INVESTIGATION INTO THE INTER-SITE AND INTER-EVENT WATER CHEMISTRY RESPONSES IN A SMALL CATCHMENT OF MIXED LAND USE IN SOUTH-WEST IRELAND

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INTRODUCTION

Water quality monitoring programmes in Ireland have until quite recently depended on fixed interval grab sampling regimes combined sometimes with continuous flow-gauging or more usually just point measurements. This form of monitoring has some applicability for measuring broad trends and is more beneficial for catchments which are dominated by relatively constant point-source contaminant discharges. However they are much less valuable when trying to make precise measurements of contaminant exports (e.g. nutrients) from rural catchments, which are dominated by diffuse source pollution and subject to continuous land use changes. In this study an intensive event-weighted monitoring programme was designed and carried out for one year in a rural catchment dominated by plantation forestry, agricultural grassland and moorland. The catchment was instrumented with five automatic water samplers and flow gauging stations, each within a sub-catchment of different land use composition. Samples were analysed for nutrients (NH3, SRP and TON) physical parameters (colour, conductivity, pH and suspended solids) and base cations (Na, K Mg and Ca).

Outlines and objectives

- To investigate the inter-site responses to the same hydrological event and attribute any differences to land use and catchment characteristics.
- To investigate the inter-event responses at each site, concentrating on preceding hydrological conditions and season.
- To investigate the behaviour of the Sodium Dominance Index (SDI) during a hydrological event, and the recovery rate as base flow again dominates discharge.

Study area

The Kilworth Catchment (Fig. 1) drains into the River Douglas situated about 30 km north east of Cork City, Ireland. The catchment covers a total area of 21.5km^2 with an altitudinal range of 60-290m. Stream gradients range around 30-40m/km: moorland tributaries are around 1m wide whilst the main channel width is 5m where it leaves the forest (Giller et al., 1992). Devonian Red Sandstone underlies most of the catchment with overlying yellowish Kiltorcan beds (Giller et al., 1996). The land use composition of the total catchment is approximately 48% plantation forestry, 14 % agricultural grassland and 39% moorland. The composition of each sub-catchment is represented in Figure 2. The conifer plantation was established in 1924, and today Sitka Spruce (*Picea sitchensis*) and Douglas Fir (*Pseudotsuga menziesii*) comprise the majority of the area planted (Cleneghan, et al., 1998). In terms of soil, brown podzolics underlie the majority of the catchment with some blanket peat, peaty podzols, peaty gleys and lithosols in upper altitudes (Giller et al., 1996). The mean annual precipitation for the area is over 1200mm and the mean daily discharge based on the gauging station at Site Doug is shown in Figure 3.

