this study, we are concerned with data obtained from the larger plot of each pair (named Laurel, Abbott, Dud and Wise). These plots had dimensions of 21.01, 115.94, 56.84 and 302.19 m$^2$, with lengths of 4.12, 14.48, 18.95 and 27.78 m, respectively. They were instrumented to monitor intra-event behaviour of rainfall, flow and nitrogen fluxes on a 1-min timestep (see Fig. 1 for an example). In addition to these four plots, a 1,500 m$^2$ first-order subcatchment (Cleese) was instrumented to monitor the same variables at a larger spatial scale to include the effects of concentrated (rill) flow as well as unconcentrated (interrill) flow. Although inclusion of catchment-scale alongside hillslope-scale results may add further complexity to the interpretation of results (for example, due to the presence of concentrated flow lines within the Cleese subcatchment, pavement cover is, on average, appreciably lower than on the hillslopes), it is considered a goal of this paper to upscale understanding across as wide a range of spatial scales as possible.

Schlesinger et al. (1996) suggest that the pattern of vegetation within a study area exerts a strong control on the spatial distribution and redistribution of the nutrients by overland flow within that area. Consequently, surface cover afforded by vegetation (as well as stone pavement and fine particles) was kept as constant as was practical when plot location was determined (Table 1). Other variables such as soil type, and plot gradient were also kept as constant as possible, though despite these efforts, some variation between plots is inevitable (Table 1). As this variability is by no means consistent between plots (Parsons et al. 2006), however, it is argued that it does not unduly bias the analysis of the effects of plot characteristics on nitrogen behaviour.

Plot boundaries and gutters were fabricated from sheet steel and aluminium flashing, buried within the hillslope to ensure that no surface flow left the plot other than through a flume sited at the downslope end. The flume concentrated flow to allow measurement of flow depth and permit the extraction of runoff samples for nitrogen analysis. Flow depth was measured using the bubbler module of an ISCO 6700 pump sampler in conjunction with a small stilling well located 100 mm upstream of the flume outlet. Flow depth was converted to discharge using rating equations-based upon a series of in situ calibration experiments which involved circulating flow through the flume at various discharges (Parsons et al. 2006). Runoff samples were taken via an intake mounted 50 mm downstream of the stilling well and between 10 and 20 mm from the flume bed depending on plot size as smaller plots tended to produce lower flow

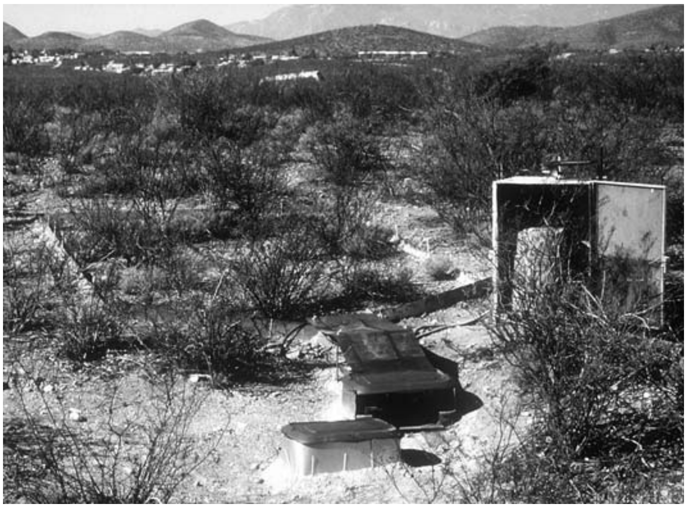


**Fig. 1** The Laurel hillslope plot (21.02 $m^2$) Lucky Hills watershed, Walnut Gulch, AZ, USA. Flume and collecting reservoirs are shown bottom centre, pump sampler and housing centre right

**Table 1** Variables describing plot characteristics, modified from Parsons et al. (2005)

| Variable | Laurel | Abbott | Dud | Wise | Cleese |
|---|---|---|---|---|---|
| Mean pavement cover (%) | 55.34 | 56.67 | 57.35 | 56.87 | 26.27 |
| Mean fines cover (%) | 24 | 14.1 | 21.7 | 16.5 | 48.77 |
| Mean vegetation cover (%) | 20.7 | 29.8 | 21.05 | 26.6 | 24.94 |
| Hillslope gradient (degrees) | 8.15 | 5.8 | 10.4 | 6.6 | 8* |

* Represents gradient of main channel

depths. Sample collection when the intake was completely submerged, was triggered by the bubbler module. Samples were removed from the field site for filtering as soon as was practical and depending upon event timing always within 4 h of the end of each event.

At the Cleese subcatchment site, a Santa Rita-type flume (Smith et al. 1982) with a stilling well was installed at the catchment outlet. A bubbler-module stage recorder from an ISCO 6700 pump sampler was mounted within the stilling well. The intake for the pump sampler was mounted in the floor of the flume and set to trigger at 25 mm flow depth in a similar fashion to the hillslope set up. Flow depth and rainfall data were recorded at a 1-min timestep, with flow being converted to discharge using a rating curve based on the flume dimensions and gradient (Smith et al. 1982).

