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An evaluation of particulate phosphorus storage in an agricultural estuary

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An evaluation of particulate phosphorus storage in an agricultural estuary

by

Suha Zoozi

A thesis submitted to Plymouth University in partial fulfilment for the degree of

Doctor of Philosophy

School of Geography, Earth and Environmental Sciences

Faculty of Science and Technology

July 2013

Abstract

Suha H Zoozi

An evaluation of particulate phosphorus storage in an agricultural estuary

Knowledge of fine sediment delivery (both timing and loading) is fundamental to the assessment of non-point source pollution in estuarine environments. This study comprised three key components that led to the development of a fine sediment and particulate associated phosphorus budget in a typical agricultural estuary. Firstly, to explore catchment inputs, turbidity and flow were monitored continuously upstream of the freshwater/saline interface on the main stem channel of the south Devon River Avon, which drains a medium sized agricultural catchment (area 340 km²), in southwest UK. Thirty-five storms were studied in detail; and the hydrological and suspended sediment load response was observed to be highly variable. Suspended sediment concentrations (SSC) reached a maximum of 804 mg L⁻¹ and sediment load varied from 3 to 227 t per hydrological event. Most sediment load was concentrated in winter months when competent flows occur frequently. Hydrological response was also variable in terms of lag, hydrograph shape and maximum discharge wherein the response to hydrological drivers was not consistent. Analysis of key storm parameters indicated that the hydrological response of the catchment was affected by the total amount of precipitation and antecedent rainfall history but the spatial pattern in rainfall across the catchment in relation to the spatial pattern of sediment sources was the key factor influencing total load. In the second component,

examination of the sediment-associated phosphorus concentrations in the surface sediment in the Avon estuary was undertaken to evaluate spatial variation in concentration as influenced by the sediment storage dynamics of key geomorphological zones i.e. saltmarshes, intertidal flats and sandy shoals. Phosphorus concentrations ranged from 1524 to 68 mg kg⁻¹ with higher concentrations found in saltmarsh. While there was no observed relationship between key sediment properties, particle size and total organic carbon within the different geomorphic units, a clear trend in particle size and particulate phosphorus concentration was observed longitudinally between mudflat zones linked to the sedimentation dynamics of the estuary. Furthermore, the relationship of particulate phosphorus concentration to organic matter content was modified by saltmarsh vegetation inputs to the sediment column. The final component of the work drew on evidence from a GIS and field-based survey to estimate (i) the total fine sediment and associated particulate phosphorus loading of the estuary and (ii), in conjunction with river flux data and literature evidence, the total fine sediment and PP storage and the annual sediment budget (inputs, storages and output) for the study estuary. The total amount of fine sediment stored in the estuary was ca. 99000 t which equated to 40 - 100 years of the annual sediment load of the river. Approximately 50% of all fine sediment that currently enters the estuary was estimated to be retained in storage supporting the important role of estuarine sediment sink zones in the attenuation of phosphorus. The total particulate phosphorus storage in estuary fine sediment was estimated to be 20 – 40 times the measured annual catchment particulate phosphorus input. Future changes in catchment sediment supply dynamics linked to catchment restoration programmes and soil conservation initiatives could destabilise estuarine sediment sinks and this has potentially

important implications for future estuarine water quality. There is a need for further work on the potential bioavailability of estuarine sediment stored phosphorus.

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- Endnote.
- Excel.
- GTA intensive course (Plymouth University).

- Scientific Writing.
- Sessions on learning academic vocabulary.
- English language support for international.
- Data analysis.
- Sond data in Excel.
- Sediment analysis.
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- TP analysis.
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Chapter 1: Phosphorus pollution in estuarine systems

1.1 General introduction

Phosphorus (P) plays an important role in the eutrophication of surface waters because it is the main element essential for plant growth. Phosphorus enters the river system mainly in particulate form and dissolved input quickly associates with sediments and may persist within the system for many hundreds of years, especially if longer-term sediment storage occurs (Daniel *et al.*, 1998). As the world population continues to increase and agriculture becomes increasingly intensive, phosphorus pollution of the environment is likely to increase (Keesstra *et al.*, 2009). Also in the UK, changes in land-use practices during the 20th century led to increases in catchment sediment yields and therefore particulate phosphorus yields (Wilby, 1995; Heathwaite & Johnes, 1996; Foster & Lees, 1999). More recently, Catchment Sensitive Farming and other catchment restoration schemes (Collins & McGonigle, 2008) have been implemented and are likely to lead to reduced sediment and PP inputs to waterways, but the impact of these on sediment and nutrient loads requires quantification and the legacy effect of past sediment inputs remains uncertain. Consequently, more information is needed on the spatial and temporal variability of the transport and storage of phosphorus by fluvial sediments to assist in the formulation and application of control and remedial measures. When considering the role of fine sediments, especially the <63µm fraction as a vector for transport of phosphorus, it is important to investigate the influence of physical and chemical properties of sediment that work to attract phosphorus (Owens & Walling, 2002). These properties will influence both the concentration of phosphorus in transported sediment, its fate in the landscape and its availability. Many studies have considered individual components of the fluvial system, such as the transport of phosphorus in

suspended sediment, the transport of dissolved phosphorus in solution, storage of phosphorus in channel bed sediments and the exchange of phosphorus between the sediment-associated form and the soluble form. More attention however needs to be given to the links between the individual components of fine sediment transport and to their roles in the transport of sediment-associated phosphorus from source to output and storage in major sink zones e.g. estuaries. The study reported in this thesis addresses this need through development of an estuarine sediment and PP budget.

1.2 Phosphorus problems: definition and rationale

Eutrophication is a major problem in estuarine systems. Excessive inputs of nutrients stimulate growth of some aquatic plants, including algae and higher plants with impacts on oxygen availability in water. Consequently, there are implications for water quality and the health of aquatic organisms (Neto *et al.*, 2008; Ferreira *et al.*, 2007). The sources which contribute most to the eutrophication of estuaries are inputs from nutrient loading from agricultural land; industrial and domestic activities via sewage treatment works and septic tanks (Neto *et al.*, 2008). The role that P plays as a limiting nutrient for algal blooms in the estuaries is likely to be influenced by P release and uptake from sediments, either in suspension or in storage, to the estuary water. This is commonly discussed in connection with certain controlling environmental factors and transformations which will occur generally when a number of factors interact together to produce the environmental conditions needed to stimulate either the release or uptake of phosphorus (Flindt *et al.*, 1999). Because sediment might act as a secondary source of P through transfer from the sediment to the water column, it is vital that management decisions are based on a good

knowledge for fine sediment and associated P storage in sediment sink zones such as estuaries.

1.3 Problems associated with phosphorus pollution of watercourses

Phosphorus is one of the main elements for plant growth and resources for a range of animal species and its input has long been recognized as necessary to maintain profitable crops and animal production (Wang *et al.*, 2009, Sharply *et al.*, 1995). In most cases, freshwater eutrophication is accelerated by increased inputs of phosphorus which is a key nutrient in eutrophication (Tunney *et al.*, 2000; Monbet *et al.*, 2009; McLusky & Wolanki, 2011). Phosphorus management is an integral part of profitable agriculture systems and continued inputs of fertilizer and manure phosphorus in excess of crop requirements have led to a build-up of soil phosphorus levels (Sharply *et al.*, 1995). Excessive phosphorus accumulation in soil presents the risk of contamination of surface water bodies and the subsequent decline in water quality by the process of eutrophication (Flaten *et al.*, 2003). These problems are dependent upon the phosphorus level in the both sediment and the water column. Awareness of the importance of the dissolved and particulate forms of phosphorus in the eutrophication of aquatic systems (Vollenweider, 1968) has led to numerous studies aimed at understanding the processes controlling phosphorus concentrations and fluxes in river systems (e.g. Osborne *et al.*, 1980). Phosphorus is strongly determined by chemical and biological processes, undergoing numerous transformations and moving between the particulate and dissolved phases, between the sediment and water column and between the biota and abiotic environment (McLusky & Wolanki, 2011). Physical deposition and re-suspension of particulates are obvious modes of phosphorus transfer between the water column and bed

sediments; but direct adsorption/desorption processes between the two compartments are also important and will depend on the equilibrium phosphorus concentration of the sediment (Pagliosa *et al.*, 2005).

1.4 Sources of phosphorus in river basins

Phosphorus enters rivers not only from diffuse catchment sources (particularly agriculture) but also from point (e.g. sewage treatment works effluent) sources. However, river systems have an important internal capacity to remove or release phosphorus from/into the water column and to transform phosphorus between organic, inorganic, particulate and dissolved forms (Jarvie *et al.*, 2005) which has important influence on the longer term nature of phosphorus-related problems in river and estuarine systems.

1.4.1 Point sources

Point sources are related to activities where wastewater is routed directly into receiving water bodies by, for example, discharge pipes; and where sewage treatment tends to be continuous, with little variability over time, they can be easily measured and controlled (Carpenter, 1998). Historically, attention has focused more on point source pollution than non-point sources (Dougherty *et al.*, 2004), largely because it has been easier to tackle and regulate. For example, point source pollution has been greatly reduced in comparison to diffuse (agricultural) sources (Jarvie *et al.*, 2005). This is because point pollution sources are easily identified, measured, collected and treated at the source (Stutter *et al.*, 2008). Even so, water quality problems remain. As further point source control becomes less cost-effective, attention is now being directed towards the contribution of agricultural non-point sources to water quality impairment (Sharpley *et al.*, 1999).

1.4.2 Non-point source pollution

Non-point source (NPS) or diffuse pollution is one of the major causes of water quality impairments relating to nutrients, which is generally linked to agricultural activity (e.g. irrigation and drainage, applications of pesticides and fertiliser, runoff and erosion) (Ribaudó *et al.*, 2001; Defra, 2007). The dominant sources of NPS pollution is derived from agriculture e.g. pollutants nutrients, sediments, and pathogens, which are driven by hydrological processes that lead to runoff of nutrients, sediment, and pesticides (Kao *et al.*, 2001). These sources are much more difficult to measure and regulate, because they originate from a variety of diverse sources (e.g. agricultural production) dispersed over wide area of land and variable in time and space due to effects of weather and the hydrologic cycle (Rwatabula, 2007). Pollution sources are often located over a large geographic area and are not readily identifiable (Loague & Corwin, 2005). Therefore, assessment and quantification of pollution NPS sources and their contribution to chemical loads to surface waters are an important aspect of remediation, monitoring, and control of water quality. An important issue to consider also is the role of sediment in non-point source pollution especially in context of phosphorus. Sediment-associated phosphorus inputs are the subject of much concern, due to the potential for phosphorus stored in sediments to become a future source of available phosphorus to plants and algae or, due to release into the water column, have a future detrimental impact on future water quality (Kaiserli *et al.*, 2002). This is due to phosphorus quickly associating with sediment, thus enabling phosphorus to persist in the environment for many years (Donnelly *et al.*, 1998). The study of sediment behaviour and input and storage dynamics is, therefore, a key factor which is required to support understanding of the P cycle in rivers and estuaries.

1.5 Sediment quality problems

1.5.1 Fine sediment as a vector for phosphorus transport

Sediment is a key factor in water quality assessment. Desorption-sorption processes lead to accumulation of various pollutants in the bottoms of rivers or estuaries through their interaction with the sediment (Kim *et al.*, 2003). Release and storage of pollutants from fine sediment to the overlying waters depends on physicochemical processes (Wang *et al.*, 2013). Similarly, it is now apparent that sediment-associated phosphorus constitutes a variable but long-term source of potentially bio-available phosphorus in freshwater (Sharpley *et al.*, 1992), as through desorption transformations which occur between the particulate and soluble forms, it has the potential to contribute significantly to the eutrophication of surface waters, which, as outlined earlier, can lead to the degradation of aquatic habitats and reduced ecological biodiversity. The fine sediment fraction (<63 µm) is considered to be the most important fraction for P adsorption and it is widely accepted that as grain size decreases, trace element concentrations increase (Owens, 2008). The finest sediment therefore is the fraction to which most phosphorus will adhere. McComb *et al.* (1998) noted that clay and silt particles in suspension and on the channel bed had higher P content due to their larger surface area and higher capacity for phosphorus adsorption. Many studies have shown that suspended sediment and sediment deposited on floodplains and channel beds can play an important role in the flux of PP and dissolved P concentrations through river systems (Owens and Walling 2002, Walling *et al.*, 2003). Therefore, sediment suspension with pollutant desorption presents a problem because the sediments act as a source of pollutants to the water (Kim *et al.*, 2004; Donnelly *et al.*, 1998; Lopez *et al.*, 1996). For example, many studies have shown P exchange between the water column and the sediment layer

with biochemical and physical reactions such as ion exchange, adsorption, and precipitation (Figure 1.1) (Kim *et al.*, 2003; Monbet *et al.*, 2009). As a result of chemical changes, pH, temperature, and redox potential permit transformations from the particulate to the soluble phase, which promote eutrophication (Haggard *et al.*, 2005; Jarvie *et al.*, 2005).

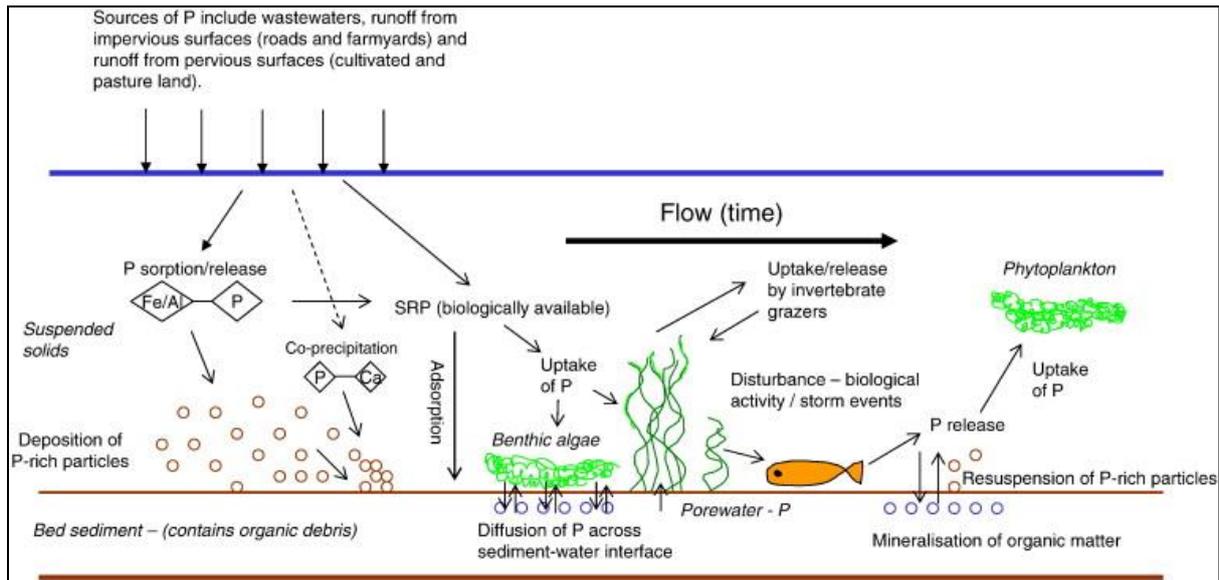


Figure 1.1 Conceptualised diagram of in-stream processes influencing P concentrations in flowing waters (Withers & Jarvie, 2008).

1.6 Policy drivers for improved knowledge of P in estuarine sediment

The European Water Framework Directive (WFD; 2000/60/EC) establishes a framework for the protection of water resources including inland surface waters, transitional (estuarine) waters, coastal waters and groundwater. The concept of the WFD has focused on the control of detrimental environmental impacts of point source pollution meaning the relative importance of diffuse inputs has increased (Foster *et al.*, 2003). The European Water Framework Directive has led to several catchment management initiatives in the UK (e.g., Catchment Sensitive Farming) that will continue to address agriculture as a primary source of phosphorus inputs to

surface waters. Although it is anticipated that this will reduce the effects of phosphorus on a river system, the WFD did not initially reflect on the possible role of sediment sinks as a secondary source of phosphorus (Collins & McGonigle, 2008; Irvine *et al.*, 2005). Existing studies of phosphorus pollution suggest that several years may pass before the effects of best management practices translate into measurable improvements in water quality (Howden *et al.*, 2009). Such time lags reflect the accumulation of high levels of P in sediment and the complexity of phosphorus redistribution through catchments due to storage and remobilisation at intermediate locations between primary sources and catchment outlets (Boesch *et al.*, 2001; Wang *et al.*, 2002; McDowell *et al.*, 2003). Likewise, sediment control strategies must be underpinned by a sound understanding of sediment sources and budgets at catchment scale (Collins *et al.*, 2001). It is necessary, however to know how such interventions are likely to influence estuarine hydrodynamics and sediment transport processes in order to then assess important management aspects such as the likely effects upon an estuary's ecology and sedimentation for example, potential accretion and dredging requirements, as these might affect the stability of phosphorus stored in the sediment column.

1.7 Project aim and objectives

The aim of this thesis is to evaluate the role of estuarine sediment sinks as stores of particulate phosphorus (PP) and, hence, potential future sources by addressing current knowledge gaps in PP delivery and storage in estuaries using a series of work packages. Each work package has a separate aim and set of objectives, which are shown below and these form the basis of the main results chapters as standalone but integrated work packages.

1.7.1 Work package 1:

Aim 1: To quantify the sediment input dynamics to a typical agricultural estuary and estimate the amount of sediment that leaves the river basin.

Objectives:

- (i) Quantify the input of sediment to the estuary system by measurement of sediment load in the freshwater channel. This is done by using high-resolution monitoring of river flow and suspended sediment concentration using in-situ monitoring equipment and storm event samplers.
- (ii) Explore temporal patterns in sediment delivery and explore the main factors that control these.

1.7.2 Work package 2:

Aim 2: evaluate the spatial distribution of fine sediment, key physical properties and concentrations of associated phosphorus in the study estuary.

Objectives:

- (iii) Characterise and delimit areas of fine sediment deposition using aerial photographs, field observations and GPS surveying to define distinct sediment depositional geomorphic units.

(iv) Collect representative sediment samples from each unit and analyse these for particle size, total organic carbon and fine (<63 µm) sediment-associated phosphorus.

(v) Create a GIS model of the Avon estuary to explore spatial patterns in key sediment properties and relationships between these and PP concentration.

1.7.3 Work package 3:

Aim 3: To evaluate the role of the study estuary as a fine sediment and PP storage zone.

Objectives:

(vi) Quantify fine sediment and PP inputs by using the river sediment load data and estimated PP concentration in suspended sediment. This will build upon information developed in objective (i) for sediment load and with addition of data from suspended sediment samples and previous studies to estimate the annual PP input into the estuary.

(vii) Quantify total mass of fine sediment and PP currently in storage in the geomorphic zones defined in objective (iii) using the geometry of cross-sectional transects to estimate the mass of sediment and extrapolating these between transects to estimate the total mass of sediment in storage.

(viii) To contextualise the total sediment and PP storage estimates within an estimate of the annual sediment and PP budget for the estuary by using annual sedimentation rate data for each storage zone from previous study and using PP input concentration in suspended sediment.

1.8 Thesis structure

The thesis is organized into seven chapters and three appendices.

Chapters 1 to 2 provide the rationale for the study and give an overview of the main problem; responses of phosphorus and sediment associated phosphorus; the role of policy to resolve the problem of the water quality. Chapter 3 provides an overview of the study experimental design focussing on the interlinked nature of the work package objectives and the main detail of the study site which is supplemented by specific detail as required within each results chapter.

Chapter 4 addresses aim 1 focusing on the relationship between temporal and spatial rainfall dynamics and discharge and sediment load based on a 2 year river monitoring programme.

Chapter 5 directly addresses aim 2 by examining of the spatial patterns in sediment grain size, total organic carbon content and phosphorus concentration in the estuary based on detailed field sampling.

Chapter 6 presents analyses and discusses sediment and PP storage data and attempts to set this in the context of an estuarine sediment budget. of phosphorus and sediment volume.

Chapter 7 provides a synthesis of the work and recommendations following this research are provided. The knowledge acquired and techniques developed are described and evaluated together with some comments regarding field and model limitations, with some suggestions for future research.

Chapter 2: Phosphorus sources and transport in river catchments and estuaries

This chapter explores factors controlling nonpoint sources of pollution and their typical transport and eventual entry to and storage within the river and estuary system.

2.1 Mobilisation and transfer of phosphorus from the catchment to the channel

The pathway of phosphorus transfer from agricultural soil to the fluvial system can be linked by soil erosion and runoff processes; runoff and soil erosion processes drive phosphorus input to surface water from agricultural land. Thus, this phosphorus delivered from the land to streams and rivers, and ultimately the estuary, could be transported to surface water in solution or with sediment movement. Dissolved phosphorus transported in runoff can originate from the release of phosphorus from soil material or vegetative material that interacts with rainfall. Particulate phosphorus is associated with soil and vegetative material eroded during runoff (Sharpley *et al.*, 1995; Gentry *et al.*, 2007). In most cases, particulate phosphorus is the dominant form of phosphorus lost (Heathwaite & Dils, 2000). For example, Sharpley *et al.* (1995) concluded in USA that 60-90% of phosphorus input by land runoff to the stream transported from agricultural soils is in the particulate form. The major factors affecting the load of phosphorus in surface runoff from agricultural land include the duration, amount and intensity of rainfall, slope, soil texture, the nature and distribution of soil phosphorus, phosphorus fertilizer history, cropping practice, crop type and crop cover density (Withers & Lord, 2002; Zaimes & Schultz, 2002). When rainfall exceeds infiltration capacity or the soil is saturated, overland flow begins and phosphorus will move downslope within soils in solution or with sediment (Sharpley

et al., 1995; Reddy *et al.*, 1995; Amano *et al.*, 1999; Sharpley *et al.*, 2001; McDowell *et al.*, 2003; Kronvang *et al.*, 2007).

For example, Shigaki *et al.* (2007) observed in the southwest of England that with an increase in rainfall intensity, there was an increase in PP loss from 0.02 to 0.3 kg ha⁻¹ y⁻¹ while Withers and Hodgkinson (2009) reported that the mean phosphorus yield was up 6 kg P ha⁻¹ y⁻¹; Also, Sharpley *et al.* (1995) in the USA found that the yield of phosphorus from an agricultural catchment was estimated to be between 0.2 - 4.6 kg P ha y⁻¹.

In a UK context, the most phosphorus transportation occurs during the winter season as rainfall increases and runoff is enhanced, when soils are fully wetted; and under these conditions, phosphorus will be transported during a few major storm events within the year. Indeed, in a UK case study on agricultural land, Withers and Jarvie, (2008) showed that export of phosphorus from a field drain was largely restricted to the main period of flow (December to April).

It is known that the spatial distribution of sediment sources is not uniform across catchments; and hence not every field in a catchment should be regarded as a source area for sediment and its associated phosphorus load. Furthermore, not all sediment that is detached and transported from its source area will be delivered to the river channel system (Walling 1983; Ballantine *et al.*, 2009). Instead, the most critical source areas for sediment-associated phosphorus in catchments will be hydrologically active areas that intersect easily erodible zones, where soil phosphorus concentrations are high; therefore source areas are generally considered to be frequently concentrated in relatively small, definable areas located close to the river network (Russell *et al.*, 2001; Pionke *et al.*, 2000). As evidence to

support these ideas, McDowell & Sharpley (2002) found that when manure was applied to fields that were relatively far from the stream network, the sediment-associated phosphorus content in runoff decreased as distance travelled increased, so that when the runoff and its sediment load arrived at the stream, its phosphorus content was reduced sufficiently for it not to be a threat to the water quality in the stream. The runoff transporting sediment from more distal parts of the catchment may not possess sufficient energy to convey the mobilised sediment from the source to the river system due to the large distances frequently involved and influence of sediment storage zones.

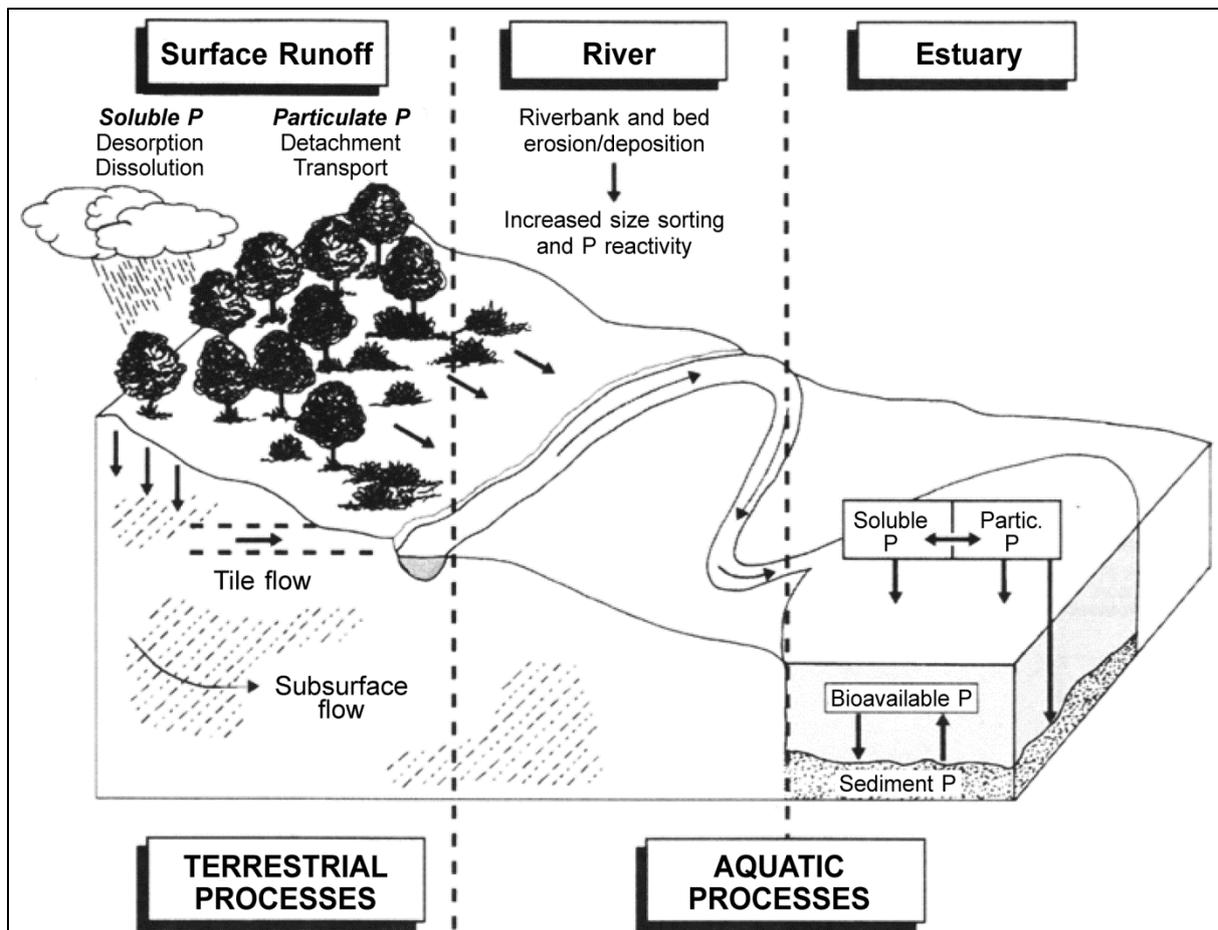


Figure 2.1: A conceptual diagram for the movement of phosphorus from land to estuary sediment sinks (Zaimes & Schultz, 2002).

2.2 Transport of phosphorus to estuaries by fluvial processes

Rivers are the main source of P to estuaries and coastal water (Figure 2.1). Most of this P is in form of particulate phosphorus (PP) (McLusky & Wolanski, 2011). Many recent investigations have shown that a large proportion of the PP load in rivers can be transported in association with sediment (Hartzell, 2009).

Understanding the variability in hydrological and geomorphological processes within catchments is an important precursor to exploring the gross outputs of water and sediment from the system. Temporal and spatial variability of rainfall and runoff response and the spatial variability of soil characteristics are key considerations (Seeger *et al.*, 2004) and owing to the complexity of these factors and their interactions, it is often difficult to find general rules that explain or predict how rainfall generates runoff, erosion and sediment transport (Gallart *et al.*, 1998; Lorente *et al.*, 2000; García-Ruiz, *et al.*, 2000). The hydrological response of a catchment is influenced by e.g., soil properties, land use, and topography, but it is also related to individual rainfall events, runoff processes and preceding conditions (Latron *et al.*, 2008). Different approaches have been used to classify the controls on hydrologic response. Hewlett & Hibbert (1967) and Woodruff & Hewlett (1970) studied rainfall–runoff relations at the event scale to define a factor of catchment hydrological response at the annual scale. Hewlett *et al.* (1977, 1984) and Hewlett and Bosch (1984) used this approach to demonstrate the role of rainfall intensity on the magnitude of the hydrological response of forested catchments. Cappus (1960) explored the relation between the storm-flow coefficient (i.e., the ratio between storm-flow and rainfall volume), rainfall depth and base flow to show the hydrological role of saturated areas within a catchment. Taylor & Pearce (1982) concluded that the storm-flow volume always correlates with rainfall amount but with varying

degrees of scatter. The scale effect of the runoff coefficient was investigated by Cerdan *et al.* (2004) in an agricultural area catchment in Normandy, while Peters *et al.* (2003) explored the relations between storm-flow, rainfall depth, water table and soil moisture dynamics in a catchment in USA. Recently, Angulo-Martínez & Beguería (2009) estimated the rainfall erosivity from daily precipitation records of the Ebro basin (Spain), and their results showed that such investigations should include kinetic energy and rainfall intensity, and their effects on the soil, as controlling factors.

The stronger relationships between rainfall and runoff may only be appropriate for short wet periods during the year as a function of the antecedent wetness of the catchment, the storm duration and the pattern of rainfall intensities. A number of the studies providing examples of the non-linearity between rainfall and runoff at the event scale have explained this as being due to the combination of the high seasonality of the climate and the generally high spatial heterogeneity of the environment. For instance, Àvila (1987) examined the seasonal hydrological response of a very small catchment in Spain, Piñol *et al.* (1997) showed the non-linearity of the rainfall–runoff relations during a wetting-up period in two paired research catchments in the Prades region of Catalonia, Spain due to the hydrograph responses of the catchments are controlled by subsurface flows. Zehe *et al.* (2005) observed that spatially variable precipitation in Weiherbach catchment south West Germany affects rainfall-runoff relation.

Ceballos & Schnabel (1998) found two different rainfall–runoff relationships, depending on the existence of saturated conditions in the valley bottom, and finally, long-term (>20) years) studies in the Vallcebre (Spain) research area, provided

insights into several aspects of catchment hydrology which is the rainfall–runoff relationship at seasonal and monthly scale, storm-flow volume and coefficient, the temporal variability of the rainfall–runoff relationship and its relationship with several hydrological variables. (e.g., Gallart *et al.*, 2002; Latron *et al.*, 2008).

Soil erosion, and thus subsequent sediment transport in alluvial channels, is the main geomorphic consequence of the runoff resulting from rainfall inputs in river basins. Kinetic energy from the rainfall increases surface runoff in the drainage network that will ultimately be responsible for the transportation of sediment yield to the basin outlet. The occurrence and intensity of erosion and sediment transport will depend on the hydroclimatic and geomorphologic characteristics of the basin, together with the availability of sediment within the catchment (Krishnaswamy *et al.*, 2001).

The transport of fine material in suspension is the major transferring mechanism of particulate material in streams worldwide (Webb *et al.*, 1995). Typically attaining more than 90% of the annual load of alluvial streams comprises fine material transported in suspension (Duvert *et al.*, 2010, López-Tarazón *et al.*, 2009, Webb *et al.*, 1995). For this reason, total sediment yields at the catchment outlet are often based purely on suspended load data (López-Tarazón *et al.*, 2009), which is also more relevant to the environmental quality investigation (Schoellhamer *et al.*, 2007).

The link of sediment flux to phosphorus flux is noted in many studies. For example, in Southwest Finland, it was shown that the bulk of total annual P flux (71-94%) in the Aurajoki catchment dominated by arable land use was particulate phosphorus (PP). Similarly, in a study undertaken in the Lake Tahoe basin, in USA, it was discovered that up to 94% of TP load was PP e.g. Hatch *et al.*, (2001); and Kronvang

(1992) showed that the particulate fraction made up 66% of the TP load in Denmark in the heavily impacted agricultural catchment of the Lynbygaards River. In the UK, Walling *et al.* (1997) reported that sediment-associated phosphorus transport accounted for up to 75% of the TP load in the Culm, Devon River; while Bowes *et al.* (2003) suggest that the particulate fraction in the UK can account for 76% of the phosphorus load based on their studies in the Swale catchment.

As alluded to above, the temporal dynamics of PP transfer are often concentrated in a few major events during the year. Jennings *et al.* (2003) demonstrated from measurements of suspended sediment load that the highest (56%) sediment transport in the river took place during winter storm events and that the lowest (4%) sediment transport was during the summer period. Furthermore, in New Zealand McDowell & Wilcock, (2004) found that during the summer, much of the sediment was stored in the channel bed and that these loadings were generally highest in summer 2228 mg TP kg⁻¹ and lowest in winter 711 mg TP kg⁻¹.

The relationship between discharge and suspended sediment concentrations, nonetheless, is difficult to define, as sediment transport is supply-controlled; and once sediment stores have been exhausted, further increases in discharge may not lead to further increases in suspended sediment loads.

In freshwater, sediment-associated P undergoes physical and chemical processes and it can move between sediment and water phases (Taylor & Boulton, 2007). In their study of PP association with sediment in Fitzroy catchment in central Queensland, Australia, Webster *et al.* (2010) found that phosphorus loading was adsorbed to clay within the sediments and it was released from river bed sediments slowly. While this

process has been reported to take a long period of time (Povilaitis, 2004; Bostrom *et al.*, 1988), phosphorus release may exceed phosphorus sedimentation for periods of weeks or months depending on supply dynamic and in certain conditions also on an annual level, this depend on oxygenated sediment retain phosphorus by fixation to iron (III) (Bostrom *et al.*, 1988; Hartzell, J.L. 2009).

Phosphorus release and uptake from sediments, either in suspension or in channel bed storage, to river water is commonly discussed in connection with certain controlling environmental factors. Transformations will occur generally when a number of the factors interact together to produce the environmental conditions needed to stimulate either the release or uptake of phosphorus (Kleeberg & Kozerski, 1997; House & Denison, 1997) and are the result of a combination of the increase in temperature, ensuing increased microbial activity, reduced oxygen and increased pH (Baldwin *et al.*, 2001). The physical properties of sediment will also have an important influence on its capacity to adsorb and desorb phosphorus; two important factors documented are, particle size and major ion chemistry. However, there is a positive correlation between phosphorus concentrations and particle size, due mainly to the increase in surface area associated with a decrease in particle size. The finest sediment, therefore, is the fraction to which most phosphorus will adhere (Owens & Walling, 2002) and particle size is a key factor to be explored in any study of phosphorus and sediment association.

2.3 Sediment and phosphorus storage in estuaries

There are many ways in which estuaries have been defined, but by their very nature, are places of transition between land and sea (Figure 2.3); no simple definition

readily fits all types of estuarine system. Perhaps the most widely used is that proposed by Mead *et al.*, (2004): “an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors: (a) a marine or lower estuary, in free connection with the open ocean; (b) a middle estuary, subject to strong salt and fresh water mixing; and (c) an upper or fluvial estuary, characterised by fresh water but subject to daily tidal action.”

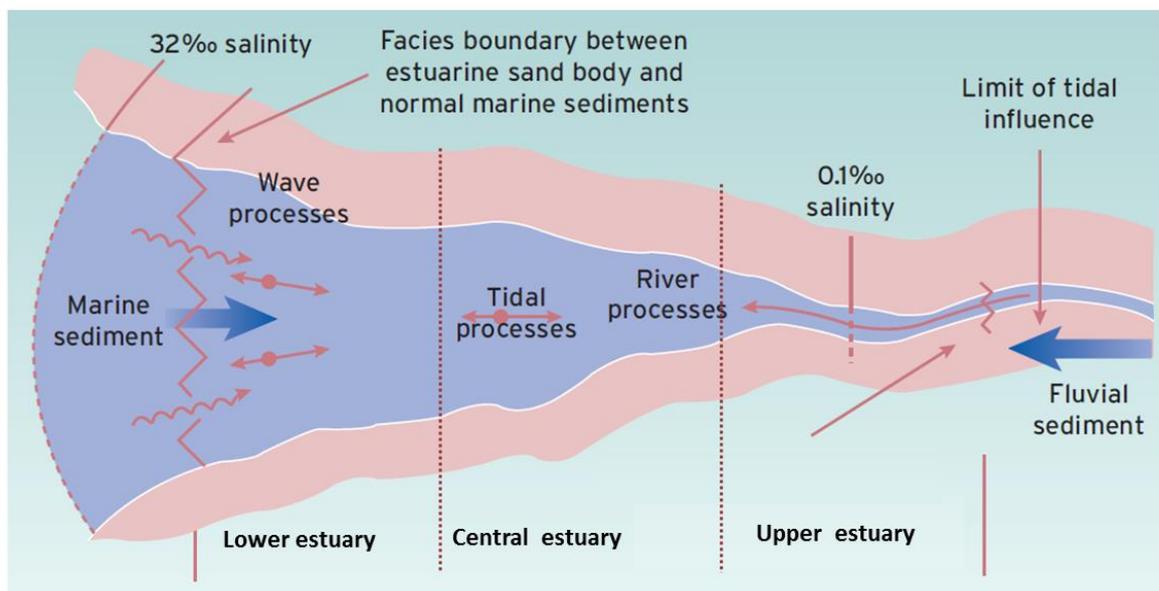


Figure 2.3: Schematic diagram of an estuary showing division into different regions (Masselink *et al.*, 2011)

In addition to determining what an estuary is, it is also necessary to consider the inner and outer limits of an estuary and the process and morphological controls on fine sediment deposition and storage dynamics. Estuaries can be described as a water bodies or basins with the marginal areas around the edge which are flooded by the tide and storm events. Water basins can assume different forms such as bays, inlets, lagoons and tidal rivers. The marginal areas include the tidal flats and mudflats; tidal salt marshes and mangroves; the upper wetlands, which are high-marshes flooded only by extreme spring tides. An estuary system can be considered

the seaward extent of a catchment that drains directly into the estuary by rivers and streams, but can also include open-coast marine systems in which the estuary is a link in the open-coast system; these systems have a major influence on the mixing of fresh and salt water in an estuary (Pierson *et al.*, 2002) and hence important influence on sediment storage dynamics. When the freshwater flows into the estuary, mixing of the fresh river water and the salt water in the receiving basin occurs. Mixing of the two water bodies depends on the velocity and density of the two masses (Pierson *et al.*, 2002) and based on these processes, three types of estuaries can be identified: (1) salt wedge estuaries; (2) partially-mixed estuaries; and (3) well-mixed estuaries (Figure 2.4).

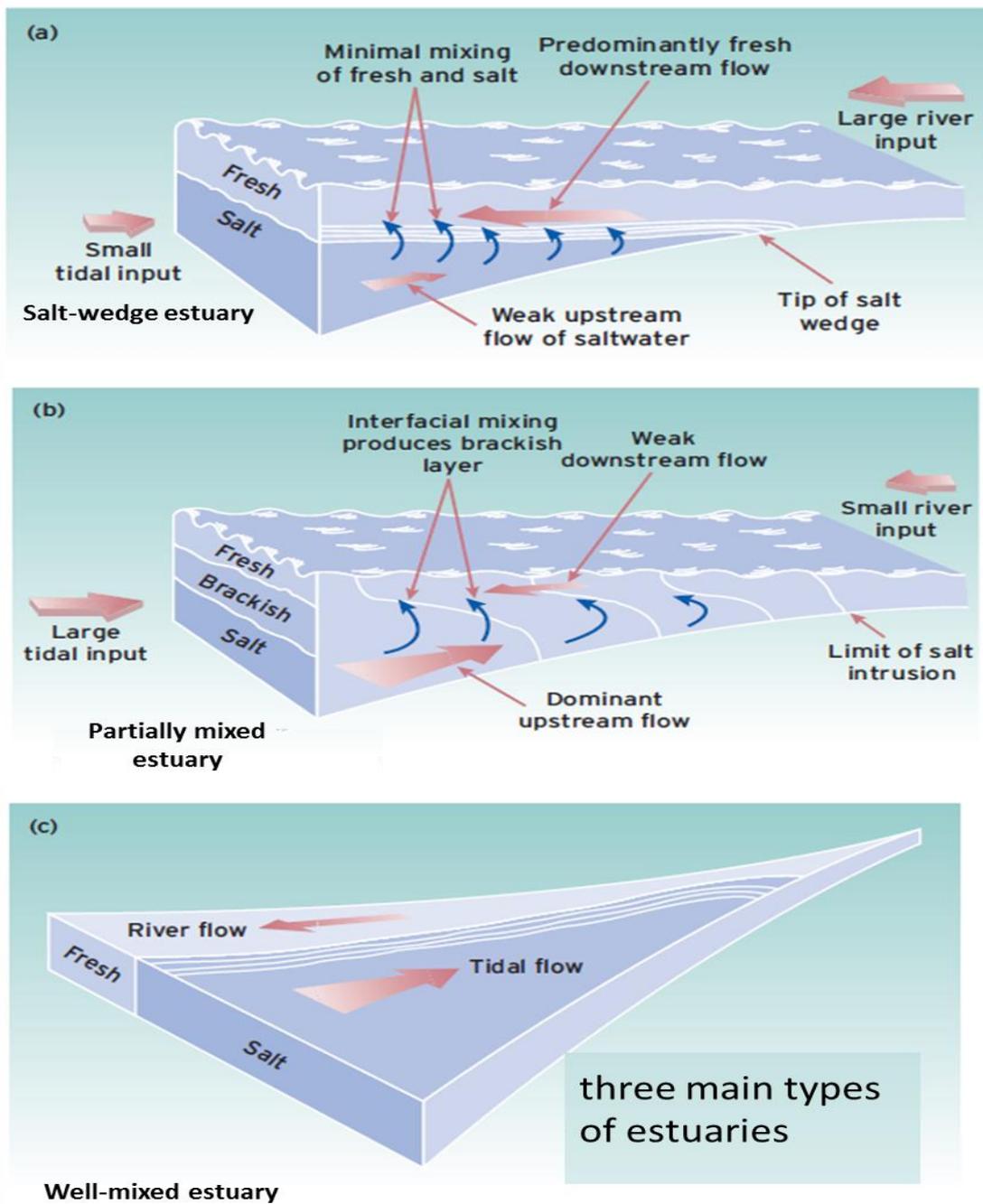


Figure 2.4: Diagrammatic representation of the three main types of estuaries: (a) stratified; (b) partially mixed; and (c) well-mixed estuary (Masselink *et al.*, 2011)

In an estuary with a large fresh water inflow and a low tidal range, the river flow tends to move over the top of saline water intruding from the sea due to the lower density of the river water. In the seaward direction from the point of fresh water entry, tidal effects become more important. The estuary may act like a salt-wedge estuary

during fluvial floods, but under low river flow conditions, the same estuary is mainly influenced by tides and tidal currents. Then, the salinity structure departs substantially from the pattern of simple salt-wedge stratification and becomes a moderately stratified or partially-mixed estuary. In an estuary with small river flow but large tides and strong tidal currents, the waters may be mixed almost completely from top to bottom. These are called well-mixed estuaries. This mixing is unsteady, because of variations in the height and strength of the tide, especially on semidiurnal, diurnal, and spring–neap scales; and because of seasonal and storm-related changes of river discharge (Richards, 2004). Thus, different mixing states can exist in an estuary at any one moment over space and at different times at the same place. The tide, wave and river flows can each vary from being dominant to non-existent. This process is very important in controlling the circulation of fine sediment in the estuary (Dyer, 1994).

Estuaries can also be classified on the basis of the relative contribution of the three major driving forces within the short-term changes: that is, the wave-fluvial- and tide-dominated estuaries (Figure 2.5). The upper part of the estuary is always dominated by fluvial processes. This classification is only partly useful for the study site, because the estuary has features that are characteristic of both estuarine types.

Wave-dominated estuaries are distinguished by higher wave energy at the mouth compared to tide energy. In the middle of the estuary, tide-dominated salt marshes and a meandering tidal channel are present (Masselink *et al.*, 2009).

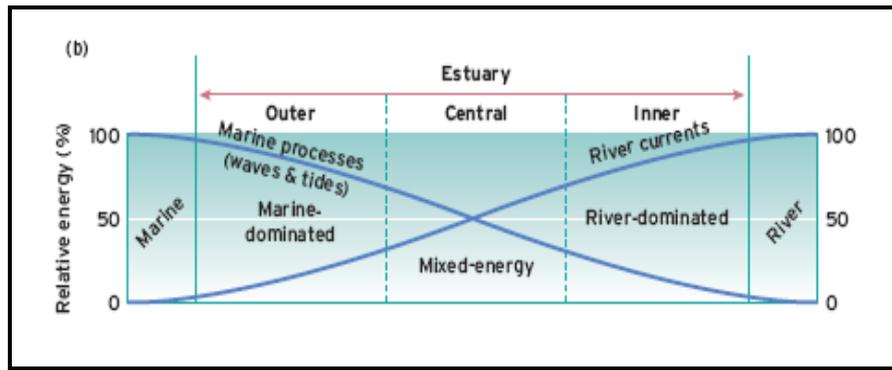


Figure 2.5: The changing mix of wave, tide and river processes along the estuary (Masselink, 2011).

2.4 Sedimentation processes and zone in estuaries

Three important physical features play a role in moving sediment inside an estuary: tides, waves and rivers (Pekar *et al.*, 2004; Uncles, 2010). The tidal currents provide a steady source of energy for sediments moving both into and out of an estuary (Uncles *et al.*, 2012). Tidal sediment transport in estuaries is a result of the interaction of both currents and waves, which is especially important in the mouth region. Inside the estuary, wave action is generally rapidly reduced. Wave-current interaction considerably complicates sediment transport predictions. However, wave action is generally much reduced inside an estuary and traditional river sediment transport equations are often applied (Taljaard *et al.*, 2009). During neap tides, maximum water velocity within the estuary is low with little sediment transport, while both velocity and transport increase towards spring tides. Fresh river water is less dense than seawater and floats over seawater (Pekar *et al.*, 2004). Therefore, when sediment that enters the estuary remains in suspension with the river water, it can be flushed out to sea quite quickly (Mead & Moores, 2004). The factors which control the concentration of suspended sediment and encourage deposition are those of flocculation (Curran *et al.*, 2004; Pejrup & Mikkelsen, 2010). Flocculation is the

physical process by which sediment particles in the water column combine and settle (Ha, 2008). It is the result of the total surface charge on the particles attracting each other much like a magnet (Dyer, 1994). Composite particles fall out of suspension and sink to the bottom as the flow meets saltwater. This is why sediment deposition is greatest near the upper reaches of the estuary. Fine grained material will tend to move in suspension and follow the flow of water. Deposition may occur at times of slack water. Coarser sediment will tend to travel along the sea bed and be affected most by high velocities in the direction of the maximum current (Figure 2.6). Retention of fine sediment is one of the most prominent features in many estuaries; and the morphological response of this sediment retention is: large areas with mudflats and saltmarsh in the upper and sheltered parts of such coastal environments.

