# Shifts in discharge-concentration relationships as a small catchment recovers from severe drought



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**Shifts in discharge-concentration relationships as a small catchment recovers from severe drought**

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**Abstract**

This paper provides evidence of the recovery of a small, moorland catchment to a severe drought, the most extreme on record in the UK. We present a detailed water quality time series for the post-drought recovery period, from the first significant storm event at the end of the drought through three very wet months during which time the catchment fully wetted up. High-frequency observations were obtained using pump water samplers, at 15-minute intervals for storm events and 2-hourly at other times. There are significant shifts in discharge-concentration response as the catchment wets up; initial behaviour is very different to later storms. Extreme drought may become more common in a warmer world, so it is increasingly important to understand water quality response during and after such episodes, if their impact on water resources and in-stream ecology is to be better anticipated.

Key words: drought, water quality, chemographs, hysteresis

**Introduction**

Climatic events occur at a variety of timescales and so it is no surprise that the response of hydrological systems will reflect the various linkages between input and output. Johnes and Burt (1993) identified several patterns in fluvial nitrate concentrations that reflect differing climatic controls: periodic variations, long-term trends and episodic response. In terms of episodes, hydrologists are mostly concerned with flood events, with a time scale typically of hours to days depending on the size of the catchment. However, episodic events may also occur on longer time scales. In some regions there is an annual cycle of hydrological response: most notably spring snowmelt in mountainous basins; and high wet-season river flow anywhere with a strongly seasonal pattern of rainfall, evaporation or both (Burt, 1992). Climatic variation can produce major deviations from normal system response that may also, like floods, be regarded as episodes. Thus, a major period of drought lasting several years can look like an individual event in a long time series. This paper describes the recovery of a small basin after an extreme drought, detailing the transition from an extremely dry state to a very wet one. Both periodic cycles and episodes can, of course, happen in a situation where there are long-term trends in external drivers; these include both climate change (e.g. global warming) and the impact of human activity within the river basin (e.g. deforestation). Long-term trends may be equated with a state of dynamic equilibrium, meta-stable where important thresholds exist (Chorley and Kennedy, 1971): slow, insidious change can lead eventually to thresholds and non-linear response. Complexity is added since the impact of an individual extreme event is contingent on the initial state of the system, which will reflect the changing long-term condition of the basin.

In this paper we use high-frequency observations from a small upland catchment in south-west England to identify patterns of sediment and solute export when the catchment is wetting up after a major drought. There is currently much interest in high-frequency observations: the combination of a new generation of field-deployable probes with data loggers and telemetry has enabled much more frequent observations over extended periods than ever before (Kirchner et al., 2004). Our data come from a different era when automatic water samplers combining simple machinery and somewhat crude electrical circuitry were the cutting-edge technology; then, high-frequency observations required an intensive field campaign reliant upon frequent collection (and subsequent laboratory analysis) of water samples. Stream stage was measured using clockwork chart recorders (comprising ink pens and paper charts), much less reliable than today's data loggers coupled to pressure transducers.

From the 1960s onwards, the use of automatic water samplers enabled sub-hourly data to be collected. Such data have provided a detailed picture of water quality variations during storm events, including inferences about the runoff processes operating (Walling and Webb, 1986). Concentration-discharge (c-Q) plots have commonly been used to infer how flow components such as overland flow, soil water and groundwater mix to produce the observed episodic hydrochemical response of small catchments (Chanat et al., 2002). Many studies have inferred the relative timing of mixing from hysteresis loops observed in c-Q plots: Evans and Davies (1998) provided a typology of hysteresis loops, illustrating how different component concentrations produce different patterns of hysteresis, while Lawler et al (2006) proposed a simple, dimensionless index ($HI_{mid}$) to quantify the magnitude and direction of hysteresis.

The severe drought which affected England and Wales from May 1975 to August 1976 was unprecedented at the time (Doornkamp et al., 1978) and remains so today. Using the Hadley Centre's monthly rainfall record for South West England and Wales (SWEP: www.metoffice.gov.uk/hadobs ; Alexander and Jones, 2001), which begins in 1873, cumulative rainfall totals up to and including August 1976 remain the lowest on record (to July 2013) for any of the following periods: 6, 12, 16, 18 and 24 months. The 3-month total June-August 1976 is the third lowest for any 3-month period. At Oxford, where the record dates from 1767 (Burt and Howden, 2011), the 16-month period May 1975 – August 1976 is also the driest on record (n=2944); only the drought of 1787-8 comes close. This extreme drought was followed by a very wet autumn and winter: the 6-month SWEP total to February 1977 is the $40^{th}$ highest on record (n=1682).

Whilst the main pre-occupation during the drought was public water supply, after the drought very high nitrate concentrations were observed in major rivers, often in excess of legal limits, causing difficulties for water supply companies (Burfield, 1977; Wilkinson and Greene, 1982; Slack and Williams, 1985). Continued concern led directly to a review of the nitrate issue by the Royal Society (1983). Droughts have also been implicated in the release of dissolved organic carbon from upland peat catchments and the 1975-76 drought was significant in this respect (Worrall et al., 2003, 2006). Working in a small catchment in SW England, Foster and Walling (1978) noted the unique solute response following the drought with concentrations rising markedly during the "autumn flush" which resulted from the heavy autumn rainfall. In their study catchment, concentrations of most solutes increased three- or four-fold, representing a rapid removal or flush of the supply that had accumulated during the drought. Here we provide evidence from the same period for another small catchment in SW England, showing how water quality recovered during the immediate post-drought period. Given projections for an increased frequency of drought in the future, evidence from rare, episodic events in the past becomes ever more relevant in seeking to understand how catchment systems might respond to climate change.

**Study catchment**

Bicknoller Combe is a small (0.6 $km^2$) catchment on the western escarpment of the Quantock Hills, Somerset (NGR 312140), UK (Figure 1). Permeable brown earth soils overlie impermeable Devonian Old Red Sandstone; as a result, the winter stormflow response is dominated by delayed throughflow peaks which follow a day or so after an immediate quickflow response (Anderson and Burt, 1978a, 1978b – both include maps and further details of the study catchment). During dry periods, stormflow is limited to this quickflow response, which is a mixture of infiltration-excess overland flow from a footpath and some saturation-excess overland flow and throughflow from residual variable source areas contiguous to the stream channel (Anderson and Burt, 1982). Vegetation cover comprises grass and bracken on steep valley-side slopes and heather on the flat interfluves where the surface soil horizon is peaty. Agricultural activity is limited to low-intensity grazing by cattle and sheep and no fertiliser is applied within the study catchment.