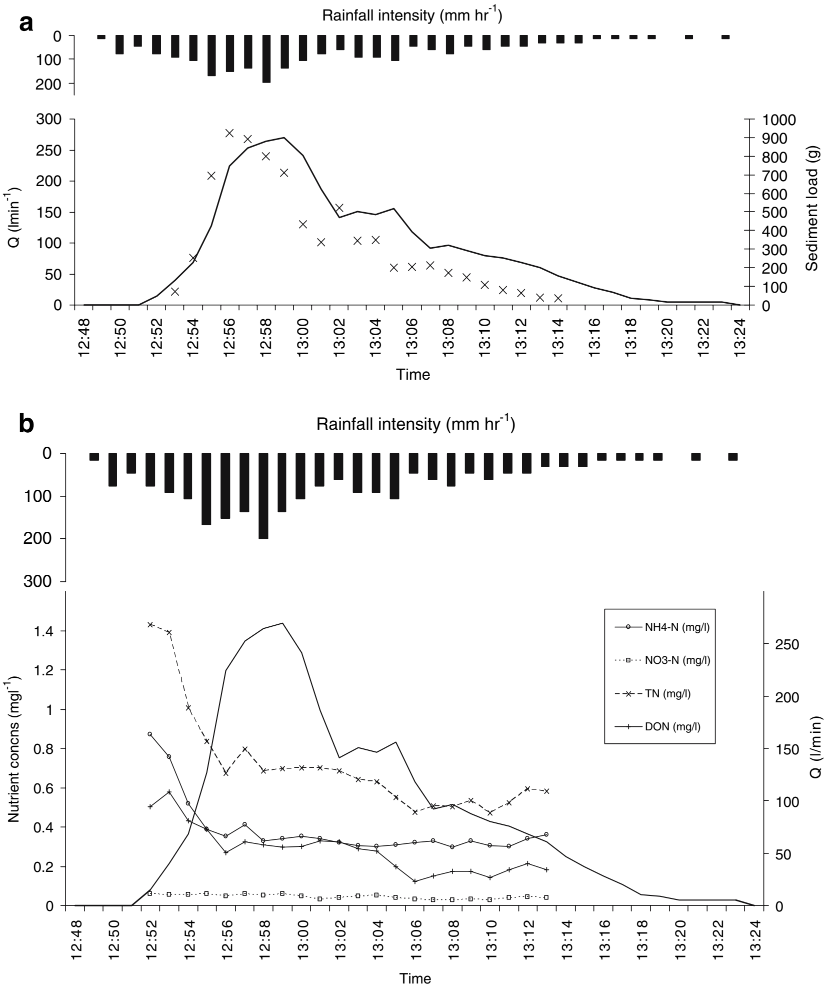
On return to the laboratory, 30 ml subsamples of the 1-l runoff samples were taken and filtered through pre-rinsed 0.45 μm Millipore HA filters into polypropylene sample bottles. These samples were then analysed for ammonium ($NH_4$-N) and nitrate ($NO_3$–N) using standard methods on a Traacs 800 Autoanalyser. Total inorganic N was taken as the sum of $NH_4$–N + $NO_3$–N. Each sample was then subjected to a persulphate digestion (D'Elia et al. 1977) and re-analysed. The difference between the digested and undigested concentrations was assumed to represent dissolved organic forms of N (DON). See Schlesinger et al. (2000) for further details and note compatibility of analytical techniques with previous work by these authors.

While 35 plot-events occurred during 2001 and 2002, due to mechanical breakdowns, only 14 events had complete records of chemistry, rainfall and discharge to include in the numerical analysis. Accepting this limitation, the dataset presented here is thought to provide a good representation of the dynamics of dissolved nitrogen behaviour during natural rainfall/runoff events in a semi-arid environment as events monitored range in runoff magnitude from 0.018 to 33.3 $l\,m^{-2}$ with return periods of between 1 and 5 years (Abrahams et al. 2006).

## Results

As an example of the event data collected during the 2-year monitoring period, a dataset for the

**Fig. 2** (**a**) Typical event data describing rainfall intensity (mm $h^{-1}$), discharge (l $min^{-1}$) shown here as the *solid line* and sediment loads (g $min^{-1}$) shown as *crosses*, from the Abbott hillslope plot, 4 August 2002. (**b**) Typical event data describing rainfall intensity (mm $h^{-1}$), discharge (l $min^{-1}$) and nutrient concentrations (mg $l^{-1}$) from the Abbott hillslope plot, 4 August 2002



