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During a winter of storms in a small UK catchment, hydrology and water quality responses follow a clear rural-urban gradient

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Abstract: This paper presents the hydrological and water quality response from a series of extreme storm events that passed across the UK during the winter of 2013/2014, in an experimental catchment with a strong rural-urban gradient across four nested sub-catchment areas. The Ray catchment in the upper Thames basin, UK, was extensively monitored using in-situ, high-resolution (15 minute) flow and water quality instrumentation. Dissolved oxygen, ammonium, turbidity and specific conductivity are used to characterise the water quality dynamics. The impact of the Swindon sewage treatment works (SSTW) on water chemistry at the catchment outlet is considerable. Hydrological and water-quality response varies considerably during the events, with the rural catchments exhibiting a much slower hydrological response compared to urban areas. A simple hydrological model (TETIS) was developed to provide insight into water sources in nested subcatchments, highlighting the disparity of the hydrological dynamics across contrasting land-uses during events. The variation in stormwater runoff sources impacts water quality signals with urban sites contributing to dilution dynamics in ammonium, whereas the more rural site experiences a peak in ammonium during the same event. Dissolved oxygen concentrations vary on a rural-urban gradient and experience a notable sag at the Water Eaton outlet (4.4mg/l) during the events, that would have resulted in significant ecological harm had they occurred during the
summer in warmer temperatures. The water-quality legacy of these storms in the wider context of the hydrological year is somewhat negligible, with markedly poorer water quality signals being observed during the summer months of 2014. Although ammonium concentrations during the events are elevated (above the ‘good’ status threshold under the WFD), higher values are observed during spring and summer months. The high flows actually appear to flush contaminants out of the Ray and its subcatchments, though the urban sites demonstrate a resupply dynamic during interim dry periods. Data suggest winter storms following dry spells in urban catchments cause some short-lived and spatially extensive deteriorations in water quality. More chronic effects, although prolonged, are only seen downstream of SSTW. These are indicative of capacity of infrastructure being reached, and from the data do not appear to be severe enough to cause ecological harm.

**Keywords:** winter flooding, water quality, rural-urban gradient, stormwater runoff, high-resolution monitoring

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1. Introduction

As technological developments have enabled the widespread deployment of inexpensive and high-resolution in-situ monitoring equipment, our potential to better understand the hydrochemical dynamics of rivers and streams in contrasting landscapes has improved accordingly (Macintosh et al., 2011 and Halliday et al., 2015). Increasingly, such networks are being deployed in urban areas to identify the impacts of urbanisation on surface water quality and associated ecosystems (e.g., Altenburger et al., 2015; Halliday et al., 2015 and
Skeffington et al., 2015). The urban contribution to global population is 54% and rising (United Nations, 2014). Hydrological impacts of urban expansion (i.e. loss of vegetation, soil sealing, artificial drainage/sewerage, and river channel simplification) have been studied for many decades (e.g. Hollis, 1975; Hollis & Ovenden, 1988; Packman & Hewitt, 1998; Miller et al. 2014). What remains uncertain is how surface water quality across contrasting land-cover varies during stormwater runoff events, as risk to personnel or damage to monitoring equipment often precludes observation during high flows (Goonetilleke et al., 2005). Butler et al., (2015) recently identified the role of terrestrial floodwater plumes negatively impacting coastal coral populations, whereby large fluxes of freshwater, sediment and nutrients contribute to the degradation of coral populations. Furthermore, they also advocated for a more holistic understanding of how stormwater quality varies during events via high-resolution monitoring, and highlighted the importance of local-scale water quality monitoring to aid in catchment management strategies.

Between December 2013 and February 2014, the United Kingdom experienced a succession of intense storms as a result of multiple Atlantic-low pressure systems passing over the country (Slingo et al., 2014). Compared to long-term averages, some parts of the United Kingdom, including the south-east, experienced 200% of average precipitation volumes for the December to February period (1961-2013). The rapid succession of storms resulted in soils in many catchments becoming saturated and runoff generation becoming very responsive to even small rainfall inputs (Huntingford et al., 2014). Much of the discussion that followed addressed issues of cause and prevention, particularly whether dredging of low-lying agricultural areas may have lessened the impacts (CIWEM, 2014). Water quality often receives limited attention during flood events, despite it being a major source of concern for ecosystem managers. However, the increasing deployment of in-situ monitoring regimes has
enabled the proliferation of data that enables identification of sub-daily dynamics that would otherwise be missed during coarser monitoring regimes, and have provided scope to determine how contrasting landscapes behave during extreme hydrological events (YSI and Loewenthal, 2008).

Through the deployment of such an in-situ monitoring network, this study provides insights into the hydrological and associated water quality dynamics during an extreme sequence of storm events. High-resolution monitoring of flow and water quality in the Ray catchment (an upstream tributary of the Thames basin in the South of the United Kingdom) was undertaken during a succession of flooding events in winter of 2013/2014 (Muchan et al., 2015). The Ray catchment (and four nested subcatchments) was monitored across a clearly identifiable rural-urban gradient across all sites. We assessed how surface water quality varied across this gradient and also assessed how water quality varies during the various stages of the flood hydrographs. We evaluate the contribution of a large sewage treatment works to pre- and post-event dynamics, and finally, assess the legacy of these significant storms on long-term water quality dynamics.