Measurements of stream discharge, slope hydrology and water quality were made at Bicknoller Combe during the period 1975-77 (Burt, 1978), most of which was a time of unprecedented drought in England as noted above. The total rainfall in the county of Somerset from May 1975 to August 1976 was only 647 mm, just 57% of the long-term average (data from Wessex Water). By contrast, 905 mm fell between September 1976 and February 1977, 160% of the long-term average. The end of the drought was marked by an intense storm on 29 August 1976; the 24-hour rainfall total at nearby Stogursey was 65 mm, equalling the rainfall received in the previous 143 days (Burt, 1978); 35.6 mm was recorded at Bicknoller Combe. Rainfall in Somerset totalled 154 mm in September (192% of long-term average), 178 mm in October (205%), 115 mm in November (115%) and 132 mm in December (142%).

Rock & Taylor™ pump water samplers were used to collect water from the stream and from well-point piezometers; sample volumes were approximately 0.3 litres. The samplers took 48 samples at intervals from 15 minutes to 2 hours. These samples were supplemented when possible by hand-sampling during storm events of various runoff sources including throughflow and overland flow. The precision of the pump water samplers for sediment concentrations is not known but there is likely to have been some degree of underestimation of high suspended sediment concentrations. After filtering using 0.45μ Millipore™ filter papers, from which suspended sediment concentrations were obtained, samples were analysed for a range of chemical determinands and cations using probes (pH, specific conductance), flame photometry ($K^+$, $Na^+$) and a Varian™ atomic absorption spectrophotometer ($Ca^{++}$, $Mg^{++}$). Very few measurements of anions were conducted because titration, a lengthy process, was then the only reliable method available. A very few measurements of nitrate concentration were made using an ion-selective probe but concentrations were very low, close to the limit of detection, and so the measurements were not continued. For the stream water, during the period 16 August to 7 December 1976, sample frequency at 2 hours or less was available for most of the time with significant gaps only for 20-27 August and 1-5 November, as it happens both rain-free periods. Stream discharge was measured using $90^o$ V-notch weirs and Munro™ chart recorders.

Previous publications have presented some of these data for particular purposes but the entire sequence has not been published before. Topics previously considered have included: the relationship between throughflow generation and the solute concentration of soil and stream water (Burt, 1979a), diurnal variation in stream discharge and solute response (Burt, 1979b), the use of mixing models to identify the contribution of throughflow in storm events (Anderson and Burt, 1982) and patterns of potassium export (Stott and Burt, 1997). Later research at Bicknoller examined soil chemical processes and the delivery of solutes (including exchangeable bases, iron oxides, manganese and exchangeable aluminium) to the stream (Burt and Park, 1999; Park and Burt, 1999a, 1999b; Park and Burt, 2000). The results presented here relate only to data collected in the period August to December 1976 inclusive.



**Results**

General solute response

Figure 2 shows stream discharge and specific conductance from 16 August to 7 December 1976 together with stream discharge. As noted above, the period from May 1975 to August 1976 was one of the driest on record in SW England. Stream discharge had fallen to very low levels by the end of August and, until the end of September, rainfall generated only a single quickflow peak; secondary delayed throughflow peaks (Anderson and Burt, 1978) only appeared from the beginning of October onwards. Specific conductance, an indicator of total dissolved solids concentration, falls steadily as the catchment wets up. High concentrations in August were an indication of the very dry state of the catchment, with subsurface discharge having fallen to a very low level. Continued evaporation had considerably increased the concentration of subsurface flow and groundwater residence times were presumably at their maximum. Over the next four months, the concentration of subsurface flow fell steadily through a combination of dilution and the shunting out of “old” water by newly infiltrated water moving downslope.

Solute response during storm events

Figure 3 shows the detailed solute response in five storms: the first three events of the post-drought period, a very intense runoff event (28th September; described in more detail below), plus the second delayed throughflow event, in mid-October. It is clear that the first two storms, produced very largely by infiltration-excess overland flow, caused the stream water to become very much more concentrated during the stormflow response, presumably because there were large amounts of soluble material available on the ground surface at the end of the long drought. Note that the peak concentration on 30th August (325 $\mu$S cm$^{-1}$) is an estimate; the nearest sample value to the peak was 283 $\mu$S cm$^{-1}$, thirty minutes earlier. Whichever value is used, the total dissolved solids concentration has effectively doubled compared to the pre-storm level. Such a dramatic increase in storm-period solute concentrations is very unusual, no doubt the result of a lack of significant surface runoff over many months: stream discharge had not even exceeded 1 l s$^{-1}$ since 19 May and had not exceeded the peak discharge seen in this storm (15.72 l s$^{-1}$) since 13th September 1975, nearly a year before. The second storm event on 10th September also shows a concentration effect, but much more subdued than the first storm. The maximum observed specific conductance was 155 μS $cm^{-1}$ with an estimated peak of only 163 μS $cm^{-1}$, an increase over pre-storm levels of 31%. By the third storm (14th September), a complex event with several discharge peaks, the stream shows a slight increase in solute concentration on the rising limb of the first, largest discharge peak. There is dilution later on during the event, suggesting that the supply of readily soluble load has been exhausted and that stream response is returning to a more typical dilution effect. Thereafter, all quickflow peaks are associated with dilution, very marked during the 28th September event. For the double-peaked hydrograph in mid-October, there is a combination of dilution, during the initial quickflow response, and a small but significant concentration effect during the delayed throughflow peak (Burt, 1979).