event recorded on the Abbott hillslope plot on 04/08/02 is shown in Fig 2a, b. One-minute rainfall intensities of up to 198 mm $h^{-1}$ were observed over a period of 38 min, generating a total flow of 3,133 l over 35 min with a peak flow of 270 l $min^{-1}$. The resultant hydrograph is characteristic of hillslope hydrographs in semi-arid areas with a steep rising limb, short lag-time between peak rainfall and peak flow (in this example within 1 min) and a prolonged (compared to the rising limb) recession. In general suspended sediment dynamics tend to precede changes to flow in a clockwise hysteretic fashion. In this example, highest loads of 925 g $min^{-1}$, occur prior to peak flow concentrations by 3 min and total yields ~7,596 g over the event. Nitrogen dynamics (shown throughout as gross yields, i.e. uncorrected for atmospheric deposition) are also at their highest—total dissolved nitrogen (TDN) = 1.8 mg $m^{-2}$ $min^{-1}$ 1 min prior to peak flow—and tend to follow the form of the hydrograph closely. This behaviour is true of all nitrogen fractions observed here, though proportions of each fraction contributing to TDN vary widely as is illustrated later.

## Spatial scaling of dissolved nitrogen behaviour

To investigate the relationships between nitrogen behaviour, hillslope characteristics and discharge an analysis of all 14 events from the five spatial scales was performed. In the first instance this work focused on a regression analysis of nitrogen yields (mg $m^{-2}$ $min^{-1}$) against plot areas. Figure 3 illustrates the relationship between instantaneous TDN yield from all events and plot area.

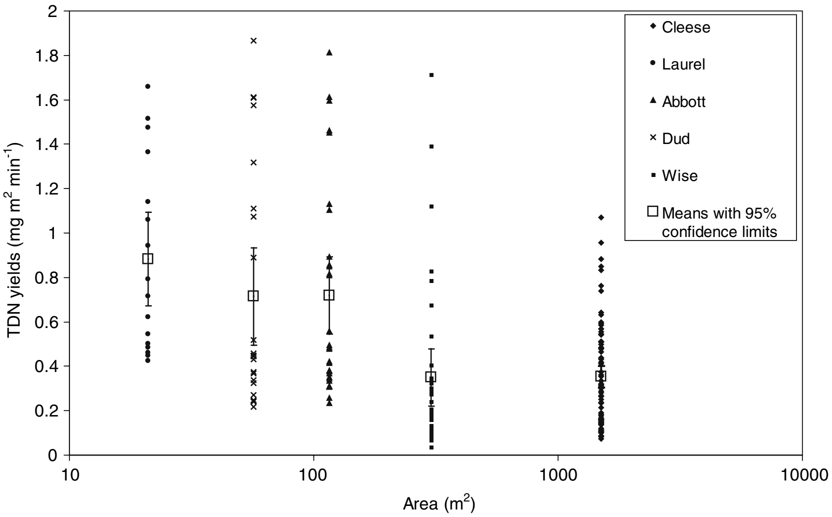


**Fig. 3** Instantaneous TDN yields (mg $m^{-2}$ $min^{-1}$) and mean values as a function of plot area ($m^{-2}$) for all events. *Box and whiskers* describe 95% confidence limits around means

For all nitrogen fractions observed a wide range of yields is evident from all plot sizes with large standard deviations around the mean and weak, positive relationships with plot area (see Tables 2, 3 for details). When described by the mean yields with 95% confidence limits (shown as box and whisker plots), Fig. 3 shows a pattern of decreasing TDN yields with plot area. Furthermore, one-way analysis of variance, to compare means between scales shows a statistically significant difference at the 95% level between the populations—$F(13.22) > F_{crit}(2.42)$.

To consider the influence of overland flow upon nitrogen behaviour instantaneous nitrogen yields were plotted against instantaneous discharge for all events across all spatial scales (Fig. 4). Although there is some evidence for a very weak positive relationship between instantaneous yields and discharges *across all spatial scales* (see Table 1), there is a high degree of variability within the dataset, particularly for low discharges: those less than 300 l $min^{-1}$ produce TDN yields of between 0.03 and 1.87 mg $m^{-2}$ $min^{-1}$. Such behaviour is similar for all fractions of N (Table 2) apart from $NO_3$–N, which shows a reasonably strong, significant relationship between discharge and nitrogen yields. However, if the influence of discharge on nitrogen yields *at each separate spatial scale* is considered, much stronger relationships are found (Fig. 4, Table 4), suggesting that the relationship between nitrogen yields and discharges identified by previous authors (Schlesinger et al. 2000), may in fact be scale dependent, as the slope of the best fit line decreases with an increase in scale. Thus, the data collected here demonstrate a general increase in TDN yield with increasing discharge, though the rate at which this increase occurs is significantly reduced as plot size increases.

