promoting access to White Rose research papers

Universities of Leeds, Sheffield and York
http://eprints.whiterose.ac.uk/

This is an author produced version of a paper published in **Hydrological Processes**

White Rose Research Online URL for this paper:

http://eprints.whiterose.ac.uk/id/eprint/77451

Paper:
Grayson, R and Holden, J (2011) *Continuous measurement of spectrophotometric absorbance in peatland streamwater in northern England: implications for understanding fluvial carbon fluxes.* Hydrological Processes, 26 (1). 27 - 39 (13). ISSN 0885-6087

http://dx.doi.org/10.1002/hyp.8106

White Rose Research Online
eprints@whiterose.ac.uk

Continuous measurement of spectrophotometric absorbance in peatland streamwater: implications for understanding fluvial carbon fluxes

Richard Grayson* and Joseph Holden

School of Geography, University of Leeds, Leeds, LS2 9JT, UK

r.grayson@leeds.ac.uk
Phone: +44(0)113 3433373
Fax: +44(0)113 3433308

j.holden@leeds.ac.uk
Phone: +44(0)113 3433317
Fax: +44(0)113 3433308

* corresponding author

Abstract

Bog systems tend to have a flashy hydrological regime with low baseflows and rapid and high storm peaks. Water derived from peatlands often contains significant amounts of organic humic and fulvic materials which largely form the dissolved organic carbon fraction of the fluvial carbon flux. However, most estimates of dissolved organic flux from peatlands are based on sampling that is infrequent and which may miss the periods of high flux during storm events. In order to better characterise the behaviour and fluxes of fluvial carbon it is necessary to operate more frequent sampling. This paper presents data from a continuously operating field based spectrophotometer simultaneously measuring absorbance across 200 to 730 nm at 2.5 nm intervals in runoff from an upland peatland stream. It is shown that absorbance at different wavelengths that have previously been used to characterise dissolved organic carbon varies rapidly during storm events. The probe is shown to even detect changes in absorbance characteristics in response to rainfall events before the stream discharge starts to rise. The high resolution behaviour of absorbance characteristics during storm events is different depending on the wavelength studied. Thus the choice of wavelength used as a proxy for dissolved organic carbon needs careful attention and it may be that automated spectrophotometric methods which provide rich time series data from across the spectrum can tell us more about fluxes, processes and sources of aquatic carbon in peatland systems in the future than traditional practices have hitherto allowed.

Keywords

DOC; water colour; UV-Vis spectrometry; peat

1. Introduction

Peatlands are important carbon stores, but as well as sequestering carbon they also release it either directly to the atmosphere or via aquatic pathways. While there have been few studies from the same site that compare the role of water borne losses of carbon to gaseous losses of carbon from peatlands, the studies that have been undertaken suggest that aquatic losses are important, perhaps accounting for a loss of 40 to 50 % of the carbon that is taken up via net ecosystem exchange each year (Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). Of the aquatic components, dissolved organic carbon (DOC) is usually the largest component, at least in catchments that are not severely degraded. Significant increases in DOC concentrations in runoff from upland peat catchments have been observed over the past few decades (Evans et al., 2006; Evans et al., 2005; Worrall and Burt, 2007; Worrall et al., 2004; Worrall et al., 2003). Numerous mechanisms have been suggested to account for these increases (Evans et al., 2005; Worrall et al., 2007b) including land management change, decreases in sulphate deposition and temperature change. The presence of DOC also results in water becoming coloured, posing a significant problem where it is used in the supply of drinking water as customers are opposed to such aesthetic problems. Furthermore, trihalomethanes are produced as a chlorination by-product when there are high concentrations of DOC and these are strictly regulated and are a costly problem (Chow *et al.*, 2003).

Estimates of DOC fluxes tend to be based on grab samples collected from streams at routine, but often widely-spaced, intervals (e.g. weekly or twice monthly). The problem is that it is highly likely that much of the DOC flux occurs during short-duration high flow events which are rarely captured by routine monitoring studies (Clark et al., 2007). Blanket peat streams have a very flashy nature with fast responding discharge events characterised by a narrow hydrograph with high peak flow and low baseflow (Holden and Burt, 2003; Price, 1992). Most of the flux of water occurs in a short period of time during high flow. It is, therefore, likely that most of the fluvial carbon flux also occurs during storm events which are not captured by most routine DOC monitoring studies. Thus there is a bias in most peatland DOC flux sampling towards baseflow which may lead to significant errors in calculating the total flux of DOC. Clark et al. (2007), for example, sampled DOC in Cottage Hill Sike, Moor House, UK, using a four-hour sampling interval for a selection of storm events over a 45 day period with an automatic pump sampler. They found that 50 % of the DOC flux occurred within 10 % of the time during high flows. This was similar to Hinton et al (1997) who found that 41-57 % of DOC was produced during the top 10 % of flows in Canadian wetlands. It is, therefore, important to improve the frequency of sampling of fluvial carbon loss from peatlands.

Aquatic DOC is comprised of various fractions which demonstrate strong absorbance across the UV-Vis range (Chen et al., 2002). Humic and fulvic acids make the largest contribution to DOC in stream waters (c. 75 - 80 %) (Thurman, 1985). While absolute DOC concentrations can be measured directly in the laboratory, such an approach does not lend itself to high resolution monitoring due to the time and costs involved. Instead UV-Vis spectrometry has been used as a proxy for aqueous DOC concentrations by both scientists and the water industry (Chow et al., 2008; Spencer et al., 2007; Watts et al., 2001; Worrall et al., 2007a; Worrall et al., 2003). Absorbance at both 400 and 465 nm

have been routinely used by the water industry as proxies for DOC and water colour (Hautala et al., 2000; Spencer et al., 2007). Although the water industry has also used absorbance at 254 nm as a surrogate for DOC for over 30 years (Chow et al., 2008; Spencer et al., 2007) absorbance at 465 nm is thought to be more powerful at discriminating different humic matter solutions than wavelengths around 250 nm (Hautala et al., 2000). Most scientific studies involve absolute measurements of DOC (using TOC analysers) to establish the relationship between absorbance and DOC. Several studies reporting increased DOC losses from UK upland peat catchments have used absorbance at 400 nm as a proxy for DOC (Watts et al., 2001; Worrall et al., 2007b; Worrall et al., 2003). The UK Environmental Change Network (ECN) use absorbance at 436 nm as a proxy for DOC, with absorbance at both 436 and 400 nm exhibiting a strong linear relationship with DOC (Worrall et al., 2003). Other wavelengths used to estimate humic substances include 272, 285 340, 360, 365, 410, 465 and 470 nm (Hautala et al., 2000; Kalbitz et al., 1999; Spencer et al., 2007; Tipping et al., 1988; Tipping et al., 1999). The SUVA254 (specific absorbance in UV light) approach normalises absorbance at 254 nm against absolute DOC concentration to give absorbance per mass unit DOC (α m^{-1}/DOC mg l^{-1}) (Weishaar et al., 2003). At the lower end of the UV-Vis range any non-organic matter and inorganic substances present can result in interference (Tipping et al., 1988).

Ratios between absorbance at different wavelengths provide valuable information regarding the aqueous DOC/DOM composition and/or the sources of this DOC/DOM. The two dominant components of DOC, humic and fulvic acids, absorb light by different amounts at different wavelengths as their characteristics differ; humic acids are more mature than fulvic acids. As a result the ratio of absorbance at 465 nm and 665 nm (465/665 or E_4/E_6 ratio) can be used to measure the proportion of humic and fulvic acids and hence the degree of humification or aromaticity (Hautala et al., 2000; Spencer et al., 2007; Thurman, 1985). Mature humic acids from soil typically have an E_4/E_6 ratio of 2 to 5 indicating increased humification, whereas less mature fulvic acids have a ratio of 8 to 10 (Thurman, 1985). In streams and rivers, fulvic acids have been found to have an E_4/E_6 ratio of 5.5 to 17 (Thurman, 1985). Wallage et al. (2006) observed high ratios in upper layers of peat indicating a high level of microbial activity and immature fulvic acids, and lower values in the deeper layers where humic acids dominated. Other humification indices include ratios of absorbance at: 400/360 nm (Kalbitz et al., 1999); 470/360 nm (Kalbitz et al., 1999); 265/465 nm (Chen et al., 2002); 254/365 nm (Baker et al., 2008); and 254/410 nm (Baker et al., 2008; Spencer et al., 2007).