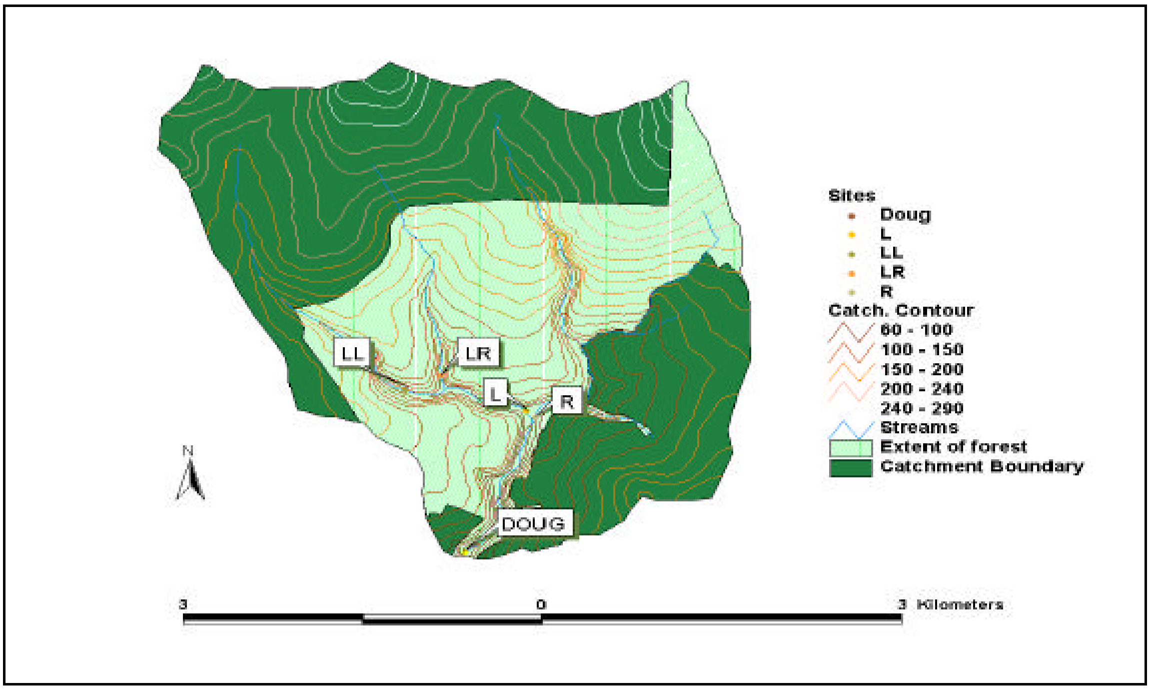

Fig. 1. Kilworth Catchment showing extent of forest, sites and contours

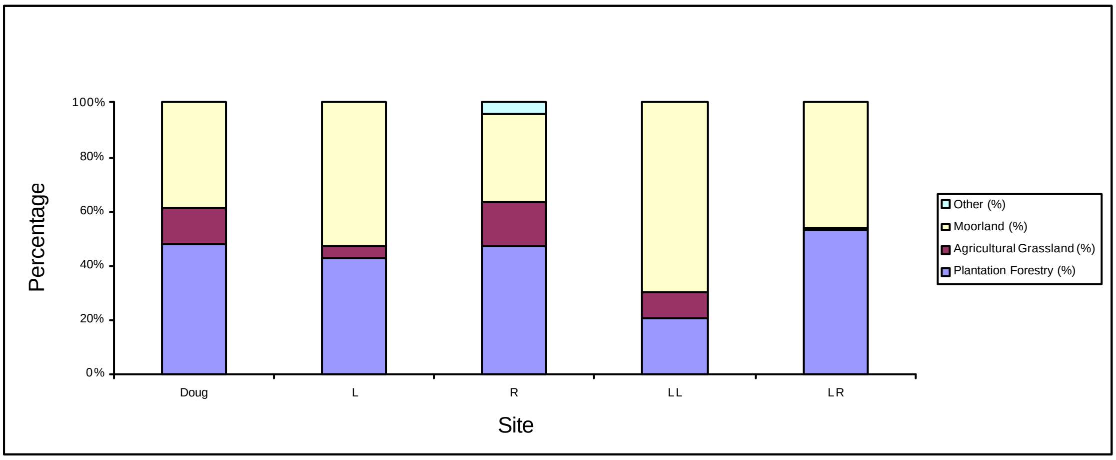

Fig. 2. Land use composition for each of the five sites

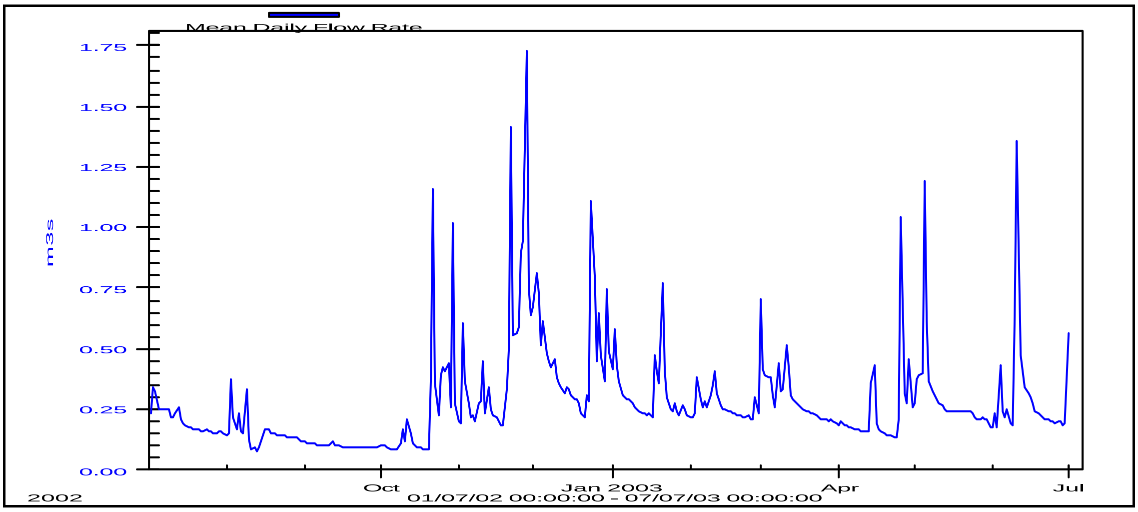

Fig. 3. Mean daily flow rate for the entire catchment

METHODS

Sampling Infrastructure

- Five ISCO 6712 automatic water samplers with 24-litre bottle configuration
- Flow gauging - horizontal weirs without end contractions and ISCO 730 Bubbler Modules
- Linked telemetrically via radio modems to a relay station at the base of the catchment followed by a landline link to lab in UCC

A sampling strategy was developed allowing synchronised discrete water samples to be collected at each of the five sampling sites triggered by an increase in stream level of approximately 5mm, thereby ensuring the first flush was collected. The sampling frequency was set to 45 minutes, which in most instances ensured samples from both the ascending and descending limbs of the hydrograph were collected, and near base flow conditions were re-established. Samples were collected from the site within 12 hours of the last sample being taken, filtered, and analysed immediately for ammonia, soluble reactive phosphate (SRP) and total oxidised nitrogen (TON) using automated flow injection. The remaining analysis was completed within two days using standard methods.

The system in place in Kilworth is also being used to test the integrity of the SDI (Sodium Dominance Index) across different flow conditions. The SDI is a measure of acid-sensitivity of rivers and is calculated as the percentage of Na^+ contribution to the total of the major cations ($Ca^+ + Mg^+ + Na^+ + K^+$). As part of a wider COFORD/EPA project the Kilworth site has been chosen to test the index variation at the reach scale across varying flow conditions. The SDI has been shown to be consistent in both base and storm flows for a given site, and a value of above 40% has been proposed for sensitive catchments (Kelly-Quinn and Ryan, 2001). For two particular sampling events (June and July 2003) the automatic water samplers were reset when the samples were collected and immediately set to sample every two hours for the next 48 hours in order to extend the sampling period. Analysis of the cations was carried out using Ion chromatography.

RESULTS AND DISCUSSION

Synchronised sampling of the five sites began in July 2002, since then a total of 17 spate events of varying magnitudes have been sampled and analysed.

Table 1:Means and ranges for nutrients and physical parameters for each of the five sites. Data from storm event conditions from July 2002 until July 2003. (LOD = Limit of detection)