**Table 2** $R^2$-values describing relationships between instantaneous flow (l $min^{-1}$), plot areas ($m^2$) and instantaneous nutrient yields (mg $m^{-2}$ $min^{-1}$)

| | Instantaneous flow (l $min^{-1}$) | Plot area ($m^2$) |
|---|---|---|
| TDN yields | 0.004 | 0.13 |
| $NH_4$–N yields | 0.001 | 0.20 |
| $NO_3$–N yields | 0.481 | 0.28 |
| DON yields | <0.001 | 0.11 |

## Temporal scaling of dissolved nitrogen behaviour: intra-event dynamics

The characteristics of a typical event are exemplified in Fig. 5a, which describes rainfall, flow, and nitrogen concentrations from the Cleese catchment on 26/07/02. Schlesinger et al. (1999) observed declines in nitrogen concentrations throughout a series of simulated rainfall events on semi-arid shrubland plots. Similar behaviour under natural rainfall events is observed here, with initially high concentrations of TDN (peaking at 2.03 mg $l^{-1}$) declining, with increasing

**Table 3** Average and standard deviation values describing yields (mg m$^{-2}$ min$^{-1}$) from each scale for each nutrient fraction observed

| | | Median values | Mean values | Standard deviation |
|---|---|---|---|---|
| TDN yields | Laurel | 0.79 | 0.91 | 0.43 |
| | Dud | 0.45 | 0.74 | 0.54 |
| | Abbott | 0.49 | 0.74 | 0.48 |
| | Wise | 0.20 | 0.35 | 0.39 |
| | Cleese | 0.31 | 0.35 | 0.23 |
| $NH_4$–N yields | Laurel | 0.29 | 0.42 | 0.26 |
| | Dud | 0.35 | 0.55 | 0.43 |
| | Abbott | 0.27 | 0.38 | 0.23 |
| | Wise | 0.10 | 0.25 | 0.32 |
| | Cleese | 0.11 | 0.17 | 0.19 |
| $NO_3$–N yields | Laurel | 0.03 | 0.05 | 0.03 |
| | Dud | 0.01 | 0.03 | 0.03 |
| | Abbott | 0.04 | 0.05 | 0.04 |
| | Wise | 0.00 | 0.01 | 0.01 |
| | Cleese | 0.09 | 0.10 | 0.05 |
| DON yields | Laurel | 0.18 | 0.33 | 0.25 |
| | Dud | 0.05 | 0.05 | 0.04 |
| | Abbott | 0.13 | 0.21 | 0.15 |
| | Wise | 0.06 | 0.12 | 0.13 |
| | Cleese | 0.12 | 0.15 | 0.13 |

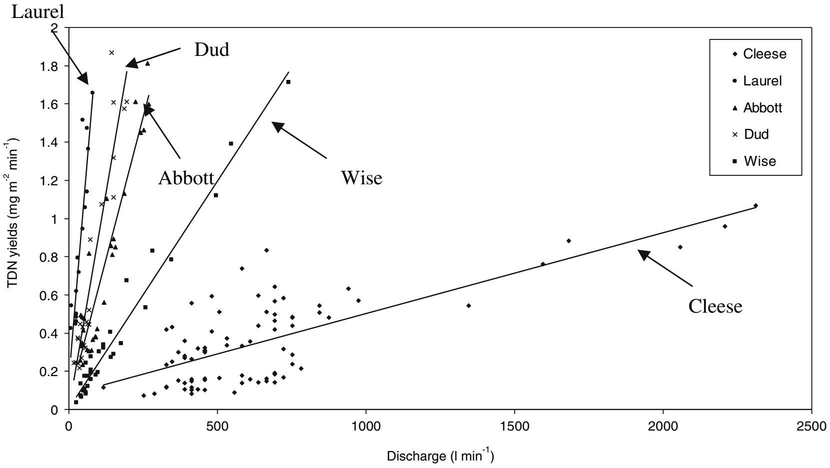


**Fig. 4** Instantaneous TDN yields (mg m$^{-2}$ min$^{-1}$) as a function of instantaneous discharge (l min$^{-1}$) for all events. *Best fit lines* describe changing linear relation between TDN yields and discharge with scale

**Table 4** $R^2$-values and equations describing best linear relationships between instantaneous discharges (l min$^{-1}$) and nutrient yields (mg m$^{-2}$ min$^{-1}$) from all plots

| $R^2$-values | Discharge versus TDN yield | Equation describing linear best-fit | Discharge versus DON yield | Discharge versus $NH_4$–N yield | Discharge versus $NO_3$–N yield |
|---|---|---|---|---|---|
| Laurel | **0.82** | $y = 0.0183x + 0.1697$ | **0.51** | **0.95** | 0.01 |
| Dud | **0.89** | $y = 0.0092x - 0.0104$ | **0.76** | **0.92** | 0.23 |
| Abbott | **0.89** | $y = 0.0059x + 0.0401$ | **0.87** | **0.89** | 0.43 |
| Wise | **0.97** | $y = 0.0024x + 0.0064$ | **0.91** | **0.97** | 0.09 |
| Cleese | **0.54** | $y = 0.0004x + 0.0782$ | 0.31 | 0.42 | **0.60** |

Bold type denotes relationships that are significant at $P < 0.01$

discharge from the catchment, to a low of 0.61 mg l$^{-1}$. Such behaviour is evident during all events observed across all of the plot scales. Initial TDN concentrations average 1.23 mg l$^{-1}$, and represent the peak nitrogen concentrations in 13 of the 14 events, whereas final TDN concentra-