Within the water industry 'online' UV-Vis spectrometry is a common practice for measuring water colour, although typically only one wavelength is measured. Several 'off the shelf' UV-Vis spectrometers are now available to continually monitor or measure part of, or the entire spectra of samples *in situ*: e.g. s::can spectro::lyser, carbo::lyser, nitro::lyser, color::lyser and multi::lyser™ and, WTW CarboVis and NiCaVis®. Such devices offer a range of benefits over traditional approaches to measuring discolouration in natural systems. First, they have the ability to make measurements with short sampling intervals if required (e.g. seconds). Second, several offer the ability to measure

absorbance across an entire spectrum (e.g. at 2.5 nm intervals), thus enabling valuable information on the different fractions of DOC present to be gathered.

The aim of this paper is to use field-based spectrophotometers to continually measure absorbance across a wide range of wavelengths in runoff from an upland peat catchment to examine the high-resolution behaviour of DOC and its components through time. We seek to test whether absorbance at different wavelengths that have previously been used to characterise DOC varies rapidly during storm events and whether absorbance ratios can be used to characterise how the composition of DOC also varies during storm events.

2. Study Site

Cottage Hill Sike (54°41'N, 2°23'W), located within the Moor House National Nature Reserve in Cumbria, northern England, has a catchment area of c. 13.5 ha and an altitudinal range of 545 m to 580 m. Cottage Hill Sike is a tributary of Trout Beck which later flows into the River Tees, 750 m downstream of the Cottage Hill Sike confluence. Lower Carboniferous sequences of interbedded limestone, sandstone and shale provide a base for glacial boulder clay at the site (Johnson and Dunham, 1963). This clay impedes drainage allowing blanket peat to develop, 98 % of the catchment is covered in blanket peat (Adamson et al., 1998; Miller et al., 2001) which is typically 3 to 4 m thick, although in places it is around 8 m thick. Slope angles within the catchment vary between 0 and 15^{o}, with the majority of the catchment (>80%) being between 0 and 5^{o}. Catchment aspect is dominated by east to southeast facing slopes.

The catchment contains an Environmental Change Network (ECN) target monitoring site where vegetation, water table, soil water chemistry, meteorology and other parameters have been monitored under strict protocols since 1992 (Sykes and Lane, 1996). Vegetation cover is most commonly *Calluna vulgaris*, *Eriophorum vaginatum* with some *Empertrum nigrum* and *Sphagnum capillifolium*. The climate is classified as sub-arctic oceanic (Manley, 1936; Manley, 1942). Holden and Rose (2010) have produced a corrected and homogenised temperature record for the site dating back to 1931. The mean annual temperature at the site between 1931 and 2006 was 5.3^{o}C compared to 5.8^{o}C since 1991 (5.1^{o}C from 1961-1990). Mean annual precipitation is 2012 mm (records from 1951-1980 and 1991-2006). Precipitation is only slightly seasonal with 57 % occurring in the winter-half year from October to March.

The mean annual DOC flux for the catchment has been estimated at 218 kg ha^{-1} yr^{-1} (1993-2002) (Clark et al., 2005). The site is being used as the key field site in a UK Natural Environment Research Council funded project exploring the role of natural pipes in carbon export from peatlands (Holden et al., 2009). The site is also one of the national "Carbon Catchments" where measurements of all the major carbon flux terms are being used to calculate the annual peatland C balance. Cottage Hill Sike flows into Trout Beck for which there is a weekly DOC sample since 1992.

3. Methods

Due to the nature of UK upland peat catchments not all UV-Vis spectrometers are suitable for measuring absorbance *in situ* within streams. Although a number of robust

spectrometers have been designed for operation within controlled environments, such as within water treatment works, they have rarely been deployed in natural streams. The deployment of such devices in upland streams poses a number of problems. For example, power supply options are often limited to batteries and/or solar panels, sites are often remote making routine visits and maintenance difficult, flows can vary widely, organic debris can hamper sensors and the build up of organic deposits on the optical components over time can interfere with measurements. High rainfall totals and varying temperature ranges also dictate that any equipment must be weatherproof and be capable of operating at low temperatures. Basic requirements for an *in situ* field spectrometer for use in a typical UK upland site are, therefore, that it must be robust enough to handle varying flow conditions, be weatherproof and be able to run off a low voltage power supply.

Scan Messtechnik GmbH (Austria) have developed a range of UV-Vis spectrometers for monitoring water. The s::can spectro::lyser™ was the first of these and is a submersible multiparameter probe which uses a xenon flash lamp to measure absorbance across the total UV-Vis range (200-730 nm). In surface waters the maximum upper range of the instrument is 300 Abs m^{-1} at 254 nm. In June 2009 a s::can spectro::lyser™ with a linked s::can con::nect controller was installed in the main channel of Cottage Hill Sike just above the gauging station. The spectrometer was installed perpendicular to flow across the channel with the measuring window in line with flow. Nylon netting was placed directly upstream of the spectrometer to prevent material collecting on the spectrometer. To ensure the optics remain clean, the s::can system uses an optional compressed air supply to clean the lens windows at set time intervals. Due to the remote location of Cottage Hill Sike a nitrogen cylinder was used (BOC, UK). The whole system was powered using an external 40 Ah 12v lead acid battery. Initially measurements were made every 15 minutes, during each measurement the mean of 3 individual measurements is stored; this interval was later extended to 20 minutes. Data was downloaded, batteries were changed and lens windows were manually cleaned every fortnight. Although the spectrometer is capable of measuring DOC in mg l^{-1} based on a global calibration, the relationship between absorbance at specific wavelengths and DOC have been found to vary between sites and many different wavelengths have been analysed (Wallage and Holden, In Review). Therefore, the full spectrum 'fingerprint' data were collected and we have not attempted to calculate DOC flux using the global calibration as we believe it be erroneous.Wavelengths analysed in this paper were chosen based on the available literature (Table 1). This allowed for comparisons of absorbance at these different wavelengths to examine their response to discharge, particularly during storm events. In addition the E_4/E_6 ratio was included as this has been extensively used to characterize the composition of DOC. Discharge was measured at 10 minute intervals on Cottage Hill Sike as part of a separate research project. Rainfall was recorded in a tipping-bucket rain gauge which recorded the timing of each 0.2 mm of rain.

4. Results

A complete discharge and rainfall record from Cottage Hill Sike is available (e.g. Fig 1). The largest discharge recorded was 0.1689 $m^3 s^{-1}$ on 31/8/2009. High rainfall totals were observed in a number of months, noticeably July and November, with the highest recorded hourly rainfall intensity of 15.6 mm hr^{-1} being measured on 1/11/2009.

Between July and December 2009 a near continual record of the complete UV-Vis range (200 – 730 nm) was collected at Cottage Hill Sike using the scan spectro::lyser. Only one significant break in the record occurred between 4-17th November 2009 due to a landslide which blocked the access road to Moor House and therefore prevented battery replacement. Sampling was discontinued in December 2009 due to severe snow and ice cover which continued through into late March 2010. Tabulated absorbance data at 2.5 nm intervals between 220 and 730 nm was available for each measurement.

Of those wavelengths previously used to characterise DOC concentrations, those below 300 nm exhibit high background values and noisy signals (Fig 2), with little differentiation between wavelengths and rapid fluctuations in absorbance over short periods of time thus limiting their ability to discriminate variations in DOC concentrations. However, at wavelengths above 300 nm (Fig 2) the signal is noticeably clearer suggesting that they have greater ability to discriminate changes in DOC. The long-term stability of the probe was demonstrated by the fact that after 10 months of near-continuous deployment and measurement the background absorbance at 400 nm remained below 0.7 Abs m^{-1}.

Correlation analysis between wavelengths demonstrates that those found close to each other are highly correlated whereas where wavelengths are widely spaced along the spectra relationships are generally weaker (Table 2). This indicates that while wavelengths across the spectra have been used as proxies for DOC they do not all exhibit similar characteristics over time, exhibiting differing responses. No strong statistical relationships were observed between temporal changes in discharge and any of the wavelengths or ratios when comparing the full data sets (all r values <0.38).

As DOC export is typically temporally restricted, with the bulk occurring during storm events (Clark et al., 2007) 24 storm events were selected from the record (July - November 2009) to establish the impacts of storm discharge on absorbance (Table 2). Absorbance at 340 and 400 nm during each of these storm events is shown in Fig 3. These two wavelengths were chosen as they have been extensively used as proxies for DOC (Table 1) and although wavelengths below 300 nm have also been widely used they were not included for reasons given above. Although the temporal response of absorbance differs between storms, many exhibit similar characteristics with absorbance decreasing on the rising limb of the hydrograph and then increasing again as discharge falls to almost baseflow.