Storm event dilution was a feature of the quickflow response for all subsequent events, with minimum concentrations typically in the range 75-100 μS $cm^{-1}$. The 14th September event was the first event to show dilution (minimum concentration 108 μS $cm^{-1}$) with the next storm hydrograph on 22nd September also a dilution event (minimum concentration estimated at 85 μS $cm^{-1}$). The 28th September event had the lowest concentration (52 μS $cm^{-1}$) for any storm hydrograph observed at Bicknoller Combe (Figure 4a). Note that the main part of this storm hydrograph was sampled at 15-minute intervals. Rainfall was very intense: 25 mm in just 15 minutes. Not surprisingly, infiltration-excess overland flow was generated, mainly from the footpath running up the valley close to the stream channel. Figure 4a includes estimates of old and new water contributing to the storm hydrograph obtained using a two-end-member mixing model (Anderson and Burt, 1982). Given the intense nature of the rainfall input, it was only to be expected that there would have been significant dilution of the stream water. Notwithstanding that the lowest concentrations occur on the rising limb, concentrations are already rising by the time of peak discharge, indicating significant, rapid inputs of old water of higher concentration, presumably from sources of throughflow and saturation-excess overland flow close to the channel.

Figure 5 shows hysteresis loops for the five storms shown in Figures 3 and 4. The loop is clockwise for the first storm (30th August), suggesting some degree of exhaustion even within this first event. Following the classification of c-Q hysteresis loops by Evans and Davies (1998), this event can be classified as C2, indicating a concentration event where surface-event water is more concentrated than subsurface water (irrespective of whether this is soil water or groundwater). Significant clockwise hysteresis is indicated by an $HI_{mid}$ index value of 0.33. The second loop (10th September) is also clockwise, although the loop is much less pronounced and the $HI_{mid}$ value is only 0.02; this is likewise a C2 event but with less dramatic concentrations on the rising limb. The 14th September event is complex, with elements of both clockwise and anticlockwise response, earlier and later in the event respectively. The major hydrograph peak yields an $HI_{mid}$ value of 0.01, indicating almost no hysteresis at all. The 28th September loop is anticlockwise, an A3 event according to Evans and Davies (1998) in which surface-event water is more dilute than subsurface sources. As noted above, maximum dilution occurs on the rising limb i.e. earlier than the maximum flow; this is sometimes referred to as a “lead” effect. The $HI_{mid}$ index is -0.28. In the 14th October event, there is again an anticlockwise loop for the quickflow peak ($HI_{mid}$ = -0.16) and a clockwise loop ($HI_{mid}$ = 0.03) for the delayed throughflow peak. Note that hysteresis loops for potassium follow a similar pattern during this period, with clockwise loops initially and anticlockwise loops later in September (Stott and Burt, 1997)

Concentration effects during summer storms are not uncommon (e.g. Walling and Webb, 1984) but the high solute peak on 30th August seems to be remarkable, an indication of the severity of the drought. It is not known whether concentration effects occur every summer at Bicknoller Combe or were just a feature of the severe drought. Water quality data are available from early February 1976, although the record is incomplete, especially in June and early July. There are data for only three very small storm events prior to the 30th August event; all displayed concentration effects. The event of 12th February (quickflow peak: 4.64 l $s^{-1}$) was large enough to be followed by a delayed throughflow peak (5.25 l $s^{-1}$, peaking 16:00-24:00 on 15th February), the first of only three such events right at the end of the 1975-76 winter season. There were two very small quickflow peaks on 19th May (0.94 and 1.19 l $s^{-1}$) and another even smaller one on 29th May (0.59 l $s^{-1}$); all three displayed concentration effects. Whether or not concentration effects are common in summer at Bicknoller Combe, the 30th August solute response seems extraordinary compared to anything else observed during the study period. Note that concentration effects were a feature of the results presented by Foster and Walling (1978) for September 1976. Burt and Worrall (2009) showed that nitrate concentrations in the Slapton Wood catchment, also in SW England, were extremely high during the 1976-77 winter.

Figure 6 provides a scatterplot of all c-Q observations during the period under consideration. Discounting outliers, all storm-period samples, there is a very narrow range of concentrations with only a small increase in concentration at the lowest discharges, all from the end of the drought period. The full range of variation is between 52 and 283 $\mu$S $cm^{-1}$, a factor of five, but 94% of 1145 samples had a specific conductance between 101 and 140 $\mu$S $cm^{-1}$. Meanwhile discharge varied by more than three orders of magnitude.

Variation in cation concentrations and pH

Notwithstanding high concentrations during and immediately after the drought, the mean specific conductance is only 125 $\mu$S $cm^{-1}$. This indicates a low-solute water (Cryer, 1986); even so, there is clearly enough calcium available in soil and regolith to maintain pH close to neutral, even during quickflow events. Figure 4b shows solute concentrations during the 28th September event. As expected, these major cations follow the pattern for specific conductance (Figure 4a) quite closely, except for potassium which always increases during quickflow rather than diluting (Stott and Burt, 1997). Note that calcium (not shown) has comparable concentrations and follows a similar pattern to sodium, but with a greater degree of dilution: for sodium, the minimum concentration is 48% of the pre-storm concentration whereas for calcium the value is 24%. Magnesium has lower concentrations but follows the same pattern of dilution during the storm event; the minimum dilution is 30%. There is a similar pattern for pH but the stream appears well buffered even during this very intense quickflow response with a minimum pH value of 6.3 compared to the pre-storm value of 7.4. This supports the observations made above that solutes become quickly available as storm runoff is produced.

| | Q | SC | pH | Na | K | Mg | Ca |
|---|---|---|---|---|---|---|---|
| Q | 1 | | | | | | |
| SC | **-0.33** | 1 | | | | | |
| pH | **-0.67** | **0.32** | 1 | | | | |
| Na | -0.13 | **0.48** | -0.02 | 1 | | | |
| K | **0.36** | **0.34** | **-0.52** | *0.23* | 1 | | |
| Mg | **-0.36** | **0.62** | *0.22* | **0.67** | **0.36** | 1 | |
| Ca | **-0.53** | **0.66** | **0.68** | 0.00 | -0.06 | **0.44** | 1 |

Table 1. Correlations between discharge and water quality determinands. Figures in bold indicate significance p<0.001; italics p<0.01; n = 193.

Table 1 shows correlations between discharge, specific conductance, pH and major cations for 193 samples where there were no missing values. The results are broadly similar to pairwise correlations which maximised the number of observations in each case. As expected from Figure 6, discharge is negatively correlated with solute concentrations, except for potassium; there is also a significant negative correlation between pH and discharge. Specific conductance correlates significantly with all cations including potassium, although in this case, despite the significance level (p=1.46E-06), the relationship is not convincing (only 11% variance explained). For calcium, there is a simple linear plot and an even stronger correlation (p=4.01E-25) with 43% variance explained.