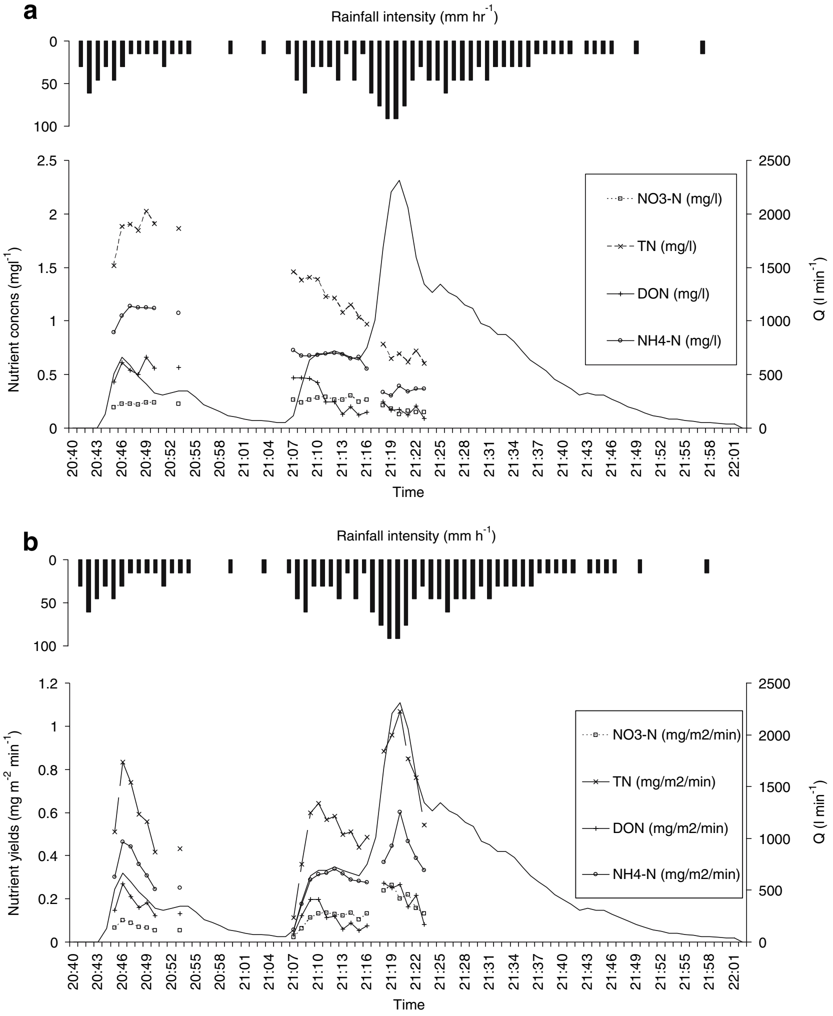


**Fig. 5** (**a**) Rainfall intensity (mm $h^{-1}$), discharge (l $min^{-1}$) and nutrient concentrations (mg $l^{-1}$) from the Cleese subcatchment, 26 July 2002. (**b**) Rainfall intensity (mm $h^{-1}$), discharge (l $min^{-1}$) and nutrient yields (mg $m^{-2}$ $min^{-1}$) from the Cleese subcatchment, 26 July 2002

tions average 0.72 mg $l^{-1}$. Furthermore, this decline is also evident within the fractions of $NH_4$–N declining on average from 0.49 to 0.31 mg $l^{-1}$ and DON declining on average from 0.38 to 0.19 mg $l^{-1}$. However, the concentration of the $NO_3$–N fraction tends to stay relatively stable during events with a slight increase on average of 0.1–0.16 mg $l^{-1}$. For all events, at each separate scale, it has been shown that discharge exerts a strong control upon nitrogen yields (Fig. 4), therefore, it is important to study the intra-event dynamics of TDN yields relative to the observed instantaneous discharges to further understanding of the temporal scaling of dissolved nitrogen behaviour within events.

Rainfall, flow and nitrogen yields for the Cleese 26/07/02 event are illustrated in Fig. 5a, b. In contrast to the decrease in nitrogen *concentration* within-events described above, there is a strong similarity between nitrogen *yields* and the form of the hydrograph illustrating how nitrogen yields are positively related to discharge during events (as was also seen on the hillslopes, see Fig. 2b for an example). Peak yields of all fractions coincide well with peak flows, which supports the findings of Schlesinger et al. (2000), who conclude that nitrogen yields are well correlated with discharge from small plots under natural rainfall in the Chihuahuan desert. This behaviour is consistent between events as was seen in Fig. 4 for TDN, but it is also true for DON and $NH_4$–N, with the exception of yields from the Cleese catchment, where coefficients of determination are low and insignificant. $NO_3$–N on the other hand, does not seem to be positively related to discharge as the near constant yields observed in Fig. 5b are replicated for all events at all scales with the exception of those at Cleese.