Clear decreases in absorbance at 340 and 400 nm coincide with increases in discharge during a large number of the storm events, with decreases in absorbance being witnessed on the rising limb of the hydrograph during storms 1, 2, 5, 7-14, 17-20, and 22-24. In storms with double peaks (5, 10, 12, 18, 19, 22 and 24) further decreases in absorbance were also observed which coincided with the second peak in discharge (Fig 3). During other storms (15 + 16) absorbance increased close to peak discharge while during others no clear pattern was observable. This indicates that during the majority of events DOC concentrations decrease noticeably during the rising limb of the hydrograph and continue

to remain low throughout much of the storm hydrograph before increasing again as flow returns to baseflow. Therefore, during storm events DOC concentrations per unit discharge are likely to be lower than those observed during regular baseflow. The observed decreases in absorbance during the rising limb of a number of storm hydrographs agrees with the response of absorbance at 400 nm in Trout Beck to the two most significant storm events captured by Worrall et al. (2003).

One of the main advantages of using a system that measures absorbance across the entire UV-Vis spectra is the ability to monitor the behaviour across several wavelengths and also to analyse the ratios of absorbance behaviour between wavelengths to provide an insight into the composition of DOC. The response of the E_4/E_6 ratio to storm events is complex (Fig 4). However, a clear seasonal trend was observed in the E_4/E_6 ratio with storms during the summer months of July and August having low ratios (<5) demonstrating the dominance of more mature humic acids (Table 3). In contrast, of those storms observed after 8th September 2009 only one had an E_4/E_6 ratio less than 5 indicating that during the majority of storms less mature fulvic acids dominated. This suggests that summer storm events may have the ability to wash out more mature humic acids that have built up during drier months as a result of microbial breakdown. However, later in the year the store of these humic acids may become depleted with less mature fulvic acids instead dominating the DOC load. During some storms (storms 3, 6, 9, 10 and 12) the initial response was a sharp increase in the E_4/E_6 ratio, suggesting an initial flux of less mature fulvic acids or surface runoff with low absorbance. In general both the 400/360 and 470/360 ratios exhibited contrasting responses to the E_4/E_6 ratio indicating that they can also be used as humification indices.

To try and understand the general response of absorbance at various wavelengths during storm events mean absorbance was calculated for the first 30 hours of the 24 previously identified storm events (Fig 5); this demonstrates that the mean response of the different wavelengths vary over time. In general absorbance of the majority of wavelengths of interest remain relatively steady during the first 3 hours of storm events after which absorbance decreases rapidly, reaching their minimum around 11 to 12 hours in to the storm, after this absorbance again increases. The response of the E_4/E_6 ratio shows some interesting characteristics (Fig 5), initially this ratio decreases during the first 6 hours before increasing to reach a maximum around 11 to 12 hours into the storm event which coincides with lowest absorbance. In both instances a further increase in average discharge at 12 hours results in a decrease in the E_4/E_6 ratio and an increase in absorbance at most wavelengths. Again both the 400/360 and 470/360 ratios exhibit a contrasting response to the E_4/E_6 ratio. Although both mean absorbance at 340 and 400 nm show similar responses over time it is clear that the magnitude of these changes differs between the two wavelengths (Fig 5) demonstrating that even for two wavelengths widely used to characterise DOC the temporal response varies.

5. Discussion

The observed rapid changes in absorbance demonstrate that DOC concentrations and composition are highly dynamic changing rapidly even over short timescales. This indicates that many sampling strategies using weekly or even daily sampling are likely to

miss significant and important changes in DOC export. In many cases the response to storm events was rapid and would more than likely be missed if weekly sampling was employed or indeed if 4 hourly sampling was employed during a few storm events. Since blanket peatlands have a flashy regime with rapid increases and decreases in discharge typically over a period of hours (Evans et al., 1999) it is therefore clear that the current DOC records from Trout Beck and Cottage Hill Sike are unlikely to properly characterise this highly dynamic and complex flux.

Despite the rapid fluctuations observed in absorbance at all wavelengths it is possible to determine some general trends in the response of absorbance during storm events. Clear links can be observed between changes in absorbance and both the rainfall and discharge records. All major peaks within the discharge record impacted absorbance across the range of wavelengths. Importantly it is evident that not all rainfall events result in significant increases in discharge within Cottage Hill Sike; however the majority of rainfall events do have an impact on absorbance. The average storm response calculated from all 24 selected storm events demonstrates that in general a decrease in absorbance is observed on the rising limb of the hydrograph (Fig 5), with further increases in discharge associated with second and third peaks in the hydrograph resulting in further decreases in absorbance. The average response of the E_4/E_6 ratio demonstrates a similar response, decreasing on the rising limb, and smaller decreases being associated with further peaks in discharge. Therefore while the response of absorbance differs per storm event and overall discharge and absorbance are poorly correlated there is a clear link between average absorbance and average discharge calculated from the 24 selected storm events. This lack of correlation between discharge and absorbance results from the fact that the response of absorbance varies over a storm event, typically increasing at the start of the event after which it either plateaus or increases.

The differences in the temporal response of absorbance at both 340 and 400 nm suggests that despite both having been widely used as proxies to characterise DOC it is perhaps too simplistic to use a single wavelength to characterise DOC. Further work is required to determine which wavelengths provide the best characterisation of DOC during continual measurements made *in situ* in peatland streams and this work is ongoing at the study site.

The global calibration used by the spectro::lyser can be used to calculate turbidity using absorbance at a range of wavelengths. However, the lack of any significant increases in absorbance during the selected storm events suggests that turbidity corrections of absorbance in upland peat catchments are not straightforward. This is particularly true for the Cottage Hill Sike catchment as the contribution from mineral soils to the suspended sediment load is very small or negligible due to the near complete dominance of blanket peat within the catchment. Local calibration is possible for this instrument and this is something that requires further investigation.

The general seasonal trend is for absorbance to decrease noticeably in late autumn and early winter. Indeed, absorbance across all wavelengths was highest between July and August and lowest in November (Fig 3), this reflects the increased availability of humic and fulvic acids during warmer summer months and the increased occurrence of storm

events from September onwards. Equally the response of many of the wavelengths and ratios to storm events varied over the period of monitoring indicating some seasonal variability. During the earlier storms observed prior to late August 2009 the impact of increased discharge is less evident; however, after this date the impacts are clearer with absorbance often decreasing during the rising limb of the hydrograph and then increasing again as discharge falls. This suggests that earlier in the year storms have a lesser impact on DOC concentrations, while towards the end of summer when microbial decomposition has taken place baseflow DOC concentrations are noticeably higher than those observed during storm events.

Within UK upland peats, humic and fulvic acids typically build up within near surface peat during drier and warmer summer months as the water table lowers allowing microbial break down of peat to occur. These humic and fulvic acids are then washed out of the peat during the first significant rainfall events after summer, a phenomena commonly referred to as the 'autumn flush' (Mitchell and McDonald, 1992). As autumn and winter rainfall continues the source of humic and fulvic acids becomes depleted. Therefore towards the later end of autumn and winter the fulvic and humic content of streams may be minimal. Extreme rainfall in mid July resulted in the occurrence of an early 'flush', with rapid increases in absorbance across a range of wavelengths resulting from high rainfall and subsequently high discharge being observed in July (Storm 3). High absorbance was also observed in mid October which may be indicative of a more 'normal' autumn flush. Indeed during Storm 17 (19/10/2009) high absorbance was observed on the rising limb of the hydrograph, with peak absorbance being almost double that seen in other storms observed in September and October. Although a link with discharge is not immediately clear, with absorbance increasing prior to any significant increase in discharge (Fig 6), this increase in absorbance does coincide with rainfall over the same time period and indicates that as rainfall increased, DOC was washed out of the peat. Initially rainfall was minimal and hence any increase in absorbance was minimal, however as rainfall became more intense so absorbance increased as DOC losses increased significantly (Fig 6). Absorbance remained high after the event indicating that even when discharge decreased DOC concentrations remained high as water with a high DOC content continued to drain from the peat.

During a number of storm events occurring after September 2009 (Storms 15, 16, 19, 20, 22 and 24) the E_4/E_6 ratio was observed to initially be above 5 indicating the dominance of fulvic acids. However, once discharge increased significantly the E_4/E_6 ratio fell below 5 suggesting that humic acids were being washed out. As discharge began to decrease on the falling limb the E_4/E_6 ratio was then observed to increase above 5 suggesting that again fulvic acids began to dominate. While an increase in the E_4/E_6 ratio later on in the year after the autumn flush might indicate an increase in the contribution of immature fulvic acids it is perhaps more realistic that this increase in the ratio resulted from an increase in surface and shallow subsurface flow with low DOC content as a result of high rainfall and saturated peat. Indeed, the concurrent decrease in absorbance for a range of wavelengths indicates that DOC concentrations decreased during this period as the source of humic and fulvic acids within the peat became depleted. Interestingly, examination of a series of three storms towards the end of August 2009 (Storms 7, 8 and 9) showed that

the E_4/E_6 ratio remained below 5 during the majority of the first event but was then often greater than 5 during the second two events. This suggests that the first event either washed out the majority of the available humic acids or the second two events are characteristic of storm events dominated by surface runoff where the peat was previously saturated by an earlier event. Sharp increases in the E_4/E_6 ratio were observed at the start of five storms occurring prior to the autumn flush. This suggests that where there is a ready supply of more mature humic acids after summer decomposition has taken place storms can result in an initial decrease in the concentration of humic acids, but that this increases as the storm continues. An alternative explanation for the observed increases in the E_4/E_6 ratio observed close to the start of several storm events is that the low DOC content of surface runoff results in a reduction in absorbance across all the spectra but particularly at the upper end where absorbance is generally lower, as a result the E_4/E_6 ratio increases significantly.