Suspended sediment concentrations

Unlike solutes, there was no clear decline in suspended sediment concentrations after the drought ended. Suspended sediment concentrations exceeded 1 g $l^{-1}$ in the 30th August event but the highest suspended sediment concentrations were observed on the rising limb of the 28th September hydrograph, reaching 6.8 g $l^{-1}$. Concentrations again exceeded 1 g $l^{-1}$ during the 30th November event, so clearly high suspended sediment concentrations are not all that unusual at Bicknoller Combe and may depend as much upon rainfall intensity as antecedent conditions. Figure 7 shows that hysteresis loops for suspended sediment concentrations are clockwise (C2 events), as expected, with the highest concentrations on the rising limb. $HI_{mid}$ indices confirm the variable nature of hysteresis loops during the post-drought period: 0.33 for the 30th August event but 0.79 for the 28th September event. Note that the delayed throughflow event in the 14th October event included a clockwise hysteresis loop for both the quickflow ($HI_{mid}$ = 0.79) and delayed throughflow ($HI_{mid}$ = 0.88) peaks. During the delayed peak, sediment sources could only be from erosion of the stream channel or variable source areas contiguous to the stream channel. There was no rainfall at this time so there could have been no sediment contribution from infiltration-excess overland flow generated on the footpath or elsewhere.

Note that further analysis of suspended sediment hysteresis in the Bicknoller Combe catchment during this period is provided in Stott and Burt (1997), including consideration of the complex relationship between potassium and suspended sediment concentrations.

**Discussion**

By the end of the 1975-76 drought, stream discharge had fallen to a very low level (minimum recorded: 0.03 l $s^{-1}$, 27th August) and the solute concentration of stream water had risen above 140 $\mu S\ cm^{-1}$, presumably as a result of a combination of evaporation and long residence time of subsurface water. As Figure 2 shows, concentrations fell steadily over the next three months, with specific conductance levelling off in the range 110-120 $\mu S\ cm^{-1}$ for baseflow conditions. Hydrologically, runoff production seems to have returned to a "normal" state rather more quickly than solute transport: delayed throughflow hydrographs, an indication of subsurface stormflow (Anderson and Burt, 1978a, 1978b), were evident from the start of October. This is testament to the very wet post-drought conditions (154 mm in September compared to an average of 80 mm). Stream water concentrations are slower to respond because of the time taken to flush long residence-time subsurface water from the system.

The 30th August storm was remarkable for its very high solute concentrations. These would have related in part to evaporation during the drought, producing soluble residues at the soil surface. There would also have been small but sustained inputs of dry deposition (particulate fallout from the atmosphere). These readily available supplies of soluble material seem to have been exhausted during the first two storm events, likewise the readily available supplies of suspended sediment. Stott and Burt (1997) note that drying of the soil surface over many months may have increased the exchangeable potassium on the surface of clay minerals, rendering potassium more available for desorption; the same process may be relevant to other base cations. Mineralisation of soil organic nitrogen increases with increasing soil moisture content. Campbell and Biederbeck (1982) observed that small showers at the end of a dry summer caused a disproportionately large flush in microbial growth and nitrogen mineralisation, perhaps because it had been extremely dry before it rained. The substrate responsible for the stimulation of this activity comes from two sources: an accumulation of dead microbial cells during the dry period; and soil organic matter newly exposed to microbial attack as a result of physical disruption of aggregates due to shrinking and swelling of the soil (Haynes, 1986). Solutes may be released at the end of a drought by a variety of processes therefore and these supplies are immediately available to surface and near-surface hydrological pathways. Whilst the evidence from Bicknoller Combe is that solute concentrations in these pathways soon return to more “normal” concentrations, it is clear that for some elements, nitrogen especially, continued soil mineralisation in the post-drought period can introduce sufficient soluble material into subsurface pathways so as to sustain much higher than normal concentrations throughout the next winter. It is not known whether there were ramifications further downstream in the study catchment but it seems likely that there would have been very poor water quality in larger rivers as a result of this first, large, post-drought runoff event, at least for a short time. As noted above, in other catchments, the effect of the drought lasted much longer, with elevated nitrate concentrations sustained throughout the following winter (Burt and Worrall, 2009), often above legal limits. Even more protracted responses for dissolved organic carbon losses from peatland after severe droughts were observed after 1976 (Worrall et al 2003, 2006); again the impact of microbial activity under fluctuating conditions is emphasised (Fenner and Freeman, 2011).

Notwithstanding the impact of an extreme drought, it is remarkable how invariant stream water concentrations were at Bicknoller Combe (Figure 6). Since concentrations vary so little with discharge, this catchment exhibits nearly chemostatic behaviour, implying that solute concentrations in stream water are not determined by simple dilution of a fixed solute flux by a variable flux of water and that rates of solute production and/or mobilisation must be nearly proportional to water flux both at storm and seasonal timescales (Godsey et al., 2009). The pH response indicates a well-buffered system, with sources of calcium sufficient in amount and availability, even during intense quickflow events, to prevent acidification episodes at times when inputs of “new” precipitation water might be expected to dominate the runoff response (Cirmo and McDonnell, 1997). On the contrary, various lines of evidence suggest a significant contribution from “old” water, including end-member mixing models (Anderson and Burt, 1982) and analysis of potassium concentrations (Stott and Burt, 1997). In some respects therefore, even for solutes, the catchment seems to recover remarkably quickly from a severe drought, with sufficient mobilisation of solutes in subsurface runoff to counter the impact of contributions from “new”, low residence-time water.