2. Study Sites

2.1 Monitoring Sites

Water quantity and quality parameters were monitored at five sites across the River Ray catchment, which is an upstream, right-bank tributary of the River Thames, draining the western part of the town of Swindon. The five monitoring sites are: (i) the river Ray at Water Eaton, which represents the overall catchment scale and (ii) the Great Western Way; (iii) the river Pry at Purton; (iv) Haydon Wick Brook at Torun Way and (v) the river Rodbourne at Nova Hreod College. The location of the five monitoring sites and the corresponding
catchment areas are shown on Figure 1 and a summary of the catchment characteristics are shown in Table 1. The sites were selected to represent varying degrees of urban land use coverage across a rural-urban gradient.

**The Ray at Water Eaton** drains the largest catchment area (84.10 km² to the catchment outlet) and discharge is continuously monitored by the UK Environment Agency (EA). The catchment contains a mixture of land uses, with grassland and arable farm land present throughout and also contains a sizable urban component in Swindon in the east of the catchment. The catchment is gently sloping and descends from a maximum height of 213.8 m Above Observable Datum (AOD) to an average elevation of 108 m AOD. Dry weather flow is sustained by groundwater from the Marlborough Downs and is further supplemented by continual inputs from the Swindon Sewage Treatment Works (SSTW) located in the middle of the catchment (Figure 1).

**The Ray at the Great Western Way** overpass is located in the upper catchment draining an upstream area of 28.20 km² and has a mix of grassland, agricultural and suburban land uses. The catchment is traversed by the M4 motorway and contains the south-west of Swindon town centre and the village of Wroughton, which is inhabited by around 8000 people (Wiltshire Council, 2011).

The **Pry** is a small tributary catchment, situated downstream in the west of the catchment, covering 3.14 km² (Table 1, Figure 1). The Pry is predominately grassland (80%) with around 10% of land use as arable, including a large organics farm (Purton House Organics, 2014). The Pry is mostly undeveloped with only 7% of land-use as suburban and no urban land-use.
By contrast, the Rodbourne catchment is heavily urbanised and covers an area of 5.88km\(^2\), containing large areas of commercial, industrial and dense housing land uses. The central Rodbourne catchment has experienced minimal development in the modern era and mostly dates to pre-1960, serviced by combined sewerage infrastructure that activates during storm flow and direct excess flows to the nearby SSTW (Miller et al., 2014).

Finally, the Haydon Wick catchment (5.65km\(^2\)) has experienced significant development since 1960 (Figure 1), resulting in a growing peri-urban area surrounding Haydon Wick brook (Miller and Grebby, 2014). Drainage pathways in Haydon Wick have been substantially altered by major drainage infrastructure upgrades following historical flooding and the northern catchment area is managed by a major storm-drain that routes water into the stream while southern sections are a combination of storm drains feeding into the heavily managed brook channel (Miller et al., 2014). Monitoring was undertaken upstream of the confluence between the two drainage areas, capturing the suburban, southern Haydon Wick catchment, covering an area of 3.07km\(^2\).

3. Data and Methods

3.1 Hydroclimatic Data

High-resolution (15 minute) flow monitoring was undertaken at the five monitoring points. Flow was derived from depth-velocity readings from Starflow™ Ultrasonic Doppler instruments fixed to river beds in selected watercourses (Pry, Rodbourne, Great Western Way and Haydon Wick). Flow at the permanent site at Water Eaton was measured by the UK Environment Agency using an Ultrasonic multi-path array installed at a crump weir, recorded at a 15 minute resolution. Rainfall was recorded by a tipping bucket rain gauge maintained by the Environment Agency, located centrally within the study area at the SSTW (Figure 1).
Data were available at a 15 minute temporal resolution providing a fully quality controlled dataset of rainfall across the monitoring period.

3.2 Water Quality Data

Water quality was measured through the temporary installation of four YSI 6600 multi-parameter sondes during December, 2013. At each site, the sonde was secured to a concrete slab and lowered onto the streambed, whilst being secured against a local landmark (typically a bridge). The sondes recorded continuously at 15-minute resolution and each sonde was equipped with a number of probes measuring a suite of water quality indicators including: turbidity, specific conductivity, ammonium and dissolved oxygen (DO). Additional data were available at the catchment scale from a permanently installed sonde at the Water Eaton outlet. Specific conductivity, turbidity and DO provided good indicators of general water quality whilst ammonium provided a useful insight into anthropogenic inputs via wastewater treatment discharges, fertilisers and animal waste from intensively managed agricultural landscapes (YSI, 2012). All calibration of the probes was undertaken by the National Water Quality Instrumentation Service (NWQIS) prior to deployment and select probes (e.g., ammonium and dissolved oxygen) were tested every two weeks to coincide with wider site visits. The four temporary sondes were checked after two weeks to ensure they had not become displaced or removed. As they were installed as loggers and not uplinked via telemetry, recorded water quality data underwent full quality control after they had been removed from the watercourse. The permanently installed sonde at Water Eaton was checked every two weeks, whereby data was downloaded onto a portable laptop, the pump system was cleaned out and batteries replaced every 4 weeks. Furthermore, newly calibrated probes replaced installed probes every 2 weeks, as recommended by NWQIS.
3.3 Spatial land-use data

A 5m resolution digital elevation model (DEM) was obtained from the EDINA Digimap service for the Thames basin (Digimap, 2014). Land use data were obtained from the UK-wide Land Cover Map 2007 (LCM2007), provided by the Centre for Ecology and Hydrology (Morton et al., 2011).

3.4 Event Selection and Analysis

Throughout December 2013, a succession of storms passed over the Ray catchment, resulting in a number of distinctive storm events (Figure 3). From these events, four identifiable events, concomitant across all sites, were chosen with identifiable rising limbs and recession periods.