6. Conclusions and Future Research

Continual measurements of absorbance across the UV-Vis spectra made using the s::can spectro::lyser™ exhibited rapid temporal fluctuations indicating that DOC concentrations and composition are highly dynamic over time. During the majority of storm events the initial response of absorbance was a significant decrease in colour, as the length of the storm continues absorbance gradually returned to levels observed prior to the storm event. Absorbance generally declined through autumn and winter and both an early flush and a more typical 'autumn flush' were observed during 2009; with the earlier flush occurring as a result of intense summer rainfall. Humic acids dominated the DOC load prior to the 'autumn flush' whereas later in the year less mature fulvic acids dominated. Despite absorbance at 340 and 400 nm both being used to characterise DOC they exhibit differing responses to storm events

Although the spectrophotometer used in this study is capable of measuring DOC in mg l^{-1} based on a global calibration, the relationship between absorbance at specific wavelengths and DOC have been found to vary between sites and many different wavelengths have been used as a proxy for DOC. Therefore, we have not attempted to calculate DOC flux using the global calibration as we believe it to be problematic in peatland systems. Instead it is our long-term goal to establish information that will improve the ability of the probe to estimate DOC fluxes in peatland systems. For example, this requires work to use spectrophotometers to sample peat DOC sources and streamflows at the same time, DOC sampling to establish how well different wavelengths/ratios sampled by the spectrophotometer actually characterise the DOC produced by peat and examination of seasonal characteristics of DOC – absorbance relationships. In the long term it is hoped that this additional information combined with the high resolution data rich approach of the spectrophotometer will enable us to produce much more reliable estimates of DOC fluxes from peatland systems than those that are currently possible. At very least the high resolution data from across the spectrum should at least help us understand more about the sources of DOC within peatland systems and the dynamic response of the aquatic carbon system to changes in hydrological conditions.

Acknowledgements
This research was funded through a Philip Leverhulme Prize awarded to JH

References

Adamson JK, Scott WA, Rowland AP. 1998 The dynamics of dissolved nitrogen in a blanket peat dominated catchment. Environmental Pollution 99: 69-77.

Baker A, Bolton L, Newson M, Spencer RGM. 2008 Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment. Hydrological Processes 22: 2325-2336.

Chen J, Gu BH, LeBoeuf EJ, Pan HJ, Dai S. 2002 Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. Chemosphere 48: 59-68.

Chin, Y.P., Aiken, G. and Oloughlin, E., 1994. Molecular-weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science & Technology 28: 1853-1858.

Chow AT, Dahlgren RA, Zhang Q, Wong PK. 2008 Relationships between specific ultraviolet absorbance and trihalomethane precursors of different carbon sources. Journal of Water Supply Research and Technology-Aqua 57: 471-480.

Chow AT, Tanji KK, Gao S. 2003 Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. Water Research 37: 4475-4485.

Clark JM, Lane SN, Chapman PJ, Adamson JK. 2007 Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates. Journal of Hydrology 347: 438-447.

Dinsmore KJ, Billett MF, Skiba UM, Rees RM, Drewer J, Helfter C. 2010 Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment. Global Change Biology 16: 2750-2762.

Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS. 2006 Alternative explanations for rising dissolved organic carbon export from organic soils. Global Change Biology 12: 2044-2053.

Evans CD, Monteith DT, Cooper DM. 2005 Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environmental Pollution 137: 55-71.

Evans, M.G., Burt, T.P., Holden, J. and Adamson, J.K. 1999 Runoff generation and water table fluctuations in blanket peat: evidence from UK data spanning the dry summer of 1995. Journal of Hydrology 221: 141-160.

Hautala K, Peuravuori J, Pihlaja K. 2000 Measurement of aquatic humus content by spectroscopic analyses. Water Research 34: 246-258.

Her, N., Amy, G., Sohn, J. and Gunten, U. 2008 UV absorbance ratio index with size exclusion chromatography (URI-SEC) as an NOM property indicator. Journal of Water Supply Research and Technology-Aqua 57: 35-44.

Hinton MJ, Schiff SL, English MC. 1997 The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry 36: 67-88.

Holden J, Burt TP. 2003 Runoff production in blanket peat covered catchments. Water Resources Research 39.

Holden J, Rose R. 2010 Temperature and surface lapse rate change: a study of the UK's longest upland instrumental record. International Journal of Climatology 30 doi: 10.1002/joc.2136.

Hongve, D. and Akesson, G. 1996 Spectrophotometric determination of water colour in Hazen units. Water Research, 1996; 30: 2771-2775.
Johnson GAL, Dunham KC. 1963 The Geology of Moor House: A National Nature Reserve in north-east Westmorland. London: H.M.S.O.
Kalbitz, K., Geyer, S. and Geyer, W. 2000 A comparative characterization of dissolved organic matter by means of original aqueous samples and isolated humic substances. Chemosphere 40: 1305-1312.
Kalbitz K, Geyer W, Geyer S. 1999 Spectroscopic properties of dissolved humic substances - a reflection of land use history in a fen area. Biogeochemistry 47: 219-238.
Korshin, G., Chow, C.W.X., Fabris, R. and Drikas, M. 2009 Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. Water Research 43: 1541-1548.
Leenheer, J.A. and Croue, J.-P. 2003 Characterizing Aquatic Dissolved Organic Matter. Environmental Science & Technology 37: 18A-26A.
Manley G. 1936 The climate of the northern Pennines: the coldest part of England. Quarterly Journal of the Royal Meteorological Society 62: 103-115.
Manley G. 1942 Meteorological observations on Dun Fell, a mountain station in northern England. Quarterly Journal of the Royal Meteorological Society 68: 151-165.
McKnight, D.M., Harnish, R., Wershaw, R.L., Baron, J.S. and Schiff, S. 1997 Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National Park. Biogeochemistry36: 99-124.
Miller JD, Adamson JK, Hirst D. 2001 Trends in stream water quality in Environmental Change Network upland catchments: the first 5 years. The Science of the Total Environment 265: 27-38.
Mitchell G, McDonald AT. 1992 Discoloration of Water by Peat Following Induced Drought and Rainfall Simulation. Water Research 26: 321-326.
Nilsson M, Sagerfors J, Buffam I, Laudon H, Eriksson T, Grelle A, et al. 2008 Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. Global Change Biology 14: 2317-2332.
Price JS. 1992 Blanket Bog in Newfoundland .2. Hydrological Processes. Journal of Hydrology 135: 103-119.
Roulet NT, Lafleur PM, Richard PJH, Moore TR, Humphreys ER, Bubier J. 2007 Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. Global Change Biology 13: 397-411.
Spencer RGM, Bolton L, Baker A. 2007 Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations. Water Research 41: 2941-2950.
Sykes JM, Lane AMJ. 1996 The United Kingdom Environmental Change Network: protocols for standard measurements of terrestrial sites. London: Natural Environment Research Council.
Thurman EM. 1985 Organic geochemistry of natural water. Kluwer Academic Publishers, Dordrecht.

Tipping E, Hilton J, James B. 1988 Dissolved organic matter in Cumbrian lakes and streams. Freshwater Biology 19: 371-378.
Tipping E, Woof C, Rigg E, Harrison AF, Ineson P, Taylor K, et al. 1999 Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. Environment International 25: 83-95.
Wallage ZE, Holden J. Spatial and temporal variability in the relationship between water colour and dissolved organic carbon in blanket peat pore waters. Science of the Total Environment In Review.
Wallage, Z.E., Holden, J. and McDonald, A.T. 2006 Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. Science of the Total Environment 367: 811-821.
Watts CD, Naden PS, Machell J, Banks J. 2001 Long term variation in water colour from Yorkshire catchments. The Science of The Total Environment 278: 57-72.
Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K. 2003 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology 37: 4702-4708.
Worrall F, Armstrong A, Adamson JK. 2007a The effects of burning and sheep-grazing on water table depth and soil water quality in an upland peat. Journal of Hydrology 339: 1-14.
Worrall F, Burt TP. 2007 Trends in DOC concentration in Great Britain. Journal of Hydrology 346: 81-92.
Worrall F, Guilbert T, Besien T. 2007b The flux of carbon from rivers: the case for flux from England and Wales. Biogeochemistry 86: 63-75.
Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, et al. 2004 Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70: 369-402.
Worrall F, Reed MS, Warburton J, Burt T. 2003 Carbon budget for a British upland peat catchment. Science of the Total Environment 312: 133-146.