		NH3-N (mg/l)	SRP-P (mg/l)	TON-N (mg/l)	Conductivity (uS/cm)	pH	Colour (Hz)	Suspended solids (mg/l)
DOUG	Mean	0.041	0.021	0.460	83.5	7.05	100.88	22.53
	Range	0.185-LOD	0.111-LOD	0.970-0.111	140.3-45.7	8.00-6.17	193.88-11.46	164.3-0.16
L	Mean	0.030	0.012	0.257	65.5	6.76	91.28	16.67
	Range	0.125-LOD	0.343-LOD	0.706-0.085	254.1-35.1	7.55-5.61	181.63-13.54	142.2-0.32
R	Mean	0.068	0.040	0.431	93.0	7.12	114.80	29.62
	Range	0.608-LOD	0.172-0.004	0.939-0.135	240.1-45.2	8.27-5.97	388.3-10.38	196.7-0.36
LL	Mean	0.034	0.011	0.267	61.0	6.57	91.40	18.8
	Range	0.337-LOD	0.119-LOD	1.319-0.028	89.1-38.9	7.51-5.34	160.2-32.08	271.5-0.76
LR	Mean	0.035	0.009	0.151	60.5	5.96	120.58	11.61
	Range	0.217-LOD	0.110-LOD	0.499-0.016	106.1-39.1	6.93-4.80	215.31-32.08	55.16-0.44

The mean concentration and range of seven parameters analysed for the five sites is summarized in Table 1.

As an example, the physical results for an event from November 2002 for Site Doug (most downstream) is shown in Figure 4. The flux of both conductivity and pH show an inverse relationship to flow rate, with pH demonstrating a lag, dropping to it's minimum (although still near neutral at this site on this occasion) six hours after peak flow conditions. Figure 4 also illustrates the close relationship between flow and suspended solid concentration and the positive association between flow and colour. This is characteristic of the behaviour of each of the sites to a hydrological event, although differences in values are apparent.

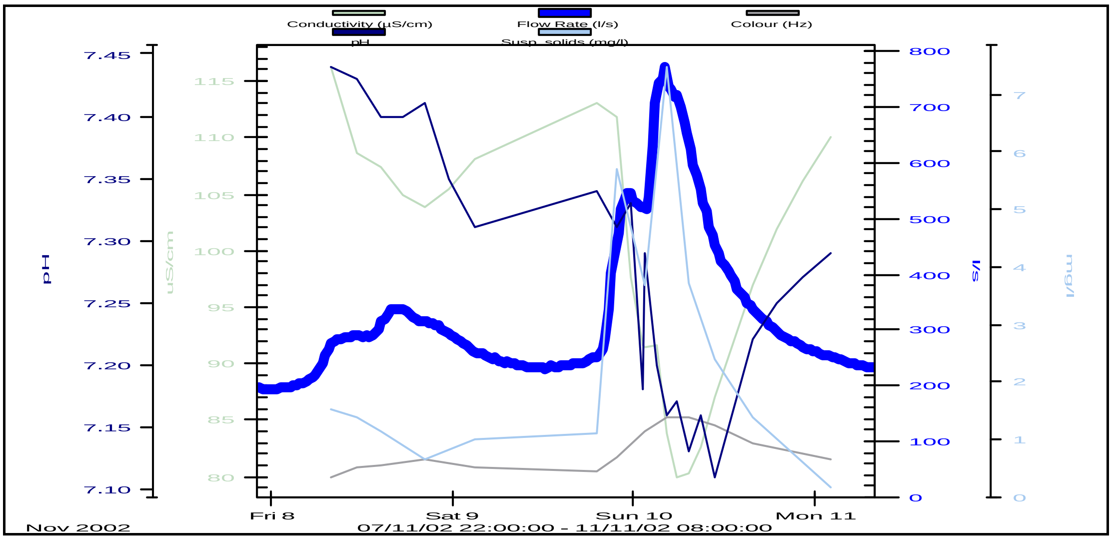

Fig. 4. Conductivity, Colour, pH and Suspended Solids at the Douglas site in Kilworth on the 8th, 9th, 10th of Nov.2002

Inter-site comparison

Figure 5 shows the difference in suspended solids and SRP between three sites: Doug, L and R, for an event in January 2003. This example shows Sites L and R which are similar in size but differ primarily in the percentage of grassland between them, 4.5 and 16.7 respectively. Site L exhibits no real peak in SRP (bottom panel) on this occasion whereas R shows a maximum of 0.102 mg/l in line with peak flow conditions. This pattern with R exhibiting higher levels, L lower and Doug intermediate is a common feature of the SRP, NH3, suspended solids, and colour data. In this example suspended solids values follow a similar trend with concentrations of 79.20 mg/l for R, 20.44 for L and an intermediate of 47.24 for the Doug site.