Small, saturated wedges persisted at the base of hillslope hollows throughout the drought (Anderson and Burt, 1980); these seem to have acted as hot spots (McClain et al., 2003) for solute production as the soils became wetter and the water table rose after the end of the drought. Being well connected to the stream, subsurface flow and its solute load would be rapidly conveyed to the channel. Burt (2005) points out that, paradoxically, the riparian zone can act as both a conduit and a barrier. In this case the riparian zone appeared to act as a conduit (Burt et al., 2010a) and there is no evidence of any buffering effect to restrict solute delivery to the stream. No doubt a variety of processes contributed to the mobilisation of solutes in the post-drought period as discussed above; mineralisation of organic matter in warm, moist soils would be particularly effective. It may also be that water tables rising into soils that have been unsaturated for a long period of time would allow interaction between immobile and mobile water, releasing solutes into subsurface flow (Anderson and Burt, 1982). On the steep slopes at Bicknoller, there is probably little opportunity for buffer-zone processes such as denitrification to operate; the soils are too well –drained and oxygenated for that to happen.

Bishop et al. (2004) argue that a particularly important function of the riparian zone is to set the stream water chemistry, since this is the last soil in contact with the water before it becomes runoff. The extent to which this happens depends upon the residence time of water within the riparian zone which, in turn, depends on the dominant flow paths operating in the area (Burt et al., 2010b). Whilst solute inputs are usually described as “non-point” or “diffuse”, they are often much more focused than generally realised. At Bicknoller, during the drought and immediately afterwards, the hillslope hollows were hot-spots of solute export and it is clear that the first few storm events provided hot moments of solute export (McClain et al., 2003). As the catchment wetted up, so the subsurface contributing areas expanded, but the hollows remained the main focus of runoff generation and solute export (Anderson and Burt, 1978a, b). In a flatter catchment, there would have been more opportunity for buffering processes to operate and so protect the in-stream environment from the initial post-drought solute loading. On the other hand, in an aquifer-dominated catchment, mineralisation would be followed by leaching to groundwater resulting in a much more complex interaction between subsurface solute sources and riparian zones (Howden et al., 2011).

The data presented in this study amply demonstrate the value of high-frequency monitoring of water quality (Kirchner et al., 2004). By their very definition, rare events occur infrequently so the best chance of observing them involves continuous monitoring (Burt, 1994). In this case, the anticipated end of a severe drought required a sustained campaign of fieldwork, keeping pump water samplers running until the first large storm arrived. Today, a combination of field-deployable probes, data loggers and telemetry makes it much more likely that a unique, unprecedented and unrepeatable event like the 30th August storm event can be captured (Burt, 1994). Given that severe droughts seem likely to become more common in a warmer world, it will be increasingly important to monitor water quality response during and after such episodes, if their impact on water resources and in-stream ecology is to be better understood.

**Conclusions**

1. The UK drought of 1975-76 was one of the most extreme on record so it is no surprise that both the quantity and quality of stream flow were significantly affected, both during and immediately after the drought period.
2. The first storm events at the end of the drought produced some dramatic and very unusual responses with very high solutes concentrations; suspended sediment concentrations, although high, did not seem to be such an uncommon occurrence.
3. Catchment recovery was surprisingly quick, both in terms of storm-runoff generation and solute response. Stream dilution during periods of storm runoff was re-established within a few events and the generation of double-peaked hydrographs

(indicating significant throughflow contribution) within a few weeks of the end of the drought.

4. Rapid solute mobilisation from lower sections of the hillslope hollows explains the near-chemostatic behaviour of this drainage basin. Riparian zones functioned as a conduit and there was no indication of decoupling of hillslope and stream in this steep, upland catchment.

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**Figure captions**

Figure 1. Location of the Bicknoller Combe study catchment.

Figure 2. Stream discharge and specific conductance at Bicknoller Combe at the end of the 1975-76 drought.

Figure 3. Stream discharge and specific conductance at Bicknoller Combe for five storm events in the post-drought period. Note that the time scale is arbitrary; event dates are indicated in each case.

Figure 4. Stream discharge and solute concentrations during the 28th September event. (a) Discharge variations including estimates of new ($Q_n$) and old ($Q_o$) water. (b) Concentrations of major cations and pH.

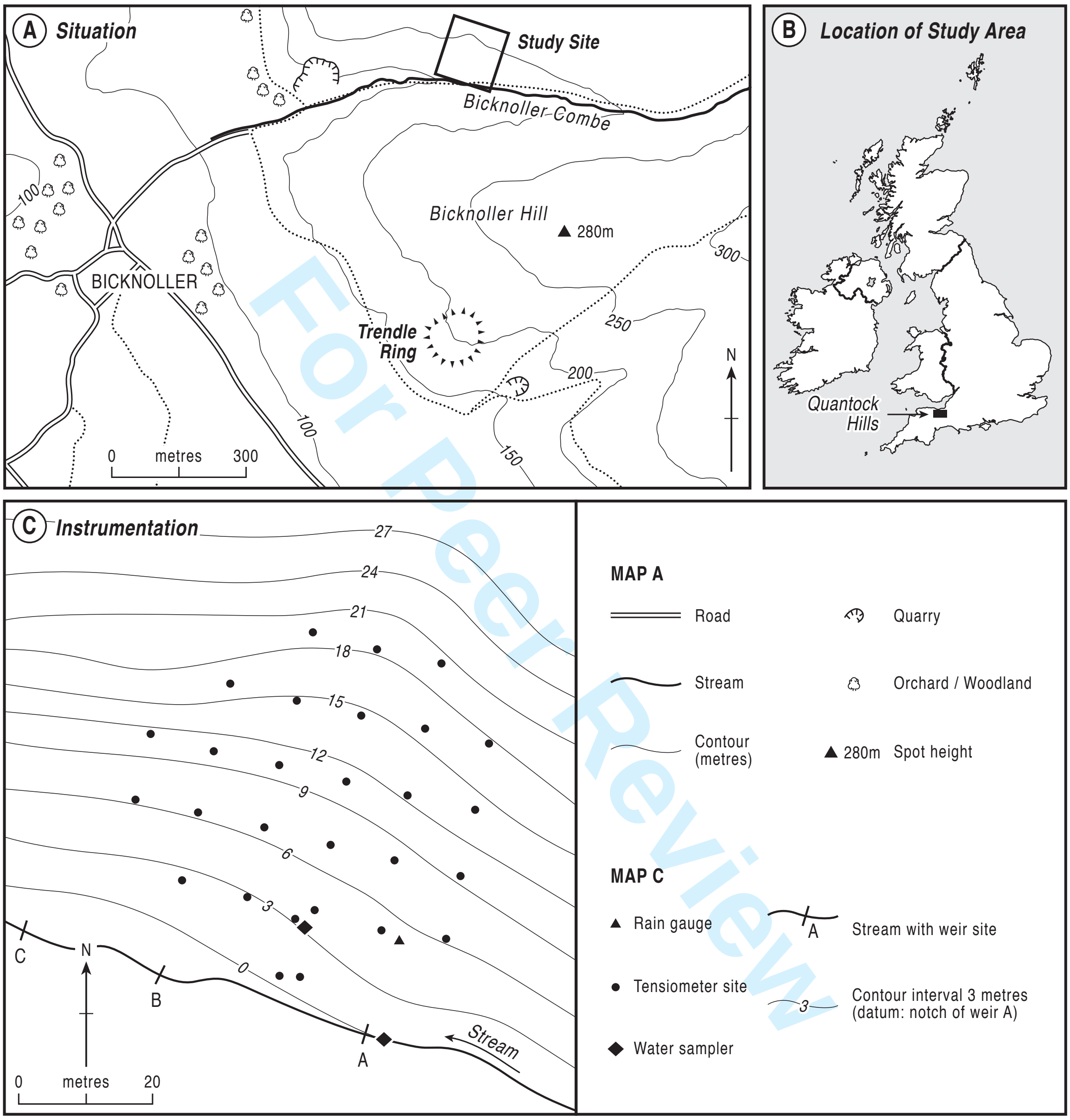
Figure 5. Hysteresis loops for discharge (Q) and specific conductance (SC) for the five storms shown in Figure 2.