Table 1. Wavelengths used in the analysis of DOC/DOM in natural waters. The majority of wavelengths are used as proxies whereas both 660 nm and 665 nm have been used along with 460nm and 465 nm to characterise the composition of DOC.

Wavelength, nm	Reference
203	Her et al., 2008
210	Her et al., 2008; Korshin et al., 2009
245	Thurman, 1985
250	Hautala et al., 2000
253	Her et al., 2008
254	Korshin et al., 1997; Spencer et al., 2007; Chow et al., 2008; Baker et al., 2008; Her et al., 2008; Leenheer and Croue, 2003; Korshin et al., 2009
260	Chen et al., 2002
272	Spencer et al., 2007; Baker et al., 2008
280	Chin et al., 1994; Kalbitz et al., 1999 Kalbitz et al., 2000; Weishaar et al., 2003; Korshin et al., 2009
285	Kalbitz et al., 1999; Kalbitz et al., 2000
300	Mcknight et al., 1997
330	Hautala et al., 2000
340	Tipping et al., 1988; Tipping et al., 1999; Spencer et al., 2007; Baker et al., 2008
350	Korshin et al., 2009
360	Kalbitz et al., 1999; Kalbitz et al., 2000
365	Spencer et al., 2007; Baker et al., 2008
400	Thurman, 1985; Hongve and Akesson, 1996; Kalbitz et al., 1999; Kalbitz et al., 2000; Hautala et al., 2000; Watts et al., 2001; Worrall et al., 2003; Worrall et al., 2007
410	Hongve and Akesson, 1996; Spencer et al., 2007; Baker et al., 2008
420	Hongve and Akesson, 1996
432	Hongve and Akesson, 1996
436	Hongve and Akesson, 1996
450	Hongve and Akesson, 1996
456	Hautala et al., 2000
460	Her et al 2008
465	Hongve and Akesson, 1996; Hautala et al., 2000; Wallage et al., 2006; Spencer et al., 2007; Baker et al., 2008
470	Kalbitz et al., 1999; Kalbitz et al., 2000
490	Hautala et al., 2000
660	Her et al., 2008
665	Wallage et al., 2006; Spencer et al., 2007a; Baker et al., 2008

Table 2. Correlation matrix demonstrating the relationships (Pearson correlation r values) between the temporal response of absorbance at those wavelengths previously used as proxies for or to characterise DOC. P values for all r values in the table were <0.005

Nm	Q	245	250	260	272	280	285	300	330	340	350	360	365	400	410	420	435	450	455	460	465	470	490	660	665
245	-0.012																								
250	-0.009	0.971																							
260	-0.007	0.955	0.956																						
272.5	-0.006	0.966	0.948	0.955																					
280	-0.014	0.967	0.959	0.935	0.959																				
285	-0.027	0.965	0.962	0.952	0.956	0.966																			
300	-0.036	0.931	0.929	0.949	0.956	0.943	0.954																		
330	0.006	0.897	0.901	0.908	0.918	0.926	0.940	0.971																	
340	0.053	0.878	0.878	0.888	0.907	0.910	0.920	0.962	0.988																
350	0.079	0.855	0.853	0.859	0.883	0.890	0.902	0.938	0.977	0.987															
360	0.123	0.821	0.822	0.824	0.846	0.856	0.869	0.907	0.960	0.973	0.986														
365	0.138	0.807	0.807	0.807	0.828	0.838	0.85	0.892	0.951	0.966	0.981	0.993													
400	0.271	0.606	0.606	0.599	0.627	0.640	0.655	0.694	0.788	0.821	0.866	0.913	0.931												
410	0.312	0.534	0.535	0.536	0.555	0.570	0.585	0.625	0.727	0.768	0.818	0.868	0.889	0.985											
420	0.322	0.478	0.476	0.481	0.501	0.511	0.528	0.566	0.676	0.721	0.774	0.828	0.850	0.971	0.989										
435	0.325	0.400	0.404	0.411	0.426	0.444	0.457	0.491	0.607	0.652	0.714	0.778	0.804	0.958	0.979	0.987									
450	0.359	0.336	0.347	0.354	0.372	0.385	0.397	0.436	0.558	0.609	0.667	0.739	0.764	0.935	0.966	0.983	0.988								
455	0.358	0.321	0.33	0.338	0.357	0.370	0.384	0.423	0.544	0.591	0.662	0.731	0.755	0.927	0.959	0.982	0.984	0.994							
460	0.372	0.306	0.316	0.323	0.342	0.358	0.370	0.406	0.531	0.581	0.647	0.721	0.745	0.927	0.958	0.977	0.988	0.992	0.993						
465	0.358	0.297	0.306	0.312	0.334	0.351	0.362	0.395	0.523	0.571	0.637	0.710	0.741	0.925	0.956	0.973	0.990	0.990	0.990	0.993					
470	0.347	0.283	0.295	0.302	0.319	0.338	0.349	0.382	0.511	0.560	0.630	0.704	0.732	0.919	0.952	0.968	0.985	0.987	0.985	0.988	0.993				
490	0.352	0.235	0.249	0.254	0.275	0.292	0.302	0.339	0.465	0.518	0.586	0.664	0.693	0.899	0.936	0.959	0.977	0.988	0.989	0.993	0.991	0.985			
660	0.369	0.086	0.107	0.123	0.141	0.159	0.166	0.200	0.338	0.399	0.47	0.561	0.594	0.829	0.876	0.908	0.936	0.955	0.959	0.963	0.963	0.963	0.973		
665	0.375	0.072	0.094	0.11	0.129	0.143	0.154	0.189	0.332	0.392	0.465	0.553	0.592	0.833	0.881	0.907	0.940	0.954	0.957	0.963	0.966	0.966	0.975	0.983	
E_4/E_6	-0.101	-0.212	-0.215	-0.219	-0.226	-0.228	-0.229	-0.233	-0.243	-0.245	-0.245	-0.245	-0.245	-0.221	-0.210	-0.200	-0.187	-0.177	-0.174	-0.17	-0.167	-0.167	-0.157	-0.133	-0.131

Table 3. Storm event details including the start and end time of the hydrograph, the mean E_4/E_6 ratio, total rainfall and total storm discharge.

Storm	Start Date	End Date	Mean E_4/E_6	Total Rain, mm	Q (m^3)
1	11/07/2009 23:41	13/07/2009 06:56	3.49	18.1	668
2	13/07/2009 23:26	14/07/2009 22:58	3.15	8.2	627
3	16/07/2009 20:58	19/07/2009 00:28	1.35	112.2	8429
4	21/07/2009 13:13	22/07/2009 12:43	3.45	25.2	864
5	28/07/2009 05:45	30/07/2009 03:05	2.48	34.3	1738
6	15/08/2009 04:17	16/08/2009 05:17	2.72	19.6	1851
7	23/08/2009 11:04	24/08/2009 21:19	3.73	14.7	828
8	26/08/2009 06:51	27/08/2009 06:36	7.16	16.2	1072
9	28/08/2009 06:21	29/08/2009 13:06	4.85	13.6	750
10	31/08/2009 06:51	01/09/2009 12:36	2.92	36.9	3325
11	01/09/2009 15:36	02/09/2009 1:36	2.35	17.3	1301
12	02/09/2009 19:21	04/09/2009 08:06	1.94	25.2	2269
13	04/09/2009 10:06	05/09/2009 04:06	1.84	10.5	845
14	08/09/2009 16:39	09/09/2009 17:09	7.67	10.2	598
15	03/10/2009 03:19	03/10/2009 20:49	6.98	24.1	1406
16	06/10/2009 09:49	07/10/2009 02:19	6.22	17.0	1204
17	19/10/2009 03:34	20/10/2009 12:02	5.48	17.0	1249
18	20/10/2009 14:02	22/10/2009 11:42	10.25	10.5	629
19	24/10/2009 09:22	25/10/2009 16:42	9.13	26.1	1324
20	25/10/2009 17:02	26/10/2009 13:42	10.32	14.5	1110
21	30/10/2009 20:02	31/10/2009 13:42	6.69	16.2	728
22	01/11/2009 05:02	02/11/2009 19:22	4.54	75.4	5117
23	03/11/2009 02:42	04/11/2009 07:42	7.43	30.0	1487
24	17/11/2009 11:28	18/11/2009 10:28	7.62	42.8	2870