Each sub catchment has it's own distinct response to each hydrological event and these patterns have shown a degree of consistency across the sampling period. For example, Site R shows consistently higher suspended solids than Site L (Figure 5), a possible explanation lies in the different land use of both sub-catchments. When looking at the differences in response to an event the management practices within each of the land use types must be considered. The majority of the grassland in this sub-catchment is utilised for dairy, cattle and sheep grazing with land drainage and fertiliser spreading both common practices. The drainage network in high flow conditions may act as a point-source, especially if the event occurs after a recent slurry application. Additionally, the lack of riparian vegetation at some points where the grassland borders the stream directly, may also lead to greater erosion and sediment transport. This may be evident in the slightly earlier hydrological response of this sub catchment (Figure 6), where a lack of impedance by the vegetation, not just in the riparian zone but also throughout the catchment results in a quicker response where surface and near-surface flows reach the stream channel quicker than a catchment with greater vegetation coverage.

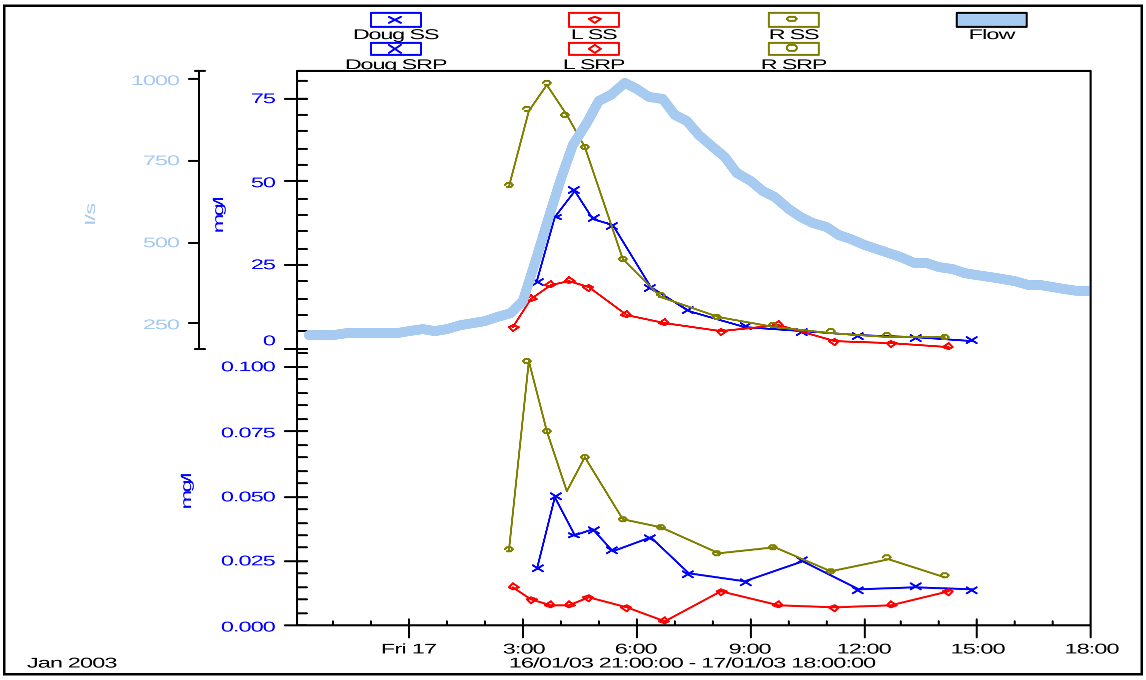

Fig 5. Suspended solids (top panel) and SRP (bottom panel) with the flow for the catchment for an event in January 2003 for three sites: Doug, L and R.