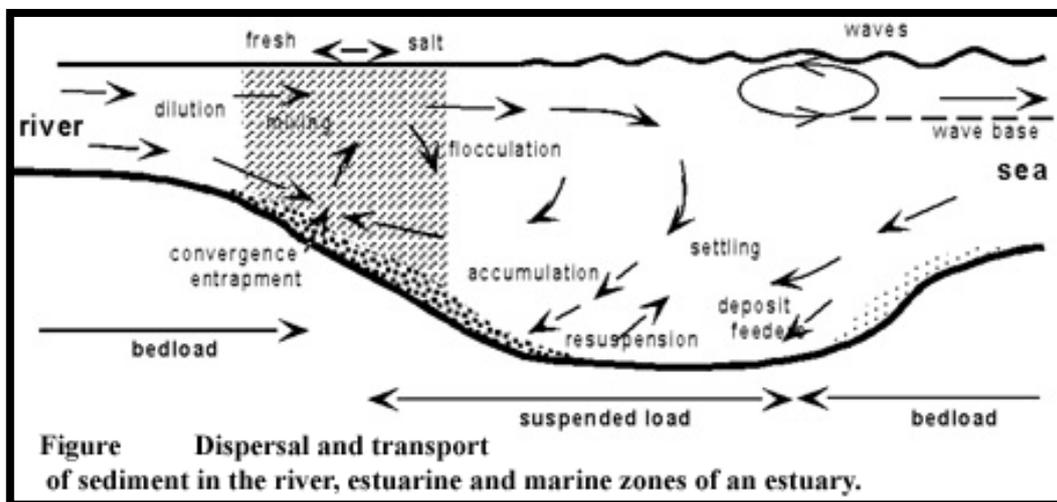


Figure 2.6: The cycle of deposition and suspension of sediment in estuaries.

2.5 Salt marsh and mudflat sedimentation dynamics

Saltmarshes and mudflats play a vital role in the accretion and storage of sediment in estuaries (Boorman *et al.*, 1998; Pejrup & Mikkelsen, 2010). These environments are typically found within sheltered bays or estuaries where the wave action and tidal currents are relatively weak, allowing for salt grass to settle and survive in the marsh (Friedrichs & Perry, 2001, Davidson-Arnott, 2002). This leads to sedimentation, which is the most important factor of a salt marsh, as without it, colonization by salt tolerant plants cannot occur. Sedimentation occurs when water movement is slowed and the suspended particles can settle. Particle size (controlled by flocculation i.e. effective particle size) and flow velocity determine how well the particle of sediment is suspended in the water. Smaller particles are more easily carried by water. Silt particles, for example, react more slowly to the velocity change and are therefore carried further in the direction of the flood (Bartholdy, 2000). These conditions allow fine sediment particles to fall out of suspension and to be deposited on the bed, creating an environment of mudflats and salt marshes (Schostak *et al.*; 2002, Hung *et al.*, 2006). The overall conclusion that can be drawn from previous studies is that increased tidal velocities increase the concentration of sediment suspended in the water and this can be further augmented by the flow conditions of the river.

Sedimentation on the marsh surface depends on various factors. Firstly, sediments carried by tidal current get deposited on the marsh surface by tidal inundation (Christiansen, 1998). Sedimentation from tidal inundation is at its maximum in the marsh located along the tidal creeks, in the direct vicinity of sediment delivery. A study by Khalequzzaman (1989) showed that the marsh within a distance of 15 – 20 m from tidal creeks received 2.8 mm/year of sediments from tidal inundation, which

was 93% of the annual required sediment to keep pace with the rising sea level of 3mm/year in Delaware Bay. Marshes away from the tidal creeks, however, received only 0.6 mm/year of sediment, 20% of annual required sedimentation, from tidal inundation.

Secondly, episodic events that inundate the marsh surface are one of the major processes by which sediments are deposited on the marsh surface. Storm inundations play a vital role in increasing sediment accumulation on the marsh surface (LeMay, 2007) especially with coincidence of high flow and suspended load in the river. Church *et al.*, (1987) found that storm events may provide sufficient sediment for marsh maintenance for a large area of the marsh, with one extreme storm depositing 30% to 165% of annual demand in a salt marsh in Kelly Island, Delaware.

Sedimentation rates are also influenced by the elevation of the marsh and its relationship to the duration of tidal flooding (Brown, 1998; Reed *et al.*, 1999). These two factors, elevation and time of inundation, are linked. As elevation is increased, the time that the area will spend inundated by the tide decreases. Therefore, the amount of sediment deposition will decrease with an increase in elevation (LeMay, 2007). A balance is required between the time in which an area is inundated and the time in which it is exposed to dry conditions. Inundation must not be too long or frequent because the chemical stress associated with water logging will prevent grass survival (Friedrichs & Perry, 2001). If inundation is too long, the result could be massive plant death due to salt intrusion or water logging. This plant death could lead to the rapid loss of elevation due to erosion forces and the reduced cohesion of the marsh sediment. The elevation loss could be in the order of 10-15 cm (Friedrichs

& Perry, 2001). Regarding the stratigraphy of a marsh in the Severn Estuary UK, Allen (1990) indicates that the rate of vertical accretion of a marsh surface is related to flood frequency of the marsh surface: the lower the marsh, the more often it is flooded and the more rapidly it increases in elevation. Cahoon & Reed (1995) show that the amount of sediment deposited on a Louisiana marsh is proportional to increased inundation time of the marsh surface; and French & Stoddart (1992) observed large increases in suspended load on tides of higher elevation. Allen (1990) hypothesizes that a relationship exists among marsh elevation, relative tidal elevation and rate of organic matter accumulation. In the extreme case of the marsh having accreted to an elevation where it is no longer flooded, 100 % of the accretion is due to organic matter accumulation. Allen (1990) does not account for the possibility of organic matter deposition from exterior sources, suggested by Cahoon & Reed (1995) to being an important contribution to organic matter accumulation on the marsh. Vertical accretion in the Hut Marsh, England, was found to vary between 8 mm/year in low areas of the marsh to 1 mm/year in higher inland areas.

The third factor that influences sedimentation on the marsh surface is vegetation type and density, which affects the sediment movement and settling on the marsh by reducing flow velocities. The total of sediment deposition has been frequently increased as more of the incoming sediment is intercepted and trapped, as the increased surface area of the vegetation causes an increase in friction. Consequently, increased friction will result in a reduction in flow velocities as well as the ability of the water to suspend and transport sediment (Boorman *et al.*, 1998). Another important aspect of the vegetation is that the presence of plants tends to reduce the re-suspension of the sediment in a marsh while adding organic matter to the surface of the marsh (Boorman *et al.*, 1998). At low flow velocities, retardation of

water flow by vegetation is proportional to vegetation height; but, with increasing water flow velocities, retardation of tall vegetation can be less than that of short vegetation (Boorman *et al.*, 1998). Mudflat areas are more complex in the behaviour of these environments (Deloffre *et al.*, 2007; Tomchou Singh & Nayak, 2009).

2.6 Particulate phosphorus storage

There is an increasing awareness of the environmental significance of fine sediment, particularly its ability to act as a sink of phosphorus into estuary systems (Berner & Rao, 1994; Zhang *et al.*, 2001; Araújo *et al.*, 2002; Jarvie *et al.*, 2005). Phosphorus has a very great affinity for fine sediment and when it is stored in the sediment it may be increased or decreased in concentration, depending on the conditions in the aquatic environment (Owens & Walling, 2002; Monbet *et al.*, 2009; Webster & Ford, 2010). Owens & Walling (2002) give details of spatial variations in TP content of sediment in different UK Rivers; they found the role of the grain size to be very important. The <63 μm fraction as critical to the transport and storage of nutrients, especially phosphorus. However there has been relatively little research on the storage of nutrient enriched fine sediment in UK estuaries, in particular patterns in phosphorus concentration within and between estuarine geomorphic units.

Fine sediment storage dynamics are complex and storage times can range from event time scales to decades. It is important to take into account the influence that the physical properties of sediment will have on its ability to distribute within the estuarine system (Reddy *et al.*, 1999; Shen *et al.*, 2008). It is well known that the spatial distribution of sediment grain size is not uniform along an estuary (Nitsche *et al.*, 2007), and not every zone in an estuary should be regarded as a sink area for

fine sediment. Since specific geomorphic units tend to have a particular sediment particle-size distribution, an evaluation of the spatial variability of phosphorus concentrations must, therefore, take into account the influence of geomorphic variation (Zhang *et al.*, 2001).

The spatial variations and transport of fine sediment are influenced by physical and hydrodynamic processes such as tidal dynamics, wave energy, river flow and sediment load, and flocculation dynamics that control sediment transport and deposition in the system (Nichols & Biggs, 1985; Dalrymple *et al.*, 1992; Bird, 2000; Masselink *et al.*, 2009). Consequently, a spatial pattern of sandy sediments near the mouth of the estuary, muddy sediments in the central section and coarser sediments with fine sediment within interstices in the fluvial-dominated upstream section of the estuary are typically observed (Nitsche *et al.*, 2007). The areas with low hydrodynamic energy will define the accumulation of fine sediments due to enhanced settlement of silt–clay particles. By contrast, areas exposed to higher hydrodynamic energy levels will be characterised by coarser sediments (Ergin & Bodur, 1999; Magni *et al.*, 2002). Moreover, the deposition of the fine mud fraction may occur within sediments due to interaction between currents, tides and salinity. Estuaries, therefore, represent a restricted exchange environment that can act as a sink or a source of sediment and sediment associated phosphorus transported to the aquatic environment (Rainey *et al.*, 2003).

As phosphorus has a strong association with sediments, the adsorption and desorption of phosphorus from sediments are two of the main processes that regulate the behaviour and concentration of phosphorus in an aquatic system

(McDowell & Sharpley, 2002). While large sediment particles including sand may be very important from a morphology perspective in an estuary, they play a lesser role in contaminant fate and transport. According to Grant & Middleton (1998), the influence of grain size on concentrations of P in sediments is well known. If the influence is not taken into account, apparent contamination differences between sites may reflect grain size rather than the extent of contamination; and samples may be grouped together purely because of similarity of sediment texture.

One approach to avoiding this difficulty involves the initial removal of coarse particles, prior to the chemical analysis of the fine fraction of the sediment (Owens & Walling 2002). Separation of the fraction <63 μm is reasonably straightforward but often does not fully remove grain size effects. The more effective procedure of separating the fraction <20 μm is rather time consuming. For these reasons, many authors have preferred to adopt some method of normalising contaminant concentrations measured in the whole sediment. This may be done using concentrations of P, and organic carbon content, or the proportion of the sediment smaller than 63 μm (Martinez *et al.*, 2009; Roussiez *et al.*, 2005). Transformations may occur within sediments when in storage in the estuarine system and much research has been carried out to examine phosphorus transformations at the water sediment interface (Dorioz *et al.*, 1989; Bowes *et al.*, 2003; House *et al.*, 1998; House, 2003; House & Warwick, 1999; Kim *et al.*, 2004). Such studies show that phosphorus is a very volatile element and once stored, its concentration may increase or decrease depending on the conditions in the aquatic environment; it is restricted to the organic fraction of phosphorus (Bostrom *et al.*, 1988; Sanei &

Goodarzi, 2006) and adsorption and desorption can be a rapid process (Scarlatos, 1997).

From the above discussion, the increasing concern surrounding fine sediment-associated phosphorus in an estuary has been demonstrated. Against this background, there is a clear need for improved understanding of the distribution of fine sediment which can provide an important insight into the understanding of the fate of sediment bound phosphorus storage in key estuarine sedimentary environments.

In the same way as sedimentation dynamics are recognised as being an important factor in environment area development, due to the accumulation of fine sediment over time, deposition of fine sediment on the saltmarsh and the mudflat area also permits the accumulation of phosphorus, carried in association with sediment. Such deposition of phosphorus on the saltmarsh and mudflat areas presents a significant environmental issue, both in terms of its potential for contaminating the deposit area and for its further remobilisation and reintroduction into the estuary system, either through channel migration and physical disturbance or through desorption reactions. Elevated suspended sediment loads at times of high flow are transported in the river and are often made up of sediment enriched by phosphorus that has been subject to accumulation and storage with subsequent enrichment transformations on the deposition environment area. Continued deposition over time with accumulation leads to an increase in the total phosphorus stock within the sediment column, which again highlights the role of estuaries as significant sinks for sediment-associated phosphorus. Venterick *et al.*, (2003); Seitzinger (1988) & Haygarth *et al.*, (1998)

have shown that phosphorus retention in the estuary environment can account for up to 45-60% of the total phosphorus load which has come from the river. In contrast, recent studies have demonstrated variable numbers in estuarine phosphorus retention, ranging from low values of 1 to 9% (Nielsen *et al.* 1995, Nedwill & Trimmer 1996, Nowicki *et al.* 1997, Trimmer *et al.*, 1998, Mortazavi *et al.*, 2000); to moderate values of 10 to 30% (Nixon *et al.* 1996, van Beusekom & de Jonge 1998); or to even higher retention values of $\geq 50\%$ (Seitzinger 1988, Wulff *et al.* 1990, Kamp-Nielsen 1992, Boynton *et al.*, 1995). Physical processes cause large variations in the concentrations of particulate P in estuaries (Stone & Droppo, 1994). The main transport mechanism of P to sediments is the settling of particulate matter; although influx of dissolved P to sediment may also occur (Conley *et al.*, 1995). Studies by Yarbro (1983) have examined the fate of such phosphorus and the principal conclusion appears to be that uptake by plants is limited and the majority of the phosphorus remains in the sediment. The flux of P into sediments occurs when P enters the estuaries and internal processes affect the cycling of P in both water and sediment (Sundby *et al.*, 1992; Mathews, 2000). The variety of processes in estuaries not only influences the total concentration of phosphorus (the higher the phosphorus content, the higher the flux); but also how phosphorus is associated within various particle-bound phosphorus phases (Conley *et al.*, 1995; Jin *et al.*, 2006).

Particulate phosphorus, in many PP environments, is largely buried and lost from short-term circulation. However, it is important to look at the differences of P forms because their differences in adsorption-desorption reactions, transportation and potential bioavailability to aquatic organisms could lead to increased eutrophication

in the aquatic system if the nutrient is released in the future (Compton *et al.*, 2000; Hartzell, 2009; Zaimes & Schultz, 2002).

Although PP is often not readily bioavailable due to the complexity of its chemical and physical binding with sediments, the variable conditions found in aquatic systems, especially pH and dissolved oxygen can result in the release of P into solution. PP may, therefore, be an important intermediate to long-term storage of P within standing waters and is of particular concern in the eutrophication issue. Hence, it is important to quantify storage of PP in the sediment sink zone of rivers and estuaries affected by agricultural activity.

2.7 Sediment and phosphorus budgets in river and estuary systems

There is an awareness of the role played by estuaries as sinks for sediment; and that sediment builds up and persists on the main deposition area. With an awareness of these problems, a number of studies have been undertaken which have documented the accumulation of sediment over time, as shown by analysis of sediment cores (Patchineelam *et al.*, 1999; Townend & Whitehead, 2003; Blaas *et al.*, 2007; Hu *et al.*, 2009; Liu *et al.*, 2002; Wu *et al.*, 1999). The results from these studies indicate that sediment supply to the estuary is determined by catchment sediment input and this sediment supply is a critical variable for investigations of habitat stability, restoration potential and contaminant fate/transport (Zedler & Callaway, 2001; Pont *et al.*, 2002; Reed, 2002; Temmerman *et al.*, 2003).

Deposition of sedimentation can result in the build-up of an area and can also accumulate sediment-associated contaminants wherever sediment is deposited (Hornberger *et al.*, 1999; Arzayus *et al.*, 2002; Taylor *et al.*, 2004). The deposition of

sediment in the estuary is a direct consequence of many factors including the sediment concentration of the tidal water, the distance an area is away from the source of sediment, the elevation and time of inundation, and the vegetation cover. In many cases it can be difficult to identify, let alone quantify, all the mechanisms that give rise to sediment transfers. It may, however, be possible to derive approximate estimates of the amounts moving to and from sources and sinks, based on measures such as transport potential and sediment demand (Townend & Whitehead, 2003). In effect, a budget is established and, as with any budget, the prime requirement is that it balances. For this reason, Pethick (1992) suggested a sediment audit as an approximate balance that could be carried out on a number of scales (e.g. local, sediment regional); and the relative importance of changes in supply and demand could then be assessed at the different scales being considered. Several authors have developed and applied the sediment budget concept to study the geomorphic work of high magnitude and low frequency events (Gilbert, 1917; Rapp, 1960; Schick, 1977); and to analyse the efficiency of processes operating in a basin and its relations, e.g., with the evolution of landscape forms (Slaymaker, 1982). However, the concept of sediment budget was not systematically applied as a theoretical framework until the work of Dietrich & Dunne (1978). They used the sediment budget approach to identify the most significant processes acting in the production and transport of sediment in a coastal basin of Oregon (USA). Since then, other studies following the same approach have been carried out (e.g., Lehre *et al.*, 1982; Reid and Dunne, 1984; Roberts & Church, 1986). Fluvial sediment budgets, following similar methodological approaches as the one presented here, have been carried out by Moore and Newson (1986), Kesel *et al.* (1992); McLean & Church (1999), among others: (a) Moore & Newson (1986) analysed the effects of land use

changes in two different sub catchments in Britain; (b) Kesel *et al.* (1992) provide an estimate of the sediment budget of the Lower Mississippi River prior to the introduction of major human modifications, dividing the study channel into 124 single reaches of similar length; and (c) McLean & Church (1999) assessed the coarse sediment transport for the lower Fraser River at three different control sections. However, few studies have identified or explored that the sediment budget of an estuary is finely balanced between the fluvial and marine exchange (Artoli *et al.*, 2008; Townend & Whitehead 2003; Patchineelam *et al.*, 1999; Boateng *et al.*, 2012). It is also known that nutrients, such as phosphorus, are transported in association with fine sediment; and in the estuary, sediment-associated P will also be deposited on the saltmarsh and mudflat area (Owens & Walling, 2002; Galois *et al.*, 2000). Deposition of fine sediment associated phosphorus has important implications. Firstly, it can result in the accumulation of this nutrient in the saltmarsh and mudflat area, which may constitute a problem, both in terms of enhanced levels of contamination and the potential for future remobilisation, due to erosion and re-introduction into the system by desorption processes; secondly, because sediment-associated phosphorus is thought to constitute a variable, but long term, source of potentially bioavailable phosphorus to plants and algae for growth (Sharpley *et al.*, 1991).

The concentration of phosphorus in river water may also have a strong influence on the transport of particulate phosphorus towards the estuaries system in suspension. Much concern has recently been directed to temporary transport of phosphorus in suspended sediments, because maximum phosphorus transport and concentrations in sediment coincide with the peak of the growing season (Drewry *et al.*, 2009). For this reason, this study examines which seasons are most important for phosphorus

transport in the river system. While there have been studies which have considered suspended sediment-associated phosphorus transport (Walling *et al.* , 2001; Evans & Johnes, 2004; & Bowes *et al.*, 2003), there have been few studies which have considered seasonal variations and variations under varying flow conditions (Webster & Ford, 2010). This trend was noted by Kronvang *et al.* (1999) and Svendsen *et al.* (1995), who both, in their studies of Danish streams, deemed that most of the retained sediment-associated phosphorus was re-suspended during storm events in the autumn and winter. Eventually, over the course of the winter, most of the stored phosphorus was exhausted, with only a small amount of residual storage remaining. This pattern of winter re-mobilization and depletion of sediment-associated phosphorus can have an additional dimension. Seasonal variation in TP stored in the sediment has been assumed by McComb *et al.* (1998) & Fogal *et al.* (1995) to be due to seasonal variations of inputs. Studies by both concluded that variability and sudden increases in TP storage in the winter time could be explained by heavy rainfall and runoff events transporting a fresh supply of phosphorus-enriched sediment from the land into the river and downstream to the estuary. During winter, when the fields are generally bare, they found that the export of such sediment-associated phosphorus was high when compared with other seasons when vegetation cover is at a maximum. While this is usually short-term storage and is likely to be flushed out in subsequent storms, most storage of phosphorus in bed sediment occurs in the summer, during the growing season, when the potential for eutrophication is at its highest (Jarvie *et al.*, 2005).

An increasing understanding of the fate of catchment-derived P and a fine-sediment budget could also provide useful information for use in producing meaningful phosphorus budgets. The deposition of sediment-associated phosphorus has

important implications because of its ability to sorb onto sediment particles; and over the long term, deposited P may potentially be released because of bioavailability (Sharpley *et al.*, 1991).

Chapter 3: Study area and research design

3.1 Introduction

This chapter provides an overview of the study experimental design to contextualise the research aims and objectives. A description of the study catchment and estuary is also provided, considering variables which may be important for sediment delivery and storage against the issues raised in chapter 2.

3.2 Choice of study area

3.2.1 Study area

The Avon catchment in South Devon was chosen to represent a typical agricultural estuary in southwest UK within which to explore sediment and particulate phosphorus delivery and storage dynamics. This catchment allowed access to the rainfall and flow monitoring data collected by the UK Environmental Agency which was supplemented by in-channel measuring equipment set up for the project. The river Avon is continuously monitored for flow a short distance upstream of the tidal limit by the Environment Agency. Rainfall is also monitored in the upper and lower reaches of the catchment.

The Avon basin is located in the South Hams, Devon, UK (Figure 3.1). The Avon river rises at within an upland area (480 m above sea-level) underlain by granite within Dartmoor National Park, a protected wetland landscape (Masselink et al., 2009). The catchment elevation drops sharply at the margins of the granite and passes through a zone of pasture land before entering the lower catchment which is dominated by cultivated land. The length of the river within the catchment is 76.1 km and the area of the catchment is 340 km². The main stem river is the primary

pathway for sediment and particulate associated nutrient delivery to the estuary which suffers from nutrient enrichment and siltation. There are also five notable feeder streams that feed directly into the estuary as well as some minor stream.

3.2.2 Geographic setting

The River Avon catchment, located in the South West of England, Devon, UK, has a medium sized catchment area of 340 km². The river rises on the upland area of Dartmoor (Figure 3.1). The River Avon rises >200 m above sea level on the Aune Head mires of south Dartmoor and flows south.

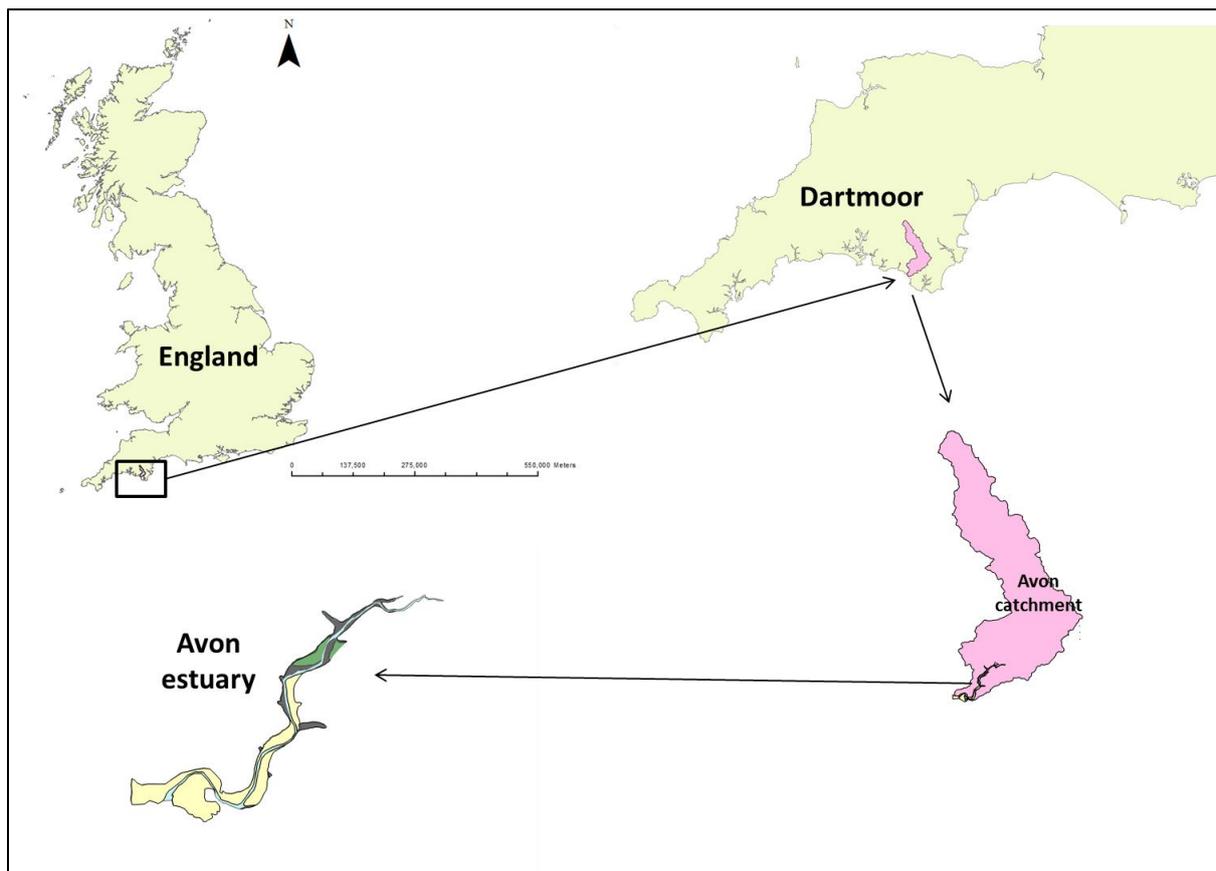


Figure 3.1: Location of the Avon catchment and estuary.

3.2.3 Geology and soil

The geology of the Avon catchment comprises three distinct geological zones (Figure 3.2): the upper catchment is underlain by granite; the middle parts of the catchment are underlain by slates, Staddon Grits; while in the lower catchment the Dartmouth slates and Meadfoot formation dominate, comprising slates with grit.

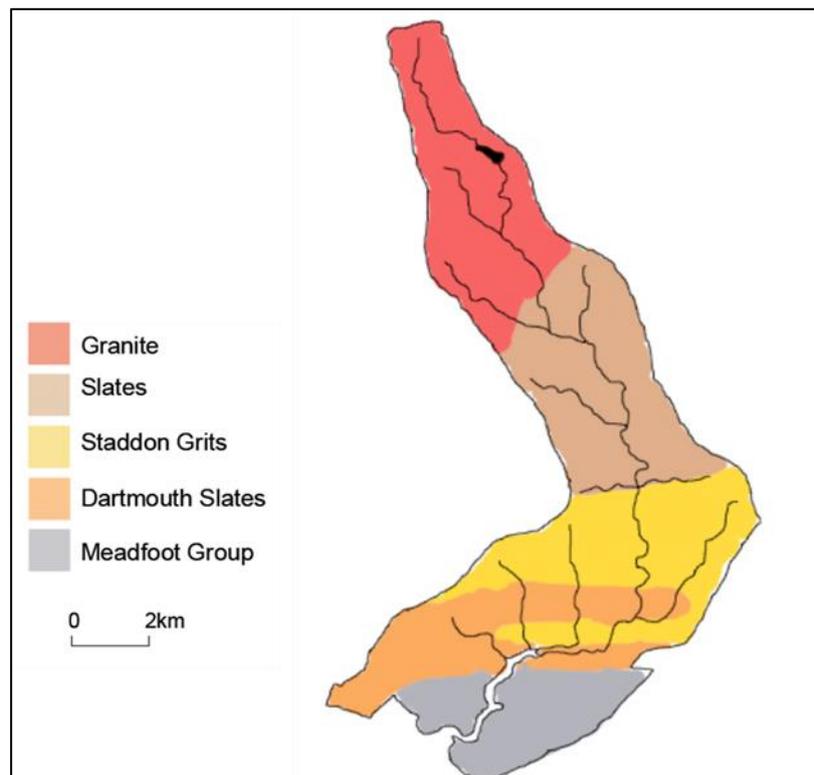


Figure 3.2: Geology of the Avon catchment

The soils in the uppermost part of the Avon catchment comprise blanket and basin peats which are thick and very acid. Upland slopes are however dominated by well drained fine loam and fine silt soils with a humose surface horizon in places. The middle parts and lower of the Avon catchment are dominated by well drained fine loamy and fine silty soils over rock or slate rubble. These soils are well suited to cultivation.

the census dates (CEH, pers. Comm.; Fuller et al 2002). The proportion of agricultural land that was cultivated increased between 1998 and 2000 (Table 3.1) from ca 20% to 40% apparently at the expense of semi-natural grassland but the noise in improved pasture data suggests some uncertainty in the comparison across the years. Indeed, in the upland moorland where blanket bogs and extensive heathland grazing dominate, (Figure 3.4) census data suggest some marked change but it is likely that much of this is down to noise and uncertainty in data and image classification approaches with development of data capture and processing technology (Fuller et al., 2002). Nevertheless, the data use data offer insights into the main pressures on the hillside soil and also spatial distribution of cultivation (Figure 3.4).

Table 3.1: Percentage of agricultural land in grass or cultivation from Centre of Ecology and Hydrology land cover data (note uncertainty and methodological issues raised in text).

Agricultural land class	2007 (%)	2000 (%)	1990 (%)
Improved grassland	42	30	42
Semi-natural grassland	16	24	35
Arable	42	45	23

Dairy and beef cattle, as well as sheep graze across the catchment but there is a focus of cultivated land in the mid to lower parts of the Avon catchment with cereals, field vegetables (including potatoes), and stock feed/maize being the more widespread land covers in this zone. Peas, beans and oilseed are also grown but in more isolated pockets. Crops are generally grown in rotation in the Avon catchment.

Within the agricultural land use types there are important temporal dynamics in land disturbance which might lead to sediment production. Cereals are generally sown in winter or spring. Winter cereals are sown between September and late autumn but the young shoots that over-winter do not provide good soil cover. With persistent rain and saturation of the soil profile, overland flow can occur throughout the winter months. Cereal fields left to spring sowing can be less prone to erosion if (i) a cover crop or grass/weeds are left over winter or (ii) the soil is ploughed after summer harvest, increasing permeability. The latter is very much dependent on weather and soil conditions after harvest. Maize crops for cattle fodder can lead to high risk of surface runoff and erosion since the crop is harvested late in the year. After harvest, wet conditions can preclude ploughing or sub soiling which means the field can be left bare and susceptible to erosion. Use of cover crops can reduce this risk significantly. Potatoes are notorious for generating overland flow due to the banking up of earth around the plants to bury tubers. This can lead to concentration of overland flow once the soil is saturated. Potatoes are generally sown in April and harvested during the summer so the main risk from this crop is later spring and during extreme summer events.

In summary, land use (agricultural practices) can result in increased sediment and nutrient run-off in the Avon throughout the year but the prevalence of cereal and cattle fodder crops means the autumn and winter months present the greatest risk and therefore highest potential sediment yields (EA, 2002).

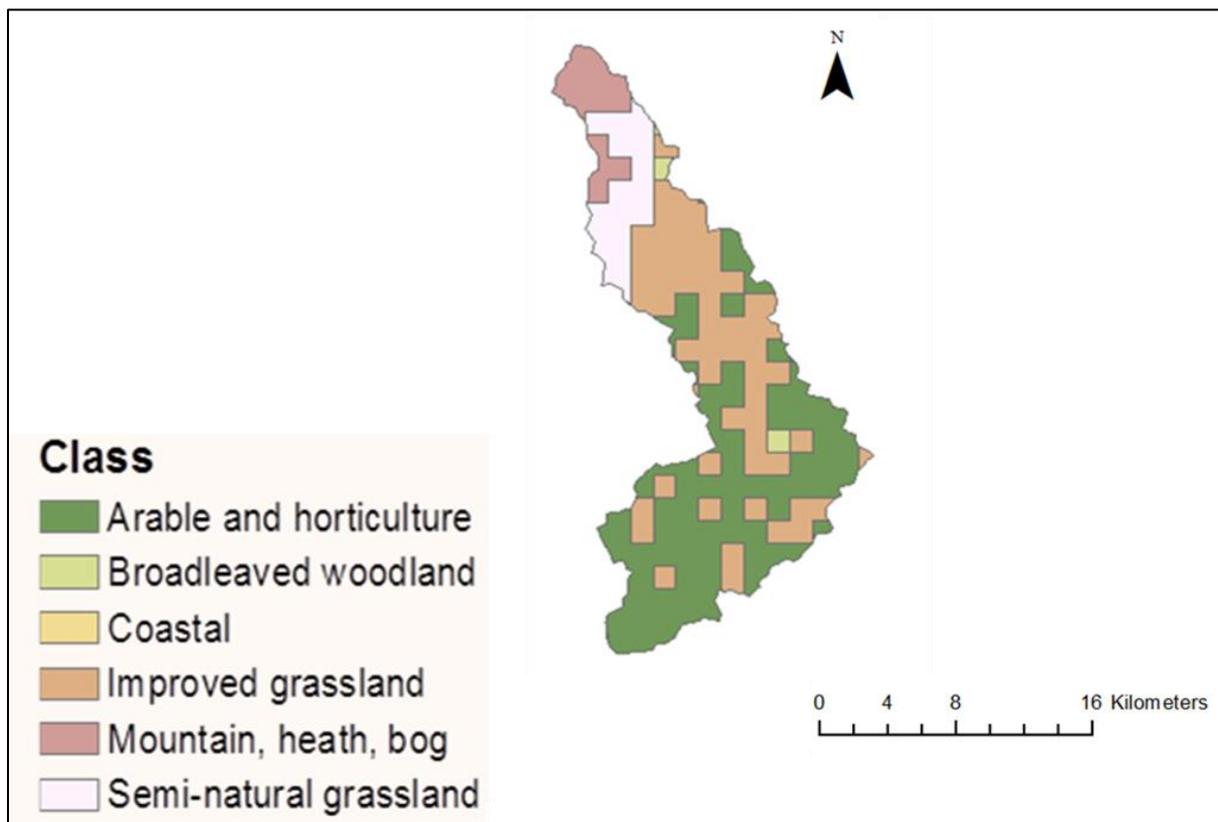


Figure 3.4: Land use of the Avon catchment (Environment Agency, 1998; land use data <http://www.ceh.ac.uk/LandCoverMap2007.html>).

3.2.5 Catchment topography and drainage network

The topography of a region plays an important role in determining the amount and rate of surface runoff and therefore the delivery of eroded material to the river channel (Walling & Kane, 1984). The river Avon rises on Dartmoor at a height of >200 m and flows in a south-east direction as a fast-flowing steep-sided stream, turning south to Loddiswell from where it starts to meander across the flatter land in a south west direction towards Aveton Gifford where it widens into the estuary (Figure 3.5).

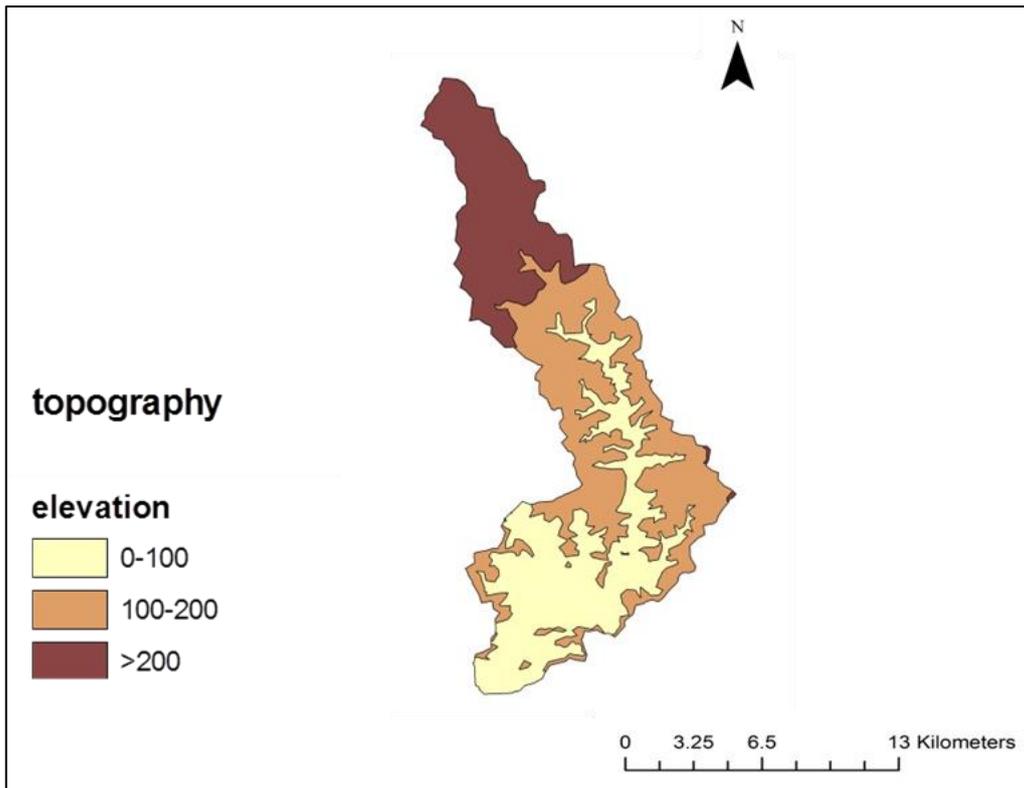


Figure 3.5: Topography of the Avon catchment.

3.2.6 Rainfall

Figure 3.6 shows annual rainfall variation in south west UK, The highest rainfall is in December and January when the sea is still warm enough to ensure high levels of air humidity and the Atlantic depressions are most active. April to July is the driest period when the sea is relatively cool. Monthly rainfall is also highly variable between years. Most months of the year have recorded totals below 20 mm in coastal districts but, for example, at Plymouth, every month has had more than 100 mm at some point in time. The south west is subject to rare, but very heavy, rainfall events lasting from five to 15 hours.

The seas surrounding the south west are the warmest of the UK with a mean annual temperature of between 11 and 12 °C. Due to Devon's proximity to the sea, the range of seasonal temperature is less than in most other parts of the UK. Very low temperatures are usually prevented due to Devon's proximity to the sea but away from the shoreline temperatures well below freezing have been recorded, such as -15.0 °C at Exeter Airport.

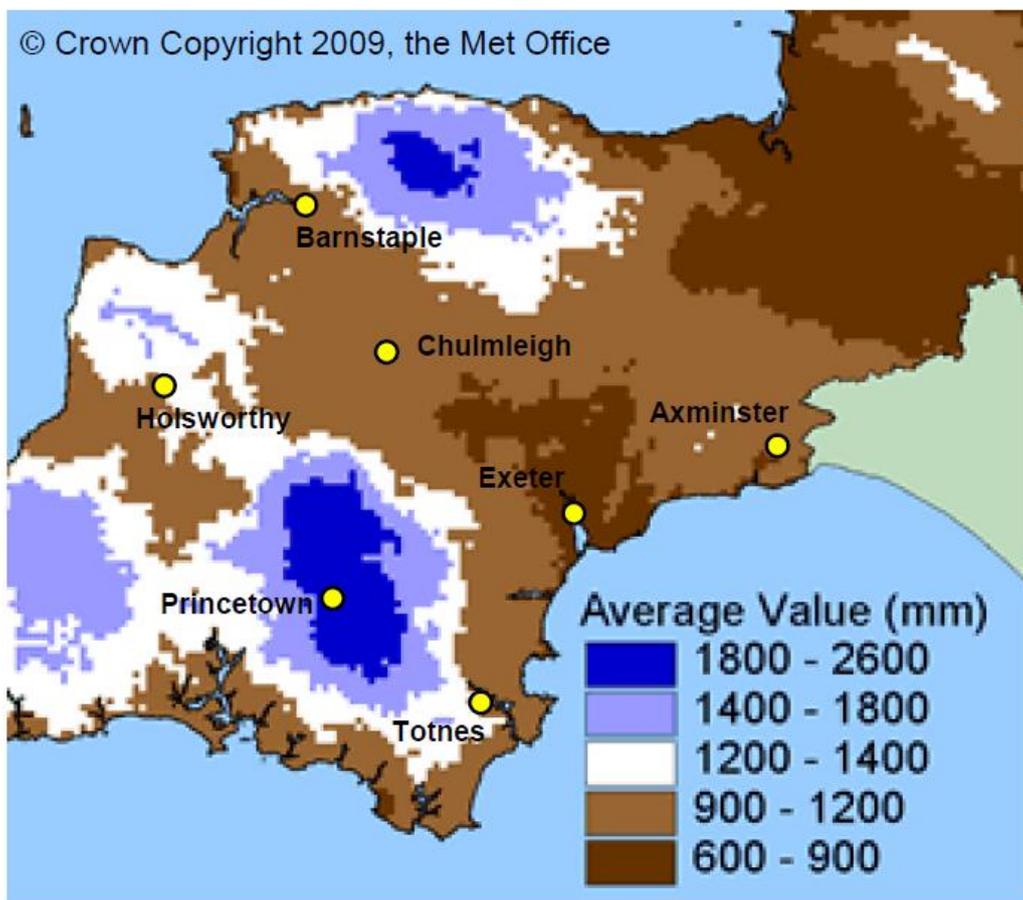


Figure 3.6: Average rainfall in UK and southwest UK (EA, 2010)

3.2.7 Estuarine geomorphology

The Avon Estuary is located approximately 24 km east of Plymouth (SX 67 45 50 16.N 03 53.W) between the river Erme and the Kingsbridge estuary and is

approximately 7.5 km long from its weir to the coastal waters at Bigbury Bay (Figure 3.7). It is a relatively small estuary with a total surface area of 213.5 ha, of which 146.2 ha are intertidal. The Avon estuary can be considered a ria (drowned river) estuary (Figure 3.8). The estuary is a ria, a river valley that was drowned when sea levels rose at the end of the last ice age (Davidson & Buck, 1997). There is a distinct ebb-tidal delta at the mouth of the estuary, with shoals to the east-west of the main channel. There is also an apparent mud basin with tidal flats and areas of saltmarsh in the central part of the estuary.

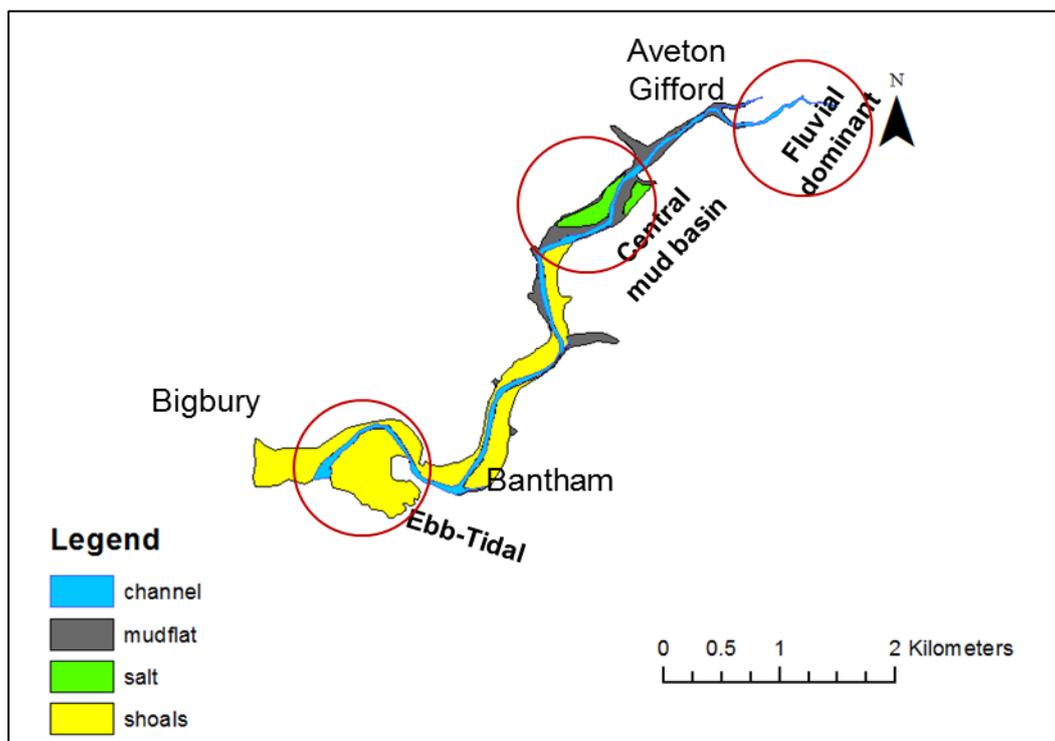


Figure 3.7: The main physical features of the Avon estuary marked by circles with saltmarsh areas marked in green, mudflats in grey and shoals in yellow.



Figure 3.8: (a) The upper and (b) lower estuary, taken from Aveton Gifford and Bantham Harbour.

Tide-dominated salt marshes and a meandering tidal channel are present in the central Avon estuary; while a wave-dominated barrier-inlet system with tidal deltas is present at the mouth of the estuary. The upper estuary is very narrow and has bank-to-bank widths of 20 m, reducing to 14 m at the tidal limit, at the weir at Aveton Gifford. The lower estuary is greatly affected by near-shore processes and the near-shore region close to its mouth is 900 m wide and has a maximum depth of 2.5 m at ODN (Ordnance Datum, Newlyn), the estuary narrows to just over 130 m and shallows slightly to 2.4 m at ODN (Masselink *et al.*, 2009; Uncles *et al.*, 2012).

3.2.8 Current problems affecting siltation in the Avon catchment

Several natural and human-induced factors affect the Avon estuary and have been perceived by local stakeholders as causing increased concentration of fine sediment and phosphorus in the estuary. There is an increase in the rate of change in siltation affecting the salt marshes and the fundus of the Avon estuary (Aune Conservation Association (ACA), 2005a). This could be due to an up-stream dam and reservoir (Uncles *et al.*, 2012). Also, there are some indications that wash from boats is causing salt marsh erosion in the Avon estuary and investigations were recently being carried out by South Hams District Council (SHDC) (EA, 2002). There is also concern about diffuse pollution from agricultural land and it is hypothesised by the ACA that this is leading to excessive growth of algae and higher plants. The Environment Agency and local Rivers Trust have identified land use issues that might be contributing to this problem, in particular connectivity between fields containing high erosion risk crops e.g. potatoes and the stream network. Other sources of sediment are poaching of the river banks by livestock, which has occurred at a number of locations in the Avon, resulting in the siltation of spawning gravels.

This may be because the total length of the river is short, 3 km up-river of Aveton Gifford.

3.3 Experimental design

This section provides an overview of the main fieldwork and laboratory methodologies that were used to address the aims of this project and how they fit together. The structure of the experimental design in relation to the specific research questions that arose from the review of relevant literature is shown in Figure 3.9 and is discussed below.