3.5 Flow Component Estimation

The proportion of flow at Water Eaton that originates from the SSTW was derived following the methodology outlined in Halliday et al., (2015), utilising daily discharge data from the monitoring at the outlet at Water Eaton and daily discharge from the SSTW, obtained from the Environment Agency.

In this study, a simple hydrological model was implemented to estimate the proportion of flow from different runoff components (direct runoff, soil water and groundwater) to analyse the contrasting catchment hydrological response and help interpret different patterns observed in the water chemistry across the catchment. The TETIS model (see Frances et al 2007 for a detailed overview), is a conceptual distributed model in which the main processes (soil water retention, infiltration, percolation, overland flow, interflow and aquifer flow) are represented by means of interconnected tanks (Buendia et al., 2015). The model was implemented on a
100m resolution grid, resampling the 50m digital terrain model from the British Ordnance Survey (digimap.edina.ac.uk) with a one-hour time-step. The spatial variation of the hydrological processes was taken into account by varying in space several model parameters, such as topography, direct runoff velocity, river network, channel slope and land cover. The spatial variability due to pedological and geological heterogeneity was not considered in this particular application given the small size of the catchment and the lack of accurate information about soil heterogeneity. Given that the focus of this paper is on the effect of urban land use, the spatial variability due to land cover was simplified, and only two classes of land cover were considered: urban and non-urban. Two land cover-dependent model parameters were identified as highly influential on model results: soil static storage and hydraulic conductivity. Based on the information available and literature values (Bussi et al., 2014), the soil static storage was set to 40mm for non-urban areas and 10mm for urban areas and the saturated hydraulic conductivity to 1 and 0.1mm h\(^{-1}\) respectively.

The model was calibrated at the catchment outlet (Water Eaton) for the most prominent flood event (24/12/2013). The calibration was carried out by adjusting the model parameters. The TETIS model has nine hydrological parameters: soil static storage, evapotranspiration, infiltration capacity, overland flow velocity, percolation capacity, interflow velocity, deep aquifer percolation capacity, base flow velocity, river flow velocity. These parameters are also called correction factors, as they do not represent the actual physical parameters but they are just non-dimensional coefficients multiplying the actual parameter values (for more information about the split-structure of the TETIS model parameters, please refer to Francés et al., 2007). This procedure has been adopted in several other studies, such as Bussi et al. (2013), Buendia et al. (2015) and Rodríguez-Lloveras et al. (2015). A local sensitivity analysis was carried out prior to the calibration stage in order to identify uninfluential
parameters (such as the overland flow velocity) and discard them for calibration. The model was validated in time at Water Eaton over the whole month of December and validated in space and time over the whole month of December and at Great Western Way, Rodbourne, Pry and Haydon Wick, and then used to analyse the land use control over the flow generation and the flow components.

4. Results and Discussion

4.1 Pre-Event Conditions

Flows across all sites remain damped during the early period of December with diurnal flows and elevated baseflow visible at the catchment outlet Water Eaton site, highlighting the impact of effluent discharge from the upstream SSTW (Figure 3d). For the more rural Pry site, the hydrograph remains damped until the second event (23rd – 24th December) whereas the urban Rodbourne site experiences small peaks in the hydrograph following small rainfall pulses during the early period of the month before the first event arrives on the 18\textsuperscript{th} of December.

In the first half of December the high-resolution data highlights key differences between baseline water quality conditions. Highest concentrations of ammonium are observed at the Water Eaton catchment as a consequence of effluent discharged from the upstream SSTW, which contributes over 50\% of baseflow to the catchment outlet during early December (Figure 5b). An early peak in the ammonium time-series at the Great Western Way site was concomitantly accompanied by a rise in specific conductivity, which was the consequence of a fire that took place at a nearby metal and timber recycling facility (Wiltshire Fire Service, 2012). This highlights a wider problem with optical sondes, whereby ionic interference likely contributed to the detection of potassium, which was present at the site during the fire whilst
sodium bicarbonate is a dominant fire suppressant agent used in Class D metal fires (HM Fire Safety Inspectorate, 1998). When present in equal concentrations, potassium will account for 10%, and sodium will account for 0.1% of the ammonium signal yielding the potential for distortion of in-situ ammonium measurements (National Rivers Authority, 1995 and Rundle, 2011). Furthermore, the Great Western Way is impacted by an adjacent construction site (which is a major upgrade to existing sewerage infrastructure) whereby spikes in ammonium are often accompanied by spikes in turbidity and drops in DO (Figure 3), indicating overflows of sewage. In the Pry, Rodbourne and Haydon Wick catchments, ammonium concentrations are relatively low and well within current EU WFD guideline values (≤ 0.6 for ‘good’ status, Halliday et al., 2015). Inputs here are small, particularly in the Pry and Haydon Wick, and much lower than the urban Rodbourne site. This is consistent with the findings of Drury et al., (2013), who identified lower values in a suburban stream upstream of a wastewater treatment plant (WWTP), compared to an urban stream upstream of the same WWTP.

Background conductivity is affected by underlying geology. The Pry sits atop fissured limestone, resulting in elevated baseline conductivity due to a higher proportion of ions following dissolution of the limestone (Krawczyk and Ford, 2006). Conductivity at the Water Eaton site is further impacted by effluent from the SSTW, where an increased concentration of chlorine ions (a strong indicator of human waste) result in elevated specific conductivities (Thompson et al., 2012 and de Sousa et al., 2014). The application of road-salts in urban areas is also a major driver of in-stream conductivity (and ammonium) during winter months (Rodrigues et al., 2010, Dailey et al., 2014 and Anning and Flynn, 2014). In Haydon Wick and Rodbourne, grit was applied to roads during sub-zero temperatures in early December and subsequently washed into adjacent surface waters following an initial pulse of rainfall,
which is evident in both the conductivity and ammonium series’ (Figures 3a and 3b). Conductivity in the urban Rodbourne catchment is higher than the suburban Haydon Wick as a consequence of a denser major road network, which are priorities for de-icer application during low-temperature conditions.