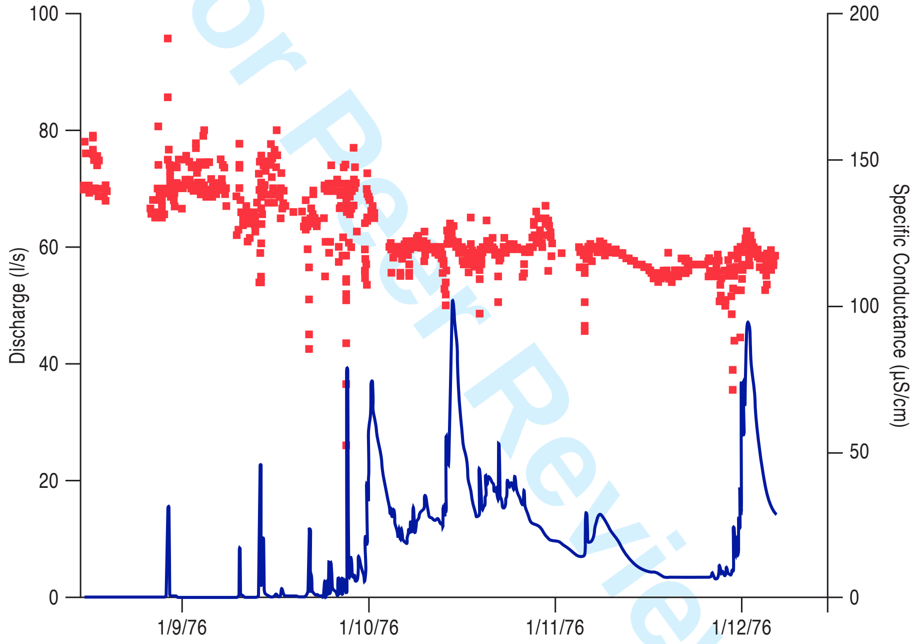
Figure 6. Plot of discharge against specific conductance for all sample values during the study period.

Figure 7. Hysteresis loops for discharge (Q) and suspended sediment concentration (SS) for three storm events.

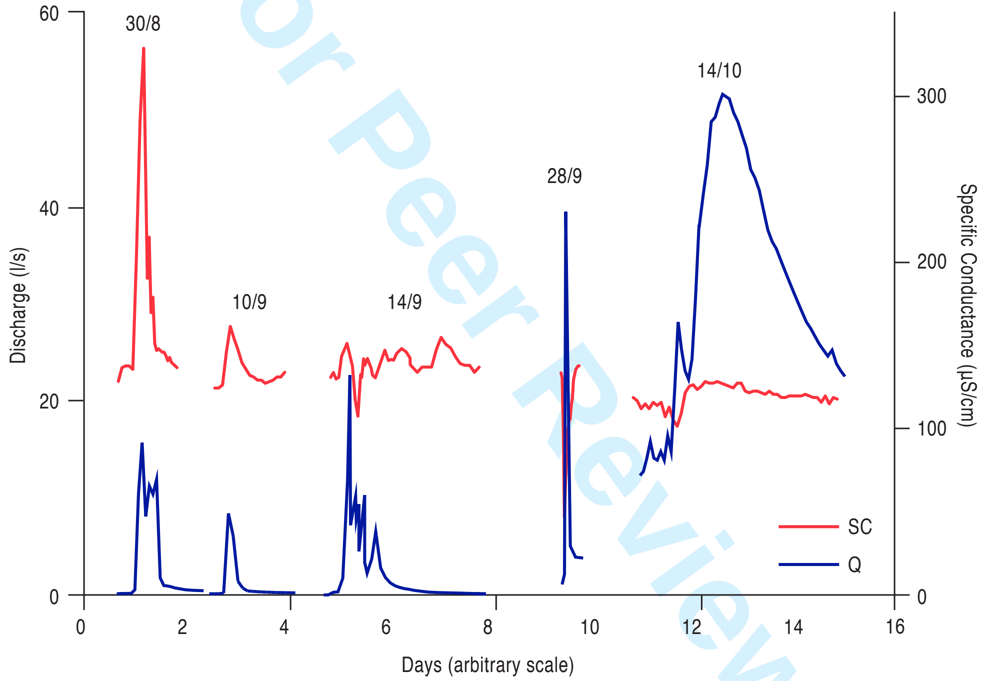
| | Q | SC | pH | Na | K | Mg | Ca |
|---|---|---|---|---|---|---|---|
| Q | 1 | | | | | | |
| SC | **-0.33** | 1 | | | | | |
| pH | **-0.67** | **0.32** | 1 | | | | |
| Na | -0.13 | **0.48** | -0.02 | 1 | | | |
| K | **0.36** | **0.34** | **-0.52** | *0.23* | 1 | | |
| Mg | **-0.36** | **0.62** | *0.22* | **0.67** | **0.36** | 1 | |
| Ca | **-0.53** | **0.66** | **0.68** | 0.00 | -0.06 | **0.44** | 1 |