During the reconnaissance field study, a pilot sampling programme of surface sediment was conducted. The findings from these pilot studies showed promise and the research strategy was refined to expand these sections of the research design.

The main phase of field research began in 28th August 2009 and Figure 3.9 shows how fieldwork and analysis themes relate to specific objectives and research questions and states the chapter in which the results can be found.

An improved understanding of temporal in suspended sediment concentrations in the river was required. The sediment analysis results were achieved by Sonde equipment and river discharge at the established Loddiswell gauging station. Sonde equipment was installed to measure turbidity, water depth, pH, and temperature. The aim is to collect 18 months data covering wet seasons to investigate how much sediment from the catchment is input into the estuary. Full descriptions of all the methods employed are described in chapter 4.

As improved understanding of the distribution of sediment-associated phosphorus on the all estuary system was required, samples were collected at several sites of

estuary in order to identify fine sediment storage area. Sediment particle size, total phosphorus and total organic content (organic and inorganic carbon) were also measured. The work involved survey, and GIS-based characterisation of the geomorphic units that the estuary comprises and then a detailed sampling strategy to characterise the sediment that was stored within those zones in terms of its particle size, total organic carbon content (i.e. basic composition) and then quality in terms of total particulate phosphorus. These data were used to generate maps of the estuary showing the main spatial patterns in sediment texture and composition and further to explore the relationships between composition and particulate phosphorus both within and between sites. Full descriptions of all the methods employed are described in chapter 5.

An improved understanding of the budget of sediment-associated phosphorus in the estuary was required. The total fine sediment and PP input, fine sediment and PP storage were used from objective 1 and 2, and cores have been used from this study and a previous study in order to gain a long-term perspective on the deposition and the annual sediment and PP budget was applied. The work involved field-based survey, GPS and cores in the saltmarsh and mudflat to measured elevation of silt/sand interface. The across-estuary distributions of sediment grain size are used in order to provide realistic values for the total mass of sediment deposition along the estuary per unit width of estuarine section.

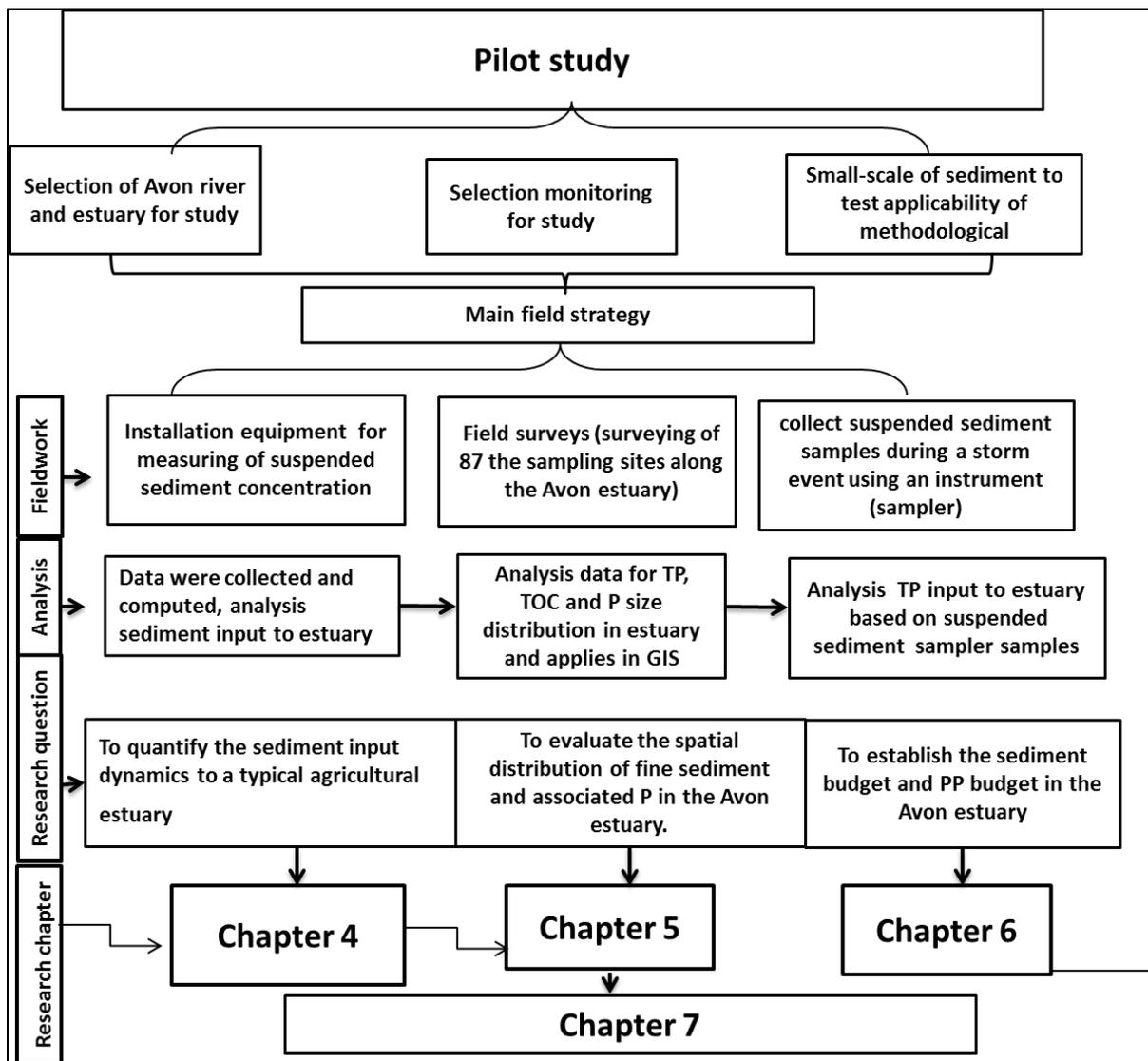


Figure 3.9: Overview of research design

Chapter 4: Suspended sediment delivery dynamics during storm-events in the Avon estuary, south west UK

4.1 Introduction

The aim of this chapter is to investigate rainfall–runoff–sediment transport relationships and to assess the nature of the hydrological and sedimentary response of the Avon river basin which has a highly dynamic response to individual storm events. Moreover, this work intends to improve our understanding of the factors that control sediment transport patterns and sediment delivery into the estuary of temperate agricultural catchments.

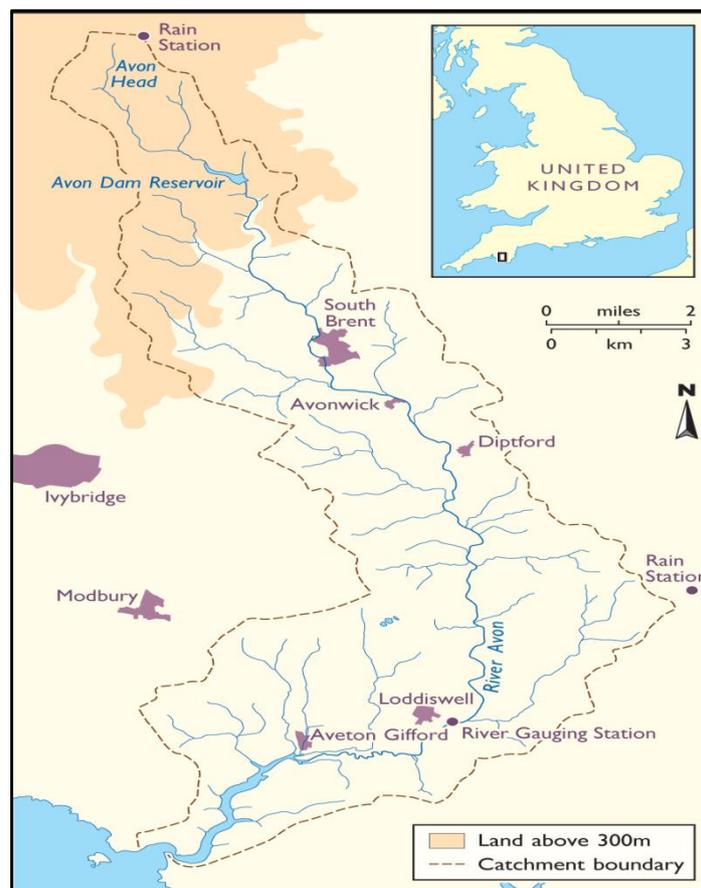


Figure 4.1: locations of two Environment Agency rainfall and river flow stations.

4.2 Methodology

4.2.1 Field monitoring

4.2.1.1 Rainfall monitoring

The rainfall data were obtained from upper (Believer station, Dartmoor) and lower (Davy Park Farm station, South Hams) catchment gauging stations (Figure 4.1 above), by the UK Environment Agency. This dataset covers a two year period from August 2009 until August 2011 with rainfall amount recorded at 15 min intervals.

4.2.1.2 Discharge and suspended sediment monitoring

Suspended sediment concentrations of the Avon River mainstem channel were monitored from August 2009 with the general aim of examining the suspended sediment transport dynamics in the highly active hydrological fluvial environment. Data collection was undertaken using a YSI meter multipara Sonde equipment which measures turbidity in nephelometric turbidity units (NTU), pH, water depth as well as temperature at 15 minutes intervals. This equipment was installed from August 2009-2011 for two years at the Environment Agency Loddiswell gauging station where river flow is also monitored continuously at 15 minute intervals (Figure 4.2). The multiparameter Sonde was suspended in the water column so that the sensors remained submerged during low flows and fixed to maintain position during elevated flow events. NTU data were not collected from April to July 2009 and from December to January 2011 owing to Sonde malfunction but flow data were available for these periods.



Figure 4.2: Sonde equipment installed on stage board at the EA gauging station, Loddiswell.

4.2.1.3 Determining the relationship between turbidity units (NTU) and suspended sediment concentration (mg l^{-1})

Turbidity data were used in order to obtain a continuous record of SSC (Ziegler 2002). Turbidity data were transformed to SSC through a calibration process. This was done using a rating curve between pair values of NTU and SSC. This relationship was derived in the laboratory, by placing the probe in suspensions of known suspended sediment concentration using material representative of the suspended sediment transported by the river, and covering a range of different sediment concentrations. The range of concentration measured was from 0 to 1000 mg l^{-1} . In total, 12 samples were placed in a large beaker and suspension was maintained with the aid of a magnetic stirrer, whilst the turbidity was recorded. The results of the laboratory calibration are summarized in Figure 4.3. A power function was used to establish the SSC-turbidity relationship since linear regression curves

can lead to large errors. Power functions based on log-linear fits are less prone to extrapolation error than linear fits (Minella *et al.*, 2008). SSC was well correlated with turbidity ($R^2 = 0.98$).

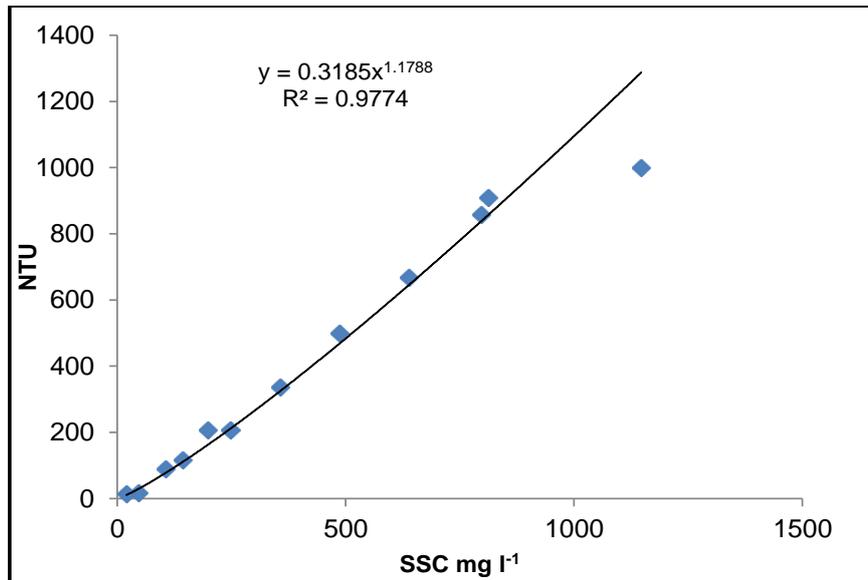


Figure 4.3: The relationship between sediment concentration and turbidity based on calibration experiments (n=12).

4.2.1.4 Storm event hydrologic analyses

This analysis focused on computing different storm response variables using data from the 35 main storm events over the two-year period having the highest peak flow (Q_p), SSC from river flow and rainfall data. The storm events were characterized using the characteristics outlined in Table 4.1. There are largely self-explanatory although those which are more involved are described in detail, in turn, below.

The kinetic energy of the maximum rainfall intensity at each storm over a 30-min period (E_{cl30}) (after Brown and Foster, 1987) was calculated with the following equations:

$$EF = 0.29 [1 - 0.72 \times \exp(-0.05 \times I)] \quad (4.1)$$

$$Ecl30 = ((\Sigma EF \times P) I_x) \quad (4.2)$$

where, EF is the kinetic energy estimated from a 30-min period, I is rainfall intensity over a 30-min period (mm h^{-1}), P is the accumulated precipitation over a 30-min period (mm) and I_x is the maximum 30-min rainfall intensity of the event (mm). The runoff generated by the rainfall was calculated by the total runoff volume of the flood (T_r , ML), and the storm flow coefficient (RC), calculated as the relation between the total amount of precipitation and the total storm runoff volume (after subtracting the base flow) of each storm) (see Appendix I).

Table 4.1 Names, abbreviations and units for the variables used to characterise storm events and to perform Pearson correlation analysis.

Rainfall related variables	Abbreviations	Unit
Duration of the event	Dur	hr
Total precipitation	P_{tot}	mm
Maximum30 rainfall intensity	$I_{\text{max}_{30}}$	mm h^{-1}
Maximum15 rainfall intensity	$I_{\text{max}_{15}}$	mm h^{-1}
Antecedent precipitation 1 day before event	P1d	mm
Antecedent precipitation 7 days before event	P7d	mm
Antecedent precipitation30 days before event	P30d	mm
Runoff related variables	Abbreviations	Unit
Total storm runoff volume	T_r	ML
storm peak discharge	Q_p	$\text{m}^3 \text{s}^{-1}$
Mean storm discharge	Q_m	$\text{m}^3 \text{s}^{-1}$
Base flow at the beginning	Q	$\text{m}^3 \text{s}^{-1}$
storm-flow coefficient	RC	%
SSC related variable	Abbreviations	Unit
Maximum flood SSC	SSC_{max}	mg l^{-1}
Total suspended sediment load	TL	t

4.3 Results

4.3.1 Temporal and spatial patterns in precipitation

Figure 4.4 presents the values for daily rainfall for the period 2009-2011. The total of rainfall in both upper and lower catchment varied over the two years. In the upper catchment (at Bellever) maximum monthly rainfall was recorded in November 2009, when 455 mm fell and minimum monthly rainfall accrued in April 2011 for the upland area of the catchment, when it represented 22 mm of total rainfall. In the lower catchment (Davy Park Farm), the maximum of total rainfall also accrued in November (2009), when total of rainfall (190 mm), and minimum rainfall April 2011 (14 mm).

As shown in Figure 4.5, the seasonal rainfall in the upper and lower catchment during the study period was varied. More rainfall fell in the winter months, and in the upper catchment (Bellever) 785 mm from November to January 2009, while in the lower catchment (Davy Park Farm), 419 mm fell in the same period. In 2011 the Bellever catchment received 433 mm in the winter while Davy Park Farm received 255 mm in the same season.

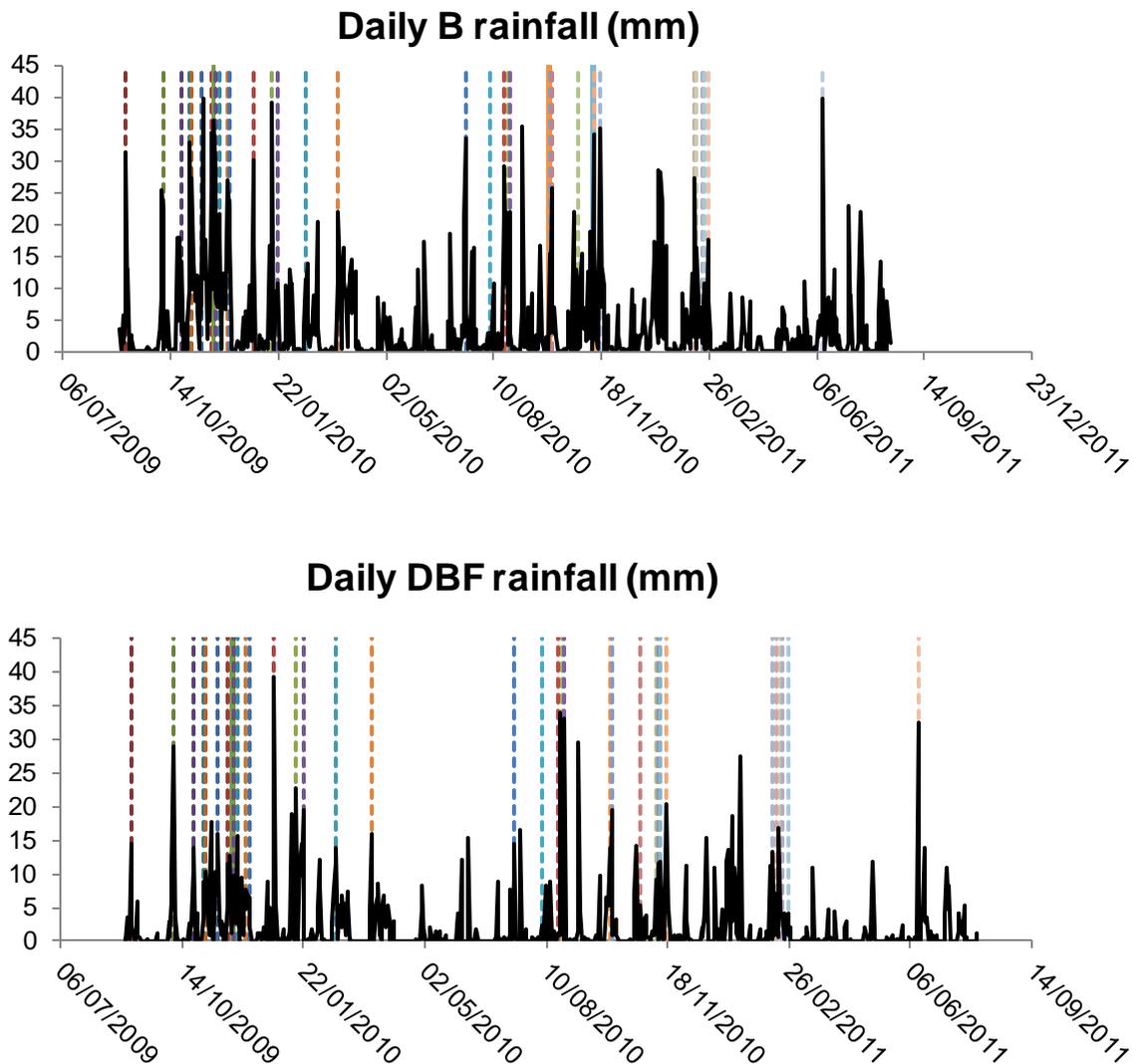


Figure 4.4: The pattern of annual precipitation in the upper (Bellever) and lower (Davy park farm) catchment during study site period. Each colour line represents major storm events analysed.

In the autumn months, the upper catchment (Bellever) received 364 mm (37% larger than lower catchment) from August to October 2009, while the lower catchment received 226 mm. in 2011 rainfall in the upper catchment was 343 mm (32% larger than lower catchment) while in the lower catchment was 233 mm. in the winter upper catchment received 785 mm (46% larger than lower catchment) and lower catchment received 419 mm in 2009. In 2011 the upper catchment was received 433 mm (41% larger than lower catchment) and 255 mm in the lower catchment. In the

spring months, rainfall falls shown in the spring months in the upper catchment 327 mm (40% larger than lower catchment) from February to April 2009, while in the lower catchment, 196 mm fell. In 2011 the rainfall was 210 mm in the upper catchment (41% larger than lower catchment) while was 122 in the lower catchment. Less rainfall falls shown in the summer months in the upper catchment 211 mm (48% larger than lower catchment) from May to July, while in the lower catchment, 109 mm falls. In 2011 the rainfall falls in the upper catchment was 274 mm (50% larger than lower catchment) while in the lower catchment was 136 mm. the annual total in the upper and lower catchment was 1687 and 950 2009, while the annual total in 2011 was 1260 and 746.

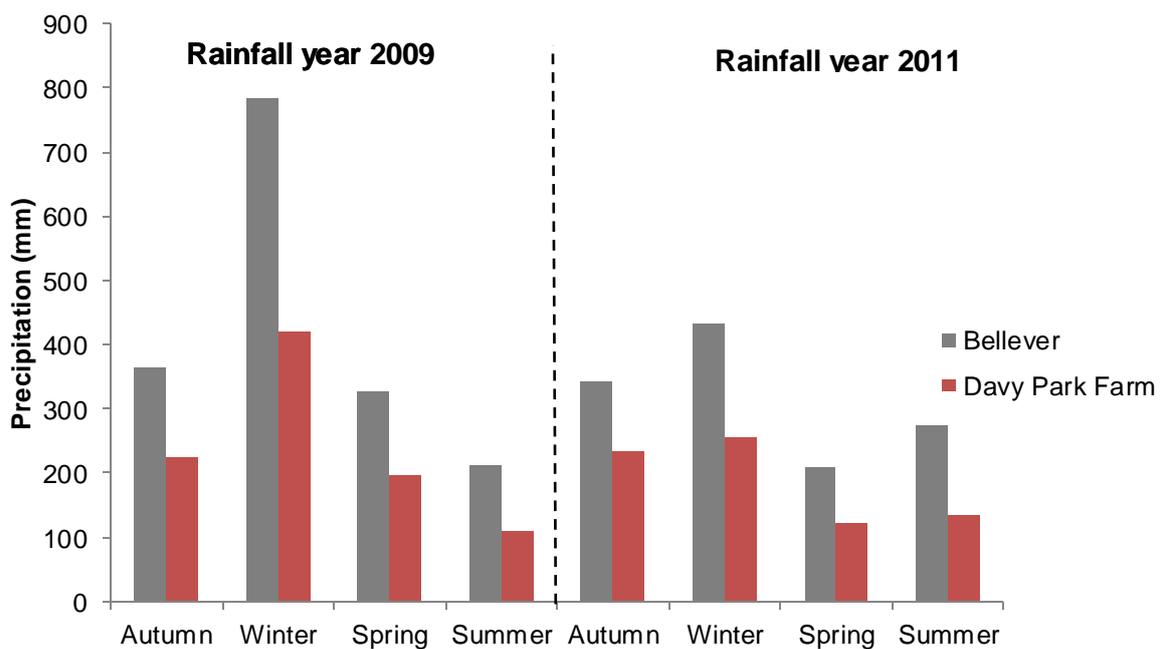


Figure 4.5: Seasonal totals of rainfall (mm), 2009-2011.

4.3.2 The annual hydrographs for each year (Q, SSC)

Temporal variability in discharge is an important consideration when examining sediment load, both in terms of energy for transportation and volume of water. Figure 4.6 presents the two years' daily flows for the Avon River; it shows that maximum flows occurred in late autumn and winter and that minimum flows occur in late summer. Times of maximum sediment transport are likely to occur at times when the flow is highest and there is a supply of material in the catchment, linked to landuse; therefore it may be assumed that the maximum sediment transport will occur in the winter, falling to a minimum in late summer. Sediment load in both years increased sharply in autumn and winter and decreased during summer.

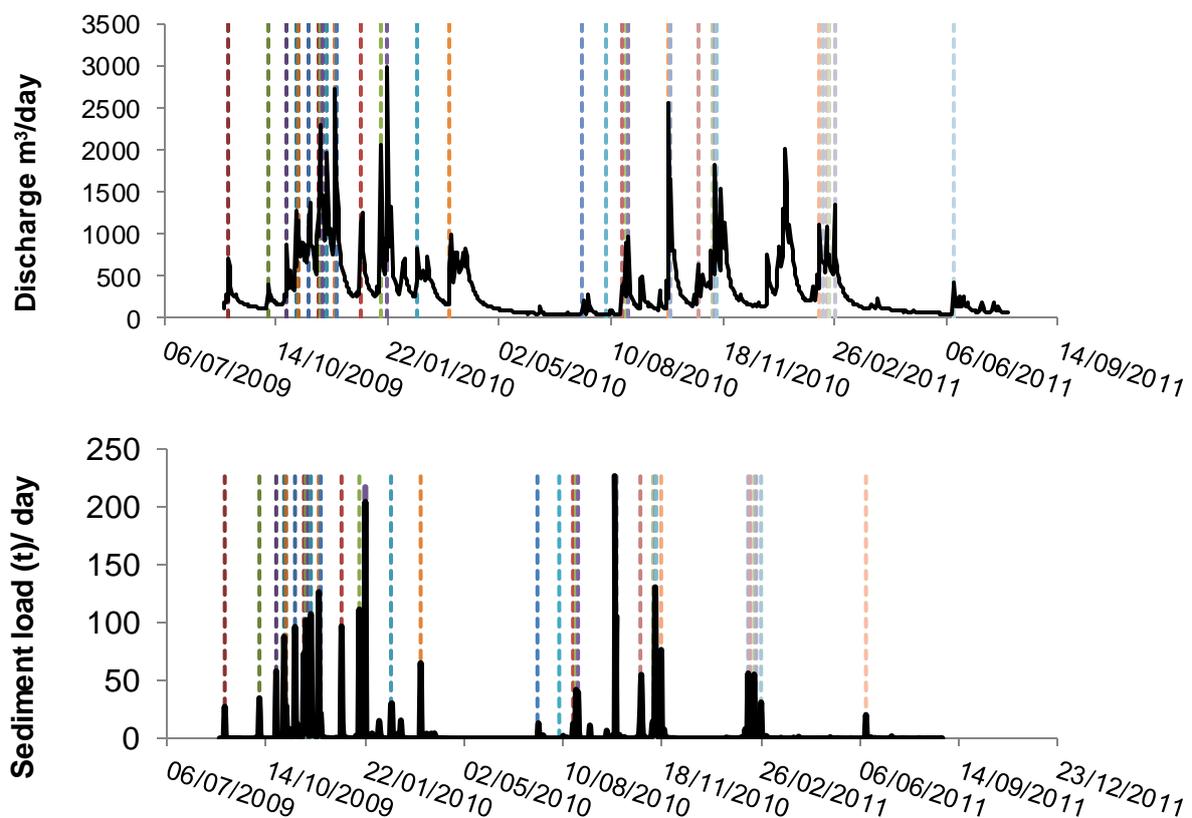


Figure 4.6: Daily discharge and sediment load for each year; each colour line represents the major storm events analysed.

Alongside Figure 4.6, the cumulative suspended sediment load and flow over the study period (Figure 4.7) further illustrates the episodic nature of suspended sediment transport by the river linked to the occurrence of specific storm events or extended wet periods. Each chart exhibits distinct steps in the cumulative curves (Figure 4.7). Flow and sediment load curve shows stepwise curves, which were fairly steep in winter but gentle in summer, because the slope of the curve indicates that sediment concentration and flow in winter were much higher than in summer.

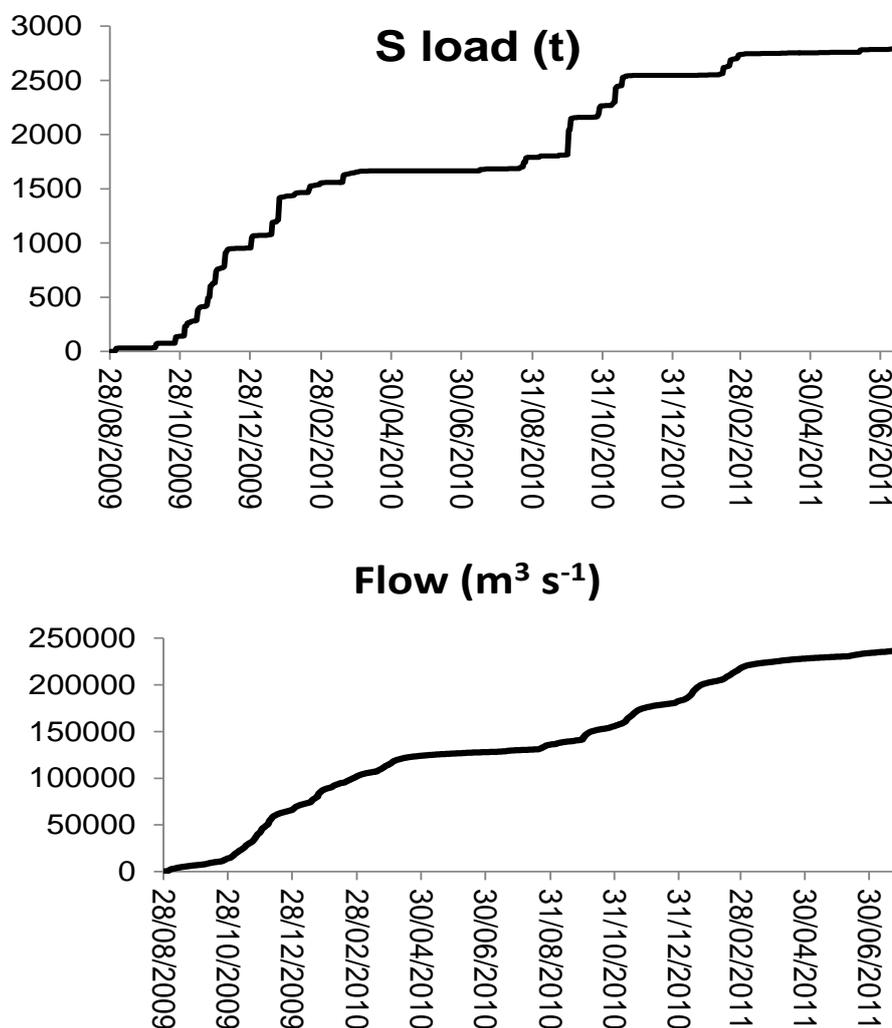
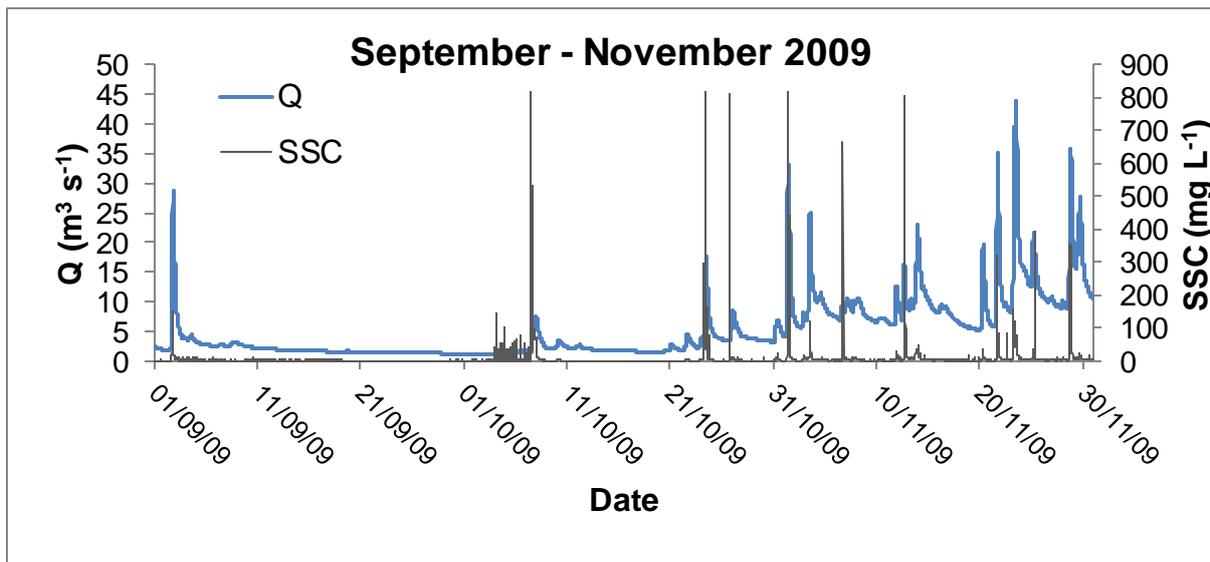
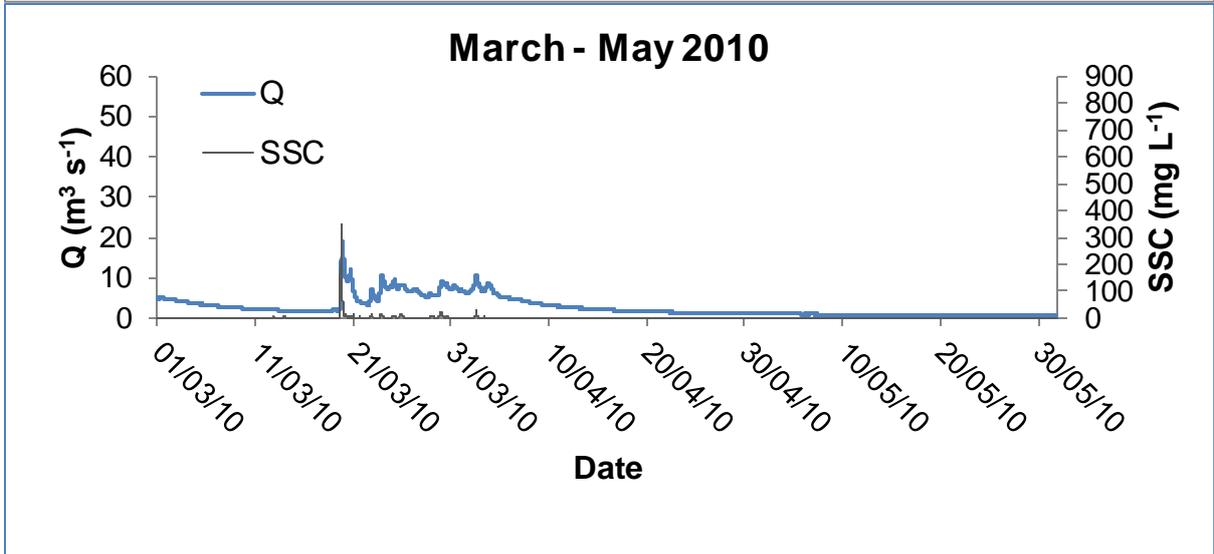
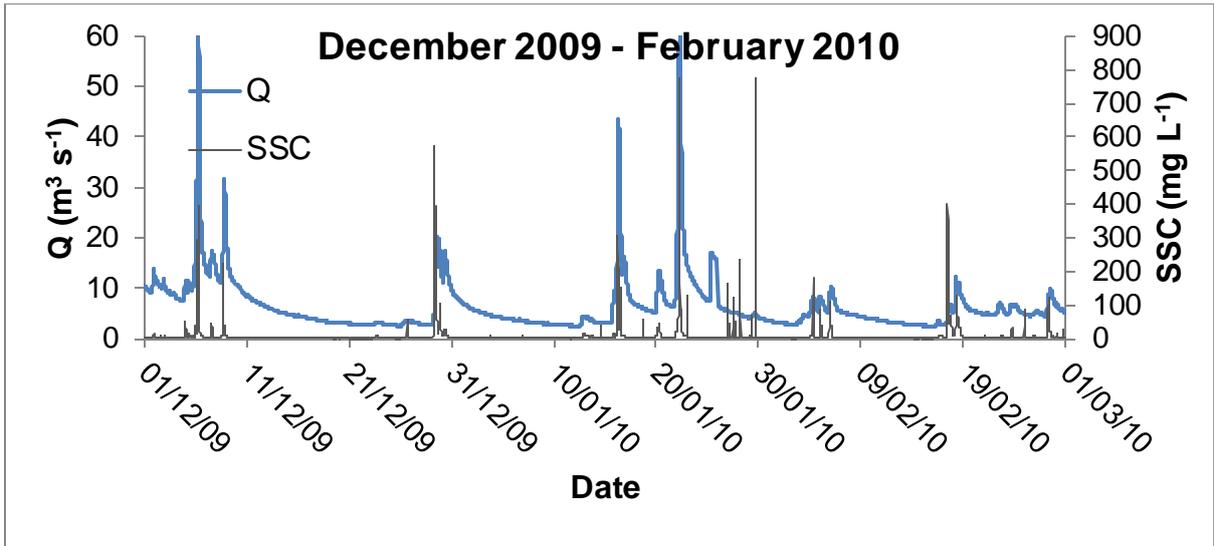


Figure 4.7: Discharge and sediment load cumulative curves for the Avon River, note that the steps in sediment load are more distinct than those of flow.

4.3.3 Temporal patterns in Q and SSL

The relationship between discharge and SSC was explored for all the individual storm events observed in the Avon River. In general, there was a highly variable relationship between discharge and sediment response different seasonal in storm events in different season (Figure 4.8). These different patterns of both express variation in probable sources of sediment throughout the catchment and the erosional response to rainfall. Analysis of 35 storm events recorded during the study period showed that there was no direct relationship between SSC and discharge ($R^2= 0.005$, P value = 0.68) (Figure 4.9).





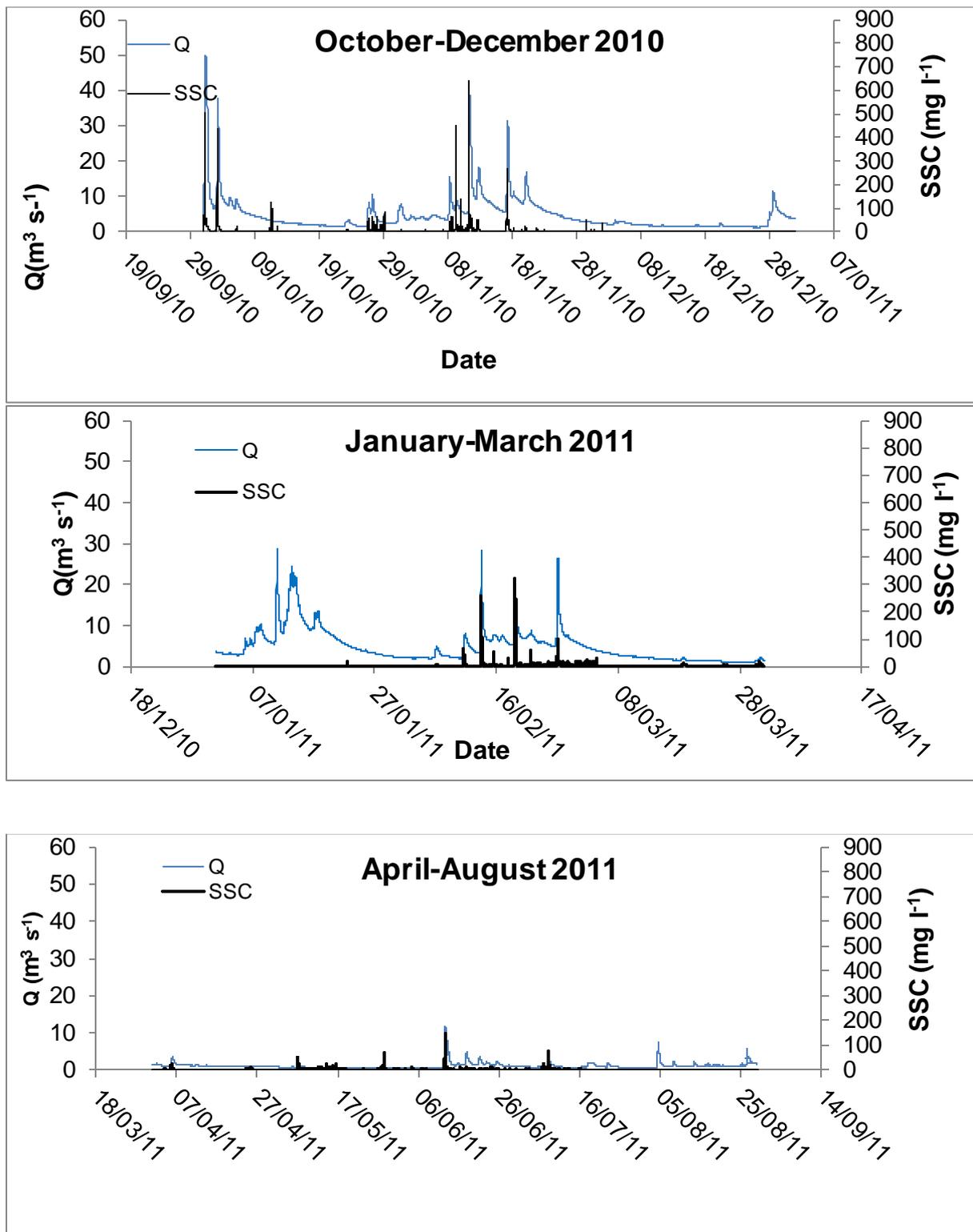


Figure 4.8 (this and preceding page): Temporal patterns in flow and suspended sediment concentration on the River Avon at Loddiswell.

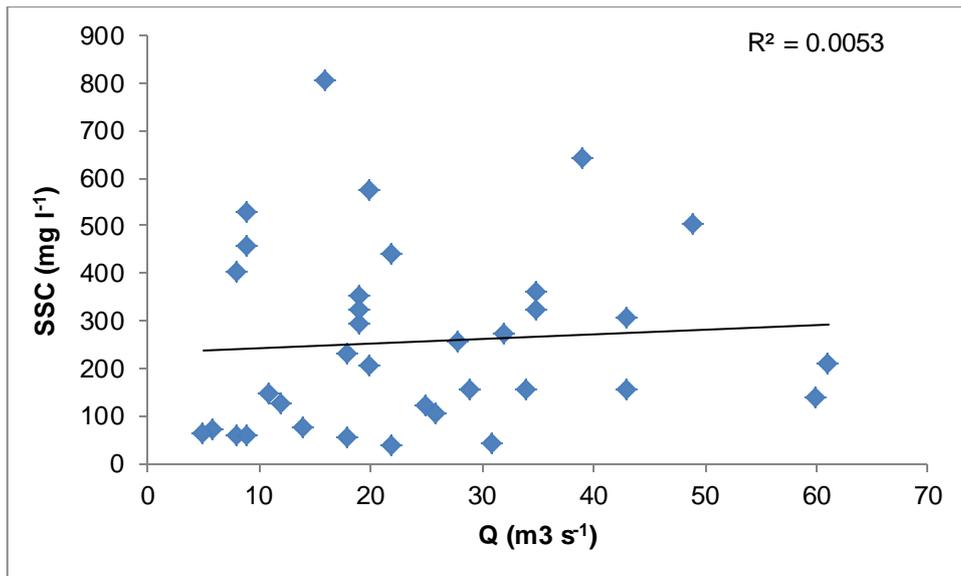


Figure 4.9: Lack of relationship between SSC and Q across all storm events

4.3.4 Monthly total precipitation, discharge and suspended sediment load

The monthly time scale values summarized general trends in total monthly sediment yield (Table 4.2). The total sediment yield for two years estimates were 10 t km^{-2} and total suspended sediment load was estimated at 3399 t for two years. Absolute monthly sediment loads, in general, increase with monthly runoff and rainfall (Figure 4.10) but as noted above, the relationship is more complex at the storm event scale. The smallest sediment loads of 0.3 and 4 t occurred in the driest months, April 2011 (22 mm rainfall at upper catchment and 14 mm at lower catchment) and May 2011 (60 mm at upper and 21 mm at lower catchment) respectively, and the greatest sediment load of 927 t occurred in the wettest months e.g. December 2009 (210 mm and 122 mm in upper and lower catchment). The preceding monthly sediment load (November 2009) was also high at 662 t, but it is notable that this month had greater rainfall than December 2009. Rainfall antecedence is important. Some of the sediment load data are missing from April to July 2010 and December to January

2011 due to Sonde failure, thus precluding a meaningful calculation of the proportion of the overall sediment load transported by the largest three of seven storm events.

Table 4.2 Monthly sediment loads, discharge and rainfall in the upper and lower catchment.

Month	Sediment load (t)	Monthly lower rainfall (DPF) (mm)	Monthly upper rainfall (B) (mm)	Monthly flow (m ³)	Sediment yield (t / km ²)
September /2009	30	27	63	6412	0.088
October	105	91	155	8130	0.308
November	622	190	455	31557	1.827
December	927	122	210	22696	2.726
January/ 2010	369	107	120	20220	1.085
February	122	101	127	13072	0.358
March	100	68	148	13279	0.292
April	Partial data	27	52	9108	Partial data
May	No data	14	30	2348	No data
June	No data	31	44	1542	No data
July	No data	64	137	2119	No data
August	138	108	146	6018	0.405
September	24	65	105	5641	0.07
October	452	84	145	14542	1.329
November	279	90	201	20330	0.821
December	No data	56	58	6854	No data
January/2011	No data	109	174	20383	No data
February	181	87	158	15075	0.532
March	11	21	30	6549	0.032
April	0.3	14	22	3507	0.001
May	4	21	60	2002	0.012
Jun	27	70	125	3967	0.079
July	5	45	89	2797	0.015
August	3	84	93	3502	0.009
Total	3399	1696	2947	241650	10
Average	189	71	123	10069	0.55

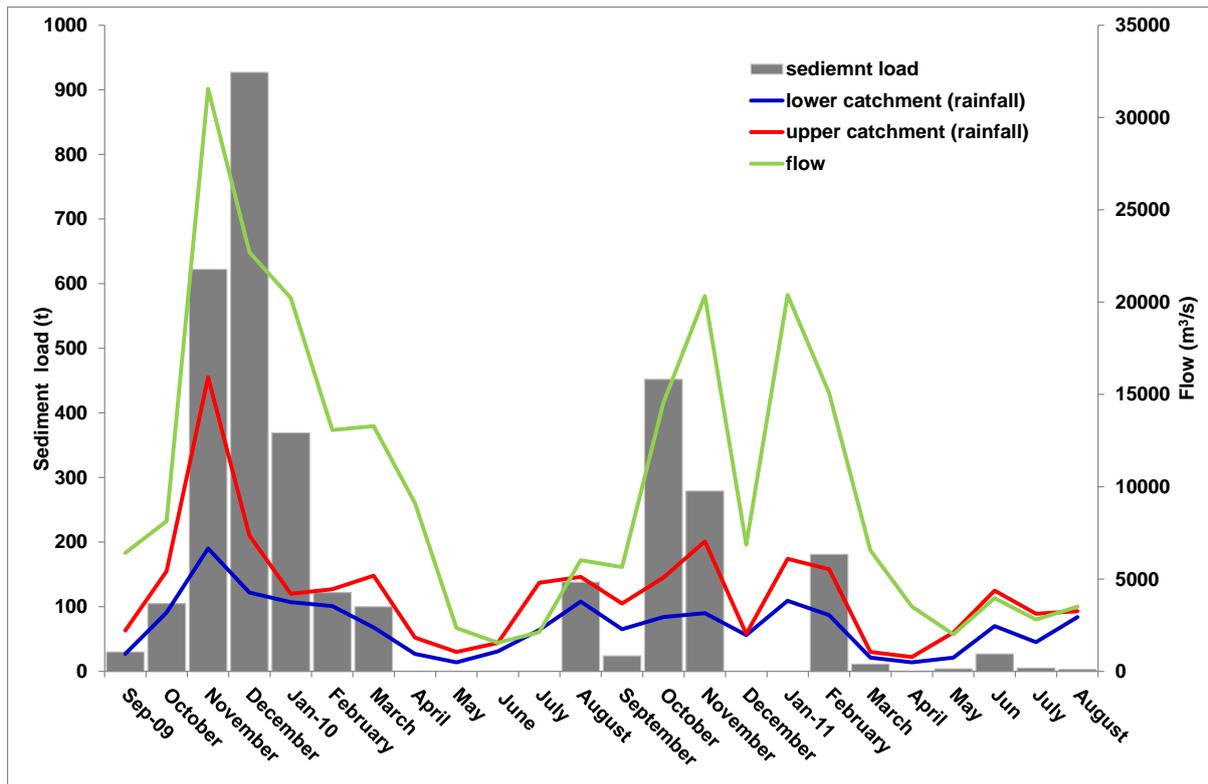


Figure 4.10: Monthly precipitation and total sediment load for the study period in the Avon catchment.