Dissolved oxygen also exhibits variations across a rural-urban gradient, with highest concentrations being observed in the rural Pry catchment and lowest concentrations occurring at the Rodbourne and Haydon Wick sites (Figure 3c). Double-peak diurnal signals are evident in DO at the catchment outlet Water Eaton site during the low-flows, highlighting the significance of effluent from the upstream SSTW, as all other in-stream drivers such as photosynthetic and respiration dynamics have typically lapsed during the winter months (Halliday et al., 2015). Sharpened DO peaks are anticipated during the winter months as a consequence of shortened days. Turbidity remains subdued during the early half of December though a clear diurnal signal can be observed at the Water Eaton site from the upstream SSTW. The Rodbourne experiences small peaks in turbidity following even the smallest of rainfall whilst the Great Western Way site experiences a large rise in turbidity on the 10\textsuperscript{th} of December (Figure 4). Although no flow data is available during this time owing to device malfunction, observed discharge remained low with no precipitation, though highly turbid discharge from a local construction site nearby was observed during site visits.

4.2 Event Hydrology and Water Quality Dynamics

The utility of in-situ monitoring devices has enabled observation of how water quality dynamics change throughout storm events for a number of parameters, elucidating how they vary across contrasting catchment land-uses. At Haydon Wick, the shallow channel presented a number of issues during sonde deployment, particularly for turbidity (Figure 4). Prolonged
recording at the upper detection limit (1200NTU) indicated that the sensor had silted up following the first event. Bio-fouling of optical sensors remains a considerable limitation to monitoring certain parameters such as turbidity (e.g., Bourgeois et al, 2003 and Murphy et al., 2015), though self-wiping sensors that reduce or prevent siltation are increasingly being used (Bringhurst and Adams, 2011 and Murphy et al., 2015).

The TETIS model was used to identify dominant subcatchment flow components for each event. The model was calibrated at the catchment outlet (Water Eaton) and validated at the Great Western Way, Rodbourne, Pry and Haydon Wick sites. The model was validated in time at Water Eaton over the whole month of December (NSE, Nash and Sutcliffe (1970) efficiency = 0.77) and validated in space and time over the whole month of December and at Great Western Way, Rodbourne, Pry and Haydon Wick (NSE = 0.75, 0.80, 0.70 and 0.82).

The resulting NSEs suggest an overall very good performance of the model (where a perfect match between modelled and observed discharge would be 1). Runoff at urban and suburban sites is dominated by direct runoff from impervious surfaces, whereas more rural sites experience greater runoff contributions from soils (Table 2).

- **Event 1: 18th December (5:30pm) to 19th December (4:30pm)**

The rural Pry exhibits very little direct runoff response during the initial storm, though a small discharge peak is observed along with a small peak in turbidity (Figure 4 and Figure 6a). By contrast, the urban Rodbourne exhibits a flashy peak due to predominance of direct runoff, which is supplemented by delayed flows from the more rural downstream areas as soils gradually begin to wet up, resulting in a double-peak in turbidity during the rising and receding limbs of the flood hydrograph (Figure 4 and Table 2). Highest turbidity is observed at the Water Eaton on the rising limb of the hydrograph, before dilution occurs as peak flows
arrives. Dissolved oxygen response is consistent across all sites, with an initial reduction followed by a rise as peak flows reaerate the streams with the exception of Water Eaton, where lowest concentrations are observed during peak flow with recovery occurring during recession. The initial drop in dissolved oxygen may be the result of turbid (and organic laden) runoff being mobilised from areas immediately adjacent to the channels. Alternatively, initial rainfall pulses may push older, subsurface water into the channel, resulting in depleted levels of dissolved oxygen across the catchments (Datry et al., 2004). Highest concentrations of DO are observed in the rural Pry as a result of increased vegetation and reduced nutrient and sediment concentrations. Specific conductivity is consistent across all sites with an inversion of the flood hydrograph being observed (with low values occurring during peak flow), with the Rodbourne, Haydon Wick and Water Eaton sites all experiencing marked drops as a result of their higher peak flows. Ammonium concentrations are lowest in the Haydon Wick, and experience a dilution during peak flow across all sites with the exception of the Pry where a small rise in ammonium is evident. During this event, the river Pry had a pronounced contribution from soil water indicating that a main source of ammonium in rural sub-catchments is that accumulated in the soil (Figure 5 and Table 2). In these areas, ammonium behaves like a diffuse-source pollutant, and its concentration increases with flow. The signal at Water Eaton is more complex with a dilution during the rising limb followed by a marked peak concentration at peak flow.