### Temporal scaling of dissolved nitrogen behaviour: inter-event dynamics

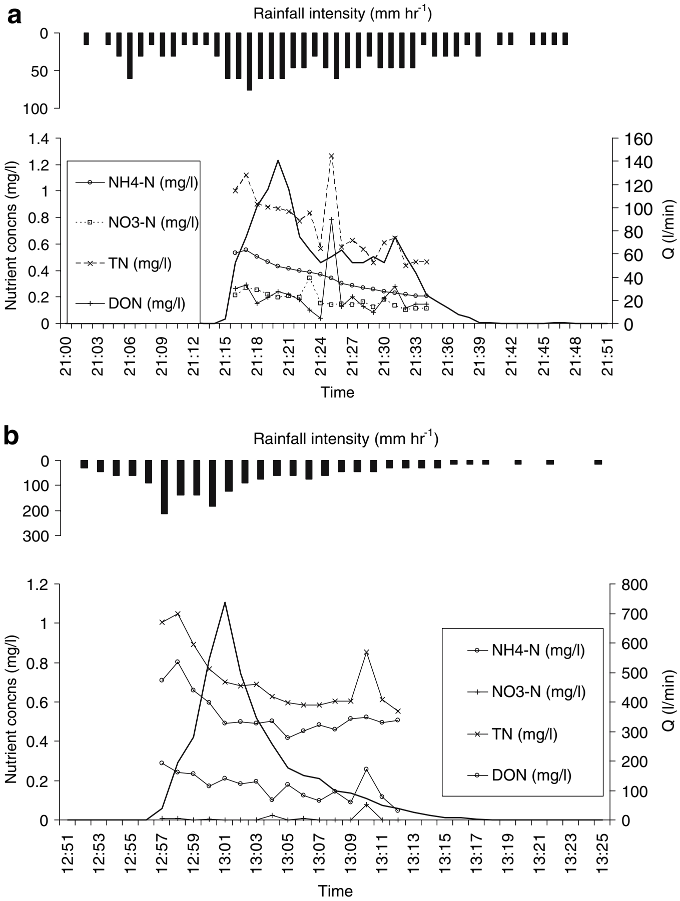
To investigate the contrast in behaviour between events, successive events on the same hillslope plot (Wise) from the 26/07/02 and the 04/08/02 are shown in (Fig. 6). The events are characterised by similar rainfall totals (29.5 and 31 mm), though very different peak 1-minute (76 and 213 mm $h^{-1}$) and average event (28 and 53 mm $h^{-1}$) intensities which generate distinct hydrograph responses. The hydrograph of the 26/07/02 event produces a total discharge of 1,385 l over a period of 28 min, with peak flows of 140 l $min^{-1}$, whereas the hydrograph of the 04/08/02 event yields a total discharge of 3,730 l over a period of 25 min with a peak flow of 738 l $min^{-1}$. Such flow characteristics lead to differences in nitrogen responses between events. Total N yield is 1,027 mg from the 26/07/02 event and 2,675 mg from the 04/08/02 event, thus, given an increase in total flow by a factor of 2.7, there is a very similar (2.6 factor) increase in TDN yield between events. Due to the limited temporal coverage of the dataset, it is not clear whether these results are true of all successive events, as only three sets of successive events were captured. However, the data shown for the Wise plot in Figs. 4 and 6a, b confirm that later events do not produce lower values of TDN than might be expected from the relationship between discharge and TDN, which is linear, and suggests that there is no notable decline in nitrogen yields on an inter-event basis.

To understand the dynamics of each nitrogen fraction that contributes to the behaviour of TDN, it is illustrative to look at the proportions of TDN from each of the three fractions analysed ($NH_4$–N, $NO_3$–N and DON), for the same events as detailed above, over all plots where observations were made (Dud, Abbott, Wise and Cleese for the 26/07/02 event and Laurel, Dud, Abbott and Wise for the 04/08/02 event). As is shown in Fig. 7a, b for the smaller event, $NH_4$–N dominates (43–57% of TDN), with the remaining contribution from DON (18–38% of TDN) and $NO_3$–N (20–25% of TDN). If we consider the proportions of TDN from each fraction from the larger event, however, consistently different behaviour is evident from all plots, with a marked increase in $NH_4$–N (52–78% of TDN) and a decrease in $NO_3$–N (1–7% of TDN), though a similar proportion of TDN from DON (21–41% of TDN). An analysis of the factors which might be expected to control the *proportions* within TDN from two events separated by only 8 days (total discharge and plot area), however, shows weak, insignificant relationships between all TDN fractions and both total discharge and plot area and the combined effect of both. Consequently, though it has been shown that plot areas and flow discharges control nitrogen yields from a hydrological perspective, it is not clear from the results presented here, what the controls upon the proportions of TDN coming from each fraction are. Although it might be relevant to consider the role of atmospheric deposition and soil mineralisation/nitrification as controlling factors on nitrogen fluxes, no such data were collected here.