4.3.5 Suspended sediment and discharge responses to rainfall events

In this section, flow discharge and suspended sediment responses to rainfall events are examined in more detail. In section 4.4.5.1 the general character of a representative selection of responses are considered using graphical techniques and in section 4.4.5.2 factors that are hypothesised to have influenced sediment responses are explored using a correlation matrix.

4.3.5.1 Descriptive analysis of suspended sediment storm responses

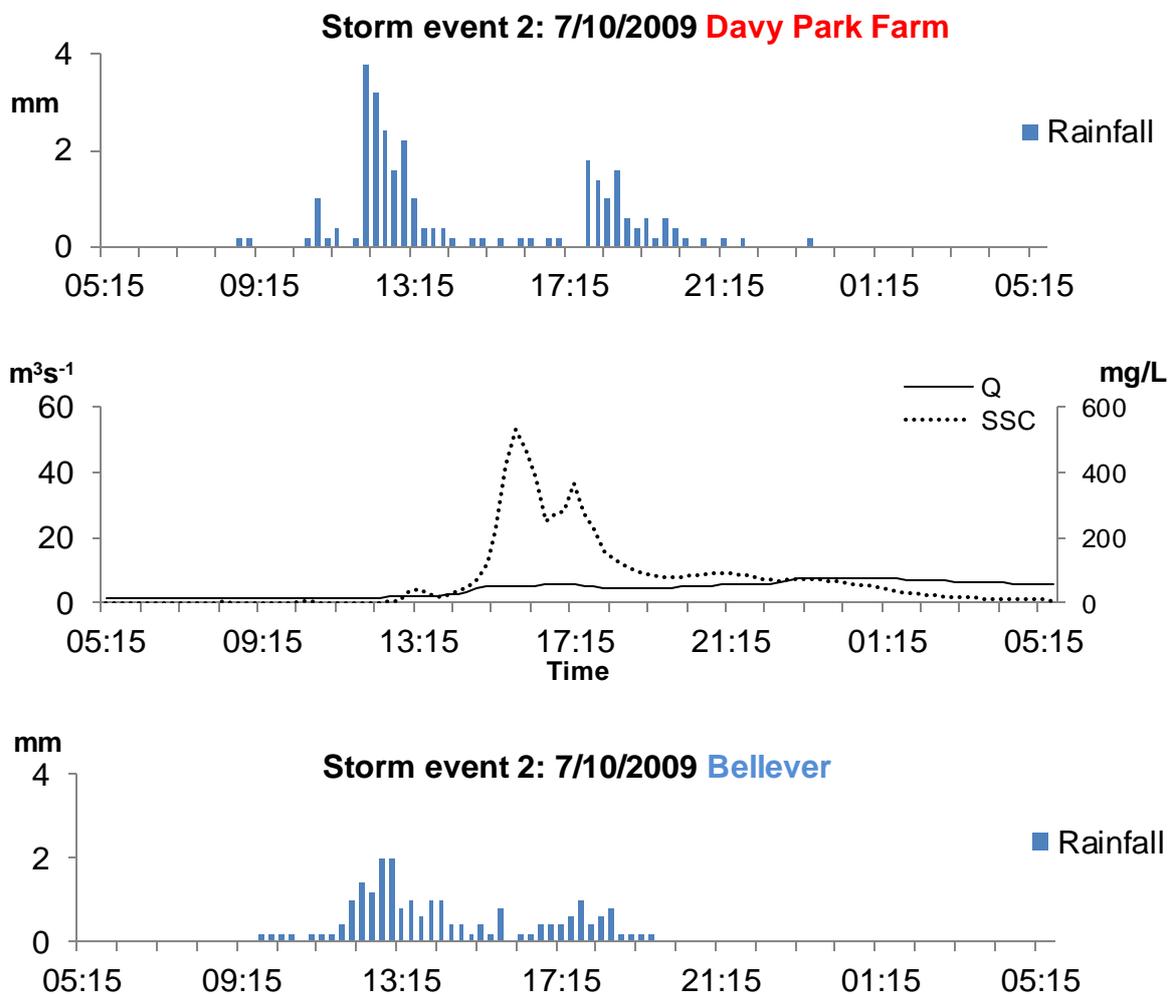
This section describes the characteristics of the 35 storm events and examines flow discharge and suspended sediment responses by analysing plots of suspended sediment concentration (SSC) varying in relation to rainfall inputs. It also considers sediment-discharge relationships and identifies patterns of transportation.

Representative suspended sediment and discharge responses to 35 storm events made by the monitored Avon River are shown and summarised in Table 4.3 and two responses made by the upper and lower catchment are shown in Figure 4.11.

The sediment concentration (SSC) typically reached their peak between 15 to 60 minutes after the start of rainfall. The highest peak SSC of the 35 events was 804 mg l⁻¹ on 12 November 2009 in response to a small storm of 17 mm total rainfall in the upper and 7 mm in the lower catchment. This storm event response coincided with high antecedent rainfall. The peak discharge for this event was 16 m³ s⁻¹. As a comparison, at a similar time of year on 01 October 2010, event with discharge of 13 m³s⁻¹ was observed with a high peak suspended sediment concentration (501 mg l⁻¹) but in response to double the rainfall in the upper and lower catchment (15 mm and 13 mm respectively). The river's relationship between storm size and sediment load, therefore, appears more complex. In Table 4.2 and Figure 4.9, the lagging time between sediment load with discharge and rainfall was observed on December 2009, with the very high suspended sediment load of 972 t for that month.

In the Avon catchment, sediment responses to rainfall in the upper and lower catchment showed variation (Figure 4.11) with a generally greater sediment response to lower than upper catchment rainfall. As an illustrative example of this, sediment concentration response can be compared between two events of similar magnitude but with contrasting spatial patterns of rainfall. The sediment response to the rainfall in the lower catchment was higher in storm event 2 which had a peak SSC concentration of 529 mg l⁻¹, while sediment concentration response to the rainfall in the upper catchment was lower in storm event 4 (Figure 4.11) which was 135 mg l⁻¹ compared with storm 2.

This example of graphical analysis of suspended sediment responses and stream flow and rainfall suggests that suspended sediment responses are determined not only by complex interactions between storm sizes, rainfall intensity and antecedent rainfall but also by supply factors such as land use and its relation to rainfall patterns. All of these factors are difficult to unravel by considering the temporal dynamic of a selection of storm events and so section 4.5.2 investigates the relative importance of different factors using statistical methods.



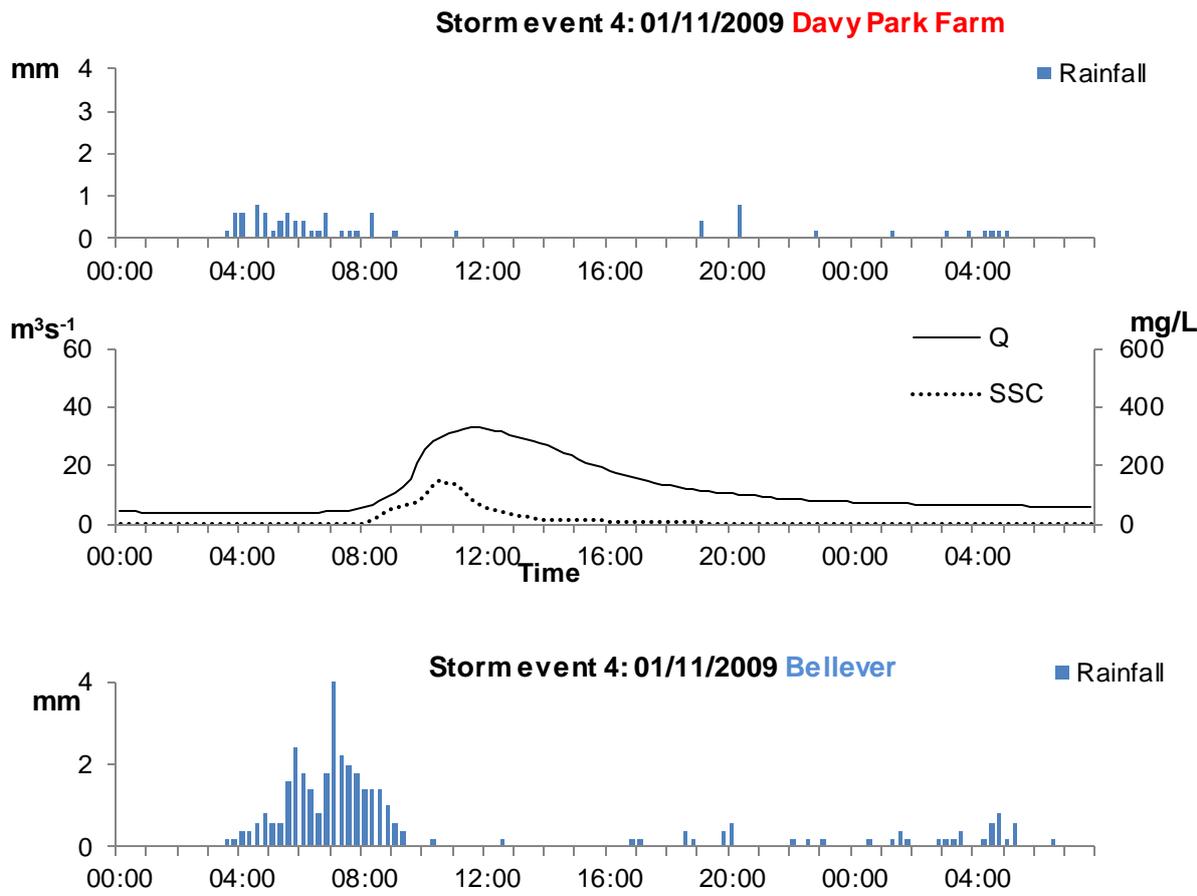


Figure 4.11 (this and receding page): comparison of suspended sediment concentration, responses to upper and lower catchment rainfall (storm events 2 and 4) see text for details.

Table 4.3: Detailed description of the storms analysis in this chapter. Bold values are maximum values on each variable.

For explain of variable and units, see Table 4.1.

P(tot) B	Dur B	IB	Max15 B	Max30 B	ECL30 B	P1d B	P7d B	P30d B	P(tot) DPF	Dur DPF	IDPF	Max15(DPF)	Max30(DPF)	ECL30(DPF)	P1d(DPF)	P7d(DPF)	P30d(DPF)	Qp	Qb	SSC	SL(tot)
22	6	4	12	6	311	5	39	97	13	5	3	7	6	73	1	6	58	29	6	153	27
22	10	2	8	4	138	25	39	46	28	2	8	16	14	397	10	20	28	9	4	529	35
13	6	2	6	3	78	3	44	119	14	5	3	7	6	73	11	17	71	19	4	293	58
30	6	5	16	8	554	10	21	154	7	3	2	3	3	12	4	8	91	34	4	155	87
22	6	2	12	6	311	10	60	194	4	3	1	5	4	32	7	0	108	25	7	119	28
17	3	2	8	4	138	7	46	210	7	4	2	1	4	32	7	45	115	16	9	804	97
29	6	4	8	4	138	26	85	327	10	4	3	9	6	73	5	61	153	35	12	322	74
35	5	3	8	4	138	10	101	350	11	4	1	6	2	8	6	30	168	43	9	154	101
5	1	3	4	2	35	28	146	397	2	2	1	2	1	0	3	29	170	22	12	35	15
18	7	4	8	4	138	14	138	422	15	5	3	6	6	73	3	41	169	35	9	358	111
22	8	4	10	5	216	27	78	412	7	3	2	5	3	12	5	51	190	60	18	138	128
17	9	2	4	2	35	23	108	441	3	2	2	2	2	8	7	40	196	31	11	38	23
21	11	3	6	3	78	2	24	182	27	6	3	7	6	73	0	45	101	20	3	575	113
28	7	4	6	3	78	2	24	109	13	4	3	5	4	32	1	15	94	43	9	305	115
10	7	1	4	2	35	10	67	167	19	7	3	7	6	73	10	24	147	61	9	206	209
4	2	1	2	1	9	11	15	101	6	4	2	4	3	24	8	7	118	8	3	403	30
16	6	3	6	3	78	11	12	65	13	4	3	7	6	73	5	59	56	19	2	350	72
29	5	6	9	4	156	21	30	60	14	5	3	6	6	12	9	18	30	6	1	68	13
21	10	2	4	2	35	21	27	90	0	2	0	1	0	0	1	12	46	12	6	125	45
4	1	19	6	3	78	22	86	119	2	1	2	11	10	203	34	39	65	20	5	202	42
19	11	3	8	4	138	4	92	122	31	5	6	11	9	183	0	48	76	18	2	231	45
29	7	4	10	7	303	6	6	149	29	6	5	14	10	203	1	2	109	14	4	75	12
15	6	3	10	8	346	0	4	105	13	3	2	5	2	12	5	17	65	49	13	501	227
25	5	5	9	7	273	3	21	124	19	4	5	16	12	268	5	36	84	22	8	439	135
7	4	2	5	5	108	13	41	112	5	2,5	2	4	1	12	5	27	89	5	5	59	7
11	6	4	10	8	346	19	49	136	9	5	2	8	6	73	10	14	54	9	6	454	84
32	9	3	5	5	108	0	57	154	10	6	2	3	2	8	0	22	63	39	5	639	205
12	10	2	4	3	52	34	89	189	11	3	3	6	3	24	12	33	75	18	9	52	46
35	8	4	6	6	156	1	57	211	18	5	3	5	4	32	0	32	96	32	8	270	75
27	11	2	6	4	104	1	28	133	11	6	1	6	4	32	0	15	69	28	5	256	56
6	6	2	3	3	39	0	49	109	4	1	4	6	3	24	1	29	65	8	6	55	4
2	2	1	2	2	17	6	63	112	5	1	5	7	6	73	16	44	64	19	9	322	55
4	5	2	4	4	69	2	38	116	3	2	2	3	3	24	4	39	73	9	7	58	3
2	3	1	2	1	9	17	38	148	3	2	2	3	2	8	1	34	82	26	8	102	31
30	13	3	5	4	87	2	21	55	17	6	5	5	2	41	0	2	7	11	5	146	20

4.3.5.2 Correlations between rainfall, runoff and suspended sediment load for individual storm events

The overview of sediment load and concentration dynamics given in section 4.4.5.1 has shown that suspended sediment responses vary between storm events and that while some insights into controls can be gained there are complex interactions between factors. To investigate in more detail the factors that determine event sediment load and peak suspended sediment concentration, a correlation matrix was created to evaluate the relationship between sediment (dependent) variables and individual independent variables. Theory suggests that suspended sediment loads will be determined (and potentially limited) by (1) the availability and ease of environment to mobilise sediment particles (linked with antecedent rainfall and rainfall intensity) and (2) stream discharge and their associated sediment carrying capacities (Gregory and Walling, 1973). Relationships between suspended sediment storm responses in the whole catchment with storm rainfall characteristics and indices of antecedent precipitation are explored in a correlation matrix giving Pearson's product moment correlation coefficients (r) and significance level (Table 4.4).

While there was a significant positive relationship between sediment load and peak discharge ($R^2= 0.6$; P-value 0.05), total precipitation (P_{tot}) at both the upper and lower catchment showed no relationship with sediment load through the year (Figure 4.8). Suspended sediment (SS) load and rainfall are not significantly correlated with each other ($R^2= 0.02$ and 0.00 for rainfall in upper and lower catchment respectively). Some relationships emerged, however, when the data were split into seasons. Table 4.5 shows that SSC_{max} , and SL, are well correlated with total

precipitation in the lower catchment with an $R^2 = 0.51$ and $R^2 = 0.52$ (P-value 0.05 for both) during the winter.

There was no discernible correlation between the discharge and precipitation in the upper and lower catchment ($R^2 = 0.24$ and $R^2 = 0.10$, P-value <0.1 for both). The total sediment load was, however significantly related to discharge (Q_p) with an $R^2 = 0.67$ (P-value 0.005), while suspended sediment concentration (SSC_{max}) was also significantly correlated with antecedent rainfall P7d (upper catchment) which was $R^2 = 0.52$ (P-value <0.05).

In the summer, suspended sediment variables were related to precipitation and discharge, but the precipitation and discharge do not show a significant relationship between each other. Table 4.6 shows, rainfall had a stronger influence on the SSC and sediment load (TL). Moreover, the sediment load (TL) and suspended sediment concentration (SSC_{max}) were correlated with total precipitation in the upper catchment (P_{tot} B) ($R^2 = 0.50$, $R^2 = 0.41$, P-value 0.005 respectively), suspended sediment concentration (SSC_{max}) was strongly related to antecedent rainfall P7d (B), and P7 (DPF) ($R^2 = 0.82$ and $R^2 = 0.86$). The total sediment load shows a positive relationship with peak suspended sediment concentration (SSC_{max}) and antecedent rainfall across the catchment i.e. P30d (B), P30d (DPF) ($R^2 = 0.50$, 0.44, and $R^2 = 0.64$, P-value 0.005 respectively). Overall, the observations in the winter showed that the suspended sediment concentration (SSC) and sediment load (SL) responded mostly to rainfall and antecedent wetness in the lower catchment, while in the summer SSC and sediment load responded to antecedent wetness in upper and lower catchment and rainfall in the upper catchment.

Table 4.4 Correlation analysis of all datasets between rainfall properties and sediment load analysis of data.

Correlation is significant at the <0.05 level for bold numbers (n=35).

	Ptot (B)	Ptot (DPF)	Ecl30 (B)	Ecl30 (DPF)	P7d (B)	P7d (DPF)	P30d (B)	P30d (DPF)	SSC _{max}	Qp	TL
Ptot (B)	1										
Ptot(DPF)	0.2121	1									
Ecl30(B)	0.0247	0.0037	1								
Ecl30(DPF)	0.0019	0.1492	0.0174	1							
P7d(B)	0.1633	0.102	0.002	0.0003	1						
P7d(DPF)	0.0453	0.035	0.1382	0.0015	0.0126	1					
P30d(B)	0.009	0.0451	0.0041	0.0876	0.6056	0.2436	1				
P30d(DPF)	0.0004	0.0069	0.0039	0.0769	0.3923	0.1382	0.8246	1			
SSC _{max}	0.0564	0.0025	0.0082	0.0719	0.039	0.0113	0.0295	0.0232	1		
Qp	0.0055	0.0031	0.2206	0.2461	0.122	0.0076	0.2206	0.2461	0.0053	1	
TL	0.0235	2E-05	0.0472	0.0025	9E-05	6E-05	0.0077	0.0157	0.3303	0.5496	1

Table 4.5 Correlation analysis between rainfall properties and sediment load in the winter (n=12).

	Ptot (B)	Ptot (DPF)	Ecl30 (B)	Ecl30 (DPF)	P7d (B)	P7d (DPF)	P30d (B)	P30d (DPF)	SSC _{max}	Qp	TL
Ptot (B)	1										
Ptot(DPF)	0.2101	1									
Ecl30(B)	0.4228	0.0184	1								
Ecl30(DPF)	0.1461	0.0194	0.0905	1							
P7d(B)	0.0004	0.1007	0.0202	0.0007	1						
P7d(DPF)	0.0376	0.0016	0.2778	0.0213	0.1657	1					
P30d(B)	0.1206	0.0309	0.2426	0.1761	0.632	0.3536	1				
P30d(DPF)	0.2561	0.0019	0.2148	0.2002	0.4429	0.0686	0.7755	1			
SSC _{max}	0.0631	0.517	0.0046	0.0097	0.5233	0.035	0.1626	0.0345	1		
Qp	0.2486	0.1063	0.3972	0.0582	0.1812	0.0143	0.2153	0.3897	0.0097	1	
TL	0.1772	0.5282	0.2125	0.0051	0.0008	0.0002	0.0101	0.1516	0.1224	0.6792	1

Table 4.6 Correlation analysis between rainfall properties and sediment load in the summer (n=7).

	Ptot (B)	Ptot (DPF)	Ecl30 (B)	Ecl30 (DPF)	P7d (B)	P7d (DPF)	P30d (B)	P30d (DPF)	SSC _{max}	Qp	TL
Ptot (B)	1										
Ptot(DPF)	0.1373	1									
Ecl30(B)	0.6591	0.5278	1								
Ecl30(DPF)	0.0663	0.698	0.0529	1							
P7d(B)	0.5236	0.1365	0.0492	0.1359	1						
P7d(DPF)	0.3461	0.117	0.1241	0.0466	0.8392	1					
P30d(B)	0.3567	0.0555	0.1241	0.3122	0.6321	0.2865	1				
P30d(DPF)	0.5639	0.013	0.0645	0.0142	0.6358	0.044	0.2592	1			
SSC _{max}	0.4137	0.1197	0.0058	0.3262	0.8253	0.8634	0.0034	0.4816	1		
Qp	0.0207	0.0426	0.0572	0.2508	0.0051	0.1061	0.9276	0.2035	0.107	1	
TL	0.5026	0.0208	0.2448	0.0377	0.3299	0.3415	0.4445	0.6487	0.5172	0.0194	1

4.4 Discussion

4.4.1 Temporal patterns in sediment concentration in the Avon River

As is clear from the results presented above, winter was the most important season in term of the sediment transport in the Avon basin, in agreement with the results from Walling *et al.* (2001), Evans *et al.* (2004), and Bowes *et al.* (2003), who all found evidence of similar temporal variation in their studies of sediment transport in South and South West England. They noted that the maximum sediment concentrations were observed in the autumn season and minimum concentrations were found at the end of February. This study also shows that there was a reduction in suspended sediment concentration was in the summer season. Results from this study are in agreement with findings reported by Jarvie *et al.* (2002), who noted much reduced soil erosion and sediment transport from the land to the river system in summer, due to reduced summer precipitation and the soil being protected by vegetation.

Discharge and suspended sediment concentration during the single storms present a complex relationship as shown in Figure 4.8 in line with observations obtained by Walling & Webb, 1981; Peterson & Walling, 1981; Walling & Kane, 1982; Peart & Walling, 1988; Walling & Webb, 1982; Irvine & Drake, 1987; Lewis, 1998; Allen & Bogen, 1994; Kostrezewski *et al.*, 1994. Often, stream bank and bed disturbance are caused which adds to complexity of sediment dynamics (e.g., Bogen, 1980, Walling & Webb, 1982 & Spott & Guhr, 1994). The study results suggest that storm event responses were related to spatial rainfall dynamics and landuse/sediment availability at respective sites.

Walling (1978) showed that, in the Dart & Creedy Rivers (UK), sediment concentrations diminished around 50% during the lag time between the sediment and the discharge peaks. In this context, Lopez-Tarazon *et al.* (2009) emphasized the importance of the proximity of sediment source areas. The role of agriculture in the lower catchment which is mainly dominated by cultivated land (e.g. winter cereals and potatoes) was a key determinant of sediment response in the winter. Heidel (1956) & Williams (1989) reported that for small streams, the maximum SSC usually occurs prior to discharge. However, other authors have suggested that SSC peaking prior to discharge reflects a progressive decline in sediment availability during storm event or an early-stage depletion of suspended sediment (Lenzi & Marchi, 2000). These explanations are considered to be not directly applicable to the Avon River.

Where there was a sequence of storms in an extended wet period (for example the period November to December, Table 4.3), the suspended sediment concentration also exhibited a trend of reduction in peak concentration and loads. Hudson (2003), Alexandrov *et al.* (2003), Gomez *et al.* (1997) and Magilligan *et al.* (1998), reported similar results. Hudson (2003) described the highest sediment concentration in the Panuco River (Mexico) occurring at the beginning of the rainy season. Alexandrov *et al.* (2003) observed that the suspended sediment concentrations recorded during a secondary storm in the Nahal Eshtemoa basin (Israel) were relatively low, due to a sediment exhaustion effect, than those observed during a primary storm. Therefore, after a period of relatively high sediment transport (supply-rich storms), sediment becomes less and less available (exhaustion phenomenon), and the sediment concentrations recorded during successive months are consequently lower (Walling, 1978). This is typified in this study by the storm event on 25/11/2009 where the peak

sediment concentration was just 35 mg l⁻¹ after a large series of events preceding this storm (Table 4.3).

The cumulative curves also illustrate the episodic nature of sediment transport with the occurrence of storm events. However, the suspended sediment load in the Avon River tends to be higher during winter and autumn than during spring and summer. In the light of these results, the existence of a seasonal sediment yield cycle composed of two phases of sediment preparation (autumn, spring and summer) and sediment transport and exhaustion (winter) can be defined. Isolated summer storms (such as those recorded August 2010) may disrupt this general pattern. Particularly high concentrations recorded in August support this observation. Asselman (1999), on the Rhine River (Germany), and Hudson (2003), on the Panuco River (Mexico), described similar sequences. Asselman (1999) observed a reduction of the suspended sediment load in the Rhine River during the autumn and winter months related to the sequence of the seasons and the storm events, whereas during the spring and summer, there was storage of fine sediment in the channel network. Hudson (2003) described the same dynamics in the Panuco River and associated the sediment cycles with the high sediment availability on the slopes at the beginning of the rainy season owing to prepare during the dry season. During early rains the sediment is quickly transported to the channel network.

A further trend common to the Avon catchment in this study is the apparent almost complete winter depletion of sediment that accumulated over the summer period. In early autumn, with the commencement of wetter weather and higher flows in the channel, it appears that sediment, which has settled on the channel bed, is re-suspended and transported further down the river system towards the outlet. This trend was noted by Kronvang *et al.* (1999) and Svendsen *et al.* (1995), who both, in

their studies of Danish streams, deemed that most of the retained sediment was re-suspended during storm events in the autumn and winter. This remobilisation and depletion was not only due to changing hydrometeorological conditions but was further facilitated by a decline in the protective cover given to stored sediment.

4.4.2 Comparison of sediment yield with other study catchments

Many authors recording results from catchment wide studies of sediment load and yield, there is much variation noticeable between all the study catchment. Furthermore, as shown in Figure 4.12, sediment yield in the Avon River varied quite considerably between the two years of study. The total load and yield were 2437 t and $7.15 \text{ t km}^{-2}\text{yr}^{-1}$ for 2009 and 986 t, and $3.30 \text{ t km}^{-2}\text{yr}^{-1}$ for 2010.

Lopez-Tarazon *et al.* (2010) in the River Isábena (Spain) which was a similar catchment area to the Avon (445 km^2) derived an annual sediment load of 54,000 t y^{-1} , with a specific yield of $121 \text{ t km}^{-2} \text{y}^{-1}$.

The Avon sediment yield was relatively low compared to other UK catchment. The suspended sediment yield for the River Swale at Catterick Bridge varied from 92.1 to $17.8 \text{ t km}^{-2} \text{yr}^{-1}$ and sediment loads were 54,000 t. In the Humber catchment, was calculated to be 699 861 t, equivalent to a yield of $15 \text{ t km}^{-2} \text{yr}^{-1}$. While the catchment located in the Mexican Central Highlands was estimated during a whole year, suspended sediment yields of upland sub catchments exhibited a specific behaviour (9.3 , and 12.0 km^2) (i.e., Potrerillos, $600\text{--}800 \text{ t km}^{-2} \text{yr}^{-1}$ and La Cortina, $30 \text{ t km}^{-2} \text{y}^{-1}$).

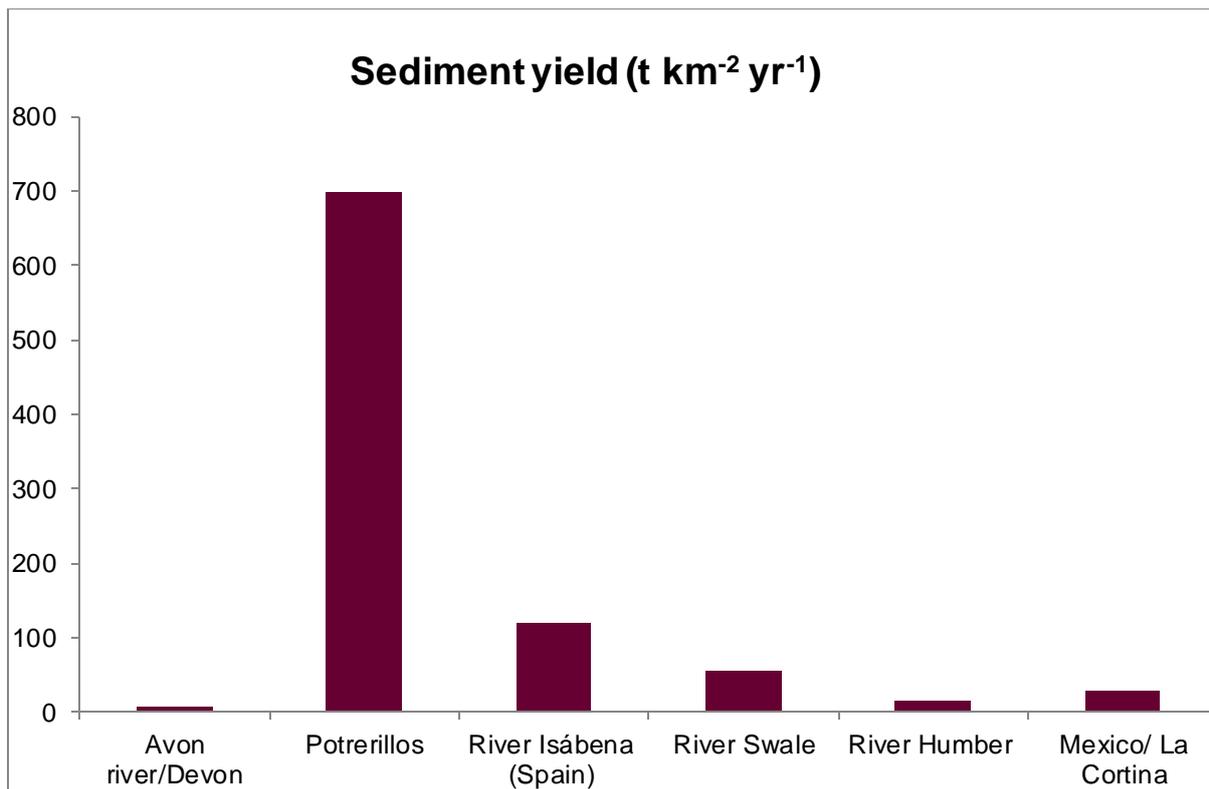


Figure 4.12: Comparison of sediment yields from this study to other agricultural catchments

4.4.3 Controls on sediment load in the Avon catchment

Table 4.4 shows a complex relationship between storm event factors and sediment response. However, correlation analysis indicates that there is little relationship between rainfall properties and sediment load across the year, but analysis of the data in seasonal blocks reveals that in the winter, rainfall in the lower catchment was a key factor for higher sediment loads. This suggests that time of year is important as, during winter, fields do not have a dense vegetation cover and when the soil surface is bare there is a ready pool of sediment that is easily eroded, similar to the idea proposed by Beuselinck *et al.* (2000) who proposed that with the season of the year and availability of sediment strongly influences the movement of sediment and nutrients. Nevertheless, most of the sediment is transported at the beginning of the wet autumn season, as the land is under preparation or the crops did not emerge to

prevent direct rain splash and runoff. At the end of the season, more of the land is covered by vegetation, and there will be less sediment produced on the hillslopes, although runoff might be higher due to the swelling of the soils and the rise of the water table at the end of the wet autumn season.

In the summer, the sediment response of the catchment was correlated with rainfall in the upper catchment where antecedent rainfall was seen to be of importance (Table 4.4). In the upper catchment where slope gradients are higher, grazing could leave some areas of the catchment susceptible to erosion and transport during rainfall events. So, correlations between sediment transport and other hydrological variables indicated that, in addition to discharge, rainfall characteristics (especially rainfall intensity) and antecedent rainfall are the most important factors controlling suspended sediment transport in the upper catchment. As shown in Table 4.4, the sedimentary response in the summer may therefore depend as much upon changes in the spatial distribution of precipitation as changes in total precipitation.

A point to note from the data is that no clear correlation between the rainfall and runoff was observed (see Appendices 1). The lack of relation is maybe due to a considerable temporal and spatial variability, exhibited by the rainfall runoff process (Sivakumar *et al.*, 2000). However, they concluded that the spatial distribution of rainfall and the accuracy of the rainfall input influenced considerably the volume of storm runoff, time-to-peak and the peak runoff (Shah *et al.*, 1996) and in this study, spatial patterns of rainfall and seasonality are a key factor in determining sediment load.

In the Avon catchment, although the rainfall amount and erosivity is generally higher in the upper catchment, the land use in the lower catchment is most susceptible to erosion and sediment generation, and winter sediment loads were most significant when the lowland areas received high rainfall. According to the Avon catchment map in section 4.2 (Figure 4.1) a large portions of the land areas, specially cultivated land, is dominant in the lower catchment and close to the main channel. In agreement with Johnes (1996) and Russell *et al.* (2001), in their study of two lowland agricultural catchments in the UK, cultivated land has often been the main surface contributing to suspended sediment loads in UK catchments. Therefore, considering the transport of sediment load in the lower catchment, the most critical areas will be hydrologically active areas which intersect easily erodible zones where sediment availability is high (Pionke *et al.*, 2000).

4.5 Conclusion

It can be concluded from the data collected that sediment response of the study catchment is complex and deserves much consideration due to related to spatial variability in rainfall and sediment source areas. The study has shown that there is spatial variation in the amount of rainfall and storm events that are restricted to the upland part of the catchment generate a large flow response but a notably lower sediment flux. In contrast, winter sediment loads are most significant when the lowland areas receive high rainfall because the land use in the lower catchment is most susceptible to erosion and sediment generation. These hydrological processes have a strong influence on the annual patterns in sediment flux, and allow the year to be subdivided into distinct seasons of transportation.

Relationships between rainfall and discharge and suspended sediment transport out of the catchment are very likely to be determined by the spatial and seasonal dynamics of the different runoff contributing areas, especially with respect to land cover and seasonal cropping patterns. The study has also shown that sediment concentrations may vary between events, and will reflect sediment supply and flow conditions in the river. The analysis of data for a two year period showed that the suspended sediment yield in the catchment and delivery of sediment to the estuary was characterized by remarkably high annual variability.

Chapter 5: Fine sediment and associated phosphorus distribution in an agricultural estuary, south-west UK

5.1 Introduction

The aim of this work package is to evaluate the spatial distribution of fine sediment and associated P in the Avon estuary. The specific objectives are:

- (i) To characterise areas of fine sediment deposition, using aerial photographs, field survey analysis and GPS surveying into distinct sediment deposition zone units.
- (ii) To collect representative sediment samples from each unit and analyse for particle size and fine (<63 μm) sediment-associated phosphorus and total organic carbon.
- (iii) To create a GIS model of the Avon estuary to explore spatial patterns in key sediment properties and sediment associated P.

5.2 Methodology

5.2.1 Sample collection

In total, 87 sediment samples were taken from key morphological zones (salt marsh, sand shoals, and mudflat) along the length of the estuary from both west and east banks from the mouth to the head of the estuary. The sediment sampling strategy was based on the representative landscape units of the estuary. All samples were bagged, labelled and returned immediately to the laboratories in the Physical Geography Department at the University of Plymouth for analysis. The samples were collected from boat and by foot, using a grab sampler and trowel as appropriate.

Approximately 200 g sediment was taken at each sampling location (full listing can be found in Appendix II) and samples represented a surface scrape of 50 mm depth. All sample site locations were recorded with a handheld GPS (Figure 5.1).

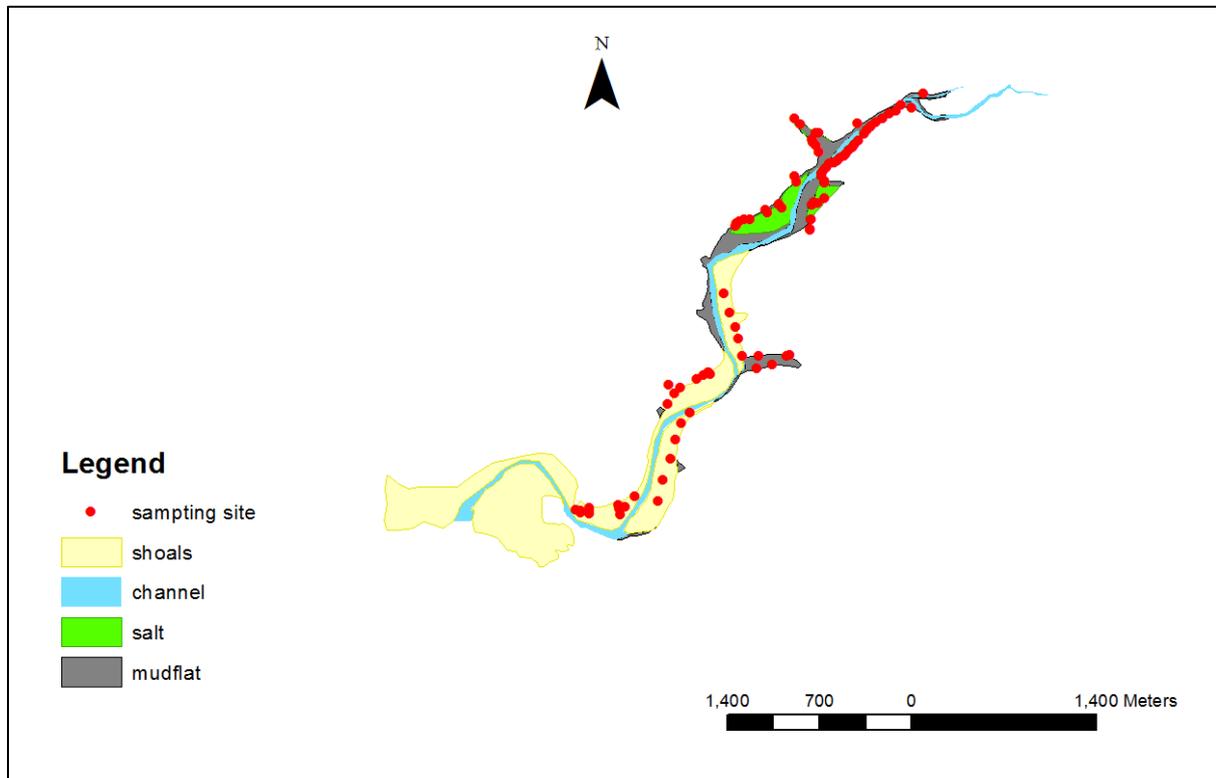


Figure 5.1: The main deposition areas of the estuary together with sample collection sites.

5.2.2. Laboratory analysis

5.2.2.1 Sediment preparation

Sediment samples were split into two sub-samples on return to the laboratory. First, a representative subsample (approximately 5 g) was taken and the weight was recorded. Then the sample was dried in a hot oven at 90 °C for one day and the dry weight was recorded. Afterwards, the dry material was gently disaggregated and sieved, using a 2 mm sieve. The weight of the material greater than 2 mm was recorded and this material was then discarded. The remaining material, which was

less than 2 mm, was sieved using a sieve to less than 1 mm. The weight of this 1-2 mm fraction was recorded. Finally, the fraction of the material less than 1 mm was analysed using the Mastersizer, following standard procedures.

5.2.2.2 Particle size analysis

Sub-samples of <1mm sediment were taken, approximately 0.25 - 0.5 g of the fine sediment, and added into a 12 ml vial. 3-4 ml of 3% hydrogen peroxide was added to remove the organic matter and the sample was left to digest for 12 hours for the reaction to occur. The vials were then placed into a water bath and heated to 90 °C for 2 hours or until the fizzing stopped. Approximately 3 - 4 ml of 6% hydrogen peroxide was added; the vials were left in the water bath and left until the reaction was finished. Particle size analysis was carried out by sieving and by laser analysis using a Mastersizer 2000 (version 5.60) laser particle-size analysis over a range of 0.1-2000 µm (Folk & Ward 1957).

5.2.2.3 Total phosphorus analysis of the fine (<63µm) sediment fractions

A second set of sub-samples was weighed, dried at 45 °C, ground in a pestle and sieved to a fine powder <63 µm prior to analysis for total phosphorus using the method of Murphy and Riley (1962). Concentrated nitric acid (10 ml) and concentrated sulphuric acid (2 ml) were added to the digestion tubes containing around 0.5 g samples. All samples were heated until the solution became colourless. Solutions were poured into a volumetric flask and made up to 50 ml with distilled pure water; blanks were used in order to correct for any errors. Samples were analysed on an AutoAnalyzer 3 (AA3) systems, run using the low level P configuration. Extracts were further diluted (1:10). This dilution was entered into the

program when operating the AutoAnalyzer (low-range phosphate configuration) to ensure final data accounted for this step (Murphy and Riley, 1962).

5.2.2.4 Total carbon content

The total organic carbon (TOC) of fine sediment samples was measured using a Skalar carbon analyser following the procedure documented by Veres (2002). In total, 87 samples were analysed. Samples weighed ranged from 100 -150 mg total carbon (TC) and from 50-150 mg total inorganic carbon (TIC). Total carbon (TC) was determined by catalytic oxidation of the sediment sample at just over 1000 ° C, converting the carbon present to CO₂ which is recorded by detectors when released. The inorganic carbon fraction (IC) was determined by acidification of the sediment sample in the IC compartment which converts the inorganic carbon to CO₂ and removes the organic carbon component. Total organic carbon component (TOC) was calculated by subtraction of IC from TC.

5.2.2.5 Spatial data analysis

The Channel Coastal Observatory and Digimap Ordnance Survey (OS, data) were used alongside aerial photography of the Avon estuary to create an Avon catchment and estuary in GIS (Figure 5.1). All samples have been analysed for grain size using the classical methods of sieving for the coarse grained material and the pipette method for the (<1 mm). Sediment classification was used to establish grain size of the sediment spatial pattern of sediment grain size for the Avon estuary. The sediments were classified according to their sand/silt/clay ratios following the classification of Shepard (1954) (Figure 5.2 and 5.3). The classification used was

originally developed by Shepard (1954), as modified by Schlee (1973). Spatial data analysis using GIS was carried out using the percentages of sand, silt, and clay sample data (Table 5.1). Interpolation on each grain size category was carried out separately, and renormalized to give a sum of 100% in order to minimize inaccuracies in the interpolation.

Table 5.1 Sediment classification output value.