- Event 2: 23rd December (00:00) to 24th December (9:00pm)

The largest of the four events, specific discharge was highest at the rural Pry site whereas comparatively damped flows occur at Haydon Wick and Water Eaton (Figure 6b). The Rodbourne and Haydon Wick both experience a double-peak flood hydrograph, highlighting the increased contribution of direct runoff and responsivity of both catchments (Table 2).
Dissolved oxygen decreases across all sites, though aeration is evident at the Pry, Rodbourne (first peak) and Water Eaton at peak flow. Conductivity experiences a dilution at the Pry whereas all other sites experience a pre-flood peak increase. Highest turbidity is observed at the Rodbourne during the first flood peak, though dilution occurs as the 2nd peak flow pushes through the system (Figure 4). The Pry experiences low turbidity, with a small peak observed during the early rise in the hydrograph (Figure 4). Ammonium dynamics across all sites experience an initial rise in concentrations before dilution takes place. From the TETIS model, a large component of the Pry’s runoff during the first two events (>80%) originates from soil-derived sources (Table 2). Following the presence of grazing cattle and application of fertiliser to fields earlier in the year, residual concentrations of ammonium remain in the soil and are subsequently mobilised following events that trigger soil-derived runoff (Biddoccu et al., 2016). Water Eaton continues to experience complex ammonium dynamics with two peak concentrations of ammonium occurring during the rising limb of the hydrograph before dilution occurs. During storm events, wastewater treatment plants are susceptible to inflow of excess stormwater, often resulting in insufficient capacity to fully treat effluent to required standards. Untreated effluent discharged into freshwater systems contains organic material that is broken down by microorganisms, reducing the DO concentrations in water (Garcia-Fernandez et al., 2015). Evidence of this occurs here, where low DO combined with concomitantly elevated ammonium and turbidity concentrations, strongly suggesting that untreated effluent is being pushed through the SSTW, exhibiting a gradual recovery as fresh stormwater pulses re-oxygenate and dilute ammonium and turbidity concentrations (Figure 4).

- Event 3: 26th December (10:00pm) to 27th December (6:00pm)
Highest observed peak flows occur at the urban Rodbourne and mixed Great Western Way (Figure 6c). Dissolved Oxygen experiences a moderate drop across all sites during the rising limb, but increase during peak flows as aeration occurs. The one exception is the Water Eaton site, whereby peak flow is accompanied by a marked reduction in DO (Figure 6c). Conductivity response is consistent, with each site experiencing an inversion of the hydrograph as peak flows dilute concentrations. The Rodbourne experiences a rapid drop in conductivity but responds during the flood recession, whereas the Haydon Wick does not return to pre-event concentrations until after the recession. In the Haydon Wick and Rodbourne, the application of de-icing road salts during cold periods has an adverse impact on conductivity. During December, sub-zero temperatures resulted in the widespread application of road and paving salt. A late example of this occurs on the 26th of December, where a sharp peak in conductivity is observed in the Rodbourne catchment following minimum temperatures of -2°C the previous evening followed by subsequent rainfall. During rainfall events, dilution of conductivities is much more severe in urban areas as a consequence of the rapid translation of rainfall into runoff, whereby quicker peaks with greater magnitudes result in much shorter and intense dilution effects. Ammonium concentrations are lower than previous events with dilution during peak flow evident across all sites aside from the Pry (which shows very little variation at all) and Water Eaton, which experiences an ammonium peak during peak flow with concentrations consistently above the 0.6mg/l status that is considered “good” under EU WFD guidelines. Highest turbidity is observed at the Great Western Way site as peak flows arrive into the system (Figure 4). During this third event, the rural Pry experiences its highest turbidity on the hydrograph recession, indicating the settling of soils and sediments washed into the stream from nearby fields following the peak flow (Figure 4).
Event 4: 30th December (00:00) to 31st December (00:00)

The highest observed peak flows occur at Rodbourne, with more damped flows occurring across the other sites (Figure 6d). The location of a significant upstream area of impervious landscape results in the rapid proliferation of rainfall into runoff, resulting in a much sharper rise to peak flow here than is visible at the other sites. Dissolved oxygen concentrations steadily decline until peak flows where aeration occurs across all sites with the exception of Water Eaton. At Water Eaton, a pronounced drop in DO is observed, with a low value of 7.4mg/l. This may be indicative of the upstream effluent contributions from the SSTW, as ammonium concentrations are equally high during this period. Water Eaton experiences elevated ammonium concentrations during peak flows, with concentrations fluctuating from pre-peak levels of 0.31mg/l to 1.28mg/l. Ammonium remains relatively damped at the Pry, though dilution in concentrations is evident at the Rodbourne, Haydon Wick and Great Western Way sites. Conductivity is damped at both the Pry and Great Western Way but Haydon Wick and Rodbourne exhibit pre-event peaks followed by subsequent dilution during peak flow. The Water Eaton experiences a protracted recovery following dilution on the rising limb. The Rodbourne experiences a significant pulse of turbid water at the onset of the final event before peak flows result in dilution (Figure 4). The Pry also experiences a rise in turbidity as peak flows arrive, though these rapidly drop again during the recession period. Despite experiencing the largest observed discharge, the Great Western Way experiences very little change in turbidity. The Water Eaton experiences a constant rise in turbidity through the rising hydrograph, which begins to dilute as peak flows arrive (Figure 4).

4.2.1 Discussion of Event Dynamics

The early mobilisation of sediment and nutrients into the streams results in pre-event sags in DO levels before peak flows reaerate the water, with a more pronounced impact in the urban
sites. Low DO is a symptom commonly associated with urban rivers and has long been recognised as a concern for aquatic ecologists, as insufficient in-stream oxygen can often result in hypoxia and widespread fish-kill in local communities (e.g., Lloyd, 1961). Here, the impact of low in-stream DO at the Water Eaton site is buffered by the low temperature conditions associated with the winter months. An inverse relationship exists between temperature and DO, and low temperatures during the winter months result in the supply of cold, oxygenated water (United States Geological Survey, 2015). During warmer conditions, oxygen concentrations at saturation are lower than in cooler waters, as noted in Owens et al., 1964. The occurrence of similarly low levels of DO during the summer months would have been compounded with low background levels on account of increased temperatures, resulting in fish-kill across the catchment area (Villate et al., 2013 and Rao et al., 2014). The relationship between dissolved oxygen and temperature is a critical driver for aquatic integrity, whereby reaeration of in-stream DO concentrations is recognised as being temperature dependant (Owens et al., 1964 and Hutchins et al., 2016). This is a key factor in water quality simulations of dissolved oxygen and is commonly applied in numerical models such as QUESTOR (Hutchins et al., 2016).