List of Figures

Figure 1. The rainfall and discharge record for Cottage Hill Sike from July to December 2009

Figure 2. Absorbance (Abs m^{-1}) in Cottage Hill Sike from July to December 2009

Figure 3. Discharge (dashed black line) and changes in absorbance at 340 (black line), 400 (grey line) nm for 24 storm events at Cottage Hill Sike

Figure 4. Changes in the E4/E6 ratio (solid grey line) and discharge (dashed black line) over 24 storm events in Cottage Hill Sike

Figure 5. Mean discharge, mean absorbance at 340 and 400nm, mean E_4/E_6 ratio and mean 400/360 and 470/360 ratio over time for the first 30 hours of the 24 storm events analysed

Figure 6. Response of absorbance characteristics for 340, 400 and 365 nm for an October 2009 storm event

Figure 1

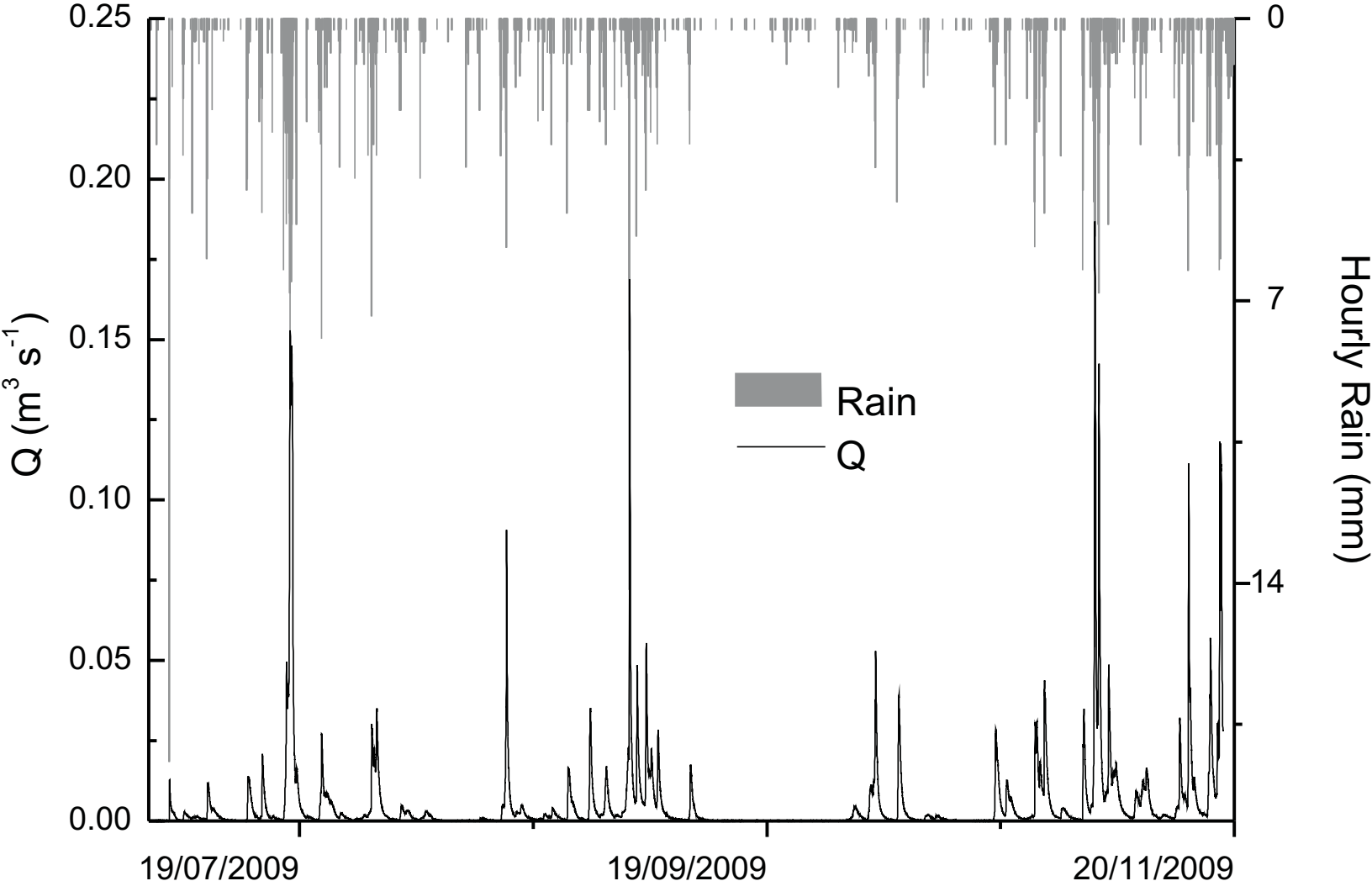

0.25
0.20
0.15
0.10
0.05
0.00
Q (m3 s-1)
0
7
14
Hourly Rain (mm)
Rain
Q
19/07/2009
19/09/2009
20/11/2009

Figure 2

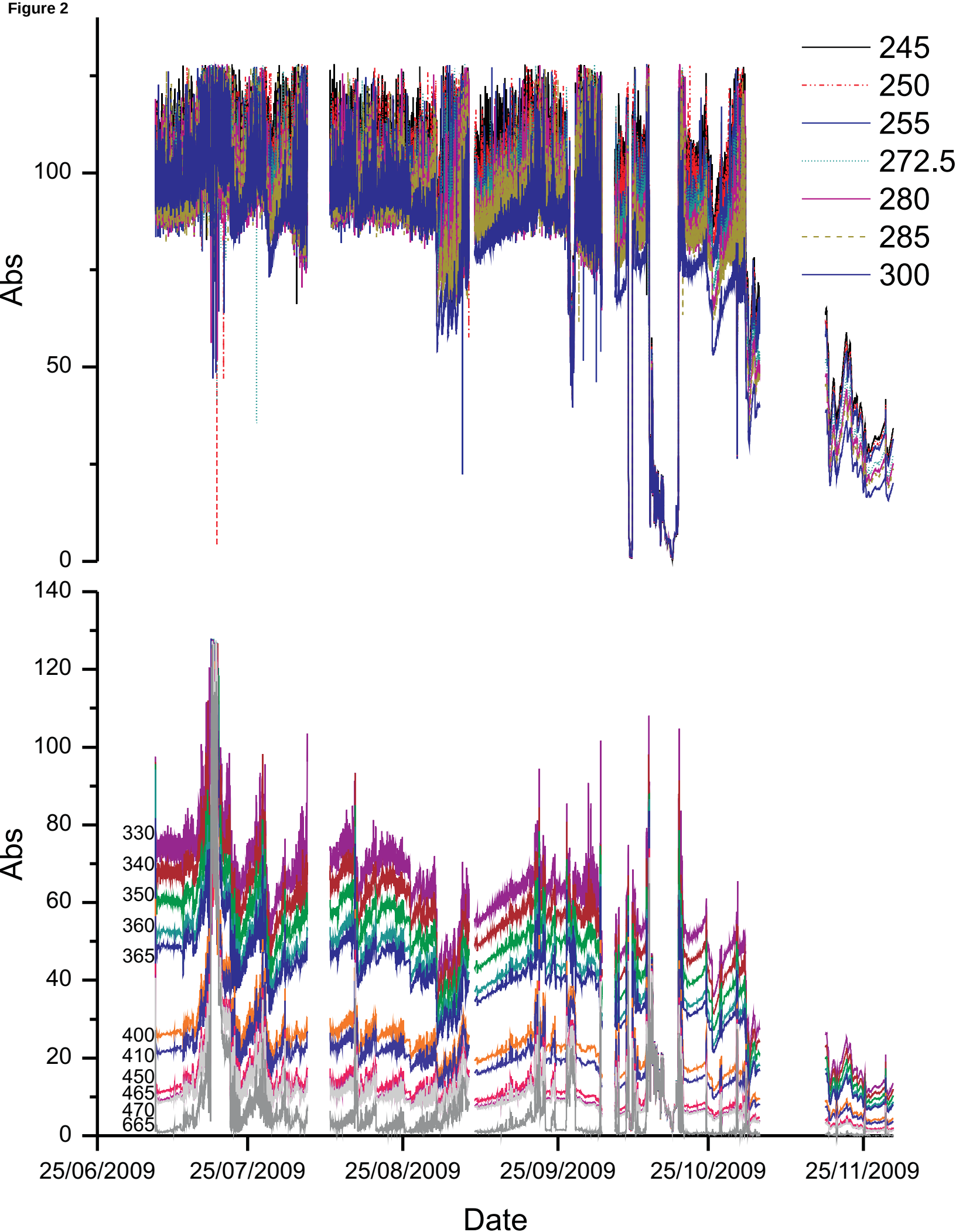

245
250
255
272.5
280
285
300
Abs
0
50
100
140
120
100
80
60
40
20
0
330
340
350
360
365
400
410
450
465
470
665
25/06/2009
25/07/2009
25/08/2009
25/09/2009
25/10/2009
25/11/2009
Date