Integer Value	Description	Sediment Classification Determination
03	Sand	Sand ≥ 0.75
04	Silt	Silt ≥ 0.75
09	Sandy silt	Sand > 0.2 AND Sand < 0.75 AND Silt < 0.75 AND Sand $<$ Silt
10	Silty sand	Sand > 0.2 AND Sand < 0.75 AND Silt $>$ Sand

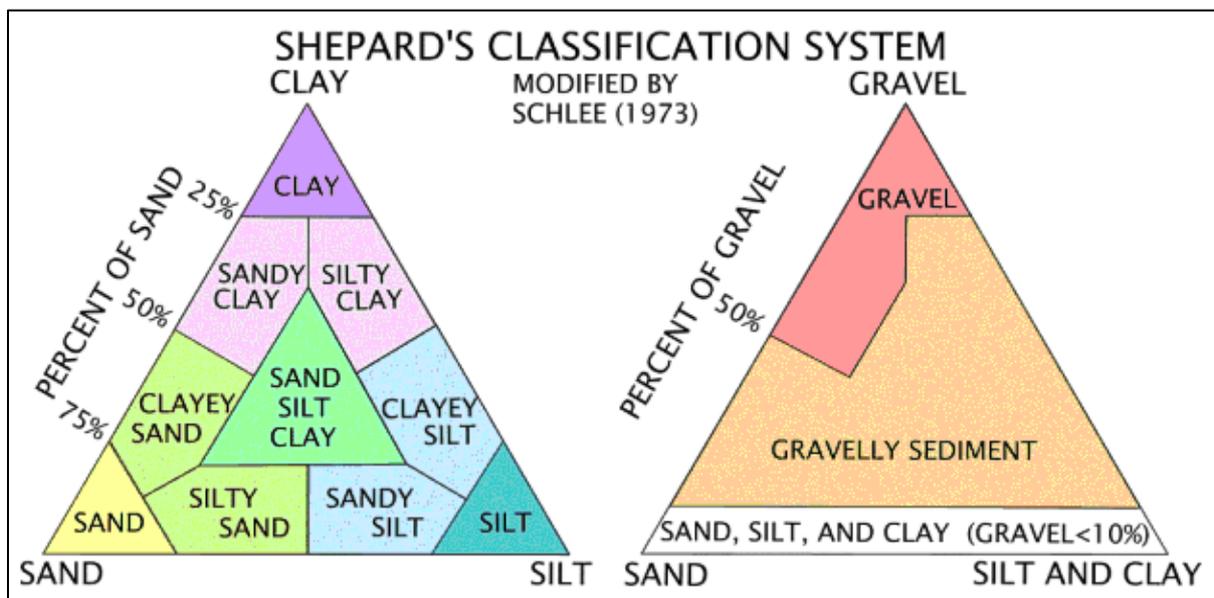


Figure 5.2: Shepard's (1954) Sediment Classification System as modified by Schlee (1973)

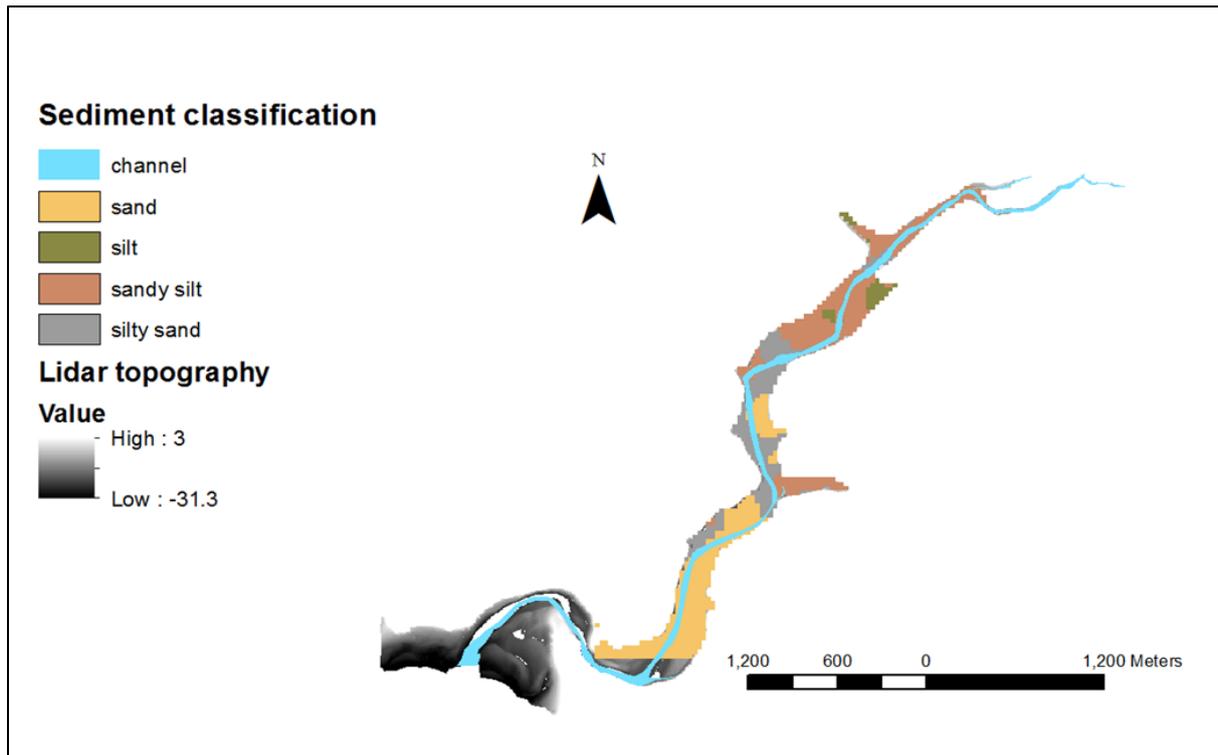


Figure 5.3: Sediment classification of the estuary (see also Figure 5.2)

5.3 Results

5.3.1. Spatial variability in sediment physical characteristics

Grain size was used to examine the sediment characteristics along the Avon estuary. As noted, the upper part of the Avon estuary was typically muddy; in the lower estuary it is typically sandy. When considering the sediment classification between sites, it appeared that silt was found in the upper estuary; sandy silt appeared in the upper and middle of the estuary; silt sand appeared in the middle and lower estuary; and sand was found in the lower estuary (Figure 5.5). In order to investigate the spatial variation of the particle size characteristics for all sites, the averages calculated on the data collected in Figure 5.6 showed that the fine fraction increased in the saltmarsh and in the mudflat, while the coarse fraction dominated in the shoal area. A maximum mean value of 80% silt was recorded in sediment samples at the

west saltmarsh site 2, and the minimum of 4% was recorded at the lower estuary at shoal site (W-SH1). Figure 5.4 shows that mean silt does not vary very much within each mudflat and saltmarsh in the upper estuary; while the mean of silt samples in the lower estuary was low at mudflat 5 and shoal (SH 1 and 2). There was found to be a low mean value of 18% recorded in sand samples in the saltmarsh, a site of west saltmarsh 2 (W-SM2) in the upper estuary, with a high mean value of 96% in sand samples in the west shoal 1 (W-SH1). There was no measurable clay fraction at the lower estuary sites; while the mean value of clay was a maximum of just 2% in the saltmarsh at the upper estuary.

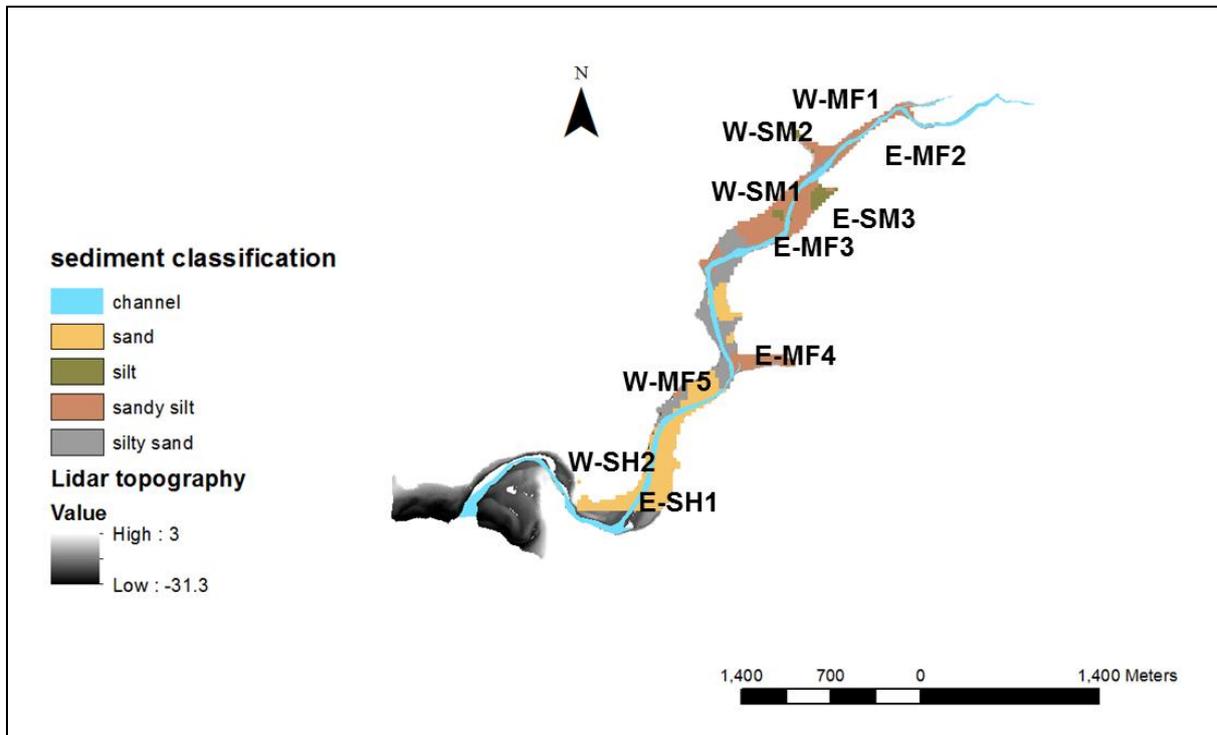


Figure 5.4: The distribution of mean sediment grain size in the estuary. The codes represent the key morphological unit sampled for P and TOC content. These samples were analysed further for P and TOC.

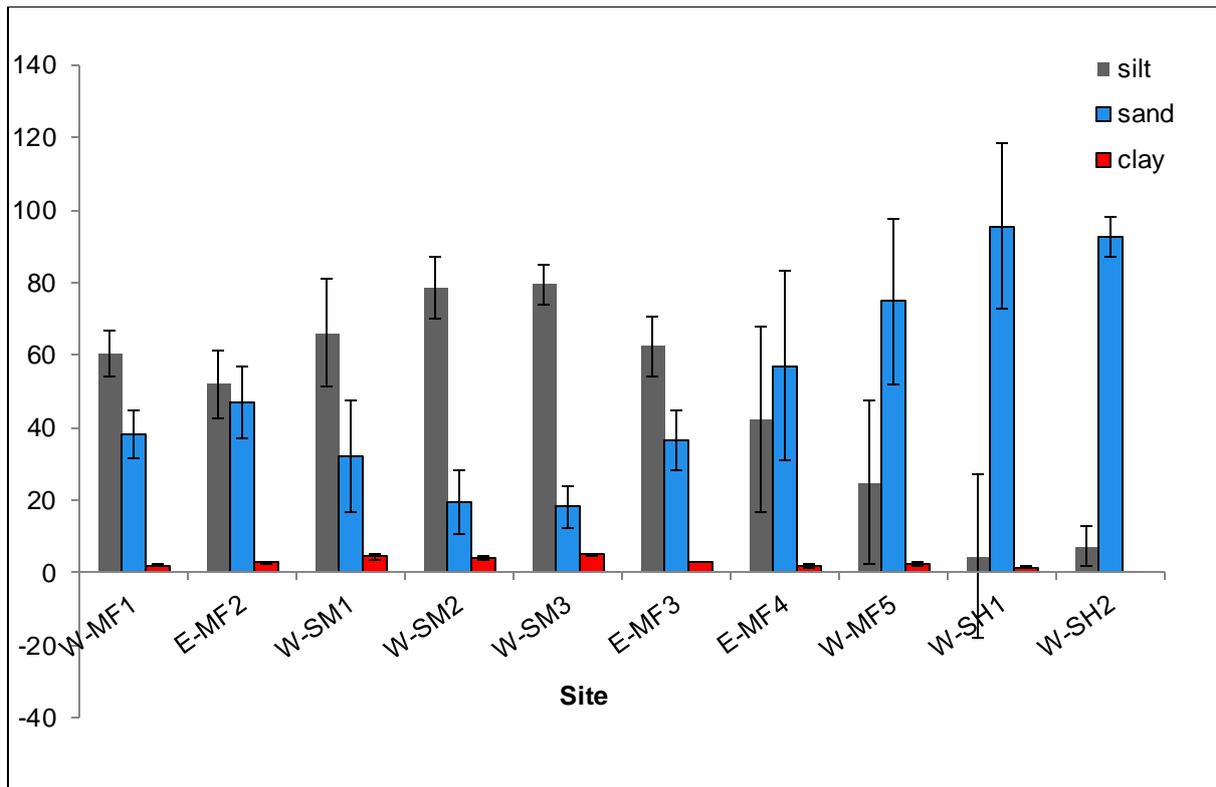


Figure 5.5: Mean and standard deviation of sediment size distribution in Avon estuary sediment (%). See Figure 5.1 for sample locations.

In order to investigate further the spatial variation of the particle size characteristics of sediment, more detailed sediment categorisation by geomorphological unit was undertaken within the Avon estuary. Figure 5.6 and Table 5.2 illustrate the distribution of mean grain size of sediment within different geomorphology zones. It shows that there is considerable variation in the particle size between geomorphology zones. Silt and clay are higher in the saltmarsh and mudflat area with less found in the shoal area. No clay deposits were observed in the shoal area. Sediment, which is rich in sand, is almost always found in the shoal area.

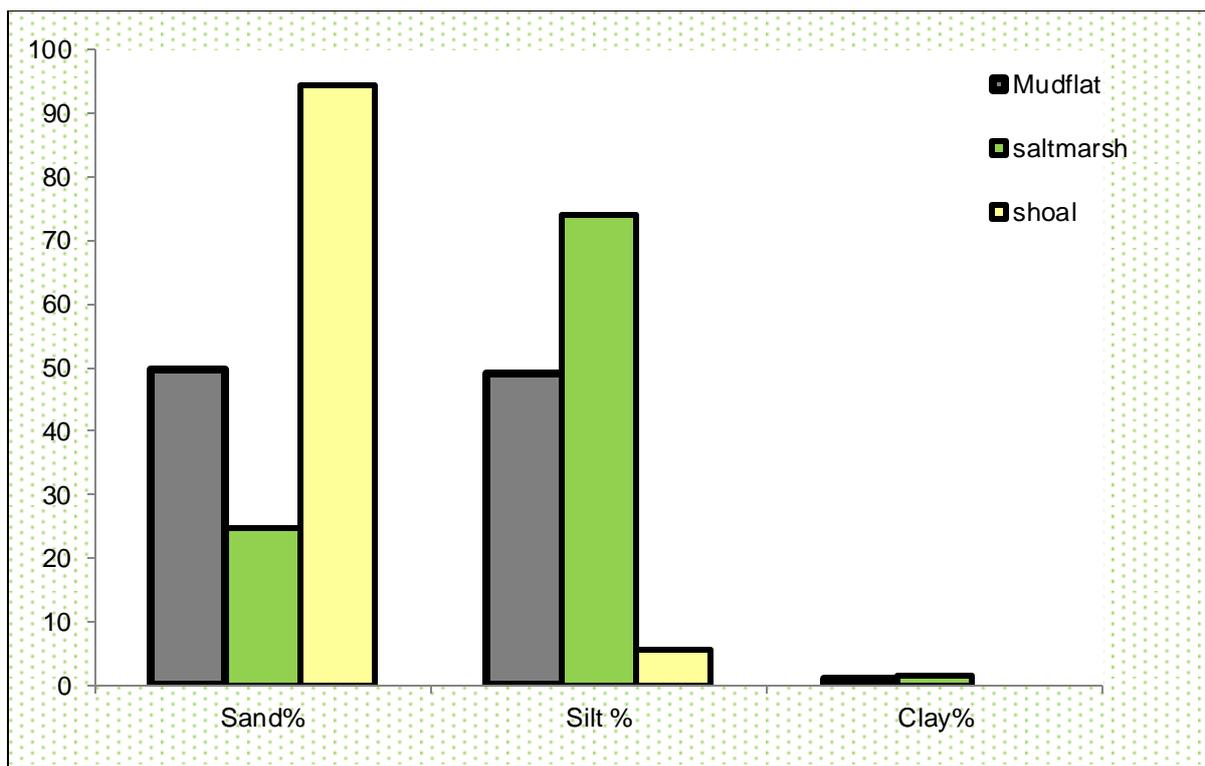


Figure 5.6: Summary particle size characteristics of sediment in the defined zones of the estuary.

Table 5.2 Mean and standard deviation (\pm) of grain size classes of sediment on different geomorphology zones of the Avon estuary.

Area	Silt %	Sand %	Clay %
Salt marsh	74 \pm 10	25 \pm 11	2 \pm 1
Mudflat	49 \pm 16	50 \pm 17	1 \pm 1
Shoal	6 \pm 2	95 \pm 2	0 \pm 0

5.3.2. Spatial variability in total carbon

The distribution of the organic carbon is shown in Figures 5.7 and 5.8. It shows higher concentrations of TC in the upper estuary and lower value in the lower

estuary. Statistical analysis shows the highest value was found in the saltmarsh and mudflat area and lowest with no measurable TC in the shoal in the lower estuary. The highest TC% was found in salt marsh (E-SM3) which was (4.4%). There was only a slight increase in the TC % in the mudflat for the site close to the saltmarsh area which is (E-MF3), which was (2.8%). Data showed a shoal (W-SH1) decrease in organic carbon concentration and no TC was particularly noticeable for sites E-SH2.

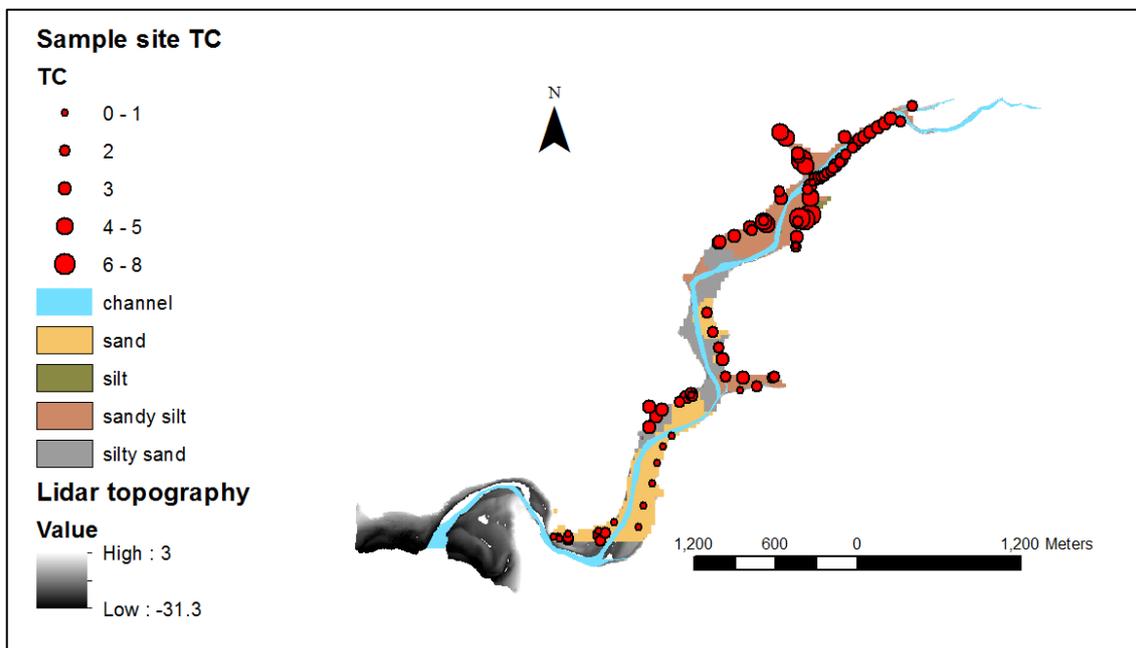


Figure 5.7: Spatial distribution of organic carbon (TC %) in estuarine sediment.

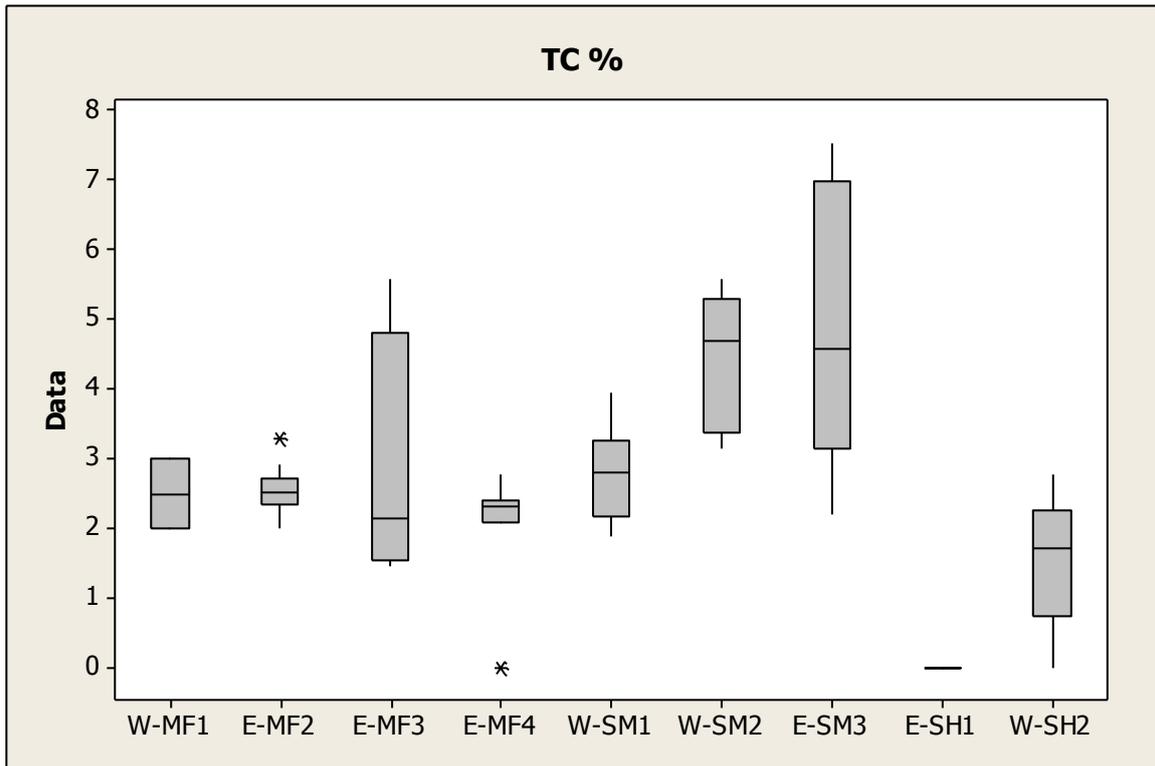


Figure 5.8: Distribution of TC sediment concentrations in the main estuary sampling zones.

Outliers are identified by an asterisk.

In order to investigate further the spatial variation of organic matter in the sediment, more detailed analysis of TC data by geomorphological zone was undertaken within the Avon estuary. Figure 5.10 illustrates the distribution of TC% of sediment on different geomorphological zones. It shows that there is considerable variation in the TC between geomorphological zones. TC is higher in the saltmarsh and mudflat area with less found in the shoal area but there is some internal variability within these units (Figure 5.9).

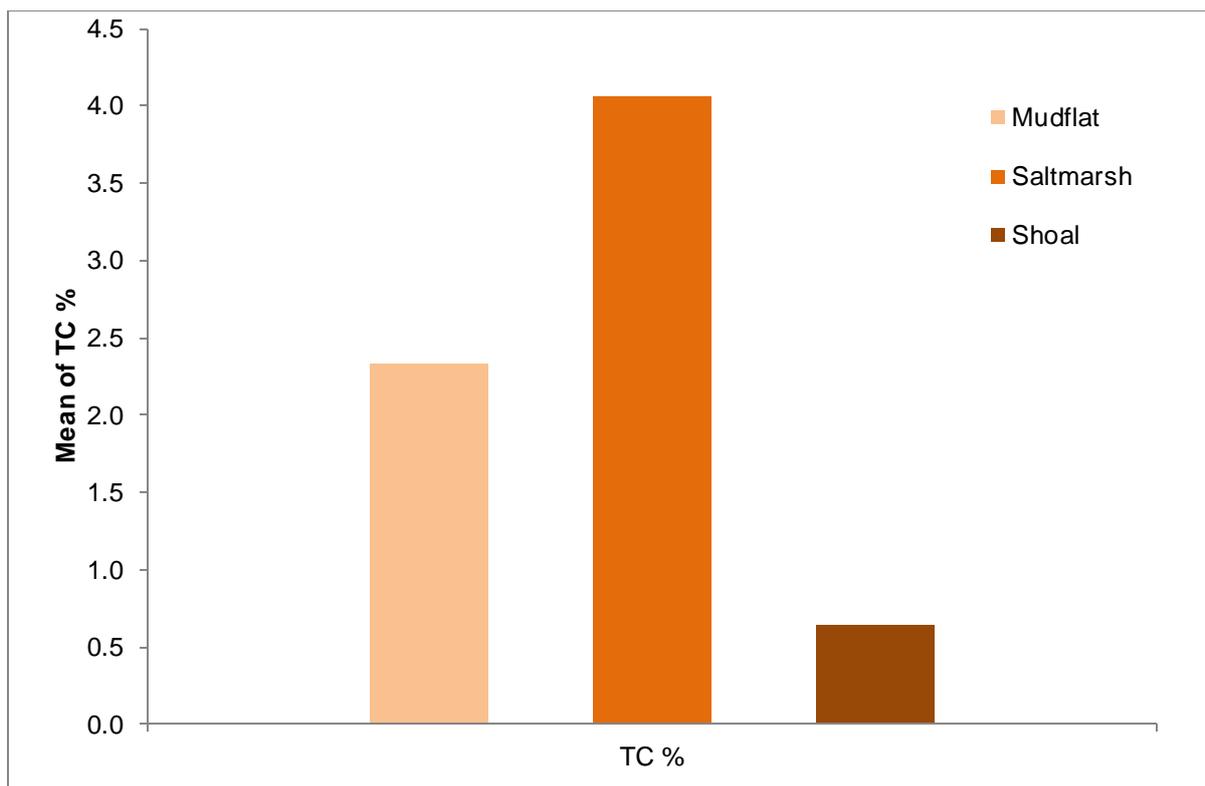


Figure 5.9: Mean TC concentrations within the key geomorphological zones of the Avon estuary.

5.3.3. Total phosphorus distribution within estuarine sediment deposits

Different distributions of the TP concentrations (mg kg^{-1}) were observed along the estuary (Figure 5.10). The higher TP was found in the upper and middle estuary and lower TP was found in the lower estuary. In the upper estuary and between the individual sites, the highest TP (mg kg^{-1}) appeared in the saltmarsh area, with the maximum value of 1198 mg kg^{-1} recorded at (W-SM1), while the minimum of 68 mg kg^{-1} was recorded at the lower estuary at the shoal area (E-SH2) (Figure 11). In terms of the geomorphology area in the Avon estuary (Figure 5.12), the highest values for TP in the sediment were found in the upper estuary in the saltmarsh area, with the mudflat area coming after the saltmarsh area in terms of the elevation of TP (mg kg^{-1}). The lowest value was obtained from the lower estuary, a site in the shoal 1 in the east bank.

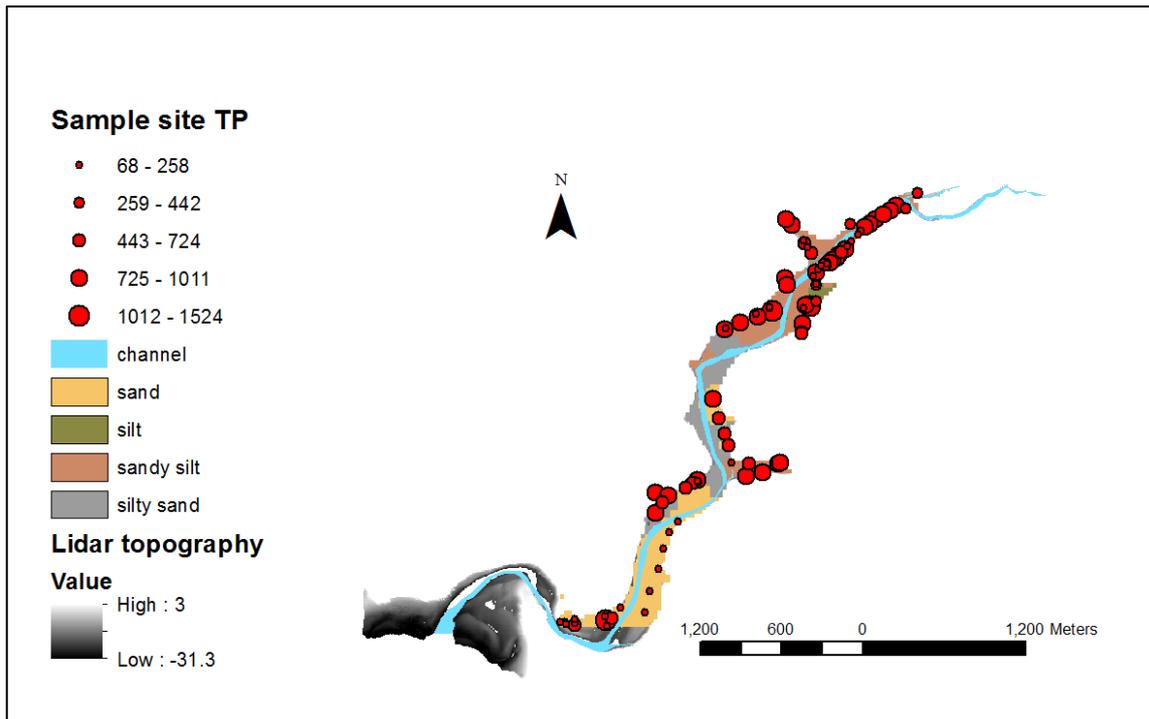


Figure 5.10: Distribution of TP (mg kg^{-1}) and the grain size content of sediment in the Avon estuary.

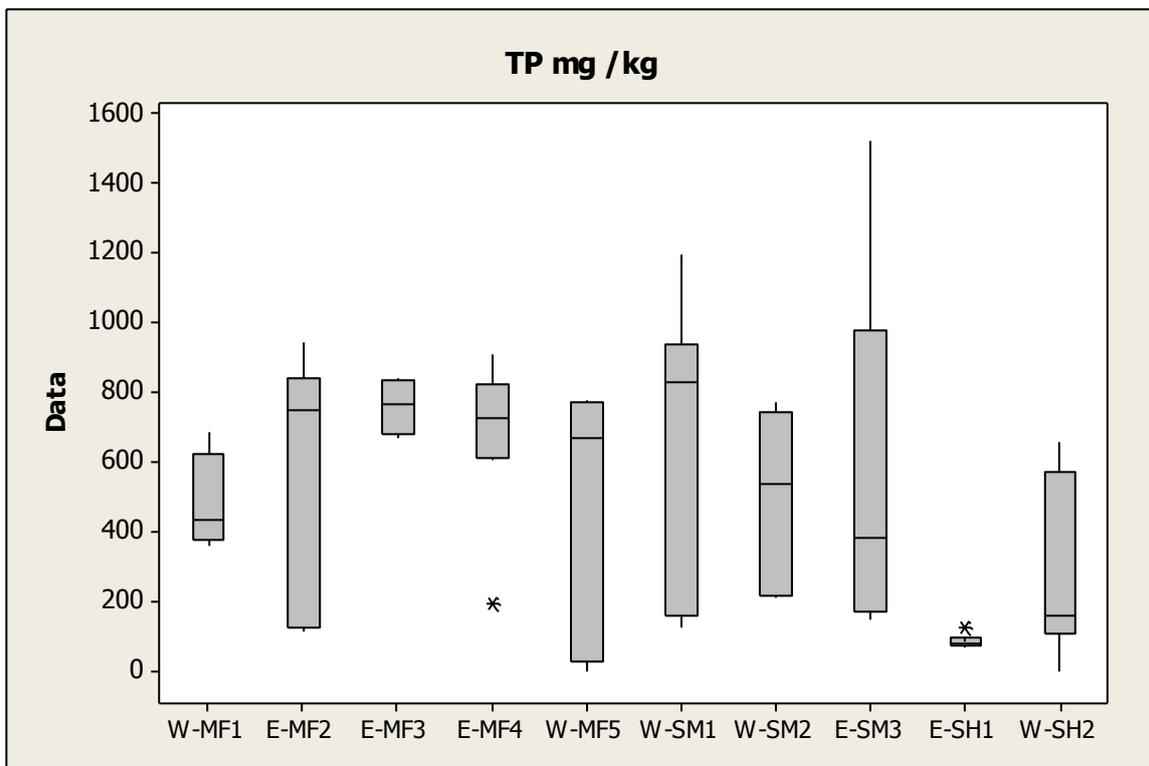


Figure 5.11: Distribution of TP in sediment concentrations in the main estuary sampling zones .

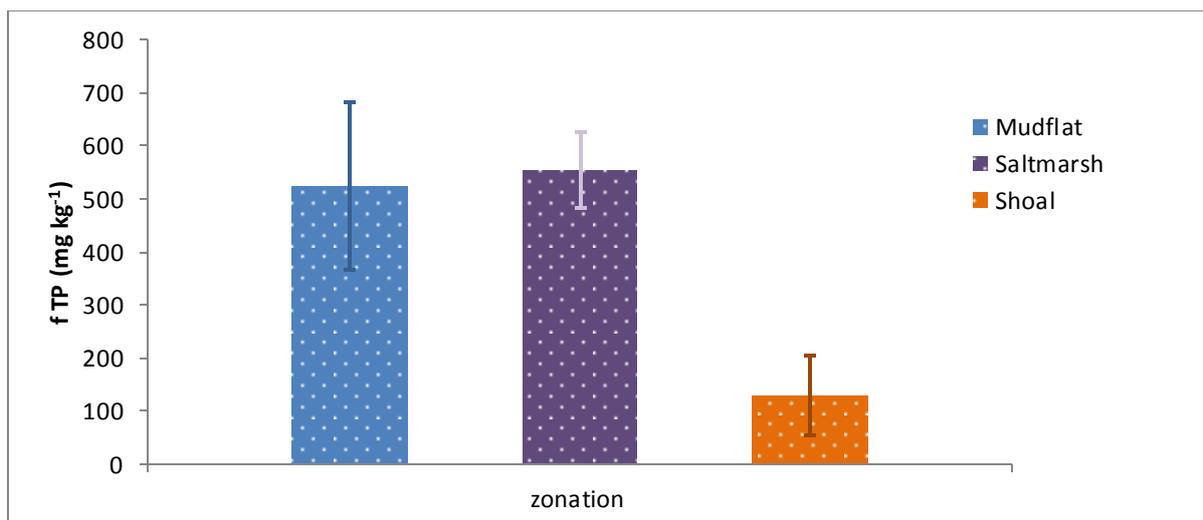


Figure 5.12: TP pattern and the zonation of the Avon estuary where error bars represent 1 standard deviation of mean.

5.3.4 Relationship between observed TP concentration and sediment properties

Table 5.3 shows key sediment properties alongside the total phosphorus concentration for each landscape unit sampled. It was observed that values for TP concentrations tended to be greater in samples from the mudflat; ($760 \pm 85 \text{ mg kg}^{-1}$) coinciding at site E-MF3 with high TC (3%) and with slightly high specific surface area (SSA) (0.13 gm^2). Higher TP concentrations (632 mg kg^{-1}) were found in the upper estuary at the saltmarsh area at site W-SM1 also coinciding with high TC (3%) , silt (79%) and low sand (15%) with high SSA (0.24 gm^2). The mean of TP in the saltmarsh at site W-SM2 was 492 mg kg^{-1} following with the highest mean of value of silt (80%) with high TC (4.4%) and lowest mean value of sand which was (18%). Lower TP ($77 \pm 5 \text{ mg kg}^{-1}$) was found in the lower estuary at site (E-SH1) with the lowest TC (0%) and high sand (93%) with lowest SSA (0.03 gm^2).

Table 5.3 summary statistics of TP, TOC, clay, silt, and sand proportions and specific surface area of sediment within the sampled landscape units.

Zone	Mean TP mg kg ⁻¹	SD/ TP	Sand	Silt %	Clay%	TC%	TC standard dev (%)	SSA gm ⁻²	SSA standard dev(gm ⁻²)	Number
W-MF1	480	142	47	52	1	2	0.6	0.14	0.02	4
E-MF2	569	338	32	66	2	2.5	0.3	0.12	0.03	22
E-MF3	760	85	57	42	1	2.8	1.9	0.13	0.02	4
E-MF4	480	188	38	60	1	2.1	0.8	0.09	0.04	11
W-MF5	332	254	75	25	0	2.3	0.9	0.01	0.04	11
W-SM1	632	422	19	79	2	2.8	0.7	0.19	0.00	10
W-SM2	492	265	18	80	2	4.4	1	0.24	0.00	5
E-SM3	536	505	37	63	1	5	1.9	0.25	0.00	5
W-SH1	184	254	96	4	0	1.3	0.6	0.05	0.00	9
W-SH2	77	5	93	7	0	0	0	0.03	0.04	6

Correlation analysis was used to examine the relationship between the TP mg kg⁻¹ and organic matter Table 5.4. Figure 5.13 shows the mean concentration of TP compared with TC; values and percentage contribution from the TP and TC measured show variation between different sites. Comparing the different sites sampled, there were distinct groupings, with a relationship between TP and TC in the mudflat area greater than others. When the measurements of TP and TC concentrations were further tested together, concentrations of TP tended to increase with an increase in TC. This relationship between phosphorus and organic carbon is reinforced by results provided by a Minitab correlation test, which shows a significant, albeit with scatter, positive relationship ($r=0.381$, $P < 0.00$). The results of the statistical analysis of the samples analysed for TP and TC are displayed in Table 5.4. This Table shows that despite the broad relationship between TP and TC between the main geomorphic units, the correlations between TP and TC was not significant within the sites; the TP concentration in individual sites was found to be different and there is no relationship within each site.

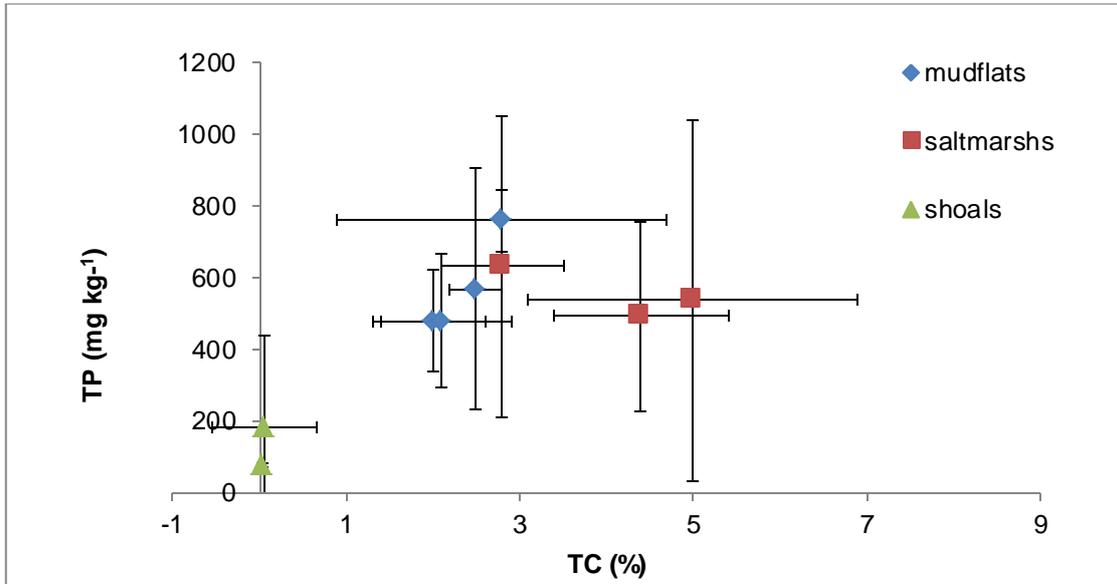
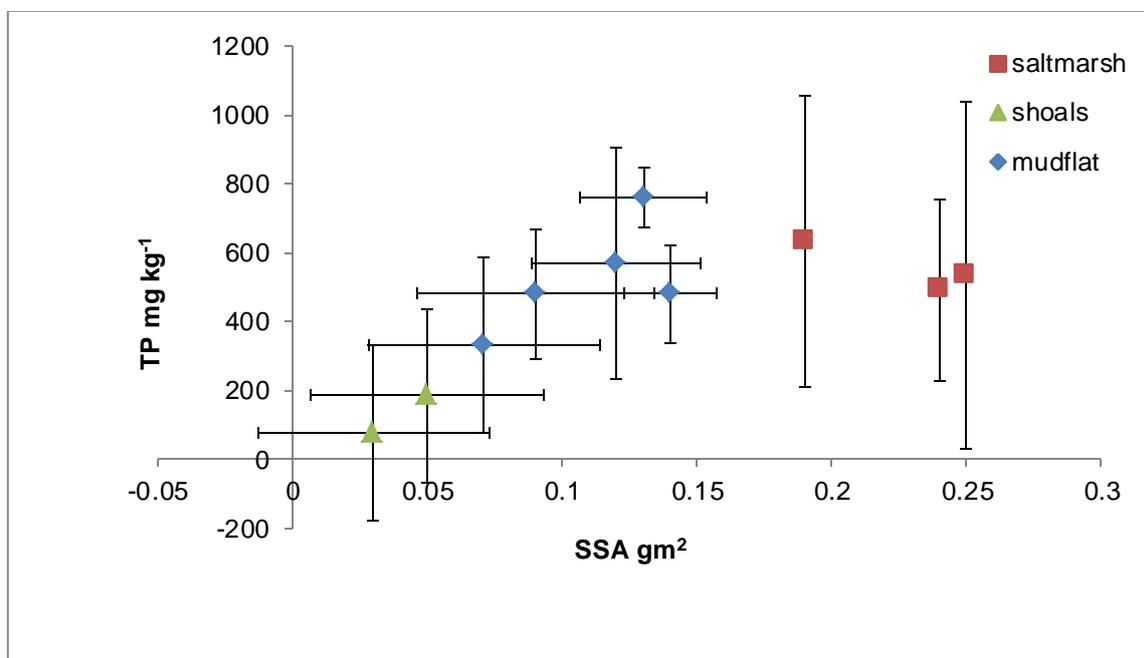


Figure 5.13: The relationship between mean TP and TC from each sample zone.

Table 5.4 correlation relationships between TP and TC % within the different landscape units.

Parameter TP-TC	Relationship r^2	P-value	Number of samples
All samples	0.381	0.00	86
W-MF1	0.350	0.20	4
E-MF2	0.174	0.45	22
E-MF3	0.640	0.36	4
E-MF4	0.203	0.57	11
W-MF5	0.500	0.20	9
W-SM1	0.071	0.84	10
W-SM2	0.180	0.77	5
E-SM3	0.535	0.35	5
E-SH1	*	*	6
W-SH2	0.638	0.03	11

Concentrations of TP mg kg^{-1} tend to increase with an increase in SSA gm^2 across the main sampling sites with the exception of the saltmarshes (Figure 5.14). The correlation analysis between phosphorus concentrations and SSA shows a weak but significant positive relationship ($r=0.261$, $P < 0.01$) which is likely to be influenced by the saltmarsh outliers. A result of Table 5.5 from correlation analysis shows that there is no significant relationship between TP and SSA within the landscape unit sites in addition to the lack of TP correlation with SSA within those sites.



Figures 5.14: The relationship between mean TP and SSA in the main sampling zones of the estuary.

Table 5.5: correlation relationships between TP and SSA within in each sampling zones

Parameter TP-SSA	Relationship (r^2)	P-value	Number of samples
All samples	0.261	0.01	86
W-MF1	0.612	0.38	4
E-MF2	0.174	0.45	22
E-MF3	0.359	0.55	4
E-MF4	-0.257	0.26	11
W-MF5	0.544	0.16	9
W-SM1	0.296	0.40	10
W-SM2	0.795	0.10	5
E-SM3	0.415	0.48	5
E-SH1	-0.059	0.86	6
W-SH2	0.638	0.03	11

5.4 Discussion

5.4.1 TP concentration and comparison to other studies

As demonstrated by the results presented above, values for the total phosphorus content of sediment collected in the whole estuary showed significantly higher values at the upper estuary sites. This pattern has been identified in other studies (e.g. Van Beusekom & de Jonge, 1998; Fox *et al.*, 1995). They identified an increase in riverine flux substantially modified by deposition in estuaries as being the cause of increased total phosphorus in the upper estuary. Nixon *et al.* (1996) and Filippelli (1997) also noted that sediment transported from the river and re-deposited elsewhere was richer in phosphorus than it had been originally. This tendency for an upper estuary increase in the TP concentrations in sediment in the Avon estuary

may reflect the relatively increasingly intensive land use and may relate to agricultural inputs of the lower Avon catchment, with an increase being obvious close to the location of the lower Avon catchment. Intensive land use is known to cause an increase in particulate phosphorus loads within a catchment; and it has been reported that sediment derived from agricultural land is present where the phosphorus content is elevated (Sharpley *et al.*, 1995). In the Avon catchment, agriculture is more intensive in the lower catchment with a higher percentage of land being given over to arable cultivation. Agricultural activities in other catchments in the UK are much less intensive. Variations in TP content in sediment attributable to land use were also noted by Bowes *et al.* (2003) in their study of the River Swale in northern England. They noted TP concentration of sediment varied with land use type, similar to the trend noticed in the Frome catchment, with a gradual increase in TP concentrations being recorded with distance from upland areas which were dominated by low intensity farming, to lowland areas where TP concentrations were much higher due to inputs from intensive farming and sewage works (Walling & Webb, 1996). Combining this idea with the knowledge that phosphorus has an affinity for fine sediment in the estuary, this would imply that higher phosphorus concentrations would be found where the finest sediment is accumulating; and this property, in combination with land use factors, could in some way explain the increased phosphorus concentrations in the upper Avon estuary. Moreover, fine sediment store samples show evidence of enrichment when compared with the lower estuary; the transport of this sediment, first to the river and then deposition on the upper estuary during storm events, will help to explain the higher TP concentrations in sediment deposited on the saltmarsh and mudflat area in the upper estuary. Comparing the TP storage of the sediment in the Avon estuary which ranged

between 68-1524 mg kg⁻¹, with other studies shows that higher TP storage was noted by many authors recording results from river sediment, and particularly phosphorus: 1430 mg kg⁻¹ Exe, Devon, UK, Lambert & Walling (1986, 1988): while Kim et al., (2003) in River Han in Korea, show that the TP was 883 mg kg⁻¹. In New Zealand, McDowell (2004) found that TP was 771 mg kg⁻¹ in Bog Burn catchment; in China, Changjiang River Estuary, the TP was 525 mg kg⁻¹ (Feng *et al.*, 2008); in USA, Okeechobee basin TP was 281 mg kg⁻¹ (McDowell and Sharpley, 2002); in Taiwan, TP in the upper river was recorded at 245 mg kg⁻¹ (Chen *et al.*, 2004), while in the lower estuary, the TP was 1240 mg kg⁻¹ (Fang, 2000).

5.4.2 Controls on TP concentration in the Avon estuary

The tendency towards retention of P in the fine sediment was noted in this study. This is similar to results reported by Ballantine *et al.* (2009) and Owens and Walling (2002), who also found that finest sediment (<63 µm) tended to have a higher P content than coarser particles. Tomchou Singh & Nayak (2009) also found that the distribution of the TP was controlled by the proportions of finer fraction of sediments. This is also in agreement with results obtained from samples taken from sites up-estuary and lower estuary for analysis of TP, where a significant relationship between fine sediment and TP was found. This is in agreement with Khalil et al., (2007) who found that variations of the TP in sediment depend on the locations, where high fine sediments were observed.

The higher concentration of TP in sediment deposited on the saltmarsh and mudflat area was more than other areas (i.e. shoal), which is similar to that found by Tomchou Singh & Nayak (2009) and Marion *et al.*, (2009), who observed that the

higher TP in the mudflat and saltmarsh can be related to retaining nutrients (particularly phosphorus) and other factors as organic matter; and sediment particle size can also influence phosphorus concentration in the sediment surface (Humborg *et al.*, 2003). Deposition of fine-grained particles occurs under low energy flow conditions and this may also contribute to the finer particle size in the upper estuary of the Avon estuary which has more concentration than the in the lower estuary, where a higher proportion of sandy sediment is found. This is in agreement with the results reported by Bates *et al.* (2004) and Nitsche *et al.* (2007) who both found that the physical properties of sediment varied with differences in particle size measurements within the estuary. They found that these variations are probably caused by flows in the main channel, perhaps due to asymmetry of ebb and tidal currents that might explain the differences in local deposition and erosional patterns in areas such as the upper estuary; this has been observed in several studies of estuaries. Also Seminara *et al.* (2001); Schramkowski & de Swart, (2002), in their study, reported a strong positive relationship between physical factors which affected the deposition of suspended sediment, as suggested by Boateng *et al.*, (2012). They noted that, once suspended, sediment and phosphorus often did arrive at the estuaries and coastal mudflats. It is assumed that potentially some fluvial sediment associated P might be stored in those depositional features. In the Avon estuary, Uncles *et al.*, (2012) found that freshwater had an increased potential for up-estuary transport and retention of fine sediment in the central and upper reaches of the estuary.

While TP concentration did seem to be strongly related to the deposition of fine sediment as shown above, this study also showed decreasing TP concentration in the fine sediment stored in the lower estuary along with decreased fine sediment

amount. This is in agreement with the results reported by Nichols and Biggs (1985) and Dalrymple *et al.* (1992) who, investigating nutrient content of sediment deposited in the mouth of estuary stated that larger amounts of sand were deposited at the mouth of estuary. In this case however, due to the fact that the material analysed was the fine fraction, it could be that the finer material stored in the same shoals has come from an external source or comprises older reworked material.