An initial spike in conductivity is evident on the rising limb, as particulate matter is washed into the stream, followed by a pronounced dilution and rapid recovery to pre-event conditions across most sites as peak flows arrive. However, at Water Eaton a much more protracted recovery is evident, as upstream flows transit through the system resulting in a much longer recession period, where land-use dictates the mechanisms and timing of rainfall-runoff conversion and the associated impact this has on water (and associated solutes) flushing through catchment systems (McGrane et al., 2014). Across these catchments, land-use is a major driver of in-stream conductivity, as urban landscapes will attenuate residues and ions
during antecedent dry periods that are subsequently mobilised into the river during first flush, resulting in higher background concentrations. These flushes will contribute to early conductivity signs at the Water Eaton which will be supplemented by slower peaks from rural areas later in the event.

Turbidity is a key water quality parameter that has been used extensively to calculate pollutographs, nutrient/contaminant fluxes and pollutant concentrations during stormwater events (e.g., Metadier and Bertrand-Krajewski, 2012 and Mather and Johnson, 2015). Here, there is a pronounced variation in turbidity across this rural-urban gradient, whereby the rural Pry exhibits very subdued turbidity throughout the month whereas the urban Rodbourne is very responsive to even the smallest flows. Water Eaton is artificially impacted by discharge from the upstream SSTW. Furthermore, Water Eaton is heavily influenced from adjacent agriculture, and intensive livestock grazing and overland traffic often contribute to considerable fluxes of sediment from the land surrounding the channel. Lawler et al., (2006) highlighted a dearth of studies on wet-weather turbidity from urban systems, which is perhaps surprising given the widely accepted role of urban sediments acting as a transport mechanism for other urban contaminants. Here, the consistently high turbidity observations in the Rodbourne highlight the constant supply of material and associated lack of exhaustion, which is often observed in rural areas (Lawler et al., 2006). The disparity in turbidity response across rural and urban sites is reflected in other water quality parameters, and highlights the need for headwater management of urban streams to reduce the fluxes of sediment and associated contaminants downstream as stormwater runoff events begin.

Ammonium concentrations are demonstrably higher at Water Eaton, highlighting the contribution of anthropogenic inputs from the upstream SSTW. In urban and suburban
landscapes, winter ammonium inputs are typically limited to road-salt wash-off, ineffective infrastructure and effluent (Lee et al., 2012). In the rural Pry, where runoff is dominated from soil-derived sources (Table 2), ammonium dynamics contradict those observed in Rodbourne and Haydon Wick. During peak flow events, the Pry experiences peak ammonium concentrations, as residual ammonium present in the soils from farming activities are re-mobilised. By contrast, urban and suburban sites experience dilutions of background ammonium during the stormwater events. High concentrations of ammonium have been demonstrated to suppress primary production in aquatic bodies in the United States and Hong Kong and pose a threat globally to aquatic ecosystems (Dugdale et al., 2012). What is, perhaps, of more concern is the measured concentrations at both the Great Western Way and Water Eaton, where concentrations regularly fail to meet the 0.6mg/l guidelines for ‘good’ water quality under the EU WFD. Whilst more detailed analysis would be required to trace ammonium source, it is likely that the influence from the WWTP has a profound impact on concentrations at the catchment outlet, particularly during stormwater events when treatment capacity may be exceeded.

Identifying the true sources of water throughout storm events is something that is inherently difficult and requires a dedicated experimental or modelling based approach, but would provide a starting point for helping to manage stormwater runoff from contrasting landscapes during events. Previous experimental approaches have utilised comprehensive upstream and downstream monitoring of WWTPs and dominant land-uses to separate local signals (e.g., Walling, 2005, Brown and Peake, 2006, Neal et al., 2010 and Sidhu et al., 2013). Other studies have sought to utilise detailed modelling studies (e.g., Sansalone and Buchberger, 1997 and Zheng et al., 2014). Combining experimental stable isotope and geochemical tracer data with distributed hydrological models has yielded some useful insights into water sources
in catchment systems (e.g., McGuire et al., 2007). Quantifying the impact of storms on in-stream dissolved oxygen would benefit from an analysis of bed sediment, in order to determine whether longer-term increase in sediment oxygen demand occurs as a result of the storms. Here, further monitoring to identify key sources of low dissolved oxygen is required to identify key drivers of adverse water quality that fails to meet the EU WFD concentrations.