Sodium Dominance Index

Figure 6 shows the calculated SDI values from four events, which were analysed for base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}). The values were then ranked in descending order for each site to illustrate the range for each site, across the four events. For these four events the first sampled on the 2nd of March 2003 and the last on the 2nd of July 2003, there is a variation between 15 and 24% for Site R and L respectively. Site Doug, the most downstream site, which is below the confluence of these two streams, falls between these two values with around 20% variation.

Variation does therefore occur in the SDI in relation to flow, but the degree of variation is not as broad as the variation found in conductivity as illustrated for a single event at Site Doug in Figure 7. Although for Sites R and Doug the range (Figure 6) spans the proposed 40% value (Kelly-Quinn and Ryan, 2001), above which the catchment is said to be acid-sensitive. Table 2 is a summary of correlations between both conductivity and colour, with the SDI. It was found the relationship was stronger at all sites between conductivity and the SDI than with colour and the SDI.

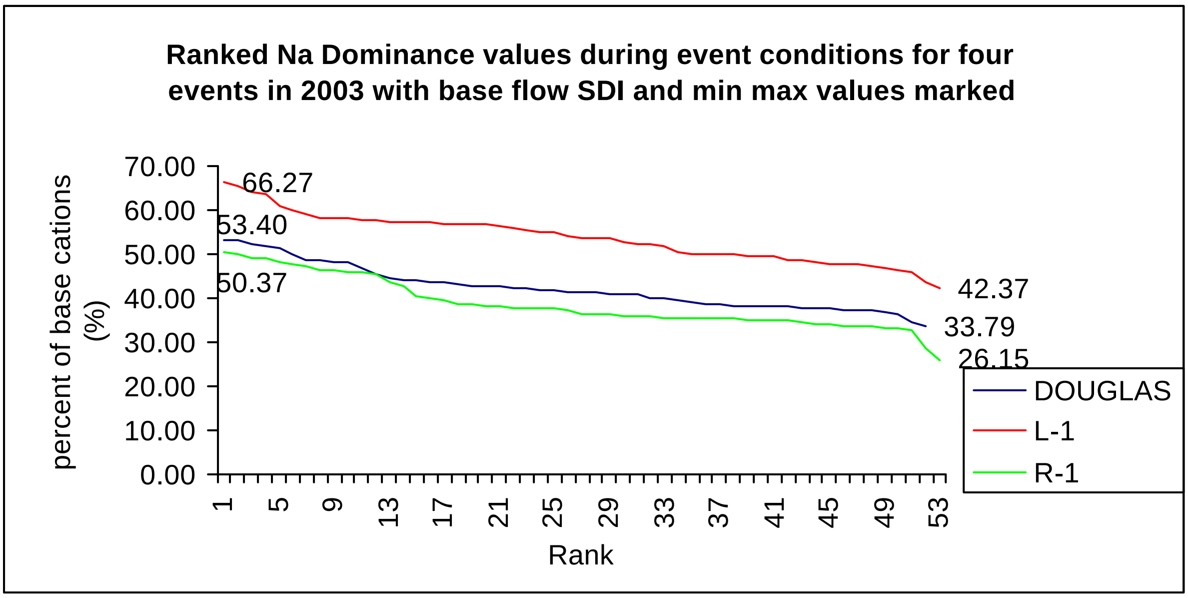

Fig. 6 Ranked SDI for three sites during four events showing min and max values for each site along with base flow values for the SDI