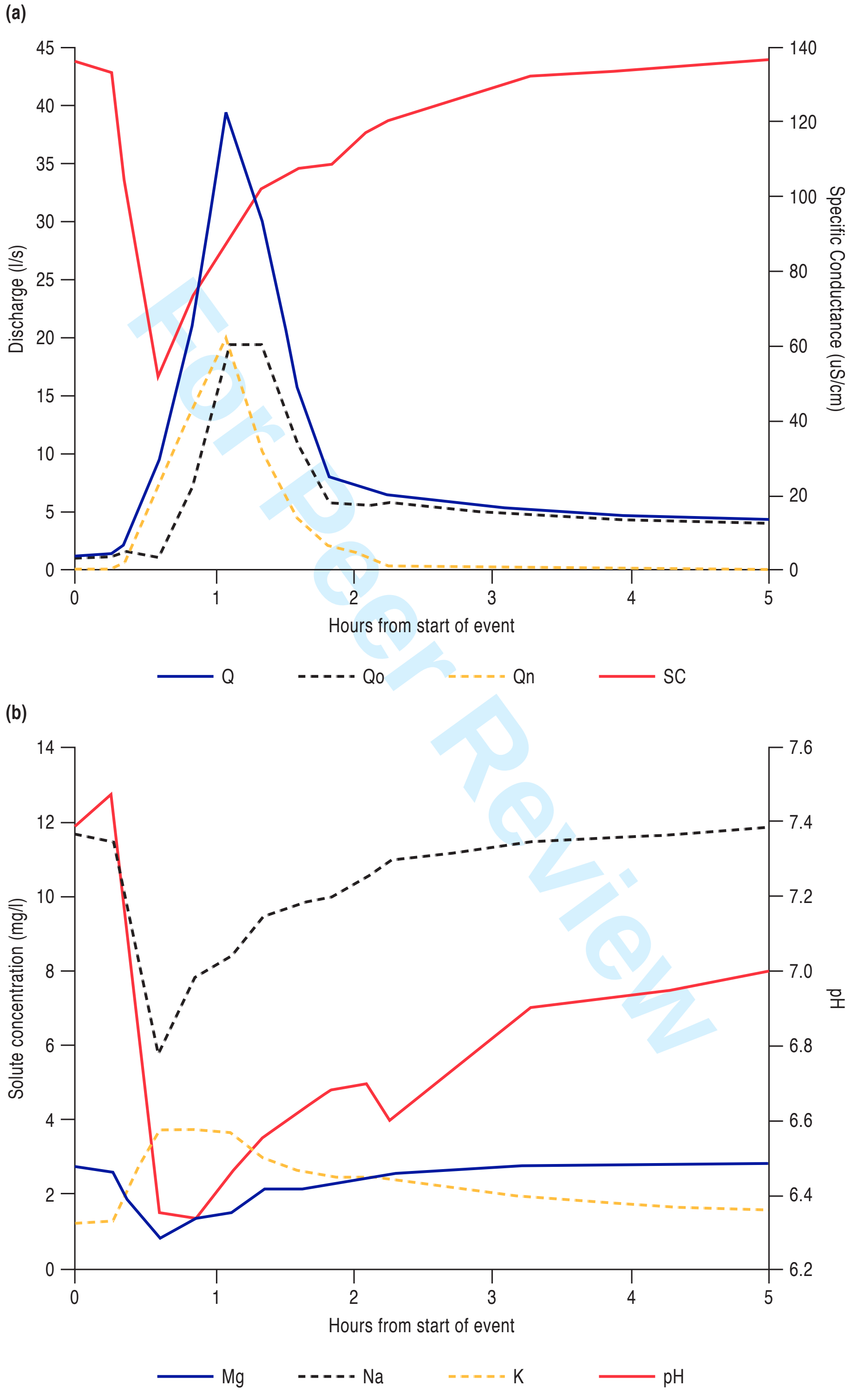
Table 1. Correlations between discharge and water quality determinands. Figures in bold indicate significance $p<0.001$; italics $p<0.01$; $n = 193$.