4.3 Events in Context of the 2013/2014 Hydrological Year

The context of the December 2013 events at Water Eaton in the wider hydrological year is presented in Figure 7. Although flow data between June and September 2014 is unavailable due to malfunction of the recording instrumentation, flows recorded during the December 2013 events were the highest observed flows during the hydrological year. Flows remained high in the catchment until March 2014, when a notable recession occurs, though observed baseflow post-event remain higher than those in November and early December 2013. Conductivity experienced a marked drop from 1166µS/cm to the lowest record value of the hydrological year during the winter events (347µS/cm). A gradual recovery is observed during the remainder of the hydrological year though peak conductivity never reaches pre-event values apart from an observed peak in August 2014. Furthermore, conductivity never reaches the same low value as that observed during the winter events as subsequent peak flows were much lower to October 2014. Despite low concentrations of DO being evident during the events (with a gradual decrease occurring toward the end of December 2013) concentrations remain higher than those observed through summer 2014. Ammonium concentrations do increase during the events, however, the high flows suppress concentrations, as observed levels during spring and summer are often higher.
During October and November 2013, baseflow conditions were depleted and effluent from the SSTW sustained flows (Figure 5b). The outlet at Water Eaton experiences direct runoff pulses from urban areas but also slower soil water pulses which dominate recession dynamics. The extent of the direct runoff and soil water responses is also temporally variable, and depends on both storm characteristics and antecedent soil moisture conditions. Following the December events, flows remain elevated through to mid-March and even periods without rainfall during this time resulted in elevated baseflow as a result of aquifers recharging during the December flood events. In water-stressed areas (including the south of the United Kingdom), flooding during the winter is increasingly being regarded as a beneficial mechanism to provide natural recharge (e.g., Prathapar and Bawain, 2014 and Dyer et al., 2015). In spite of their oft-catastrophic consequences, flood events during the winter months are valuable for reconnecting streams and aquifers in water stressed areas (Desilets et al., 2008).

Whilst ammonium concentrations during December exhibit small peaks, sources of ammonium remain limited during the winter months and average ammonium concentrations are marginally lower than those exhibited during the summer months, when fertiliser applications increase and in-stream concentrations increase (Wang et al., 2011). The high flows that prevail through January and February contribute to a continued dilution effect but the storms exhibit no prolonged impact on ammonium concentrations. Dissolved oxygen experiences pronounced sag, c.2mg/l, well into January and experiences a protracted recovery. The increase in temperature during the summer months results in a chronic decrease in DO levels with episodic, dangerously low concentrations below EU WFD guidelines. In May, peaks in discharge are accompanied by concomitant peaks in ammonium and significant drops in both DO and specific conductivity. The widespread application of
fertiliser to fields, gardens and parklands during early spring results in a ready source that is mobilised into streams following rainfall events (Environment Agency, 2007). Specific conductivity experiences a marked drop during December and recovery is very protracted through the remainder of the year. The magnitude of these events flushes much of the conducting particles out of the system, failing to return to pre-event concentrations until the end of the summer period, exhibiting a cleansing effect on catchment water quality.

5. Conclusions

High-resolution monitoring of flows and water quality during the winter of 2013/2014 across a well-defined rural-urban gradient has provided a unique dataset revealing a range of water quality responses. Water quality shows a marked contrast with wastewater effluent having a much more significant, lasting impact on water quality than observed first-flush dynamics from more developed areas. Resupply is evident in urban and suburban areas, where dry periods between events allow build-up of ammonium, turbidity and associated conductivity, particularly following cold periods and road-salt application. Overall, stormwater runoff provides some benefits by facilitating recharge to depleted groundwater stores and cleansing catchments by flushing large volumes of suspended material out of the channel. Water quality impacts are short-lived for storm events and the greater impact to water quality is the effluent being discharged from the upstream sewage treatment works. There exists a potential capacity issue for sewage treatment works, whereby hydraulic push occurring during large storm events results in untreated effluent being discharged. Had similar floods occurred during the summer months, the ecological consequences from poor local water quality may have been much more pronounced as a consequence of increased temperatures and lower DO concentrations. However, it remains unclear how such stormwater quality dynamics would vary across the same gradient during the summer months, and whether first flush dynamics
during this more biologically active period may pose a greater threat to aquatic integrity and in-stream ecosystems, highlighting a considerable seasonality challenge to aquatic managers. Furthermore, as urban areas continue to grow and wastewater loads to WWTPs increase accordingly, there remains an uncertainty regarding how treatment efficiencies may be impacted and what consequences this may have during future flood events. A clearer understanding is required of how urban expansion will continue to impact on water quality, (both via diffuse and point-source inputs) in order to better mitigate against stormwater inputs to receiving water bodies.