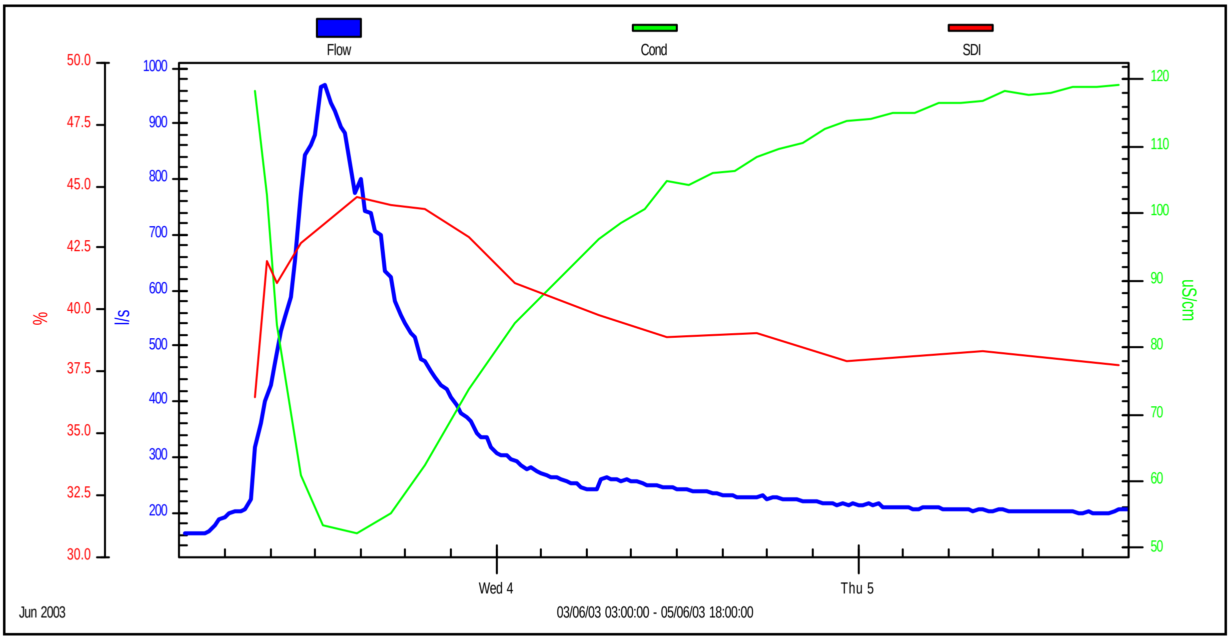

Fig.7 Flow, conductivity and SDI for an event the 3rd of June 2003 for Site Doug

Further investigation would be necessary between sites and across seasons to understand the SDI and it's response to differing hydrological conditions more fully. Grab samples were taken during a weeklong dry period on the 23rd of June 2003 and the SDI values do not fall at the lower end of the storm event ranges as would be expected, but well within the extremes of the range: Doug = 42.86%, L = 50.34% and R = 42.58%.

Table 2. Summary of correlations between both conductivity and colour with SDI for three sites for an event in June 2003

Site	Correlation	r^2
D	Conductivity & SDI	0.8902
	Colour & SDI	0.8126
L	Conductivity & SDI	0.9288
	Colour & SDI	0.7824
R	Conductivity & SDI	0.6954
	Colour & SDI	0.5862

CONCLUSIONS

Inter-site differences

At this explorative data analysis stage, patterns in response to hydrological events do seem apparent, with consistently higher levels of NH3, SRP and suspended solids for Site R, which is the site with the greatest percentage of grassland. Although further analysis would be necessary to attempt to identify the underlying processes.

Sodium Dominance Index

Within the Douglas catchment and sub-catchments the SDI does appear to vary to some degree with flow, and ranges by approximately 20% during storm events for each of the three sites looked at. This correlation is lower than other standard measures of acid-sensitivity during such events.

Inter-event comparison

When looking at the same site across the sampling period, at this stage there does not seem to be any clear seasonal patterns in the data other than those directly associated with flow. Further analysis may elucidate such patterns including for example estimates of seasonal nutrient export rates.

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