While TP concentrations did seem to be strongly related to the deposition of sediment as shown above, this study showed an increase in TP deposition along with an increase in the total sediment deposition and deposition of the <63 μm fraction. Hence, perhaps supply and concentration are interlinked.

This study shows a clear link between specific surface area measurements and phosphorus concentrations in surface sediment between landscape units sampled. This supports the idea proposed earlier that TP has an affinity for the fine fractions of the sediment, although there was no significant relationship within the specific sites in the estuary. This suggests that sorting effects on TP concentration only occur longitudinally in the estuary at the large scale. Sediment phosphorus concentrations increase with an increase in specific surface area, which is similar to an observation by Ballantine, *et al.* (2007), who reported that TP increases with an increase in specific surface area, because finer particles contain more sorbed phosphorus and less primary mineral phosphorus of lower availability than clay-sized particles: this is a product of the higher TP concentration and is not surprising. Horowitz (1991) has emphasized the importance of particle size and SSA in exerting a fundamental control in the ability of sediments to adsorb contaminants, stating that as SSA increases, the amounts of phosphorus that collect on the surface of the sediment also increase; this in agreement with the findings presented by several other authors

(e.g. Dong *et al.*, 1983, Cripps, 1995). Spatial variations in TP content of sediment may also in some part be attributable to trapping of phosphorus enriched sediment in organic matter, as was reported by Berner (1982) and Stephens *et al.*, (1992). This in particular might explain why the saltmarsh sediment is outliers from the main TP and SSA relationship (Figure 5.12). Their work suggests that the total organic carbon content of a sample was largely dependent on the proportion of fine sediment within the sample, regardless of its position. In contrast, Zhou *et al.* (2007) found that total phosphorus (TP) had irregular variation in its spatial distribution, where the TC, concentrations were highest in the high marsh zones and lowest in the bare flat areas. Despite the fact that the relationship between sediment grain size and organic carbon is well known, according to (De falco *et al.*, 2004), it was found that an evaluation of the spatial distribution of sedimentary organic carbon at the basin scale in relation to the sediment dynamics can contribute new knowledge both to coastal zone and management issues.

5.5. Conclusion

The results presented in this chapter show that significant amounts of phosphorus can be incorporated into fine sediment deposits on the saltmarsh and mudflat area within agricultural estuaries. Because of the quantities of phosphorus delivered to the upper estuary and the interactions that occur in the critical area, saltmarsh and mudflat can become a significant long-term sink for sediment-associated phosphorus.

This critical area can become major stores for phosphorus and could then be a source of phosphorus within the estuaries through water interactions. The study has shown that there is spatial variation in the amount of phosphorus deposited on the upper estuary area with variation between sites, though variation is not consistent

between sites. There is a general increase in TP concentrations in fine sediment in the upper estuary, while in the lower estuary TP concentration decrease is identifiable. These differences are likely to be controlled to a large extent by particle sorting effects although there is also potentially a sediment provenance control which requires further investigation (Rotman *et al.*, 2008).

The study has provided some evidence on controls of particle phosphorus concentration in the sediment estuary. As TP concentration patterns vary, this will reflect specific surface area and organic matter. Deposition on the saltmarsh area can demonstrate that for the entire site there is relationship between the SSA and TOC contributions to TP. The relationship between specific surface area and TP concentrations shows that grain size did seem to be an important influence in TP concentrations in sediment, with increases in specific surface area accompanied by increases in total phosphorus concentration and decreasing towards the lower estuary.

The improved understanding of spatial variations in phosphorus deposition provided by this study will help to quantify the storage dynamics of phosphorus delivered from the river system. It provides a foundation upon which to develop further understanding of the fate and delivery of sediment-associated phosphorus in the estuary system.

Chapter 6: A fine sediment and phosphorus budget for the Avon estuary

6.1 Introduction

The aim of this chapter is to develop a fine sediment and particulate phosphorus budget for the Avon estuary, south Devon, UK. The specific objectives are to:

- (i) Quantify fine sediment and PP inputs using sediment load data from Chapter 4 and PP load from previous work and field measurements.
- (ii) Quantify total fine sediment and PP storage by assessing the volume of fine sediment in the Avon estuary using transect cross-sections and mean PP sediment content.
- (iii) Quantify the annual sediment and PP budget of the estuary (input and storage) using annual sedimentation rate from previous work and mean suspended sediment concentration PP.

6.2. Methodology

6.2.1 Sampling strategy

As mentioned in previous chapters, storage of fine sediment and phosphorus content was observed to be greater in the upper estuary, the main deposition area. Bugler (2006) identified three main saltmarshes in the Avon estuary (Figure 6.1). These three salt marshes located downstream of Aveton Gifford in the upper part of Avon estuary (Main marsh, Stadbury marsh and Milburn Orchard Marsh). These marshes, located in the upper part of Avon estuary, are investigated in this study because of their potential role in attenuating transport of fine sediment from Avon catchment to

the coast through their retention of sediment in the central and upper reaches of the estuary; and because they are also sheltered from wave exposure, allowing salt marsh and mudflat sediments to accumulate.

Main marsh is located within the main river channel and is the largest of the four marshes. The uppermost part of the marsh is being actively eroded by the main river channel, producing steep sided banks. At the seaward end of the marsh there is active deposition on the inside of the meander bend, causing the marsh to migrate downstream.

Stadbury marsh is located furthest downstream, on the inside of a meander bend. It is the smallest of the marshes, with growth restricted spatially by the river channel and cliffs. The marsh shows a progression from the small cliff face, where high salt marsh grasses dominate, to mudflats which gently slope down to the river channel.

Milburn Orchard Marsh is located furthest from the coast within the upper estuary, out of the main channel and is nested with Dukes Mill Creek: this location decreases the influences of the incoming tide. The present conditions produce a brackish marsh, decreasing in salinity up-stream with increasing dominance of freshwater inputs (Bugler, 2006).

South Efford marsh is located within the upper part of the estuary within the main channel; the marsh at South Efford has been influenced by the low tide (EA, 2010).

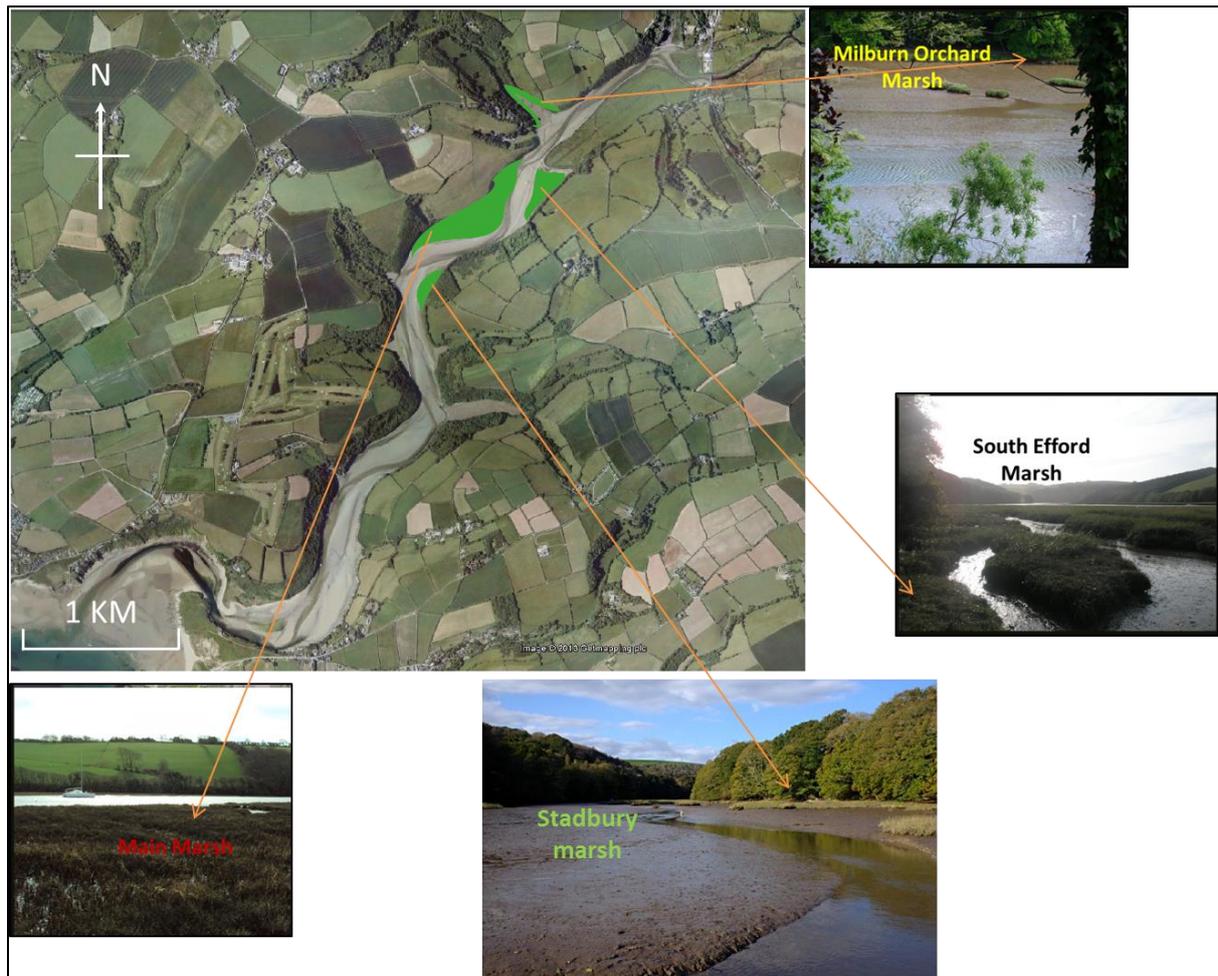


Figure 6.1: The Avon estuary and the main saltmarsh environments.

6.2.2 Applying the sediment budget concept to the Avon estuary

Figure 6.2 provides a schematic representation of the linkage between the various elements of the sediment budget of an estuary system. The way that the sediment budget of the Avon estuary was established in this study was a quantitative relation between sediment input and output and the storage of sediment in the sink zone. Data on annual suspended sediment load (i.e., sediment input from the Avon River to the estuary) and sediment stored in the sink zone of the estuary (i.e., annual sedimentation rate) were used to estimate the sediment budget of the Avon estuary

and are described in more detail in the following sections. Sediment output (i.e., sediment output to the coastal zone), was calculated by subtracting storage from the sediment input. The literature-based hypothesis tested was that a significant proportion of the sediment transported by the river to the estuary was stored in sedimentary sinks zone in the estuary with a smaller proportion of fine sediment transported toward the coastal zone.

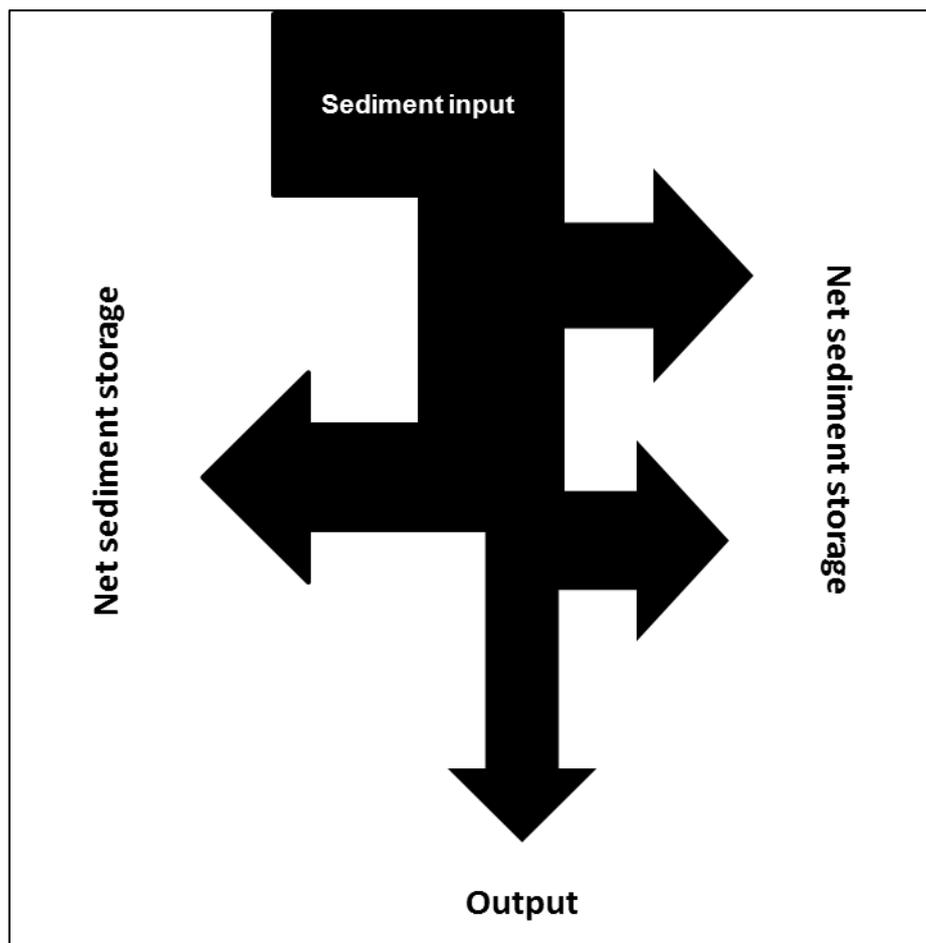


Figure 6.2: Schematic representation of the model followed by this work to construct the sediment budget of the Avon estuary.

6.2.3 Quantifying the total mass of stored <math><63\mu\text{m}</math> sediment and PP in estuarine sinks

6.2.3.1 Determining the elevation of the sand/silt interface

A key factor to determine the cross-sectional area of the silt deposits, to underpin volume and mass estimations, was estimation of the elevation of the sand-silt interface. To quantify the elevation of interface between silt/mud and sand data were collected and supplemented by data already collected (Bugler, 2006). Forty-six cores were used to establish the stratigraphy of the salt marshes in the upper estuary (secondary source) and twelve cores were collected from saltmarsh and mudflat area using a gouge corer (primary source). Figure 6.3 shows the location of the coring undertaken in this study and also secondary source data from Bugler (2006). Sediment texture was assessed in the field in order to determine vertical changes in fine sediment properties (silty clay component). The typical types of grain size sediment observed was silt clay starting in the top with a gradual change into the sand moving toward rock bed. Each core location was plotted using GPS.

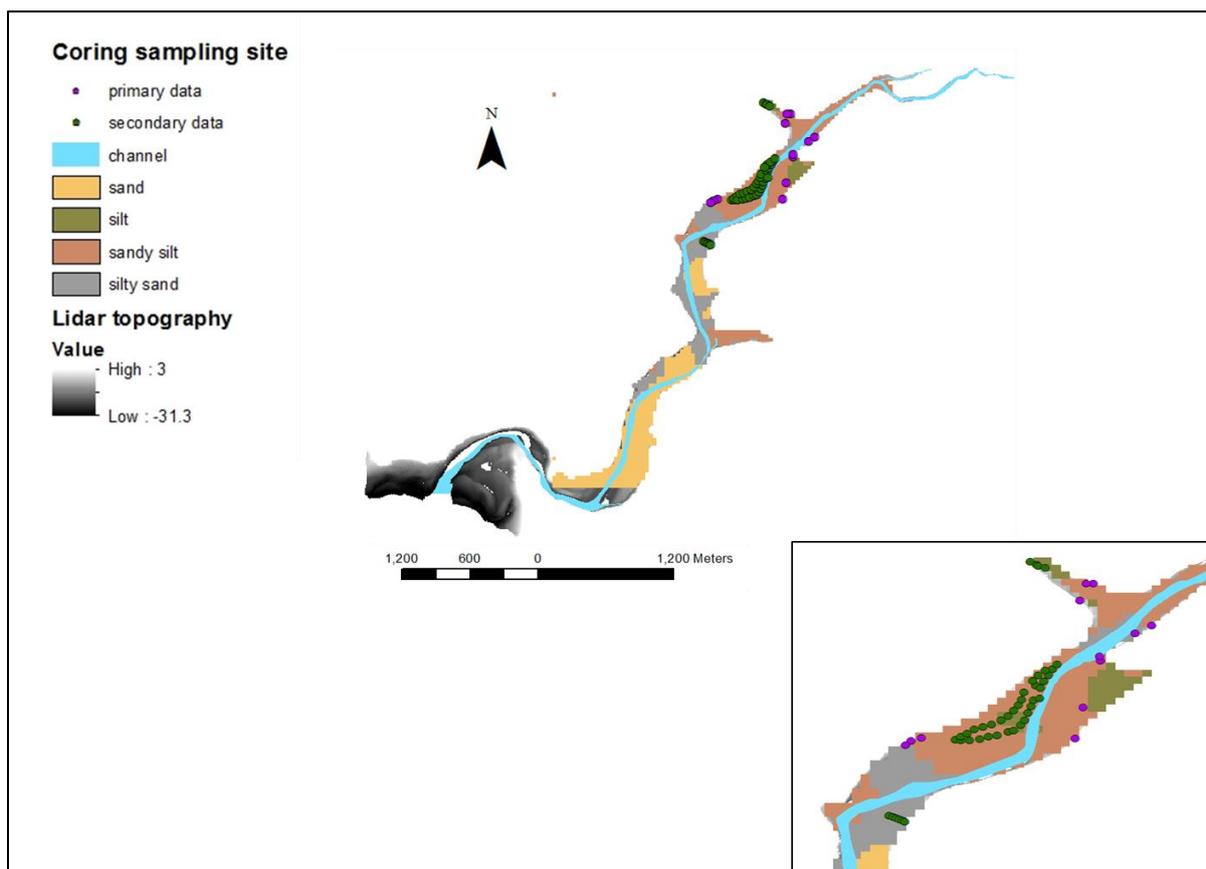


Figure 6.3: Data points for determining the elevation of the silt/sand interface.

6.2.3.2 Quantifying the cross-sectional area of fine sediment deposits

Twenty-one estuary cross sections were used to estimate volumes of fine sediment based on average elevation of the interface between silt/mud and sand (i.e. metres above ODN determined as described in 6.3.2.1) and the topography and the known spatial extent of the deposition zones from aerial photographs and the GIS. Survey data from previous work (Atkins source data) was used to determine elevation of the channel. The channel width was measured based on the GIS measurement. The cross sectional data truncated by the mean of the elevation of sand/silt interface were combined in GIS and used to calculate the cross-sectional area of the mud section which was multiplied by the length of the relevant estuary reach to get

sediment volume (Figure 6.4). The cross-sectional area each mud wedge was determined using the trapezoidal rule. The length of each section (m) was based on a transect between section which has measured in GIS and represented (Figure 6.5). Total sediment volumes determined for each reach were then transformed to the volume of fine sediment as described in the next section.

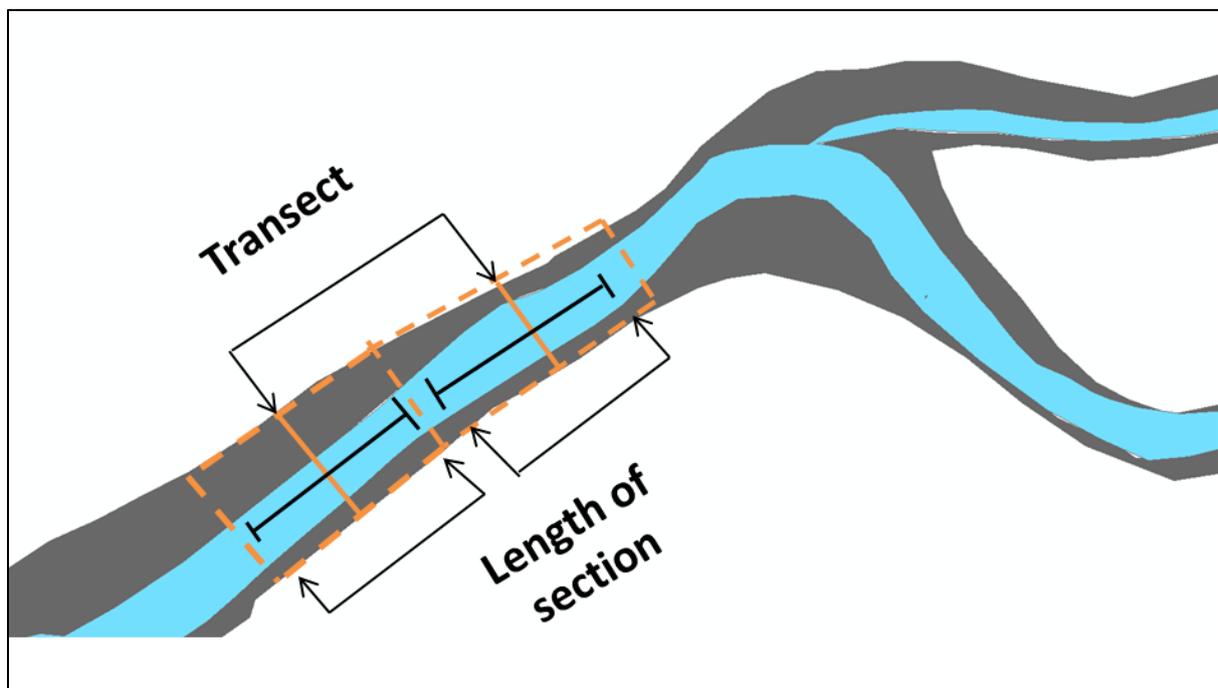


Figure 6.4: diagrammatic representation of measurement of the length and distance of the section in the Avon estuary

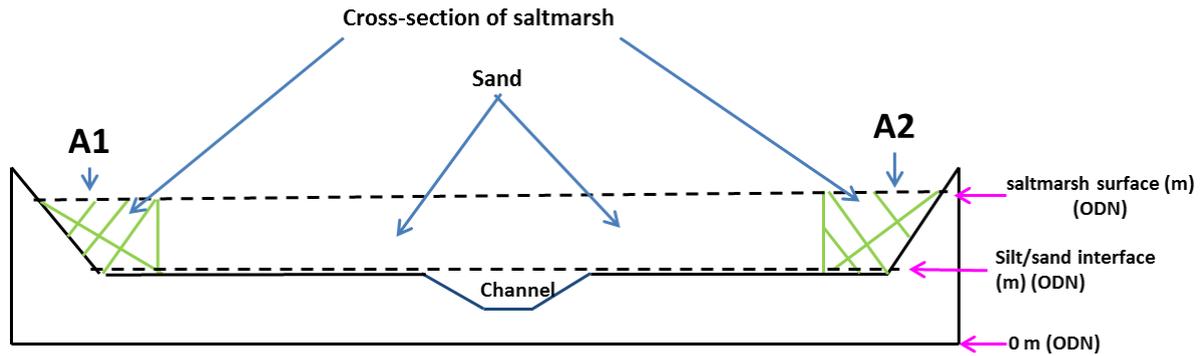


Figure 6.5: Diagrammatic representation of the measurement of silt deposit cross-sectional area

6.2.3.3 Mass of fine (<63 μm) sediment in storage

The measured area of sediment (m^3) was converted to the sediment mass (ton) using representative dry-bulk density based on Flemming & Delafontaine, (2000). Next, the mass was corrected to that of just the <63 μm sediment component by applying the proportion in the specific storage zone as determined in chapter 5. The calculation for total mass of fine sediment in storage (MS) can therefore be given as:

$$MS = (V \times BD) \times (P < 63)$$

Where V is volume of sediment (m^3);

BD is bulk density (t m^{-3}) and P <63 μm is the proportion of sediment <63 μm .

6.2.3.4 Mass of PP in storage

In total, 87 sediment samples were taken for analysis of the PP concentration of stored sediment (Figure 6.6) (full details in chapter 5). The mean value for each

landscape unit was applied to the total mass of fine sediment storage to estimate the mass of P in storage.

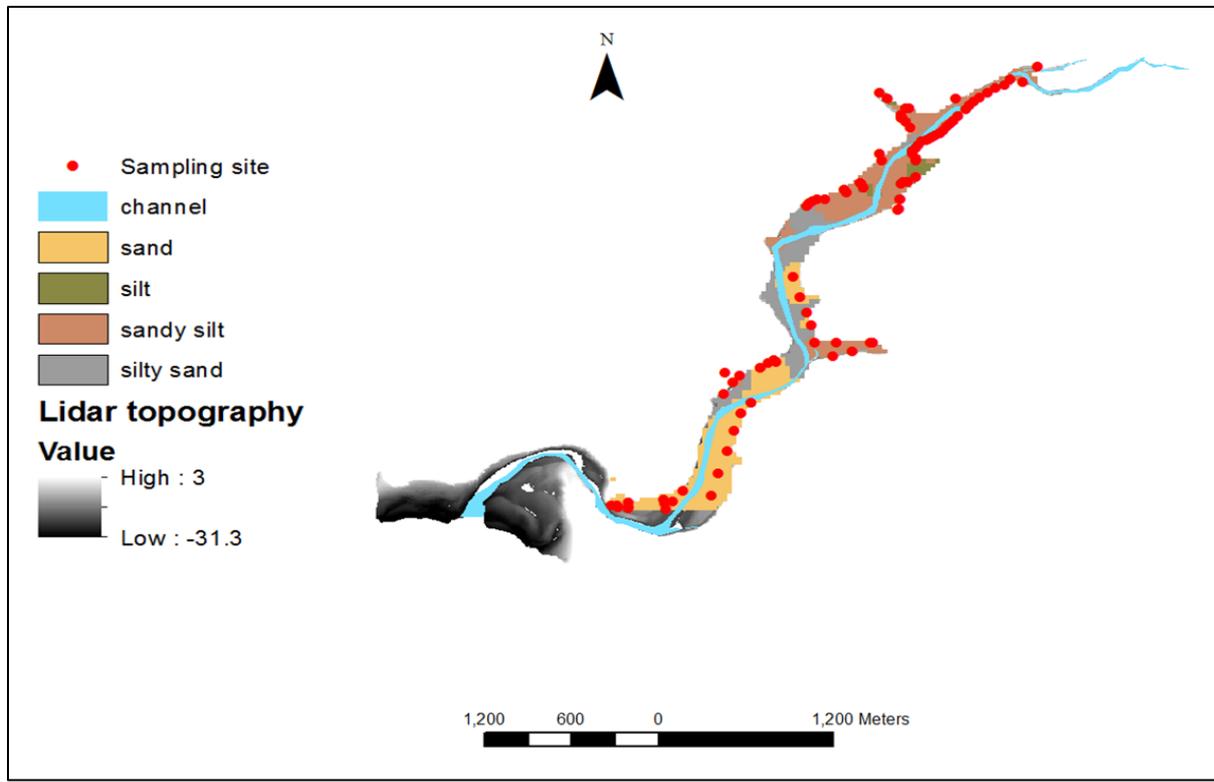


Figure 6.6: Locations of sediment samples collected for TP (mg kg^{-1}) analysis.

6.2.4 Sediment and PP budget

6.2.4.1 Input (fluvial SS and PP loads)

As estimate of river sediment load is a key part of the estuarine sediment budget. As described in Chapter 4, suspended sediment transport was monitored in the Avon estuary from 2009 to 2011 in order to estimate sediment load input. Full details of the equipment and data processing can be seen in chapter 4.

Information from the literature and field data based on in-stream time integrated samples was used together to develop an improved understanding of the characteristic PP content of the suspended sediment. The sediment samplers operated in situ, and two tube samplers were installed in the Avon River (Figure 6.7).

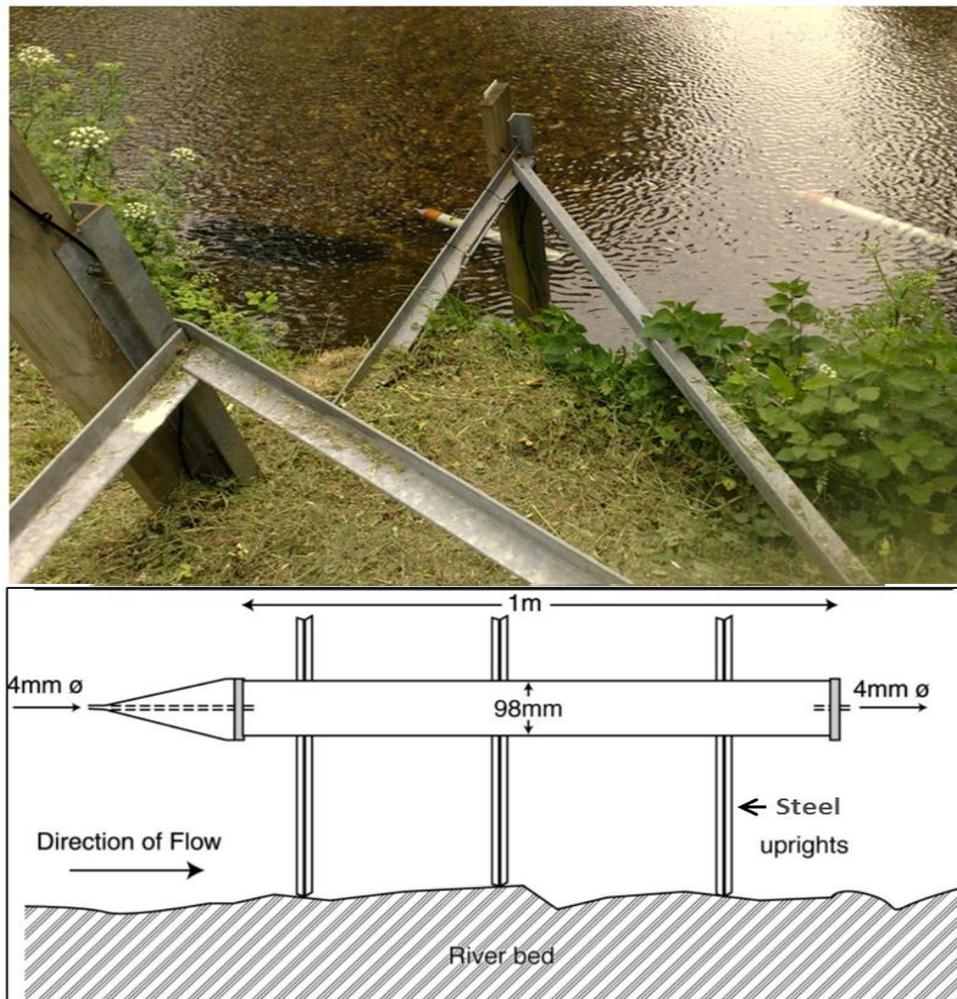


Figure 6.7: Suspended sediment sampler in the Avon River

When emptying the traps, each tube sampler was disconnected from the uprights and completely removed from the stream. In the laboratory, the samples were dried at 45 °C and analysed for total phosphorus following the method described in chapter five.

Total phosphorus loads (kg) were estimated by calculating TP (mg kg^{-1}) per season (winter-summer) and multiplying these two values by the monthly sediment load (kg). The seasonal pattern of TP with significantly higher concentrations in winter and lowers concentrations in spring and summer has been frequently reported in the literature (e.g. Arheimer & Lidén, 2000; Chen *et al.*, 2003).

Due to the Sonde equipment failure, no SSC data were collected from April, June, until July 2009 and December until January 2010. Hence a power regression function was used to establish the monthly sediment load relationship and applied for unknown-data (Figure 6.8). The relationship between sediment load (t) and flow (m^3) was significant ($R^2 = 0.76$, $P < 0.00$).

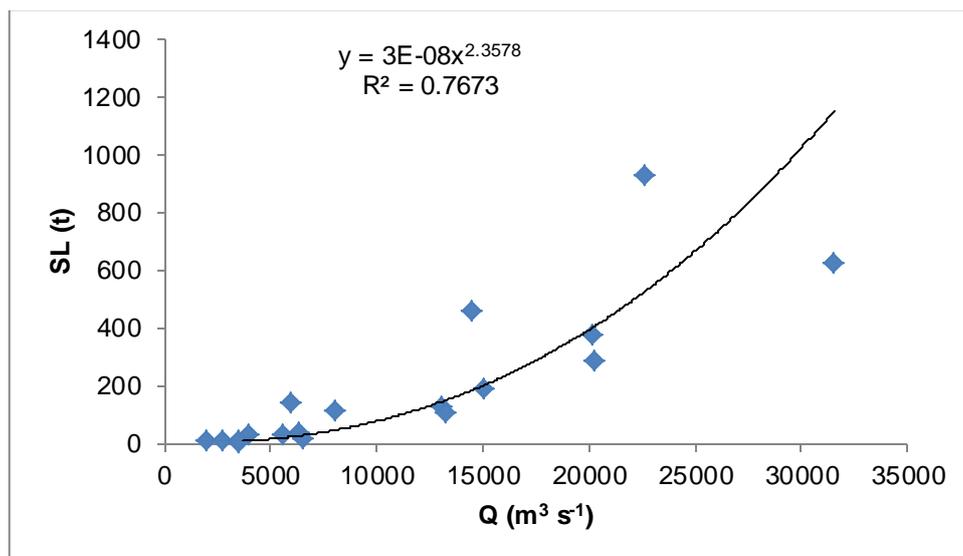


Figure 6.8: Relationships between monthly sediment load (t) and flow ($\text{m}^3 \text{s}^{-1}$).

6.2.4.2 Annual accretion rates of the sediment storage zones

Saltmarsh and mudflat accretion rates from previous work in the study estuary and similar environments were assessed and applied (Bugler, 2006; Jouanneau *et al.*, 2002) to estimate sediment budget (SB) (t) within the storage zones:

$$SB = AR * BD * A$$

Where AR is accretion rate of sediment ($t\ yr^{-1}$) BD is bulk density ($kg\ m^{-3}$) A is the area of the deposition zone (m^2).

6.2.4.3 Total PP inventory ($kg\ m^{-2}$) (PPI)

To calculate total PP inventory in the storage zones, ($kg\ m^{-2}$) (PPI) the following equation was used:

$$PP\ I = \left(\frac{TP \times MS / 1000}{A} \right)$$

$$PPI = PP\ inventory\ (kg\ m^{-2})$$

Where TP is mean P concentration at the site ($mg\ kg^{-1}$), MS is the mass of sediment $<63\ \mu m$ (kg) and A is the area of the deposition zone (m^2).

6.2.4.4 Output of sediment and PP

Output (O) of fine sediment (t) from the estuary to the coastal zone was calculated based on the input and storage of sediment samples following by:

$$O = I - S$$

Where I is annual input of sediment (t) from the Avon river, S is estimated amount of annual storage of sediment ($t\ m^{-2}$) from section 6.3.3.2.

The output of phosphorus budget (O) was then calculated:

$$O = I - S$$

Where I is annual input of PP (kg) in suspended sediment, S is total PP inventory ($kg\ m^{-2}$).

6.3. Results

6.3.1 Temporal variations in fine sediment and PP input from the catchment

The monthly values for TP concentrations in samples collected result from literature and suspended sediment samples are presented in Table 6.1 and Figure 6.8 along with estimated TP yield from the catchment (kg km^{-2}) and sediment load (t). The results presented show that there was variation in the PP load values within the sampling period largely driven by sediment load: the maximum PP load was noted in winter, of 836 kg in 2009; and the minimum in the summer, of 1 kg, in 2011. Monthly P kg values started increasing from October and decreasing around March, with a distinct peak in the winter (November-December-January 2009); while for the rest of the sampling period, little variation is apparent, with a lesser peak in summer (Figure 6.9). The total P yield in two years in the Avon River was 10 kg km^{-2} , with the variation of relative contributions from individual seasons of P yield estimated as highest (2.46 kg km^{-2}) in the winter of 2009, while in the summer of 2011 the total P yield is expected to be significantly the lowest (0.01 kg km^{-2}). Figure 6.9 presents TP kg in the study period, where a clear seasonal trend is apparent.

Table 6.1 Monthly sediment load, phosphorus concentration, and phosphorus load from the catchment. Highlighted data in bold are results of regression data.

Month	Monthly sediment load (t)	P mg kg ⁻¹	Estimated P load (kg)	Catchment P yield (kg km ⁻²)
September /2009	28	465	13	0.04
October	50	1357	67	0.43
November	1216	1357	1651	2.46
December	559	1357	759	1.22
January/ 2010	426	1357	578	1.47
February	152	1357	207	0.48
March	158	1357	214	0.40
April	65	465	30	0.01
May	3	465	1	0.02
Jun	1	465	0	0.02
July	2	465	1	0.02
August	24	465	11	0.09
September	21	465	10	1.21
October	196	1357	266	1.11
November	431	1357	585	0.94
December	33	1357	45	0.06
January/2011	434	1357	589	0.06
February	213	1357	289	0.04
March	30	1357	40	0.04
April	7	465	3	0.01
May	2	465	1	0.01
Jun	9	465	4	0.04
July	4	465	2	0.01
August	7	465	3	0.04
Total for two years	4071	21864	5369	10.23
Average	170	911	224	0.43

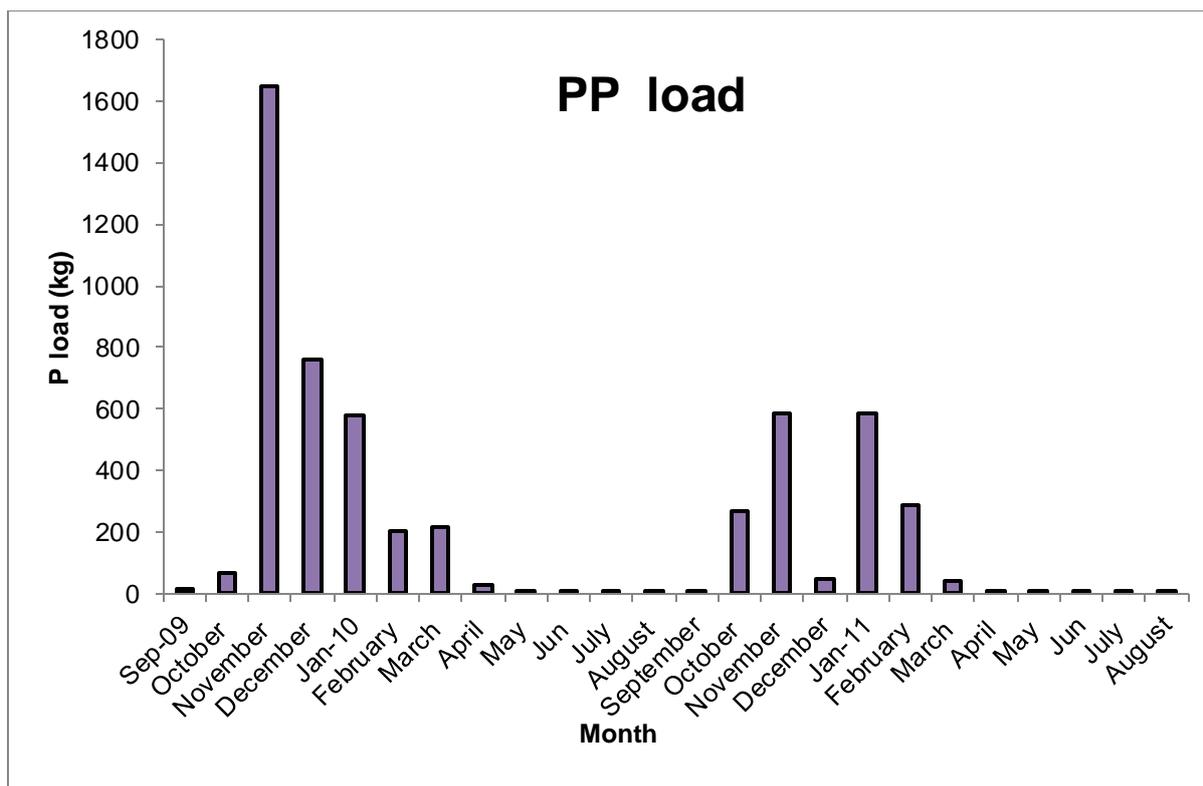


Figure 6.9: Monthly particulate P loads in collected sediment at river site in the Avon catchment.

6.3.2 Sediment storage

6.3.2.1 Deposition zone stratigraphy

Locations of all coring samples are displayed in Table 6.2. No difference in grain size with depth was observed between mudflat and saltmarsh. Generally, the stratigraphy shows a progression of grain size sediment from the sediment surface to the bedrock material in the saltmarsh and mudflat deposits area. The silt and clay component increases up core and occasionally is concentrated into lenses and gradually alters to the sandy silt. A sharp boundary exists between the gravels and a silty sand layer above. Large quantities of shell fragment are present in the silty sand, occasionally concentrated in layers. The basal sediments consist of sandy gravels dominated by slate fragments. The colouration also changes from being grey in colour to a dark appearance (light grey to dark grey).

Table 6.2 GPS coring location of the 12 and core texture descriptions.

Site	Location	Description
1	N 50.305204 W 3.84959	0-17 cm : light brown mud 17-47 cm : brown silty clay 47-68 cm : hard silty clay brown
2	N 50.306361 W 3.851472	0-5 cm : light brown mud 5-22 cm : silty clay grey brown 22-44 cm : dark grey silty clay 44-45 cm : light brown clay
3	N 50.307028 W 3.850889	0-10 cm : mud loose 10-20 cm : silty clay with gravel 20-47 cm : silty clay with very fine sand and slate fragment 47-55 cm : loose silty clay grey
4	N 50.307028 W 3.851222	0-10 cm : mud loose 10-20 cm : loose silt clay 20-33 cm : dark grey silty clay
5	N 50.300944 W 3.858639	0-5 cm : mud 5-22 cm : silt clay fine sand 22-51 cm : hard silty clay dark grey with plant material and grabble 51-67 cm : silty clay sand brown 67-78 cm : dark to light sandy clay very light brown
6	N 50.300667 W 3.859361	0-5 cm : mud 5-35 cm : sandy silt clay dark grey with organic matter with grabble 35-65 cm : silty clay with sand dark grey 65-65 cm : silty clay light grey with sand and big gravel 85-90 cm : sandy clay with gravel 90-98 cm : sandy silt light brown
7	N 50.304056 W 3.850444	0-17 cm : light brown mud 17-98 cm : silty clay sand 98-1 m : gravel
8	/	0-10 cm : mud 10-38 cm : silty clay with sand and getting sand 38-60 cm : silty sand clay grey and sandy and more gravel in the bottom
9	/	0-12 cm : mud 12-29 cm : silty clay with sand and the rest gravel
10	N 50.303945 W 3.84904	0-8 cm : mud 8-26 cm : loose silty clay with sand 26-50 cm : silty clay with sand gravel and plant material
11	N 50.301053 W 3.85148	0-53 cm : brown mud with shell 53-83 cm : silty clay and getting sand to the bottom 83-134 m : silty sand with clay very fine sand
12	N 50.30223 W 3.85118	0-10 cm : mud 10-37cm : silty clay dark grey getting sand to bottom 37-73 cm : silty sand with clay grey getting to bottom 73-94 cm : sandy silt clay with shell 94-116 m : silty clay with very fine sand

6.3.2.2 Elevation of the silt/sand interface

The estimated elevation of silt/sand interface shows that the range had a median of 0.6 m, a mean 0.6 m, and a standard deviation of 0.4 m, and the sampling minimum was 0.01 m and the maximum was 1.3 m (n=12). The elevation of fine sediment is similar to that found in the supplemented with additional data from previous work (Bugler, 2006) that fine sediment samples for all runs range, with a median of 0.9 m, a mean of 0.8 m, and a standard deviation of 0.3 m and minimum 0.4 m (n=46), and maximum elevation 1.7 m. Figure 6.10 shows a histogram of sediment elevation above of ODN for the 58 cores which was used to derive a mean depth of fine sediment of 0.8 m. The maximum elevation of silt/sand interface was 1.66 m which gives an indication of the margins of error in this analysis.

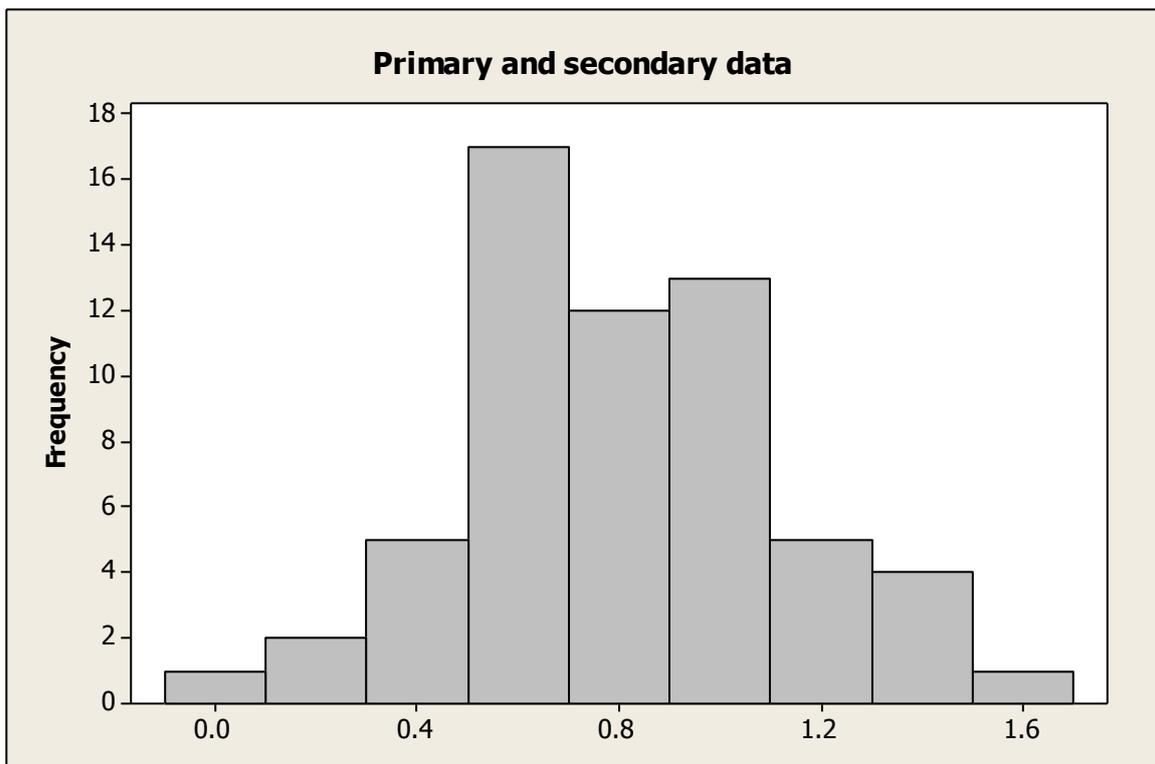


Figure 6.10: Frequency histogram of sediment elevation above of ODN for 58 cores from Avon estuary.