Figure 3

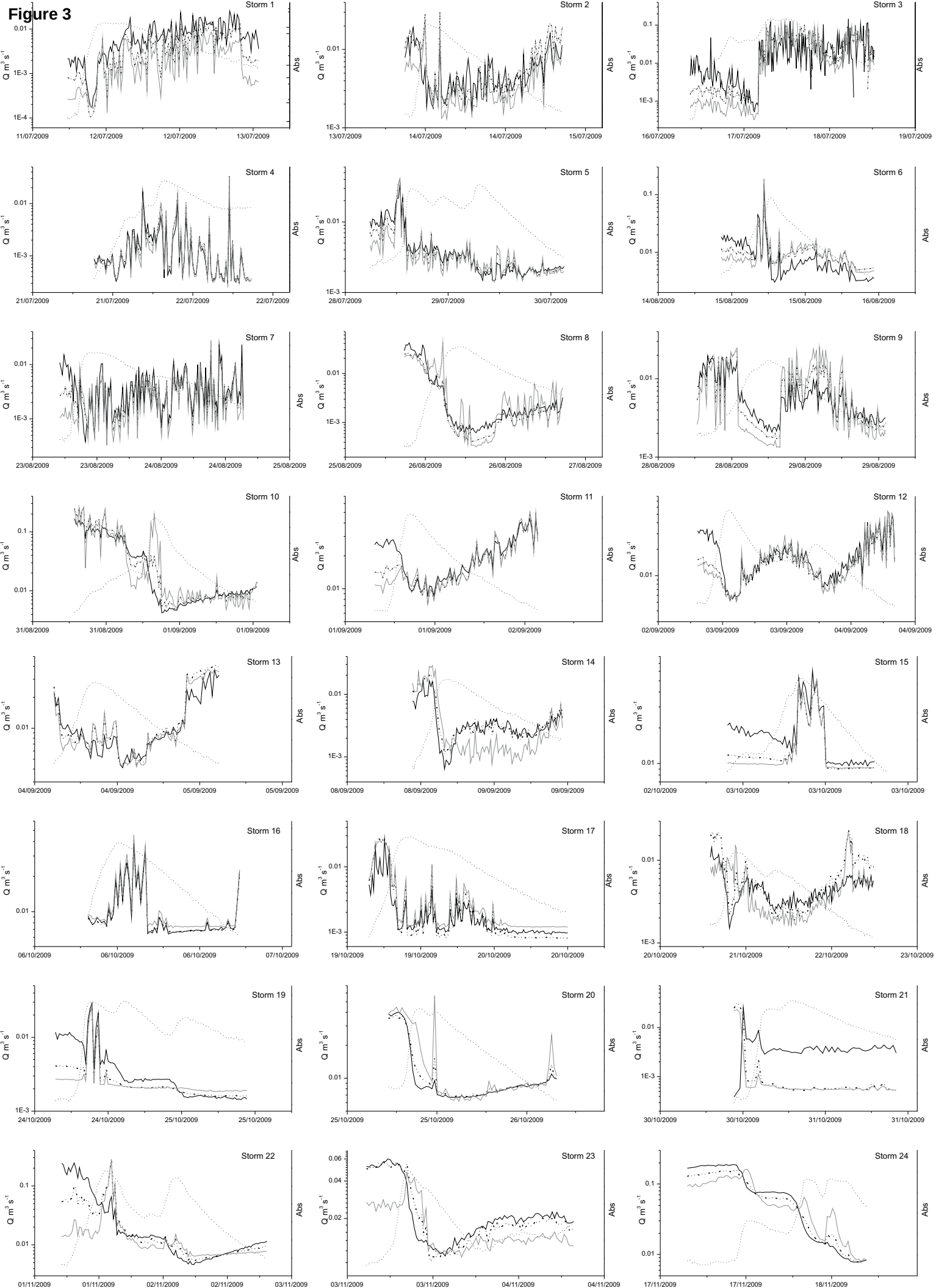

Storm 1
Storm 2
Storm 3
Storm 4
Storm 5
Storm 6
Storm 7
Storm 8
Storm 9
Storm 10
Storm 11
Storm 12
Storm 13
Storm 14
Storm 15
Storm 16
Storm 17
Storm 18
Storm 19
Storm 20
Storm 21
Storm 22
Storm 23
Storm 24
Q m3 s-1
Abs

Figure 4

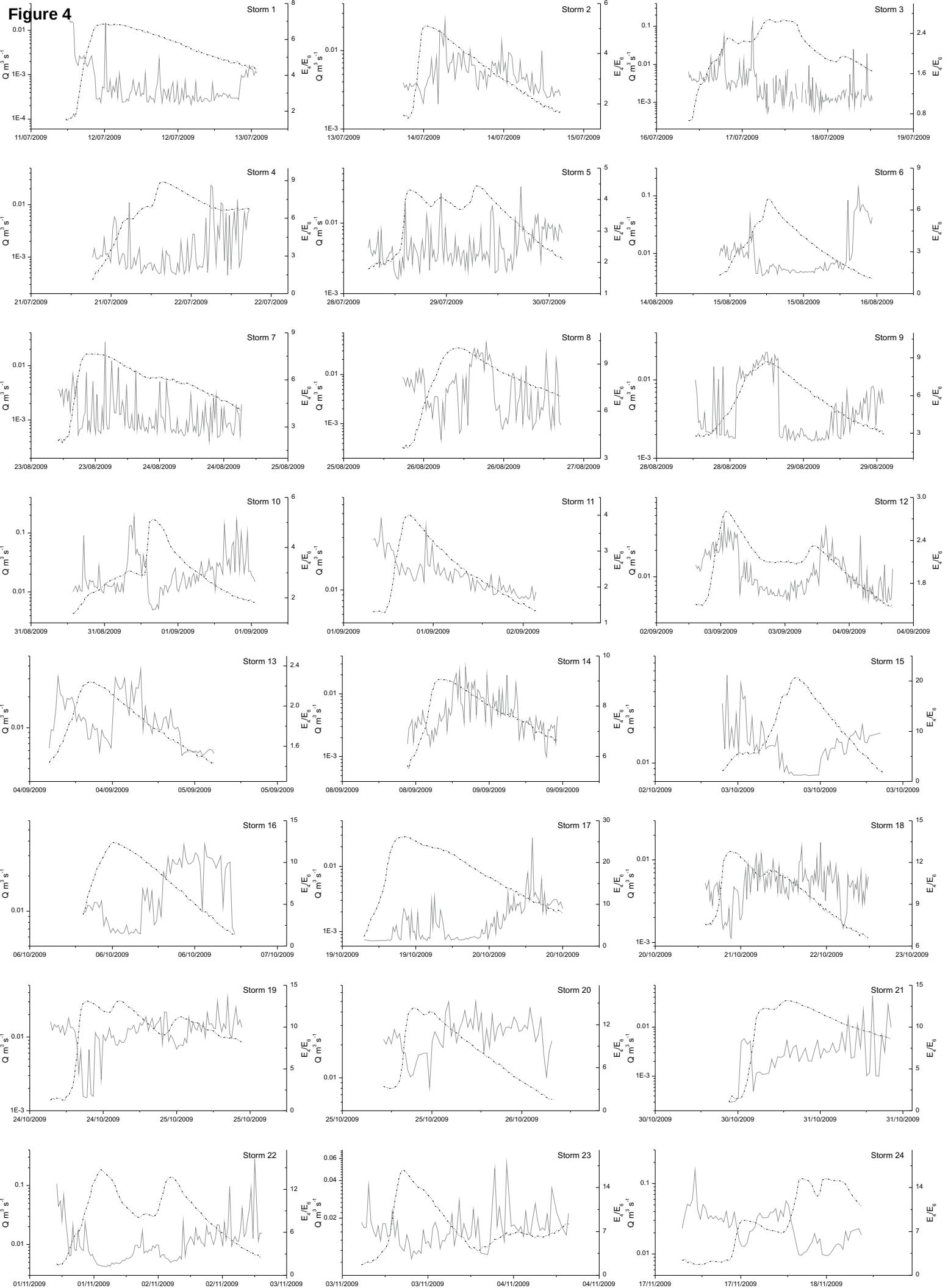

Storm 1
Storm 2
Storm 3
Storm 4
Storm 5
Storm 6
Storm 7
Storm 8
Storm 9
Storm 10
Storm 11
Storm 12
Storm 13
Storm 14
Storm 15
Storm 16
Storm 17
Storm 18
Storm 19
Storm 20
Storm 21
Storm 22
Storm 23
Storm 24
Q m3 s-1
E4/E6