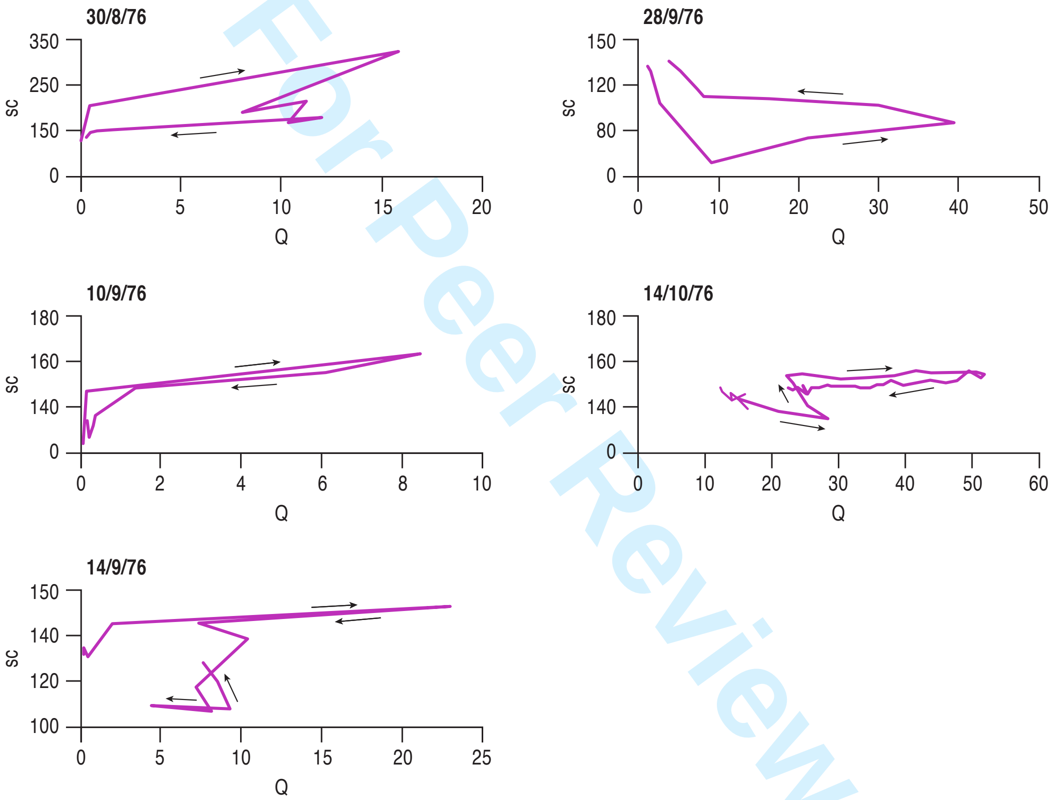

A Situation
Study Site
Bicknoller Combe
Bicknoller Hill
280m
Trendle Ring
BICKNOLLER
100
150
200
250
300
N
0 metres 300
B Location of Study Area
Quantock Hills
C Instrumentation
27
24
21
18
15
12
9
6
3
0
C
N
B
A
Stream
0 metres 20
MAP A
Road
Quarry
Stream
Orchard / Woodland
Contour (metres)
280m Spot height
MAP C
Rain gauge
A
Stream with weir site
Tensiometer site
3
Contour interval 3 metres (datum: notch of weir A)
Water sampler

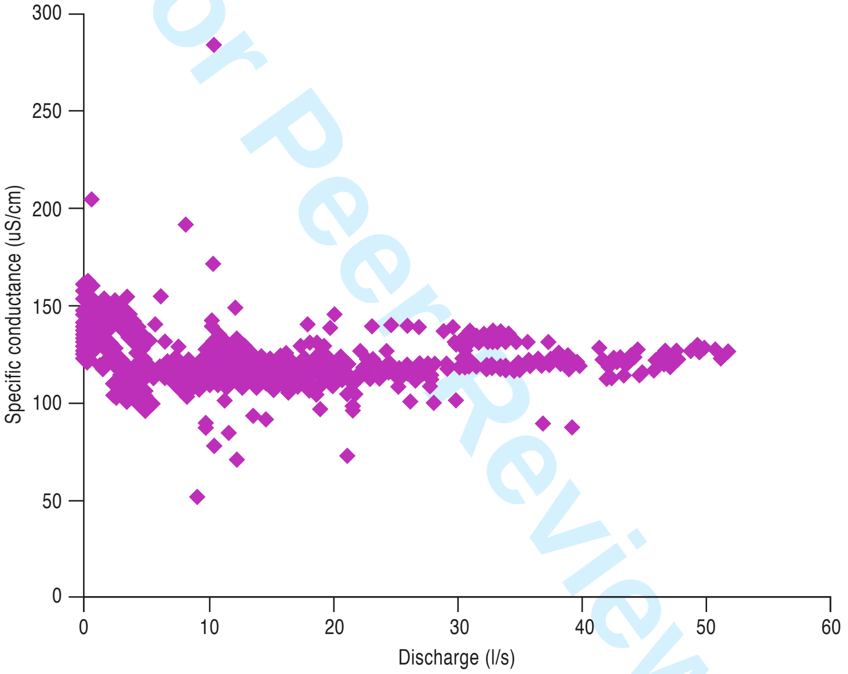


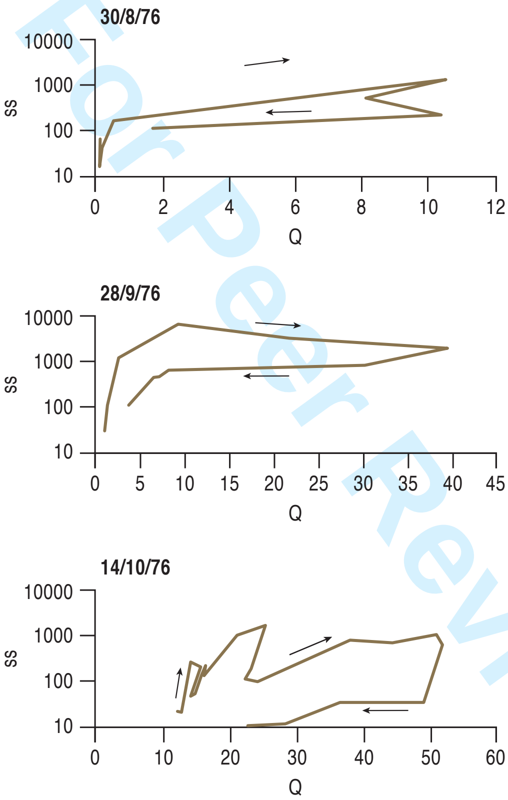
100
80
60
40
20
0
Discharge (l/s)
200
150
100
50
0
Specific Conductance (µS/cm)
1/9/76
1/10/76
1/11/76
1/12/76


30/8
10/9
14/9
28/9
14/10
Discharge (l/s)
Specific Conductance (µS/cm)
Days (arbitrary scale)
SC
Q
0
20
40
60
0
100
200
300
0
2
4
6
8
10
12
14
16


(a)
Discharge (l/s)
Specific Conductance (uS/cm)
Hours from start of event
Q
Qo
Qn
SC
(b)
Solute concentration (mg/l)
pH
Hours from start of event
Mg
Na
K
pH


30/8/76
350
250
150
0
sc
0
5
10
15
20
Q
28/9/76
150
120
80
0
sc
0
10
20
30
40
50
Q
10/9/76
180
160
140
0
sc
0
2
4
6
8
10
Q
14/10/76
180
160
140
0
sc
0
10
20
30
40
50
60
Q
14/9/76
150
140
120
100
sc
0
5
10
15
20
25
Q


300
250
200
150
100
50
0
Specific conductance (uS/cm)
0
10
20
30
40
50
60
Discharge (l/s)


30/8/76
ss
10000
1000
100
10
0
2
4
6
8
10
12
Q
28/9/76
ss
10000
1000
100
10
0
5
10
15
20
25
30
35
40
45
Q
14/10/76
ss
10000
1000
100
10
0
10
20
30
40
50
60
Q