6.3.2.3 Fine sediment volumes based on estuary cross section analysis

The estuary cross-section (Figure 6.11) is an example to illustrate the way volume of fine sediment in the estuary was derived. The larger volumes of fine sediment tend to be directed upward in the central and upper estuary (see Appendix III). Up-estuary, the greatest volume of fine sediment in a cross-section area was found at upper estuary section 4 which is a consequence of storage fine sediment in the upper estuary (Figure 6.12; estuary section 4); while, no fine sediment deposit was found in the mouth of estuary at section 16 (Figure b 6.12 lower estuary section 16).

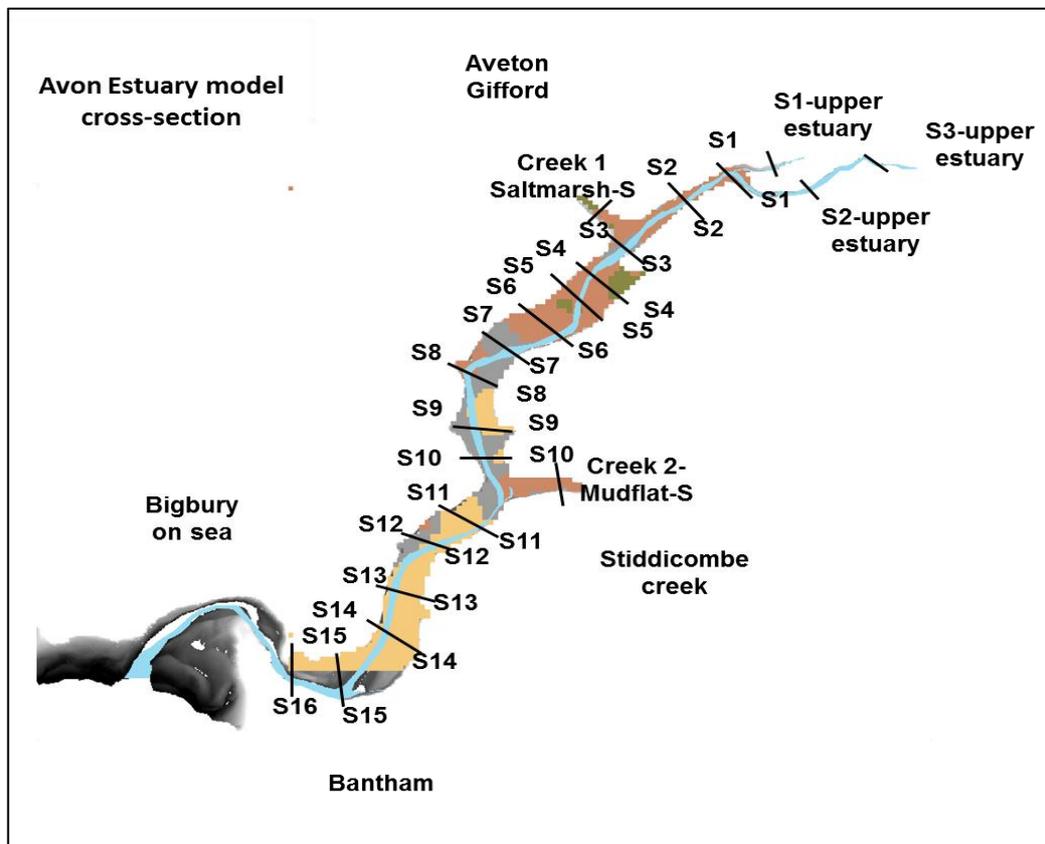


Figure 6.11: Locations sections drawn across the estuary define nodes used by dashed and continuous lines. Cross-estuary distributions of sediment grain size were measured over the sections shown as continuous lines.

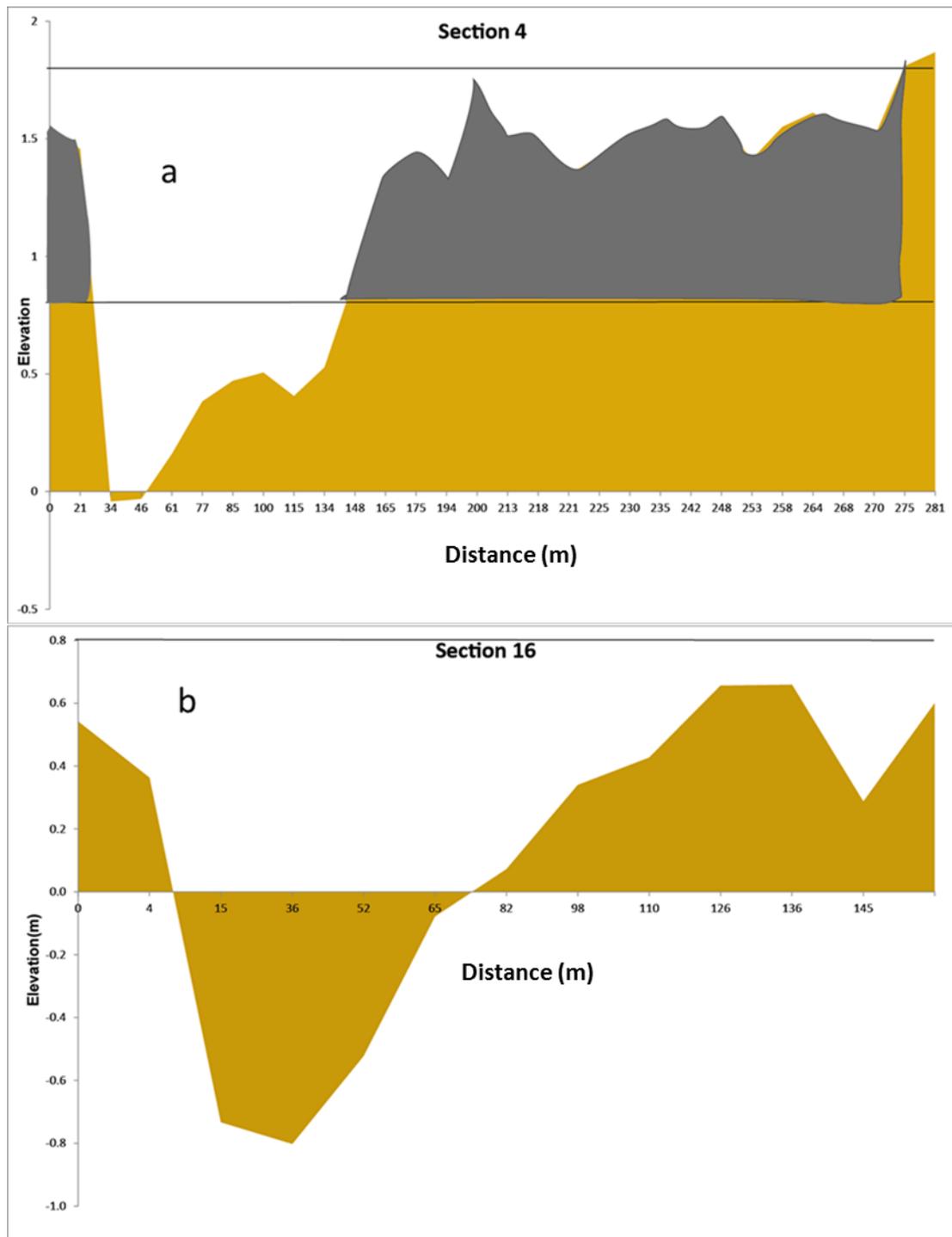


Figure 6.12: Example estuary channel cross-section upper at the saltmarsh (a) and at the mouth (b) of the estuary sites.

6.3.2.4 Mass of sediment storage and associated phosphorus

The total fine sediment for the estuary storage zone was ca. 99000 t. This represents 40-100 years of the current annual sediment flux from the catchment given the two annual loads of 2413 t and 986 t determined in the catchment sediment flux work package (see chapter 4). Estimates of total stored PP (PP kg) on the estuary sites were calculated by TP concentrations and deposition of the less than 63 μm fraction of sediment, all shown in Table 6.3. The total PP for the estuary storage zone was 72754 kg. This represents a minimum of 20 and 40 years of the current annual load based on the two annual loads of 3500 and 1800 kg. The difference in the total annual flux stored between sediment and P is likely to reflect more recent increases in PP load with agricultural intensification or loss of P from the sediment column. In the Table 6.3 shown, the deposition of the <63 μm fraction of sediment was different from site to site, with the value for the upper estuary being higher than that for the lower estuary site, ranging from a minimum of 125 (t) to a maximum of 34593 (t).

The total stored PP associated with the <63 μm fraction was higher in the upper and middle estuary, with a maximum of 22866 kg and a minimum of 13 kg in the lower estuary, a result of 0.98 from correlation analysis using a Pearson's test, shows that there is a significant relationship at the 0.00 level between total stored PP and mass of the <63 μm of sediment fraction. It is possible that upper estuary patterns for PP storage, described above, may be due to changes in the particle size composition, and statistics describing these characteristics are also presented in Table 6.3. There are appreciable differences in the particle size composition between the sites, which might explain the spatial pattern in sediment-associated P. Figure 6.13 shows that maximum and minimum PP storage do coincide with maximum and minimum fine sediment storage.

Table 6.3: Calculation of sediment volume, phosphorus concentration and phosphorus storage for each estuary section.

Section label	Cross-section area (m ²)		Total cross-section area (m ²)	Section length (m)	Volume of sediment (m ³)	Proportion fine sediment (<63µm)	Mass (t) <63µm	Mean TP (mg kg ⁻¹)	Mass of PP (kg)
	West	East							
Upper estuary 1	7	10	17	280	4760	0.52	3713	1046±479	3880
Upper estuary 2	10	9	19	291	5510	0.52	4297	1056±461	4540
Upper estuary 3	2	20	22	285	6578	0.52	5131	1113±22	5710
Creek 1-saltmarsh	10	6	16	105	1680	0.82	2066	632 ± 422	1310
Creek 2-mudflat	4	0	4	280	1120	0.43	722	688 ± 188	500
1	3	12	15	190	2850	0.53	2266	569 ± 338	1290
2	3	3	6	138	828	0.68	845	488 ± 342	410
3	2	3	5	160	800	0.82	984	661 ± 336	650
4	9	80	89	316	28124	0.82	34593	661 ± 336	22900
5	40	8	48	190	9120	0.60	8280	549 ± 462	4510
6	30	0	30	196	5880	0.60	5292	549 ± 462	2900
7	20	35	55	298	16390	0.60	14751	866 ± 174	12800
8	12	60	72	165	11880	0.43	7663	739 ± 141	5660
9	3	10	13	214	2782	0.43	1794	866 ± 174	1550
10	6	60	66	176	11616	0.25	4356	739 ± 141	3220
11	1	3	4	236	944	0.25	356	726 ± 85	260
12	4	10	14	217	3038	0.25	1139	536 ± 334	610
13	7	0	7	230	1610	0.25	604	97 ± 27	60
14	1	4	5	336	1680	0.07	176	74 ± 5	13
15	3	3	6	347	2082	0.04	125	318 ± 266	40
16	0	0	0	208	0	0	0	0	0

* All data after proportion (<63 µm) column multiplied by bulk density (1.5)

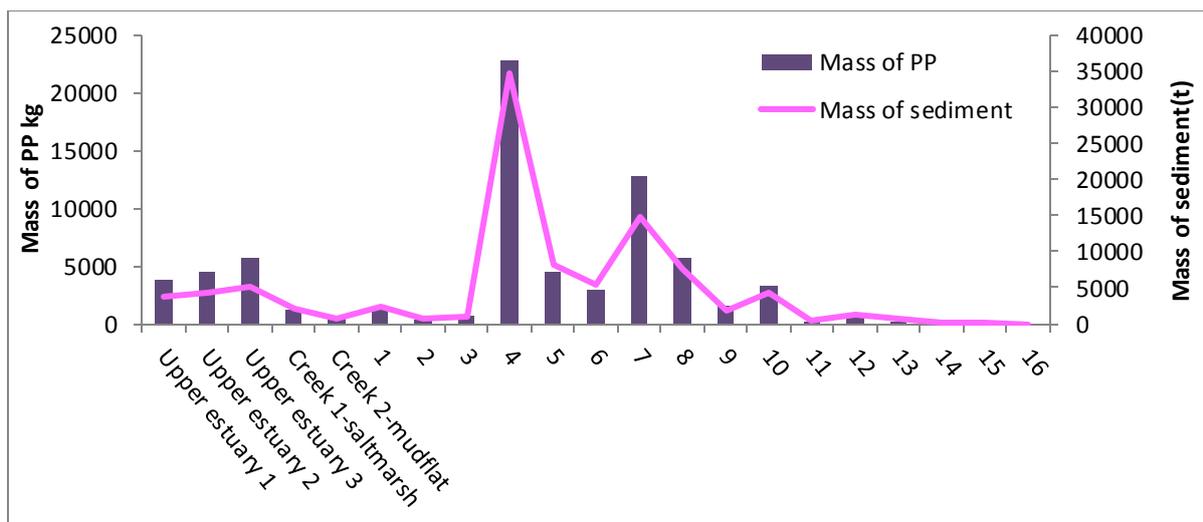


Figure 6.13: PP deposition and sediment deposition along the Avon estuary

6.3.2.5 Annual sediment budget estimation

The information provided by the annual sediment input and annual sediment storage from a previous study (Bugler, 2006; Jouanneau *et al.*, 2002) has been integrated to establish an annual sediment budget for Avon estuary and the final sediment budgets for the Avon estuary are detailed in Figure 6.14. Table 6.4 summarises all the rates estimated in saltmarsh and mudflat area and gives details of their area. As expected, the majority of the sediments entering the Avon estuary pathway originates from the Avon catchment sediment input which calculated from the maximum annual suspended sediment load measured (in 2009-2010)(see section 4.5.2) would reach 2437 t yr^{-1} , the storage in the deposition area can reach up to 1271 t yr^{-1} , finally sediment output was calculated by subtracting sediment input from sediment stored and delivered to the out of estuary (e.g., 1166 t yr^{-1}). From these analyses, of the estimated sediment storage in the Avon estuary, 99079 t more than

half of the fine sediment <63 μm supplied in the year with the greatest sediment load was potentially trapped in the deposition area, with about 30% on the saltmarsh area and 70% on the mudflat area.

Table 6.4: Distribution of the annual sedimentation and phosphorus storage within the Avon estuary derived from data presented in this section.

Zone	Annual sediment accretion (cm yr ⁻¹)	Annual accretion (g cm ⁻² yr ⁻¹)	Annual sediment accretion (kg m ² yr ⁻¹)	Area (m ²)	Annual sediment accretion (kg yr ⁻¹)	Annual sediment accretion (t yr ⁻¹)	Proportion (<63µm)	Annual <63 µm sediment accretion (t yr ⁻¹)	Mean PP concentration (mg kg ⁻¹)	PP input to storage zone (kg)
SM(Main marsh)	0.39	0.585	5.8	63923	78895	79	0.66	52	1245 ± 594	65 ± 31
SM (Milburn marsh)	0.49	0.735	7.4	10734	373950	374	0.79	295	1245 ± 594	367 ± 175
SM (Stadbury marsh)	0.27	0.405	4.1	13614	55137	55	0.80	44	1245 ± 594	55 ± 26
Mudflat 1	0.40	0.60	6.0	11488	68928	69	0.25	17	1245 ± 594	21 ± 10
Mudflat 2	0.40	0.60	6.0	157511	945066	945	0.52	491	1245 ± 594	611 ± 292
Mudflat 3	0.40	0.60	6.0	41368	205116	205	0.63	129	1245 ± 594	161 ± 77
Mudflat 4	0.40	0.60	6.0	34186	163860	164	0.42	69	1245 ± 594	86 ± 41
Mudflat 5	0.40	0.60	6.0	27310	248208	248	0.7	174	1245 ± 594	217 ± 103

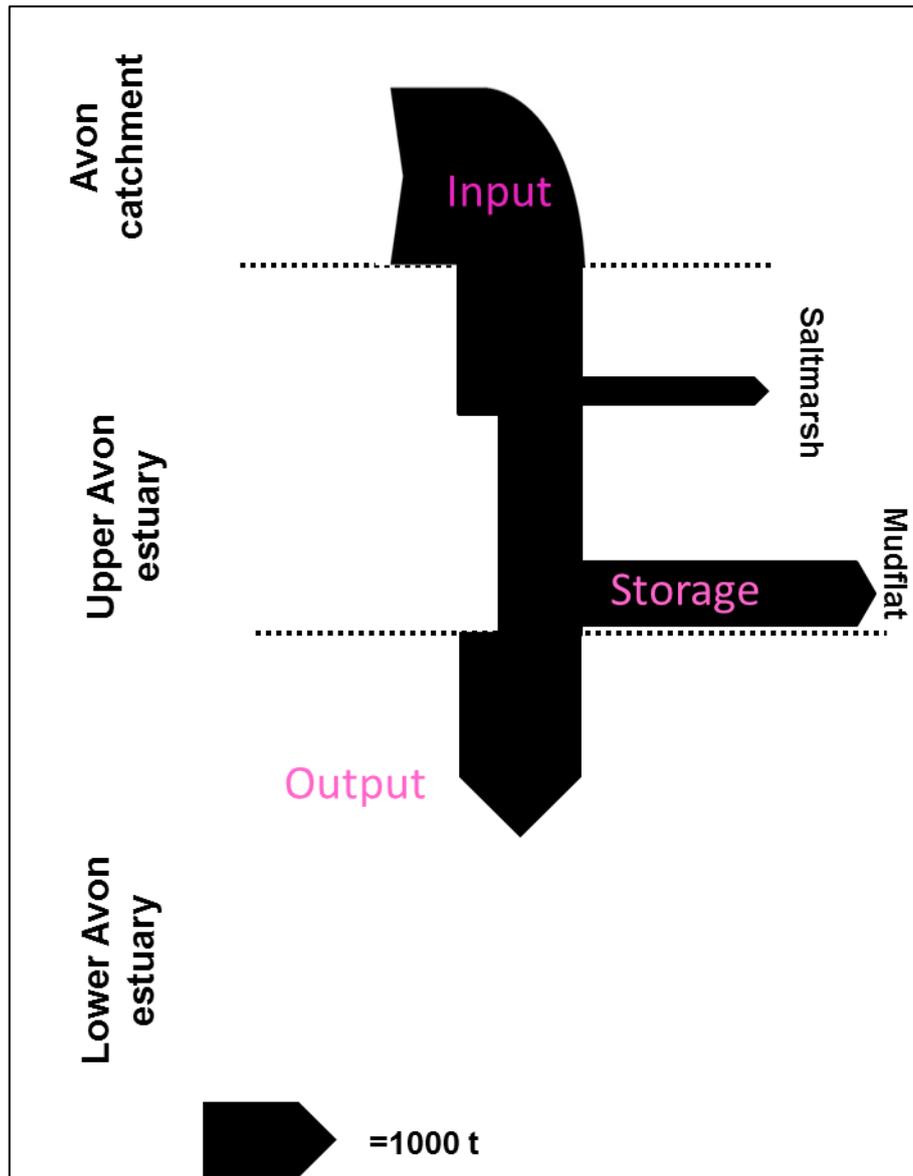


Figure 6.14: Annual sediment budget of the Avon estuary. Thickness of arrows is approximately proportional to total sediment mass.

6.3.2.5 The annual PP deposition on the estuaries sediment

The annual PP input was obtained from average values for TP concentration in suspended sediment from the two events sampled and is represented in (Table 6.4).

The particulate P input ranged between 825 - 2035 mg kg⁻¹ (1245 mg kg⁻¹ on

average). These estimations show in Figure 6.15 that PP input is transported by the river to the estuary was 3034 kg yr^{-1} .

Estimation of PP storage appeared that the zonation in the estuary received of PP input from the river and sediment was 1582 kg yr^{-1} with highest PP storage in mudflat area was 1452 kg , this implies that because there were high amounts of sediment deposited because there were higher surface area and showed an increase in PP storage along with an increase in total deposition of the $<63 \mu\text{m}$ fraction.

An estimate of the PP output can be made by subtracting PP input with PP stored to give 1452 kg yr^{-1} export. This suggests that approximately less than half of the PP that reaches the channel actually leaves the estuary in any one year.

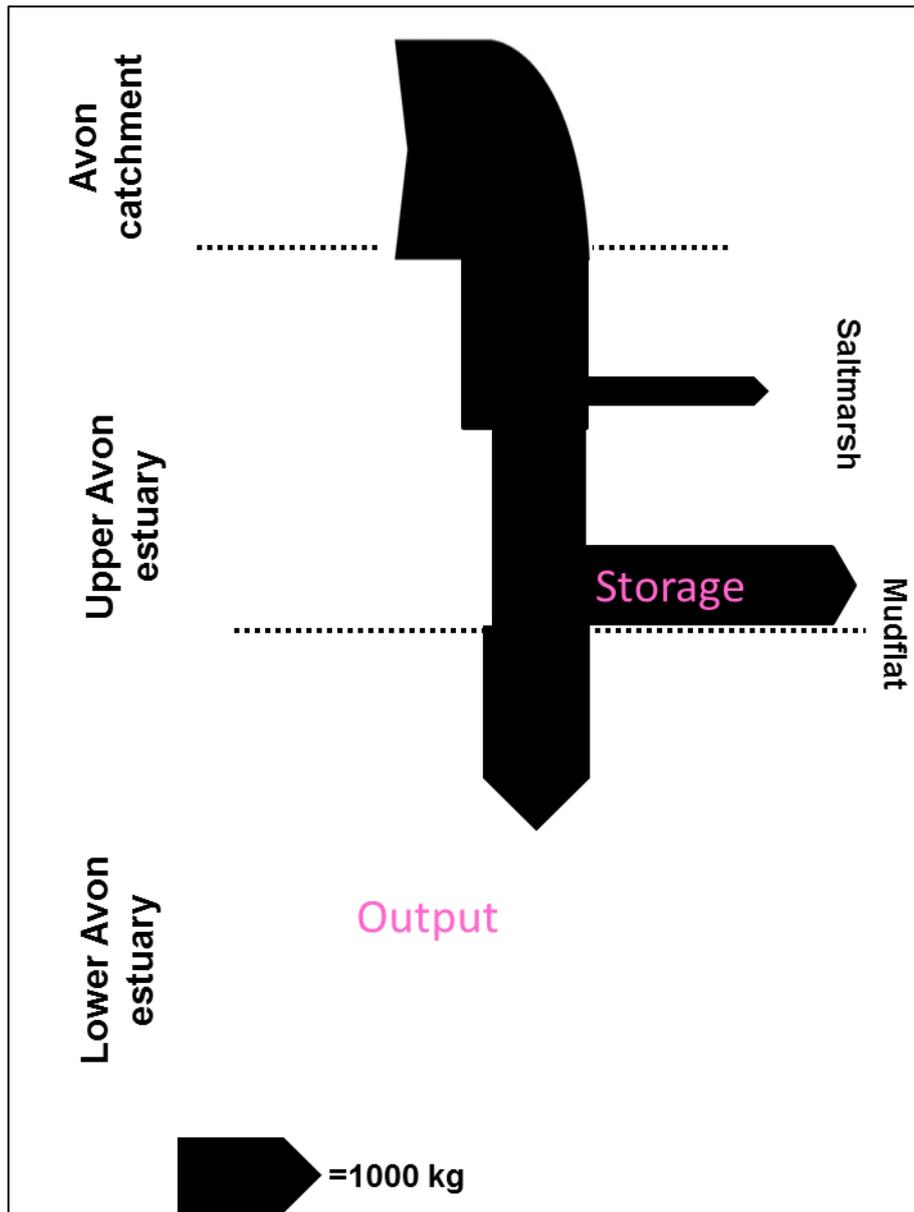


Figure 6.15: Annual PP budget of the Avon estuary. Thickness of arrows is approximately proportional to total phosphorus mass.

6.4 Discussion

6.4.1 PP estuary input dynamics

It has been demonstrated that PP fluxes in river systems are temporally variable (Evans & Johnes, 2004; Bowes *et al.*, 2003). The result above shows that there is variation in the TP values between sampling periods for the whole two years and that the maximum TP load input was noted in winter in accord with a higher sediment

load. This is more in agreement with what was found by Jarvie *et al.* (2002) who observed, in a study of the Kennet, high winter concentrations of particulate phosphorus in suspended sediment; while others claim that winter concentrations are lower than those found in the summer months. Coupling of information on sediment-associated phosphorus content with that on the total sediment load in transport allowed an assessment of the total sediment-associated phosphorus flux.

6.4.2 Comparison of PP concentration with other study catchments

This study and other authors have written about the variability of total phosphorus levels in rivers according to different locations. Values of PP for data recorded by Walling *et al.* (2003) in their study of the Rivers Aire and Calder, however, were generally higher than recorded in this present study and in global studies. In their comparison of the nutrient content in various UK Rivers with global rivers, Russell *et al.* (1998) noted variation in the contribution of the various fractions of phosphorus measured to PP. It was concluded that in catchments where land use was dominated by intensive agriculture, the dominant phosphorus fraction present was the inorganic one, due to inputs from fertilizers. Owens and Walling (2002) and Owens *et al.* (2001) identified an increase in urbanization as being the cause of the elevated levels of phosphorus detected. Dong *et al.* (1983) noted variation in TP concentrations of suspended sediment in the Menomonee catchment, attributable to various point sources; while Cheung *et al.* (2003), in a study in the Pearl River Delta in China, noted variation in phosphorus content at different sampling sites, which were traceable to specific point inputs. However, in contrast, spatial variation in PP content of sediment in Avon catchments cannot be explained by distinct point sources throughout the catchment. Bowes *et al.* (2003) reported similar increases in

phosphorus concentrations in a downstream direction in a study along the River Swale in the North of England, which they attributed not to inputs from point sources, but to transformations from dissolved phosphorus to sediment-associated phosphorus (Figure 6.16).

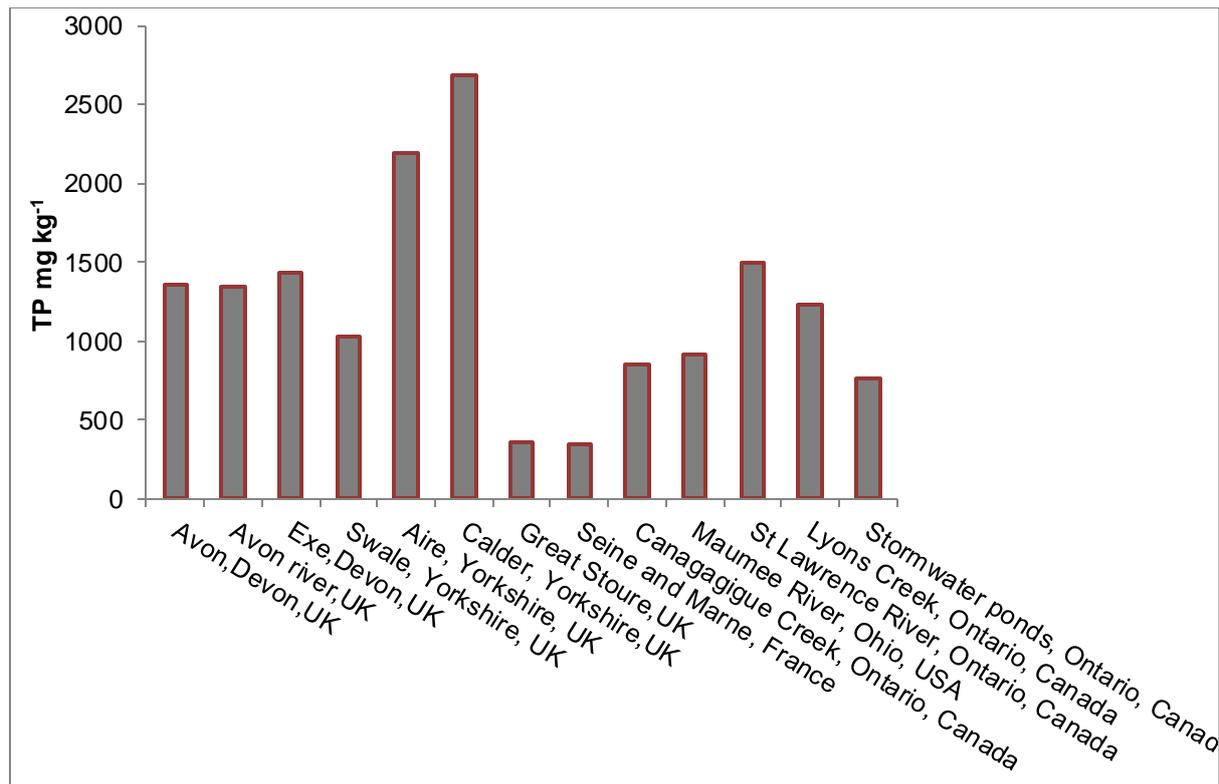


Figure 6.16: Mean TP content of river sediment for this study compared to UK and global rivers.

The results presented in Figure 6.17 show how the TP kg ha⁻¹ yr⁻¹ measured were higher than other catchments for the different land use types. There is much variation apparent within each of the catchments and land use types, but it is clear that TP export is higher for cultivated land than for the other land use types. For example, Walling, (2005) and Heathwaite, 1997, showed that TP yields were often 43, 68, 75 kg ha⁻¹ yr⁻¹ in agriculturally dominated watersheds in Avon (Warwickshire); Seven catchment, Exe and Dart: while, in the Ouse, TP was 55 and Swale was 33

kg ha⁻¹ yr⁻¹. From Don, Dee, and Ythan in the UK, TP was 67, 69 and 79 kg ha⁻¹ P year⁻¹. In Europe, Heckrath *et al*, 2008, found that TP export was 30, 50, 50, and 110 P kg ha⁻¹ year⁻¹ in Denmark, Norway, Sweden and Finland. Sharpley *et al.*, 2001; Sims and Pierzynski, (2005) found that TP export from agricultural land in Arkansas, USA was 104 from grassland and 200 P kg ha⁻¹ yr⁻¹ from cultivated land. Overall, in this study, findings are the smallest of all other catchments, which was 7.8 kg ha⁻¹ yr⁻¹.

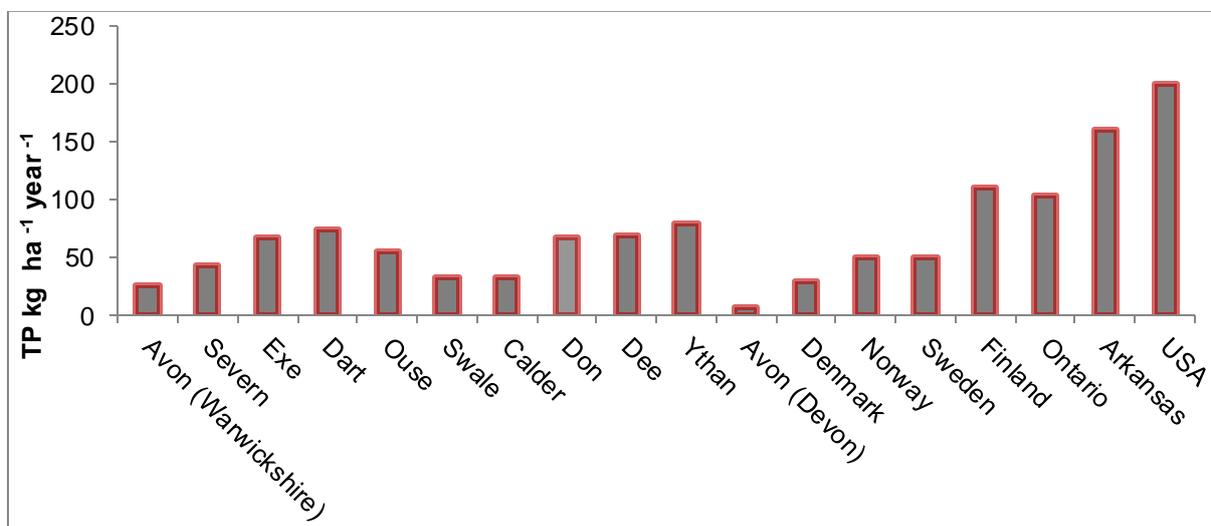


Figure 6.17: Comparison of TP yield between this study and other catchments

6.4.3 Area of fine sediment accumulation

At the upper part of the Avon estuary site, in cross-section, the volume of fine sediment storage per square meter was high in the upper estuary area at section 4, which suggests that there was an intertidal area of fine sediment that has been transported by water and is stabilized by vegetation (Boorman *et al.*, 1998). This tendency for an increase in the silt-clay concentration in sediment has been noted by other authors (e.g. Bryce *et al.*, 1998). Appendix III illustrates the fine sediment was also high at site 7 and 10: this suggests that the tidal creek delivers sediment to and

from the central area of the estuary or explains the extreme shallowness of the channel between the central and upper estuary (Friedrichs & Perry, 2001; Uncles *et al.*, 2012). In the lower estuary, the amounts of fine sediment deposition are seen to be low. This suggests that there is dependence on the direction of sand transport at a location within the estuary (Uncles *et al.*, 2012) and therefore, a relatively low proportion of silt-clay in the sediments associated with changes in gradient channel along the estuary, with changes in the sediment-deposition capacity of each section. The lower PP concentration of the silt that is stored in these areas suggests the silt may be derived from an external source or is reworked material.

However, a reduction of the total volume of the sediment deposits is responsible for morphological change (Masselink *et al.*, 2009; Mertes *et al.*, 1996). Trapping of fine sediment in sites 8 and 9 in the lower estuary deposit was associated with cross-estuary movement; this suggests that the secondary circulation during the flood tide pushed sediment onto the shoal on the west side (Woodruff *et al.*, 2001). The amount of fine sediment storage in the estuary was low where annual sedimentation was very high.

Net deposition of sediment on a marsh is a function of the availability of sediment and the opportunity for deposition. Rates of sediment deposition in saltmarshes frequently increases as more of the incoming sediment is intercepted and trapped as the increased surface area of the vegetation causes an increase in friction (Boorman *et al.*, 1998). This tends to increase in the upper estuary, a salt marsh area having a larger surface area to volume ratio; fine particles

can adsorb a much higher concentration of nutrient than suspensions of particles having greater grain size. This could skew sedimentation patterns toward higher

deposition of fine sediment in the upper estuary more frequently because of the vertical sediment exchange between the suspended sediment and salt marsh sediment and could provide an explanation as to why more of the fine sediment is deposited (Flemming & Delafontaine, 2000; Van Ledden, 2004). Table 6.5 and Figure 6.14 show that the rates of sedimentation across a marsh are not uniform and the high rates of net sediment accumulation at the mudflat zone, this may be because of the net accretion rate may also have diminished as a result of increasing sediment compaction over time (Marion *et al.*, 2009).

Sedimentation rate is a consequence of a range of factors (Brown, 1998). These factors include the vegetation cover, the distance from the source of sediment and the concentration of sediment (Davidson-Arnott *et al.*, 2002; Friedrichs and Perry, 2001; Reed, 2002; van Proosdij *et al.*, 2000). These creeks allow for tidal fluxes to deliver nutrients, microorganisms and sediment into the marsh system.

The highest amounts of P are deposited across the upper estuary; this suggests that PP increases are dominated by increases in a deposition of sediment: those points closer to the source of sediment will have a higher concentration of PP within the sediment (Friedrichs & Perry, 2001). Thus, sedimentation will occur constantly at the boundaries closer to the source.

As demonstrated by the results above, PP deposition is widely reported to be strongly related to the deposition of sediment. This is exemplified by the results reported by Steiger and Gurnell (2003) who investigated the nutrient content of sediment deposited on the floodplains of the Garonne. They found that with higher sedimentation rates, larger quantities of phosphorus were deposited, regardless of sediment texture. Also Kronvang *et al.* (1999), in their study in the Gjern catchment,

reported a strong positive relationship between total sediment deposition and PP deposition. Figure 6.13 also shows that almost the maximum and minimum PP depositions coincide with the maximum and minimum sediment deposition rate. This implies that PP deposition is highly dependent on supply of fine sediment at each site and hence source of material is a key consideration. This is well demonstrated at Lower Bockhampton, in the catchment of the River Frome, where the highest concentrations of TP were recorded. Sediment deposition was low; therefore the total amount of phosphorus deposited on the floodplain was also low. In direct contrast, the TP concentration in sediment at Chilfrome was the lowest measured in the two catchments, yet because there were high amounts of sediment deposited, the quantity of phosphorus introduced annually to the floodplain was high (Ballantine *et al.*, 2009).

6.4.4 Sediment and PP budgets

Results from this study showed a sediment budget input to the Avon estuary where the highest input of sediment recorded for one year was estimated to be 2437 t y⁻¹. The total storage data suggest that between 40 and 100 years of river sediment load are currently stored in the estuary which a significant storage given the known history of saltmarsh growth in the twentieth century (Chapter 3). This trend is in keeping with the work of Bostock *et al.* (2007) who demonstrated that most of the fine sediment generated into the estuary is currently coming from the Fitzroy River, southeast Australia. In contrast, in the River Isábena in Spain, however, there is much less of the sediment input to the coastal zone (e.g., 235 t y⁻¹, 600 t yr⁻¹) (López-Tarazón *et al.*, 2012; Furnas, 2003). This could suggest that fluvial loads have been sufficient to fill the estuarine basin and have resulted in large amounts of

sediment being stored in the deposition zone areas; and that one can expect that it may take tens to hundreds of years for this stored sediment to move through these systems to the estuary output (Nichols *et al.*, 2013). The data suggests storage of 1271 t yr^{-1} of fine sediment is high similar to estimates of fine sediment storage of the Fitzroy River estuary of 1420 t yr^{-1} (Bostock *et al.*, 2007). The annual budget implied that greater than 50% of the sediment input load was stored in the sink zone.

The amount of PP storage in the deposition areas was high. It is suggested that sediment-associated phosphorus accumulating may persist within the system for many hundreds of years, especially if longer-term sediment storage occurs (Daniel *et al.*, 1998). It is believed that saltmarsh and mudflat areas represent storage zones for sediment-associated phosphorus in the longer term. It is noteworthy that the total PP storage in the contemporary system equated to ca. 20 – 40 years' worth of the annual PP flux for the catchment i.e. half that of the sediment flux. This discrepancy could be linked to more recent increases in PP load in the river.

The annual particle phosphorus storage in the estuary was about $1600 \text{ kg P yr}^{-1}$. This is high when compared with the other studies in different environments; for example, Cooper *et al.* (2002) found that approximately $600 \text{ kg as PP yr}^{-1}$ was stored in the UK; while, Bennett *et al.* (1999) found that annual PP storage was 575 kg P in Lake in USA; while Nemery *et al.* (2005) found that $319 \text{ kg of P yr}^{-1}$ was deposited on the alluvial plain in France. This could suggest an increase in supply of TP, suspended in the river system and related to agricultural activities, as phosphorus concentrations are known to increase in parallel with the intensity of land use. This is in contrast to what was reported by Thoms *et al.* (2000) in a study of floodplain sedimentation in the River Murray, Australia. They noted an increase in phosphorus

content in overbank sediment in distal areas of the floodplain. Heavy metals interact with fine sediment in a similar manner to phosphorus and have the same relationship: i.e. contaminant content increases with an increase in specific surface area; Zhao *et al.* (1999) also observed increases in contaminant content with distance from the channel. In agreement with this present study, Nemery *et al.* (2005), who considered phosphorus deposition on the floodplain in a study of the Marne watershed in France, reported reduced phosphorus deposition with distance from the channel.

6.5. Conclusion

The results presented in this chapter suggest that significant amounts of phosphorus can be stored in estuary sediment sinks due to fine sediment deposition. This major phosphorus store has the potential to become a source of phosphorus in the estuary through chemical exchanges processes between the sediment and the water column.

It should be recognised that there are several sources of uncertainty within the sediment budget calculation as presented and the conclusions must be considered within this context. The sediment inputs to the estuary were based on just two years of high resolution monitoring and there was a notable difference between the loads reported. The derivation of total sediment stored was based on assumptions of sediment wedge shape and also assumptions of uniformity between transects. More detailed surveying would permit quantification of this uncertainty. The sediment budget evaluation has also not assessed the potential impact of sediment erosion from saltmarshes and the reworking of material by tidal currents which will also add an element of uncertainty to the budget. These could be further constrained through application of sediment source tracing approaches and high resolution dating of

saltmarsh and mudflat deposits to explore spatial variability in the age and residence time of stored material.

Notwithstanding the above limitations, saltmarsh and mudflat areas represent important storage zones for sediment and sediment-associated phosphorus in the longer term with current storage amounts equating to several decades of sediment and associated P. The continued inputs to the storage zones mean it could therefore be regarded as permanently stored in the system but future changes in sediment supply due to land management or climate change could disrupt this.

Destabilisation of deposition areas by erosion are an important future consideration as sediment-associated phosphorus may be reintroduced into the water. Also, with the potential for desorption to occur with wetting and drying of the sediment, the sediment could become a source of dissolved phosphorus to the water. The bioavailability of the PP stored in estuarine sediment needs attention (Monbet *et al.*, 2009). The improved understanding of the sediment and phosphorus budget provided by this study helps contextualise the importance of quantifying inputs of fine sediment associated phosphorus from the river and will contribute further to understanding the fate of sediment-associated phosphorus in the estuary system.

Chapter 7: Thesis summary and conclusions

The overall aim of this project work was to develop knowledge of phosphorus inputs to and storage in the estuary of an agricultural catchment, using the fine sediment budget as the framework. Regarding this aim, three research objectives were formulated to address the research needs. The preceding chapters have presented the results of the investigations designed to address each of the project research objectives. The aim of this chapter is to present a summary of the main findings from the investigations, explore some limitations and to suggest areas for future research and analysis.

7.1 Project Summary

7.1.1 Quantifying the fluxing of sediment and particulate phosphorus from the catchment to the estuary

Chapter 4 provided information on temporal variability in the suspended sediment concentrations and loads of the river channel that delivers material to the estuary from the study catchment. Parts of chapter 6 developed and extended this further by exploring the phosphorus content of fluvial suspended sediment as a basis for estimating the particulate associated phosphorus input to the estuary.

The examinations of the annual hydrographs of sediment load showed that seasonality in rainfall and land use cover was the main contributor in variability in the sediment flux. The combination of high flow and suspended sediment concentration in the river network during winter meant that sediment transport was highest in winter, which was the season when contributions to sediment and phosphorus loadings in the river in line with other studies. The cumulative flow and suspended sediment load

curves showed the episodic nature of sediment load transport with the occurrence of storm events.

Examination of the correlation analysis of the relationship between the rainfall characteristics, runoff dynamic and sediment load showed that there was little relationship between rainfall properties and sediment load across the two years of study; but analysis of data in seasonal blocks revealed that in the winter, rainfall in the lower catchment was a key factor for the higher sediment loads. This was driven by the greater proportion of land in cultivation in the lower catchment which was susceptible to erosion and sediment export during this period. In contrast to winter, the summer sediment response of the catchment is correlated with rainfall in the upper catchment, where antecedent rainfall is seen to be of importance.

The examination of Individual storm hydrographs supported the important influence of spatial rainfall patterns. For example, a significant winter event, where the rainfall in the lower catchment was high (28 mm), had a greater sediment response (529 mg l⁻¹) when compared with an event with a lower sediment load (155 mg l⁻¹), where the rainfall in the upper catchment was greater (30 mm). The total load and yield were 2437 t and 7.15 t km² yr⁻¹ for 2009 and 986 t, and 3.30 t km² yr⁻¹ for 2010. Catchment PP yields were 6.7 kg yr⁻¹ for 2009 and 10.2 kg yr⁻¹ for 2011.

The study was limited by the two year high resolution monitoring period. A longer record would permit a better insight into the temporal dynamics of sediment delivery and the processes controlling this. Those could be coupled with a sediment source apportionment study to help confirm the conclusions about spatial patterns in landuse and rainfall.

7.1.2 Spatial variability of sediment-associated phosphorus concentrations in estuarine sediment sinks zones

In Chapter 5, the particulate phosphorus concentration for sediment was assessed in the study estuary. Comparing the TP storage of the sediment in the Avon estuary which ranged between 68-1524 mg kg⁻¹, with other studies shows that higher TP concentrations were noted by many authors recording results from river sediment, and particularly phosphorus: 1430 mg kg⁻¹ Exe, Devon, UK, Lambert & Walling (1986, 1988). The spatial variation in key sediment compositional properties (i.e. sediment grain size and total organic carbon) and the phosphorus content of surface sediment concentration was explored with a view to developing insights into the key controls on spatial variability.

An examination of sediment particle size classification data confirmed typical estuarine sedimentary zonation in that it showed that fine-grained sediment (mostly silt and sandy silt) were deposited in the upper estuary whereas most of the middle to lower estuary deposits were silty sand and sand. The exception was the deposits found within the tidal area of estuary feeder streams or creeks which run directly into the main estuary. These were dominated by silt, albeit small pockets, as per the upper estuary. Silt storage areas were dominated by saltmarsh, while sand was found in the shoal areas.

The results of spatial variation of the concentration of phosphorus in the fine sediment fraction showed that the higher concentrations (1524 mg kg⁻¹) were present in the upper estuary, with lower concentrations (68 mg kg⁻¹) in the lower estuary. There was no significant correlation between total particulate phosphorus and total organic carbon or particle size across the full estuarine fine sediment dataset nor within the data from each specific sediment storage unit that was

sampled. Comparison of fine sediment summary data between the sites, however, showed that higher concentrations of the phosphorus were present in the mudflat zones ($760 \pm 85 \text{ mg kg}^{-1}$) which was very close to saltmarsh zone, with lower concentration ($77 \pm 5 \text{ mg kg}^{-1}$) in the shoal area. Furthermore, mean particulate phosphorus concentrations of each sediment storage unit were seen to correlate closely with the fine sediment, specific surface area and organic matter where in the latter appeared to be influenced by saltmarsh vegetation. Estimates of total phosphorus storage in the estuary vary spatially between individual sites and show a strong relationship with the total amount of fine sediment in storage at each site. No inorganic carbon was noted in the estuary.

The results provided some insights into the compositional controls on particle phosphorus concentration in the estuary sediment. Particular, deposits on the saltmarsh area can be noted: that for the entire site there is a relationship between the SSA and TOC contributions to TP. An examination of the correlation relation between TP and SSA found that the relationship between specific surface area and TP concentrations shows that grain size did seem to be an important influence in TP concentrations in sediment, with increases in specific surface area accompanied by increases in total phosphorus concentration, decreasing toward the lower estuary.

The study showed that there was spatial variation in the amount of phosphorus deposited per unit area within the estuary sedimentation zones and while proximity to the catchment input was key factor i.e. upper estuarine sediments were enriched in phosphorus, there was an overall relationship between particulate phosphorus concentration and particle size when considering the mean data of each group. Interestingly there was no relationship between particle size and particulate phosphorus within the sites which, coupled with the above observation, suggest that

particle size controls occur at the estuary scale. There was general increase in TP concentrations in fine sediment in the upper estuary, while in the lower estuary TP concentration decrease is identifiable.