Figure 5

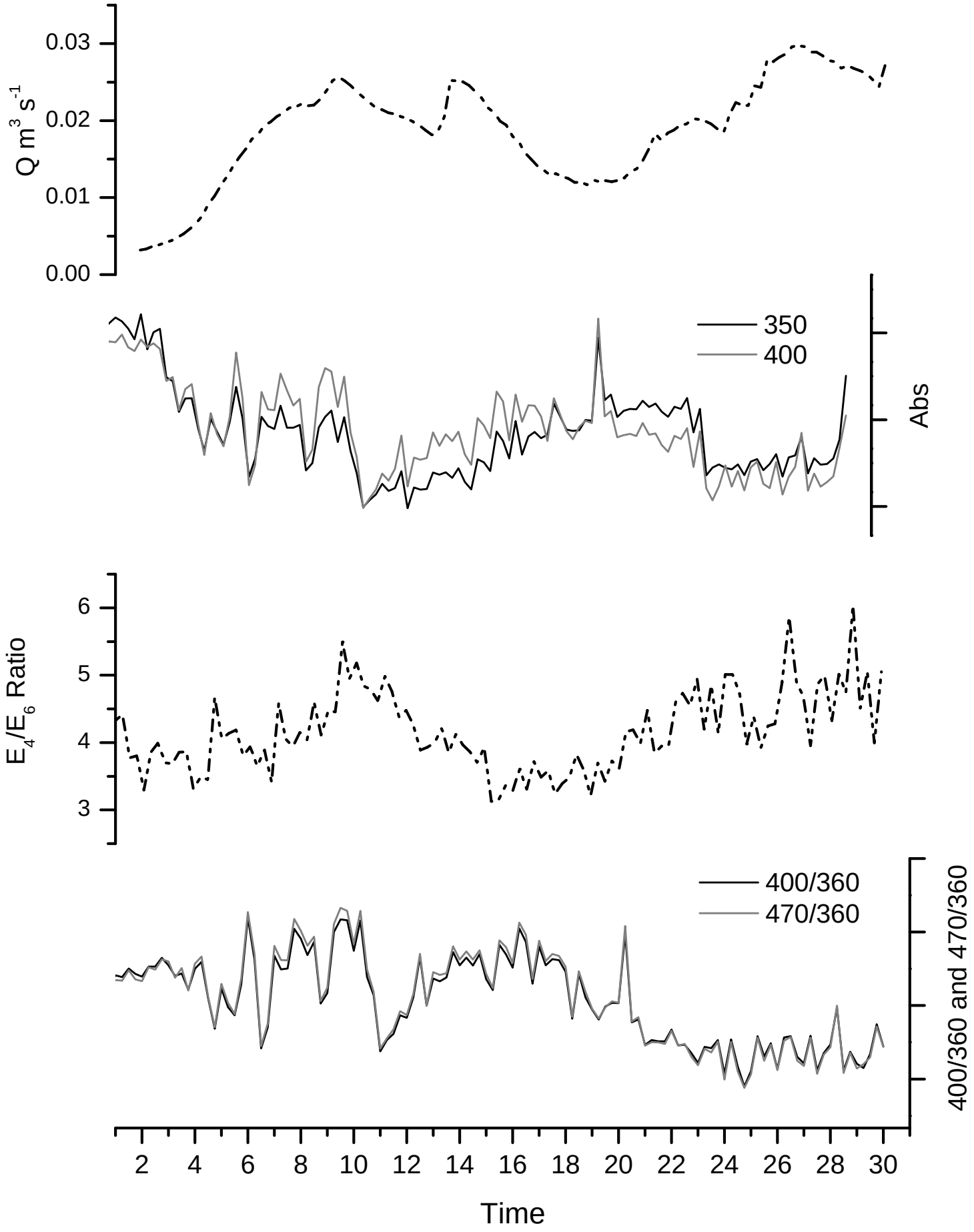
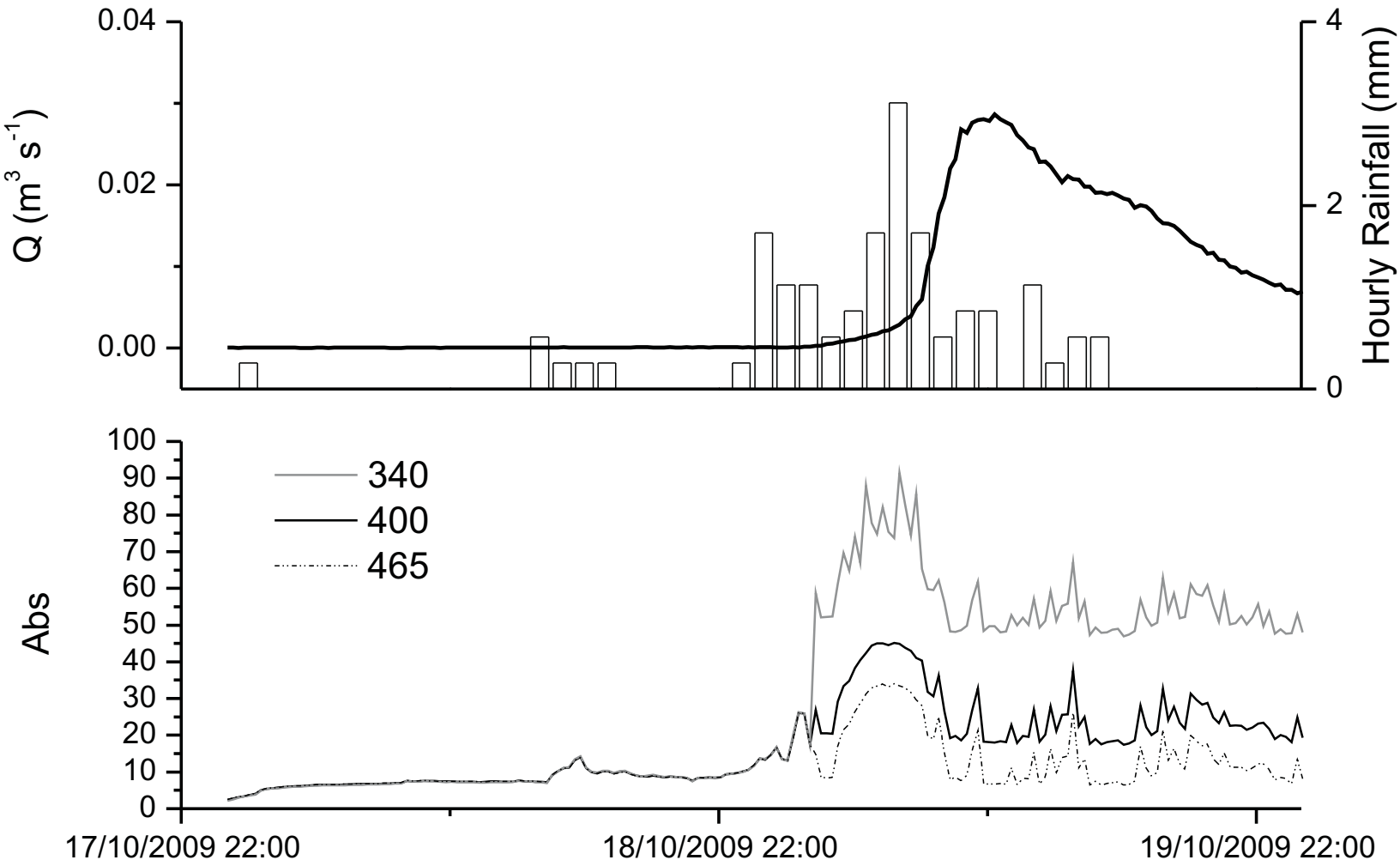

Q m3 s-1
0.03
0.02
0.01
0.00
350
400
Abs
E4/E6 Ratio
6
5
4
3
400/360
470/360
400/360 and 470/360
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Time

Figure 6


0.04
0.02
0.00
Q (m3 s-1)
4
2
0
Hourly Rainfall (mm)
100
90
80
70
60
50
40
30
20
10
0
Abs
340
400
465
17/10/2009 22:00
18/10/2009 22:00
19/10/2009 22:00