Acknowledgements
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Figure 1: Location map showing the Ray and subcatchments (Rodbourne, Haydon Wick, Ray at Great Western Way (GWW) and Pry) relative to the wider Thames basin (insert). Urban extent for catchment derived using the CEH Land Cover Map 2007 database for the full River Ray catchment (National River Flow Archive site 39087)
Figure 2: Cumulative rainfall statistics for winter (December - February inclusive) period in the upper Thames basin, showing average cumulative rainfall (1961 - 2013) and rainfall for winter storms of 2013/2014. Long-term average based on British Atmospheric Data Centre (BADC)/UK Meteorological Office data and 2013/2014 data based on observational tipping bucket gauge data and Met Office station data.
Figure 3: Time-series of flows and water quality parameters of dissolved oxygen, ammonium and specific conductivity for nested sub-catchment sites across the Ray and catchment outlet with selected events highlighted.
Figure 4: Flow and turbidity time-series’ for December 2013 at the Pry, Rodbourne, Great Western Way, Haydon Wick and Water Eaton monitoring locations. Haydon Wick experienced a number of problems during its deployment, continually recording at the optimum sensor range during low flows highlighting either a silting of the sonde or operation out of the water.
Figure 5: Simulated proportion of runoff from each site during December 2013, highlighting direct runoff (blue), soil-water runoff (green) and groundwater contributions (grey) with observed discharge (black) and simulated discharge (red) also plotted for reference.
**Figure 5b:** Discharge (m$^3$/day) from both the Swindon Sewage Treatment Plant (SSTW, red) and The Ray at Water Eaton (black), with the percentage proportion of flow (grey) also highlighted.
Figure 6a: Flow and water quality matrix for 5 sites during event 1: discharge is represented by the line plot (left Y axis) and water quality parameters via the dot plots (right Y axis).
Figure 6b: Flow and water quality matrix for 5 sites during event 2
Figure 6c: Flow and water quality matrix for 5 sites during event 3
Figure 6d: Flow and water quality matrix for 5 sites during event 4
Figure 7: The December winter events (red) in context of the hydrological year from October 2013 to October 2014 at Water Eaton - from top to bottom: ammonium, dissolved oxygen, specific conductivity and flow.
Table 1: Catchment Characteristics across Study Sites at subcatchment and catchment scales – data from a 5m Ordnance Survey DEM (Edina, 2015) and the Centre for Ecology and Hydrology LCM 2007 (Morton et al., 2011)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Pry</th>
<th>Ray at Great Western Way</th>
<th>Rodbourne</th>
<th>Haydon Wick</th>
<th>Ray at Water Eaton</th>
</tr>
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<tbody>
<tr>
<td>Area</td>
<td>km²</td>
<td>3.14</td>
<td>28.21</td>
<td>5.88</td>
<td>5.65</td>
<td>84.10</td>
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<td>Mean Elevation</td>
<td>mAOD</td>
<td>122.1</td>
<td>120.6</td>
<td>102.7</td>
<td>107</td>
<td>108.1</td>
</tr>
<tr>
<td>Max Elevation</td>
<td>mAOD</td>
<td>145</td>
<td>212.1</td>
<td>142.1</td>
<td>147.6</td>
<td>213.8</td>
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<tr>
<td>Mean Slope</td>
<td>°</td>
<td>1.8</td>
<td>2.19</td>
<td>0.97</td>
<td>2</td>
<td></td>
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<tr>
<td>Land Use</td>
<td>(%)</td>
<td>2.9</td>
<td>4.5</td>
<td>0.7</td>
<td>0.6</td>
<td>2.2</td>
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<tr>
<td>Forestry</td>
<td></td>
<td>9.5</td>
<td>19.3</td>
<td>0</td>
<td>9.5</td>
<td>16.3</td>
</tr>
<tr>
<td>Arable/ Horticultural Grassland</td>
<td>(%)</td>
<td>80.6</td>
<td>49.1</td>
<td>16.3</td>
<td>19.2</td>
<td>44.5</td>
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<tr>
<td>Water</td>
<td></td>
<td>0</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>0.2</td>
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<tr>
<td>Suburban</td>
<td></td>
<td>7</td>
<td>18.3</td>
<td>61.9</td>
<td>67.3</td>
<td>26</td>
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<tr>
<td>Urban</td>
<td></td>
<td>0</td>
<td>5.7</td>
<td>14.8</td>
<td>2.4</td>
<td>9.3</td>
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<tr>
<td>Industrial</td>
<td></td>
<td>0</td>
<td>1.3</td>
<td>5.3</td>
<td>2</td>
<td>1.5</td>
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Table 2: Percentage flow components (direct runoff, soil water and groundwater) from the TETIS model by sub-catchment and by storm event

<table>
<thead>
<tr>
<th>Water Eaton</th>
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<th>Rodbourne</th>
<th>Great Western Way</th>
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<td>Event 1</td>
<td>Event 2</td>
<td>Event 3</td>
<td>Event 4</td>
<td></td>
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<tr>
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<td>Direct runoff</td>
<td>Direct runoff</td>
<td>Direct runoff</td>
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</tr>
<tr>
<td>Soil water</td>
<td>Soil water</td>
<td>Soil water</td>
<td>Soil water</td>
<td>Soil water</td>
</tr>
<tr>
<td>Ground water</td>
<td>Ground water</td>
<td>Ground water</td>
<td>Ground water</td>
<td>Ground water</td>
</tr>
<tr>
<td>30% 63% 8%</td>
<td>25% 67% 8%</td>
<td>13% 59% 28%</td>
<td>5% 63% 32%</td>
<td>5% 89% 7%</td>
</tr>
<tr>
<td>61% 32% 7%</td>
<td>51% 40% 8%</td>
<td>28% 45% 27%</td>
<td>11% 57% 32%</td>
<td>5% 85% 8%</td>
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<tr>
<td>71% 23% 7%</td>
<td>61% 31% 8%</td>
<td>33% 40% 27%</td>
<td>14% 55% 32%</td>
<td>7% 85% 8%</td>
</tr>
<tr>
<td>25% 69% 7%</td>
<td>21% 71% 8%</td>
<td>11% 61% 28%</td>
<td>4% 64% 32%</td>
<td>2% 69% 29%</td>
</tr>
<tr>
<td>5% 89% 7%</td>
<td>5% 85% 8%</td>
<td>2% 69% 29%</td>
<td>1% 67% 32%</td>
<td></td>
</tr>
</tbody>
</table>
Journal of Hydrology: Highlights

High-resolution monitoring of hydrological and water response to the 2014 UK winter storms in nested catchments across a rural-urban gradient

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- Unprecedented storms with 200% average winter rainfall had little impact on overall water quality
- Wastewater effluent key driver of water quality at catchment outlet
- Storms yield some benefits by flushing catchments and recharging aquifers
- Colder winter conditions protected aquatic ecosystems from hypoxic conditions