## Discussion

Schlesinger et al. (2000) monitored nitrogen yields from small (4 $m^2$) plots under natural rainfall events and used these results in combination with atmospheric deposition data, to calculate net gains/losses of N to/from the landscape in units of kg $ha^{-1}$ $year^{-1}$. Results showed that losses of dissolved nitrogen in runoff were potentially significant (0.43 kg $ha^{-1}$ $year^{-1}$) if extrapolated to the landscape scale. However, data presented here suggest that the relationship between the size of plot where observations are made and the magnitude of those observations may be more complex than has previously been assumed. In fact, the relationship between discharge and nitrogen losses varies significantly with the scale of observation across the range of plot sizes from 21 to 1,500 $m^2$. This result brings into question the approach of upscaling results from such small plots to the landscape scale, which is an area of work that requires much care (Wainwright et al. 2000; Müller et al., in press). A key finding of this

**Fig. 6** (**a**) Rainfall intensity (mm h$^{-1}$), discharge (l min$^{-1}$) and nutrient concentrations (mg l$^{-1}$) from the Wise hillslope, 26 July 2002. (**b**) Rainfall intensity (mm h$^{-1}$), discharge (l min$^{-1}$) and nutrient concentrations (mg l$^{-1}$) from the Wise hillslope, 4 August 2002



study is that extrapolation of results from small spatial-scale experiments using either simulated or natural rainfall events may be misleading if only one spatial scale of observation is used. Parsons et al. (2004) have demonstrated that for soil erosion it is the explicit consideration of hillslope length (and therefore of particle travel distance), that allows scaleable predictions of sediment yields to be made. Herein it is suggested that a similar approach is taken to upscaling understanding of nitrogen yields, with direct consideration of plot/catchment areas and therefore variability in runoff behaviour being made in order to provide larger scale estimates of dissolved nitrogen losses in overland flow that do not underestimate potential losses by ignoring the effect of spatial scale.

It is likely that the most direct control on decreasing nitrogen yields with increasing spatial scale, is the reduction in runoff coefficients as plot size increases, or the spatial scaling of runoff that was observed by Parsons et al. (2006), Wainwright and Parsons (2002), Yair and Kossovsky (2002) and Yair and Raz-Yassif (2004) in relation to soil erosion. As spatial scale increases, observed increases in discharge will occur through more concentrated flowpaths, and deeper overland flow. Dissolution of nitrogen held in the soil, however, may only occur in the lower layers of runoff that are in contact with the soil leading to a lower concentration of nutrients in larger volumes of water. Furthermore, in dry environments where $NO_3$–N in particular has accumulated in soils over the dry season from nitrification and mineralisation processes, the upper layers of the soil may be the main source of TDN (Riggan et al. 1985; Avila et al. 1992; Holloway and Dahlgren 2001). Consequently, as catchment areas increase, the effect of this flushing of $NO_3$–N from the soil is reduced, with the reduced runoff coeffi-

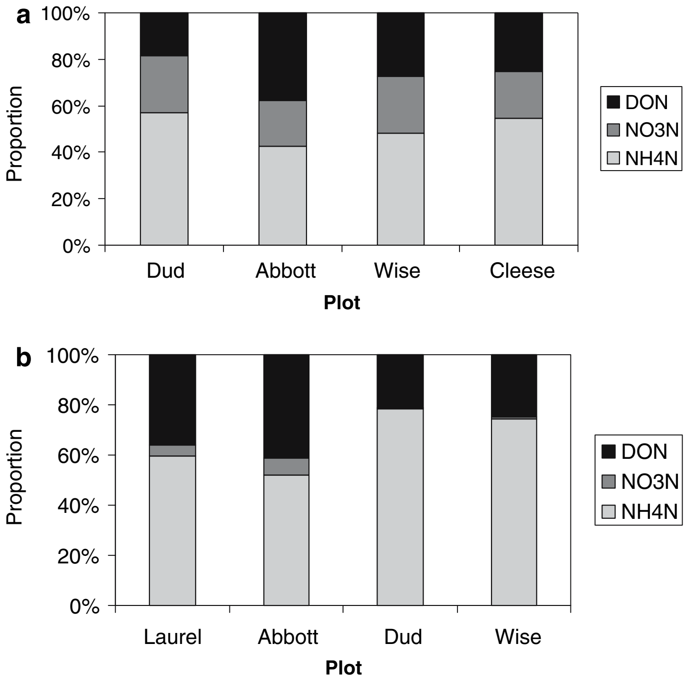


**Fig. 7** (**a**) Proportions of mean TDN from $NH_4N$, $NO_3N$ and DON from Dud, Abbott, Wise and Cleese during the 26 July 2002 event. (**b**) Proportions of mean TDN from $NH_4N$, $NO_3N$ and DON from Laurel, Abbott, Dud and Wise during the 4 August 2002 event

cients. Similar observations were made by Fenn and Poth (1999), Meixner et al. (2001) and Meixner and Fenn (2004) to explain spatial patterns at larger spatial scales. This is a tentative explanation for the reduction in the slope of the best fit line describing the relationship between flow discharge and TDN yields (Fig. 4) and it is also a mechanism which would explain the control exerted by the form of the event hydrographs observed upon the accompanying nitrogen yields. Clearly, more detailed datasets describing N mineralisation/nitrification and the deposition (both wet and dry) of N, and the interaction of these processes with surface runoff are required to enhance understanding in this area.

Across all spatial scales, observations of nitrogen dynamics during single, natural rainfall events suggest that initial fluxes, associated with the rising limb of event hydrographs produce the highest concentrations of all nitrogen fractions. These findings support the conclusions of Schlesinger et al. (1999) who found concentrations of both TDN and DON in runoff to be at their highest within the first 5 min of simulated rainfall events and to decline thereafter. Supply limited behaviour such as this has commonly been observed in relation to suspended sediments in dryland channels (Alexandrov et al. 2003) and erosion rates on semi-arid hillslopes over both simulated events (Parsons et al. 1994) and during natural rainfall events (Parsons et al. 2006). Similar observations in relation to nutrient behaviour were made by Schlesinger et al. (2000) from small plots under natural rainfall in semi-arid New Mexico. In addition these authors found that such behaviour led to higher nutrient yields from shrubland areas, due to increases in discharge, rather than concentration. Data collected here support these findings at a range of spatial scales (from 21 to 1,500 $m^2$), demonstrating that the exhaustion of nitrogen during events occurs independent of spatial scale, and that the yields of dissolved nitrogen from natural events at each spatial scale increase with discharge, though at a decreasing rate as plot size increases.

Little support is evident, however, for any inter-event or seasonal decline in nitrogen losses, as was observed by Fisher and Grimm (1985) who recorded significant decreases in DON over the course of three events within the Sonoran desert. Results described here also contradict the findings of Li et al. (2006), who published data from a chaparral watershed demonstrating seasonal exhaustion of nitrogen where successive storms occur closely together (within 3–4 months). However, these findings are supported by the work of Parsons and Wainwright (2005) who found a seasonal decline in $NH_4$–N concentrations in runoff under grassland, but found no significant seasonal variation in concentrations of $NH_4$–N under tarbush and creosote bush shrub species (similar vegetation types to this study). Here, DON contributes largely the same proportion of TDN between the consecutive events observed, though unfortunately none of the plot datasets covers an entire season to elucidate whether or not a seasonal exhaustion effect is prevalent. From the limited data available on successive events, it seems unlikely that this is the case, however, as nitrogen yields appear to vary consistently with hydrological behaviour regardless of event timing or position within the season.

## Conclusions

This paper describes the behaviour of dissolved nitrogen associated with overland flow at a range of temporal and spatial scales. In so doing it addresses the problem of up-scaling results from small-plot experiments to provide larger scale estimates of nitrogen yields by demonstrating that observed nitrogen behaviour is particularly sensitive to the spatial scale at which it is monitored. Dissolved nitrogen yields increase with increasing discharge but at a declining rate related to increasing plot size. Therefore, if results from small-scale plot experiments are extrapolated to the landscape scale, it is likely that misleading estimates of nitrogen yields (overestimations) will be made. Small spatial-scale experiments do not consider the retention of water-borne nutrients within the landscape, nor changing abilities of deeper flows to pick up proportionally more nutrients.

Observations describing the temporal scaling of nitrogen behaviour show that event-based nitrogen concentrations are initially high and decline through events. This finding indicates that nitrogen exhaustion occurs, in a system that can be described as supply limited on an event basis. Nitrogen yields are strongly controlled by event hydrology, so that even when concentrations are at their highest (typically on the rising limb of the hydrograph), dissolved yields are low, only reaching their peak when discharge increases. As desert soils tend to be low in nutrients and, in the present case have suffered from accelerated erosion over the last 100–150 years, such behaviour is understandable and agrees with the existing datasets that describe event dynamics at single spatial scales from rainfall simulation experiments.

On an inter-event basis, there appears to be little support for the hypothesis that nitrogen yields will decline either between events or across the monsoon season. This finding is in line with an, albeit limited, literature and suggests that though nitrogen supply may be exhausted in the short-term (i.e. during an event), seasonal exhaustion does not occur. Therefore, large events, whenever they fall during a season, will yield significant nitrogen losses. This may be due to the role of nitrifying bacteria in replenishing the supply of $NO_3$–N in the soil, once the rainy season has started (Hartley and Schlesinger 2000) and the accumulation of extremely high amounts of soil $NH_4$–N during the dry season due to the mineralisation of organic N in the soil (Fisher et al. 1987).

A key outcome of this work is an improved empirical understanding of the effect of spatial scale and hydrological behaviour upon the dynamics of dissolved N in overland flow. Ongoing work will incorporate this understanding within a modelling framework to permit the prediction of nitrogen losses at larger spatial and longer temporal scales. This work will utilise the empirical understanding presented here in addition to further data (currently being collected), which describe the role of N mineralisation/nitrification and wet/dry deposition of N to address landscape scale questions.

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