The improved understanding of spatial variations in phosphorus deposition provided by this study will help to quantify sources of phosphorus from the river system and will contribute further to understanding the fate and delivery of sediment-associated phosphorus in the estuary system but there remain unanswered questions about the stability of the stored phosphorus in the sediment column.

The augmented particulate phosphorus concentration of the stored estuarine sediment means these deposits could pose a risk to future water quality through potential release to the water column. This could be driven by physical disturbance of the stores perhaps caused by changes in sediment supply or increased storminess and erosion of sediment deposits. Release could also be driven by changes in the geochemical partitioning studies (Monbet et al., 2009). Exploration of the stability and bioavailability of sediment-associated P would be the next logical step in this investigation.

7.1.3 Estuarine fine sediment and particulate phosphorus budgets

Chapter 6 considered the total storage of fine sediment and phosphorus associated with sediment deposition in the estuary in the context of the annual river loads. As with suspended sediment, temporal variation was noted in the phosphorus concentration and did show elevated concentration in the winter.

The examination of phosphorus content and storage associated with sediment were reported. Generally it was found that both the fraction of phosphorus in stored sediment mirrored that of phosphorus associated with suspended sediment.

The total amount of PP and fine sediment in the storage area was 27000 kg and 99000 t, and this represents many times (between 40 – 100 years load) to the annual river input, as measured in the two study years, which was a maximum of 3034 kg yr⁻¹ P input and 2437 t y⁻¹ sediment input. Using accretion data for the main storage zones, the annual storage rate in the Avon estuary was 1271 t yr⁻¹ of fine sediment and 1582 kg yr⁻¹ of PP storage.

As with fine sediment and phosphorus storage in the estuary, because phosphorus storage is correlated with the amount of sediment stored in the estuary, variation in the storage of phosphorus is shown to vary from site to site according to the inputs of sediment.

A large part of the sediment storage (99000 t) represents the sediment budget in the Avon estuary; this storage is of a more long-term nature and is only likely to be remobilised and reintroduced to the estuary system by, for example, physical disturbance with a change in sediment supply or increased storminess. This emphasises that the deposition area has notable control over the temporal storage and magnitude of the sediment transport out of the system, showing the need for taking this key geomorphic element into account in the estimation of sediment budgets of Avon estuary.

Equally important is the need to consider phosphorus storage in sediment in any nutrient budget study, because although such storage is temporary and does not represent a net loss to the system on the annual scale, it can add up to significant

amounts. Deposition of sediment in the estuary causes the long-term storage of sediment and its associated phosphorus load, thus enabling phosphorus to persist in the environment for many years. While the sediment is likely to be more susceptible to physical disturbance, the P stored within might be released by changes in environmental conditions within the sediment column through biotic or abiotic processes. This is a critical area for future investigations.

The conclusions of this work package rest on a series of assumptions made within the sediment budget calculation including, most importantly, uniformity of sediment deposit depth and shape between transects and a minimal influence of erosion, scour and fill processes and reworking of material by tidal currents. These aspects and the limited temporal scope of the input monitoring period require further attention to refine the conclusions made in this thesis.

7.2. Future work

Future work needs to focus on (i) aspects relating to limitations in the current study and (ii) new questions arising from the current study.

With regard to the first aspect, the above sections have identified a need for a longer temporal record of sediment inputs to help constrain this key term of the sediment budget. The exploration of other processes that might affect sediment movement between the storage zones, e.g. saltmarsh erosion, translocation of material and reworking of old material by tidal currents also require attention to refine the sediment budget. Alongside this, high spatial resolution dating of sediment cores from tidal flats and saltmarshes would give a better insight into the age of the depositional features and spatial variability in past and current accretion rates. All

these aspects would lead to a more informed quantification of uncertainty in the derived sediment budget.

With regard to the second aspect of future work, a study to address the role of estuarine sediment as a secondary source of phosphorus would build logically on the sediment-associated phosphorus storage amounts and distribution in the estuary as determined by this study. Further studies could be extended to potential for release of phosphorus-associated sediment again to the water through application of sequential extraction techniques or bioassay experiments. There is great potential for remobilisation of phosphorus-associated sediment for chemical exchanges associated with changes in estuary chemistry (e.g. pH, redox potential), which may occur naturally. Such changes are more likely to affect storage sediment than suspended sediment because of the extended period of contact between sediment and water. Also this study only considered one nutrient. Further studies could be extended to encompass a wider range of fractions of phosphorus or to consider other nutrients or contaminants e.g. heavy metals or pesticides.

Across both of these aspects, in several areas of this study work, questions about the source of sediment have arisen, in particular in relation to the lower PP concentration of sediment that was stored, in low proportion, in the sand deposits. Other studies have recently demonstrated that sediment accreting on saltmarshes can be sourced from other sediment storage zones within the system (e.g. Rotman et al., 2008) and that reworking is important. This has implications for the sediment budget and also the P content and geochemical stability. A detailed analysis of sediment provenance of the different zones of deposition to explore contemporary catchment versus internal reworked sediment and/or externally sourced fine

sediment would improve understanding of the development of these important PP sinks.

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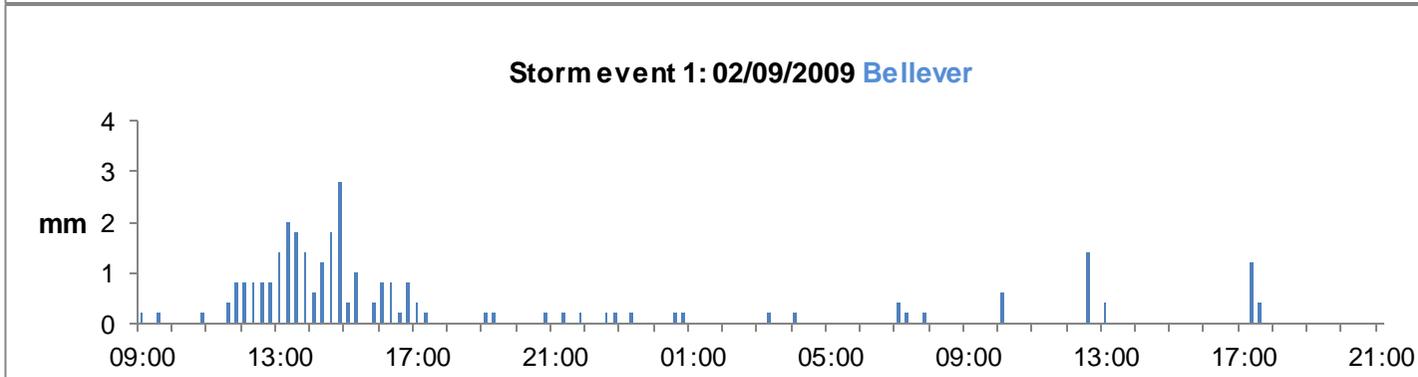
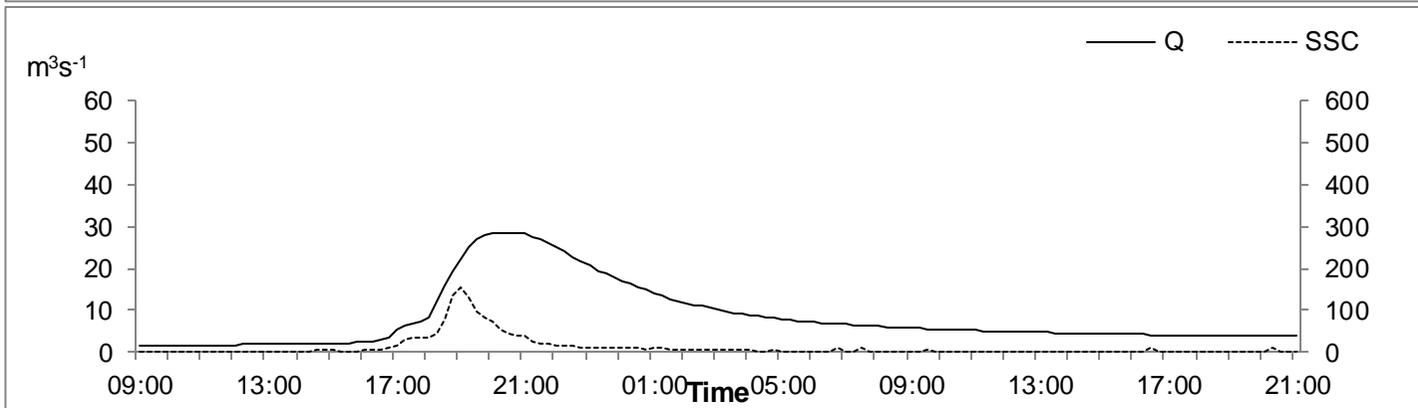
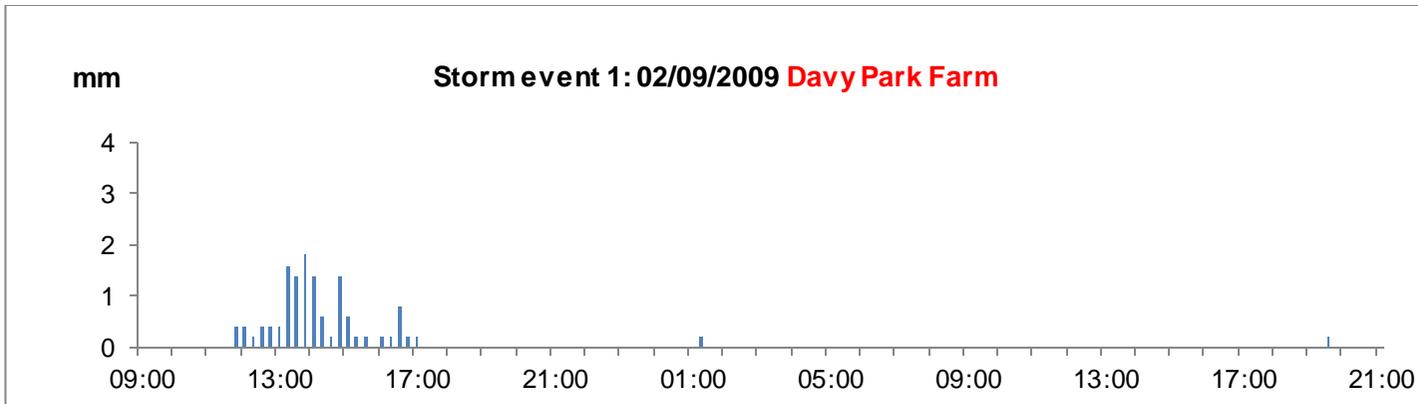
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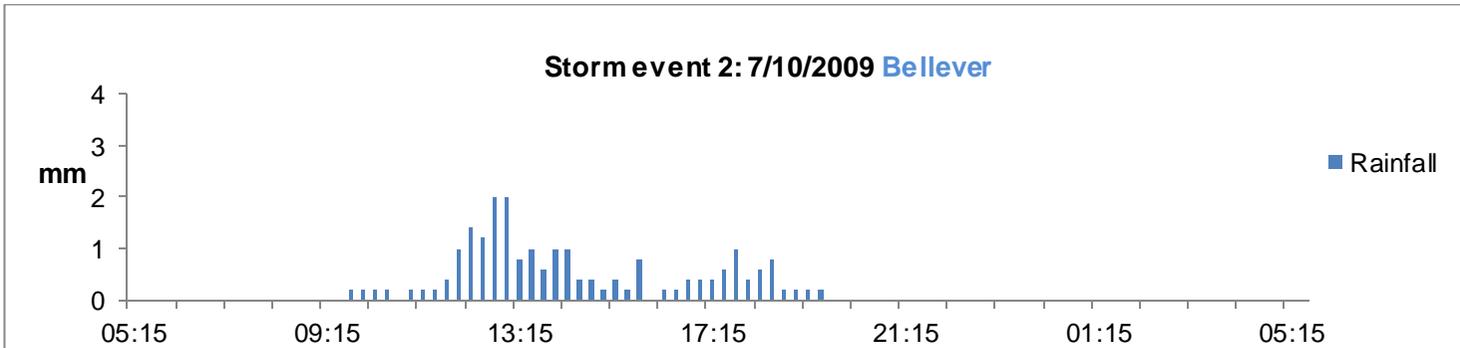
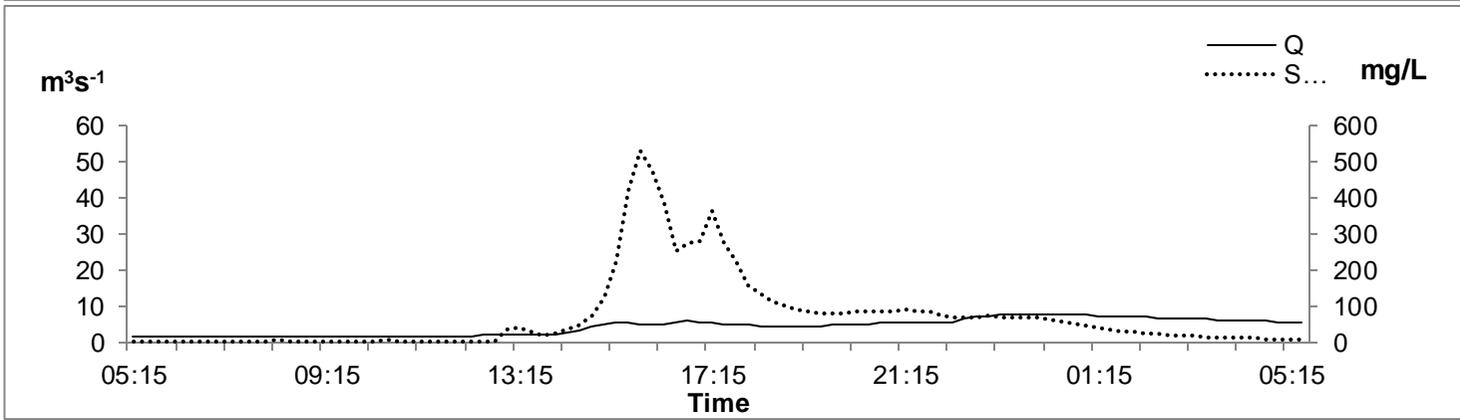
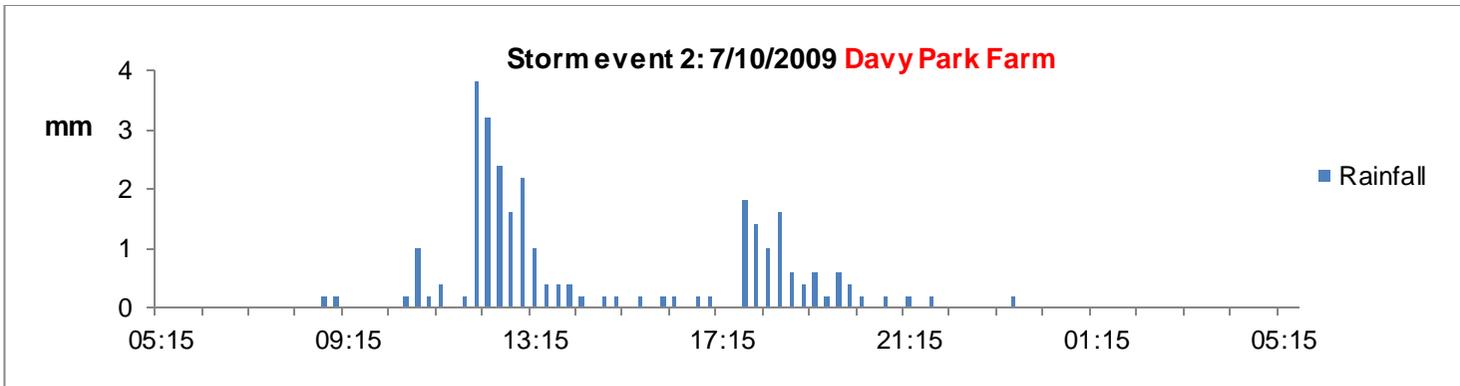
Appendixes

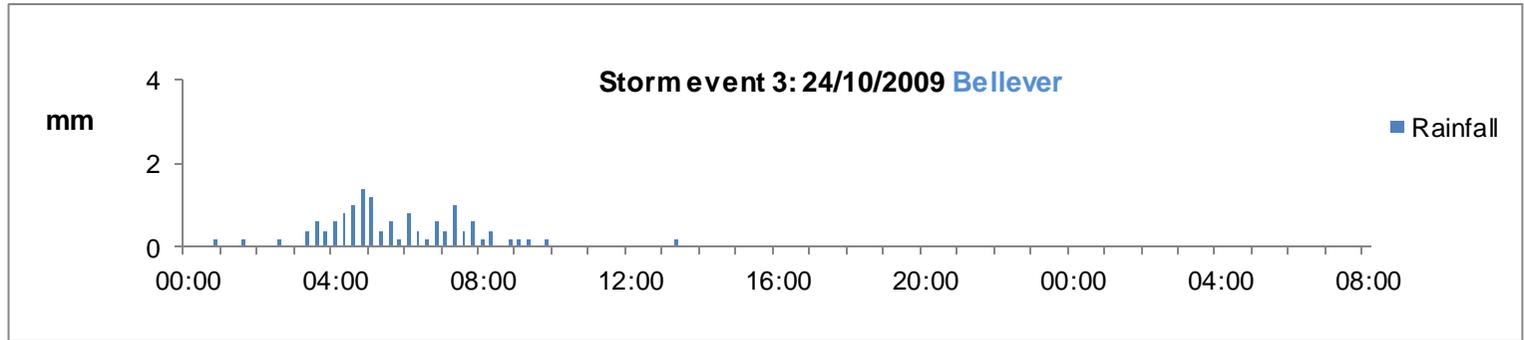
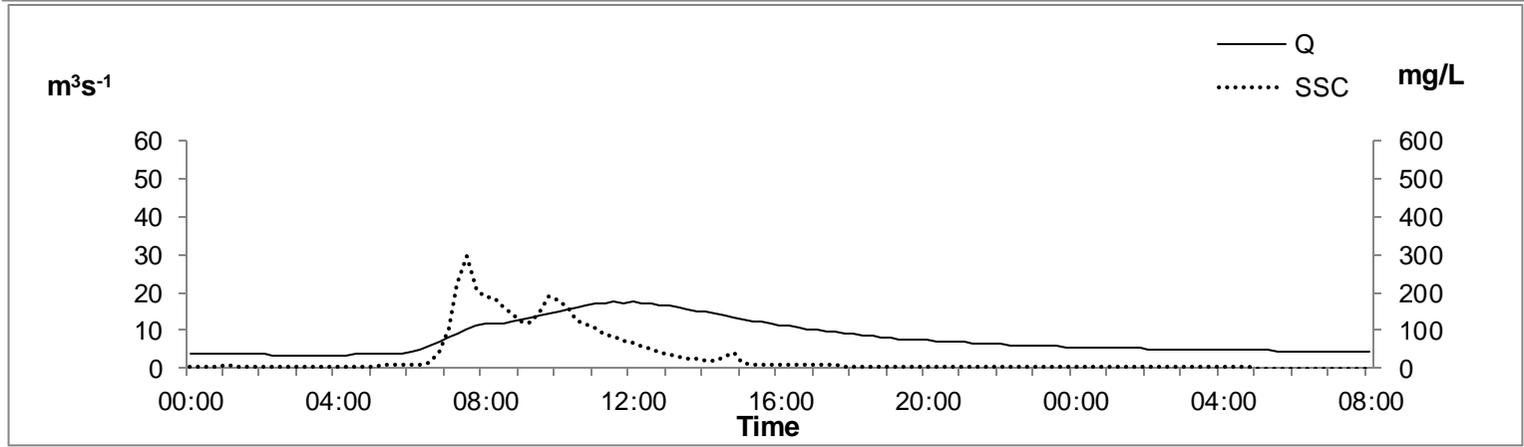
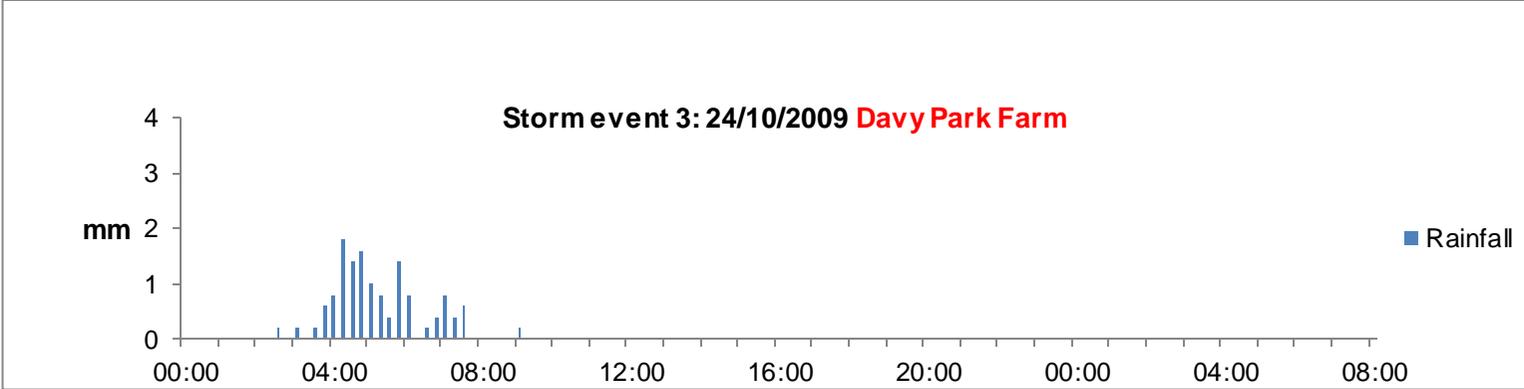
Appendix I: storm event hydrologic analysis

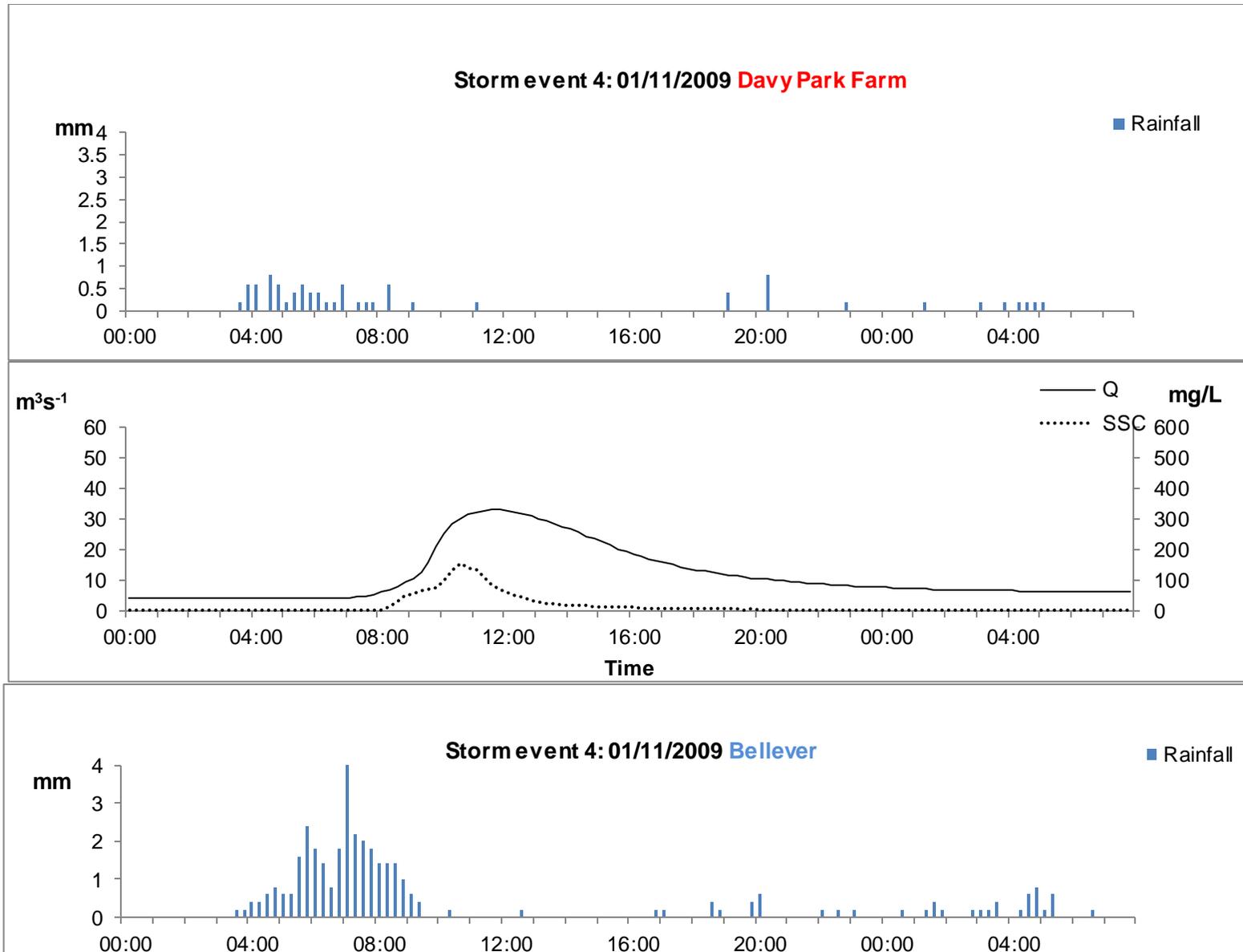
Date	Bellever					Day Park Farm					
	Daily rain	P1d	P7d	P30d		Daily rain	P1d	P7d	P30		
1	02/09/09	31		5	39	97	13		1	6	58
2	07/10/09	22		25	39	46	15		10	20	28
3	24/10/09	14		3	44	119	14		11	17	71
4	01/11/09	33		10	21	154	6		4	8	91
5	03/11/09	27		10	60	194	4		7	0	108
6	12/11/09	12		7	46	210	7		7	45	115
7	21/11/09	34		26	85	327	10		5	61	153
8	23/11/09	36		10	101	350	5		6	30	168
9	25/11/09	8		28	146	397	2		3	29	170
10	28/11/09	22		14	138	422	15		3	41	169
11	06/12/09	26		27	78	412	6		5	51	190
12	08/12/09	18		23	108	441	3		7	40	196
13	29/12/09	30		2	24	182	19		0	45	101
14	16/01/10	39		2	24	109	13		1	15	94
15	22/01/10	11		10	67	167	18		10	24	147
16	17/02/10	10		11	15	101	6		8	7	118
17	19/03/10	22		11	12	65	11		5	59	56
18	15/07/10	34		21	30	60	14		9	18	30
19	20/08/10	29		21	27	90	0		1	12	46
20	23/08/10	6		22	86	119	2		34	39	65
21	25/08/10	22		4	92	122	31		0	48	76
22	06/09/10	35		6	6	149	29		1	2	109
23	01/10/10	15		0	4	105	7		5	17	65
24	03/10/10	26		3	21	124	19		5	36	84
25	27/10/10	8		13	41	112	5		5	27	89
26	09/11/10	18		19	49	136	9		10	14	54
27	11/11/10	34		0	57	154	10		0	22	63
28	12/11/10	17		34	89	189	9		12	33	75
29	17/11/10	35		1	57	211	16		0	32	96
30	13/02/11	28		1	28	133	8		0.2	15	69
31	15/02/11	16		0	49	109	4		0.6	29	65
32	19/02/11	2		6	63	112	5		16	44	64
33	21/02/11	11		2	38	116	3		4	39	73
34	26/02/11	9		17	38	148	3		1	34	82
35	12/06/11	39		2	21	55	29		0.2	2	7

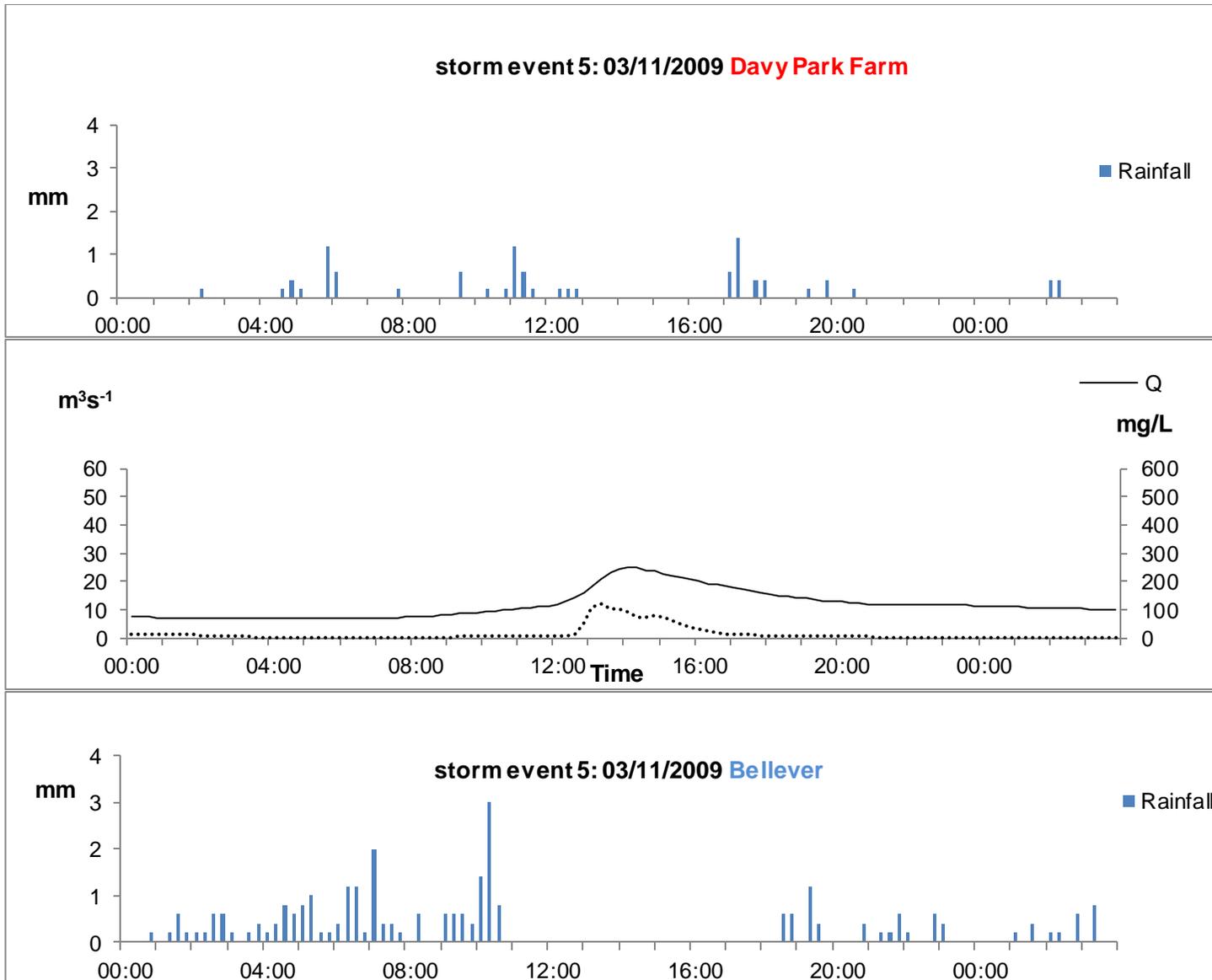
	Davy Park Farm					Believer				
Date	Tr ML	Tb ML	TS ML	Ptot ML	RC %	Tr ML	Tb ML	Ts ML	Ptot ML	RC %
02/09/09	641	194	447	4420	10	641	194	447	7480	6
07/10/09	280	202	78	5100	1	280	202	78	7480	1
24/10/09	590	173	417	4760	9	590	173	417	4420	9
01/11/09	839	155	684	2380	29	839	155	684	10200	7
03/11/09	558	230	328	1360	24	558	230	328	7480	4
12/11/09	787	378	409	3060	13	787	378	409	2380	17
21/11/09	871	464	407	3400	12	871	464	407	9860	4
23/11/09	1707	475	1232	3740	33	1707	475	1232	11900	10
25/11/09	737	516	221	680	33	737	516	221	1700	13
28/11/09	1278	476	802	5100	16	1278	476	802	6120	13
06/12/09	2026	1073	953	2040	47	2026	1073	953	7480	13
08/12/09	1036	497	539	1020	53	1036	497	539	5780	9
29/12/09	873	170	703	6460	11	873	170	703	7140	10
16/01/10	1287	413	874	5100	11	1287	413	874	9520	9
22/01/10	2443	853	1590	6120	26	2443	853	1590	3400	47
17/02/10	437	123	314	2380	16	437	123	314	1360	23
19/03/10	697	97	600	3740	13	697	97	600	5440	11
15/07/10	100	32	68	4760	1	100	32	68	9860	1
20/08/10	737	516	99	136	72	737	516	99	7140	3
23/08/10	523	185	338	2720	12	523	185	338	1360	25
25/08/10	887	127	760	10540	7	887	127	760	6460	12
06/09/10	465	170	295	9860	3	465	170	295	9860	3
01/10/10	2123	831	1292	2380	54	2123	831	1292	5100	25
03/10/10	1322	488	834	6460	13	1322	488	834	8500	10
27/10/10	279	158	121	1700	7	279	158	121	2380	5
09/11/10	374	281	93	3060	3	374	281	93	3740	2
11/11/10	1506	324	1182	3400	35	1506	324	1182	10880	11
12/11/10	561	348	213	3060	7	561	348	213	4080	5
17/11/10	1315	590	725	5440	13	1315	590	725	11900	6
13/02/11	767	216	551	2720	20	767	216	551	9180	6
15/02/11	260	150	112	1500	4	260	150	2040	2040	0
19/02/11	560	310	250	1700	15	560	310	250	680	37
21/02/11	437	384	53	1020	5	437	384	53	1360	4
26/02/11	700	302	398	1020	39	700	302	398	680	59
12/06/11	245	144	101	9860	1	245	144	101	10200	1

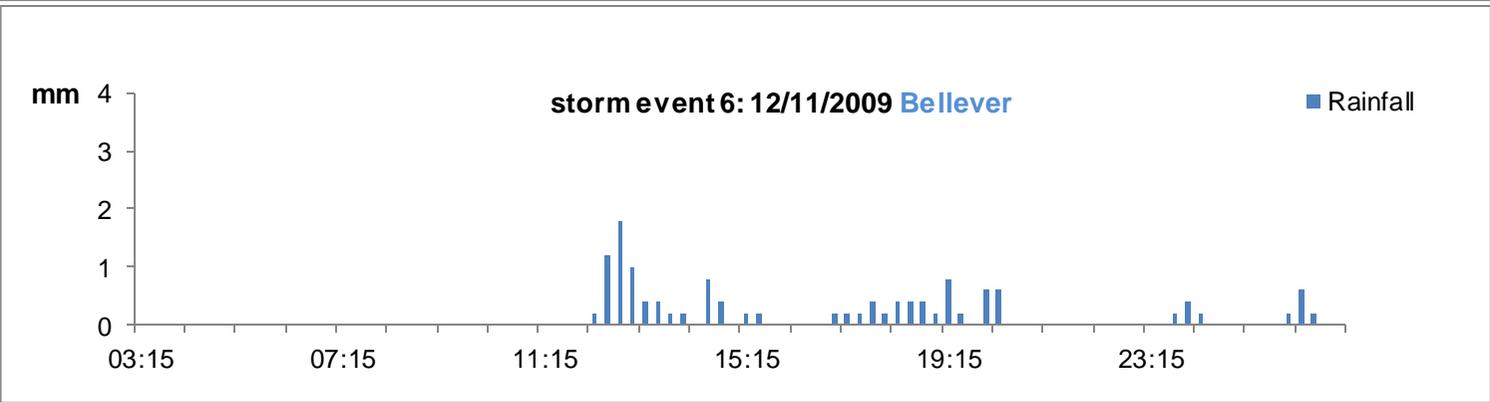
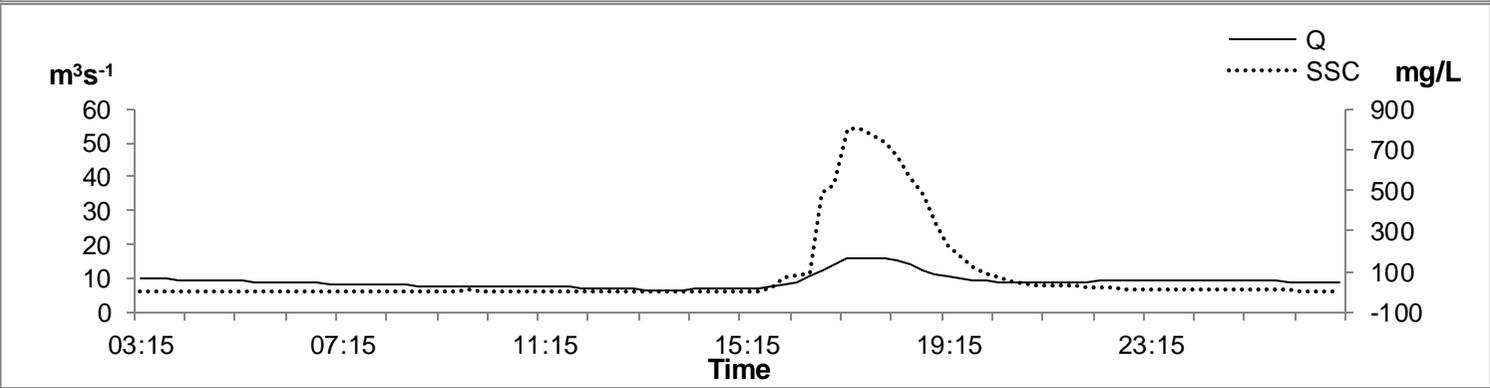
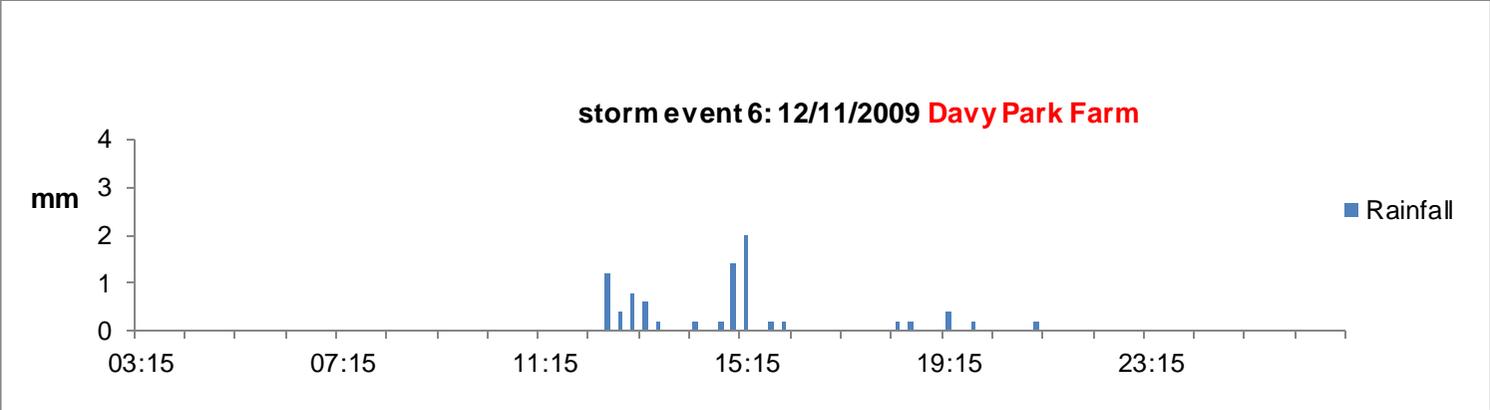


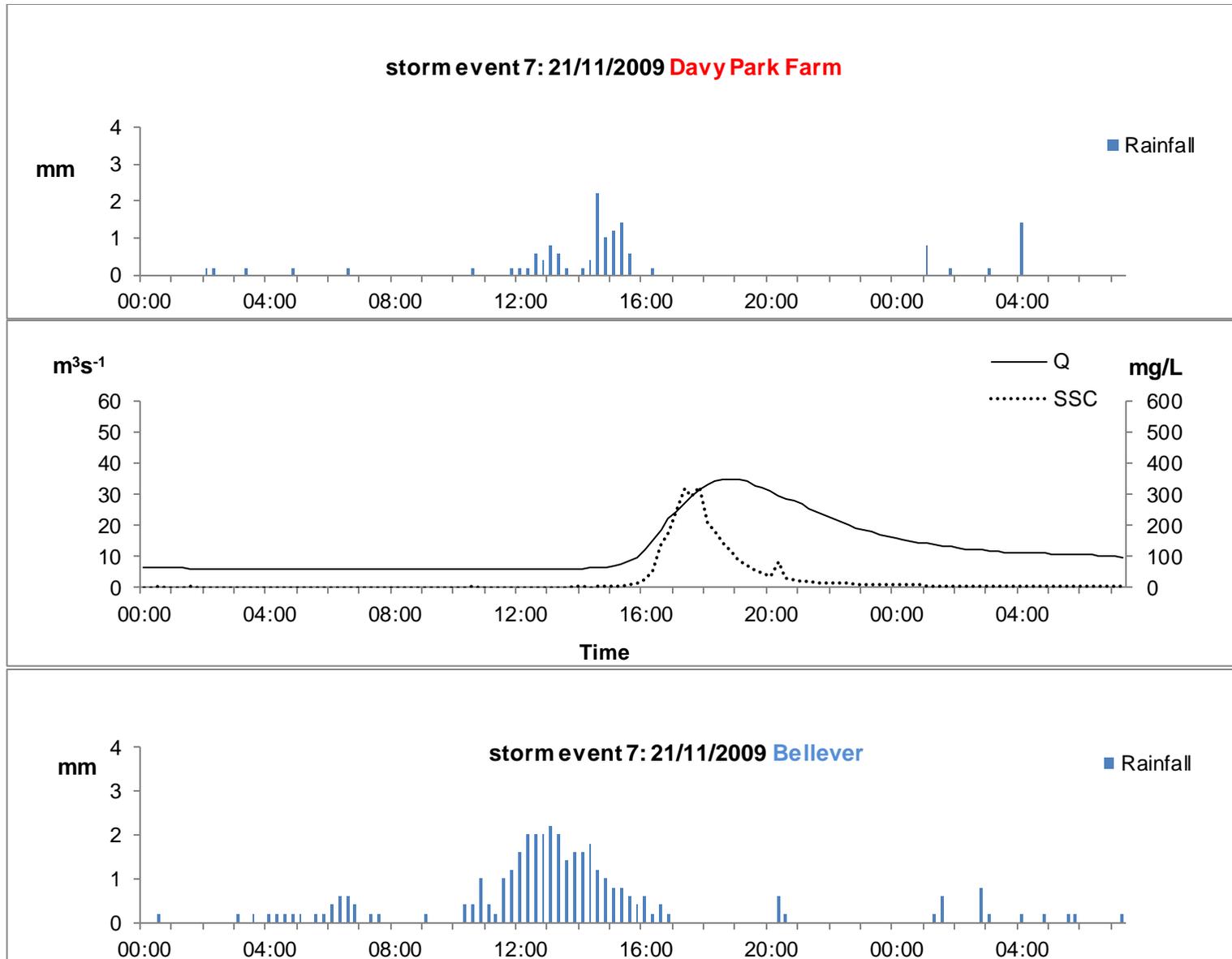


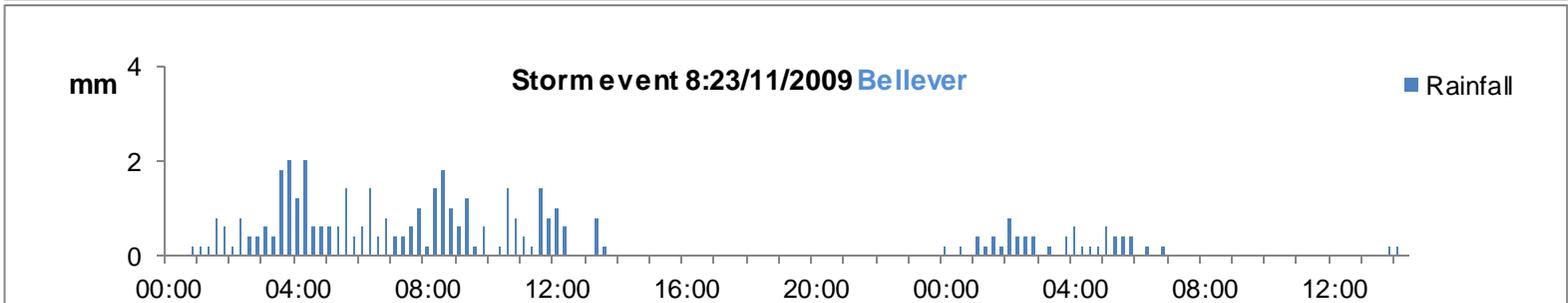
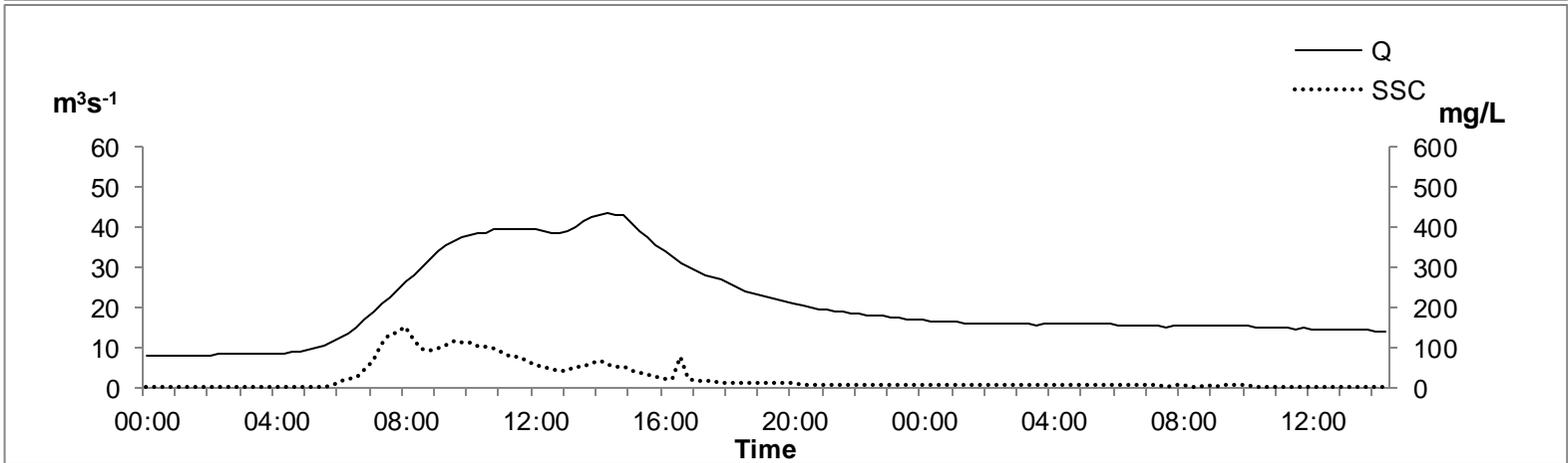
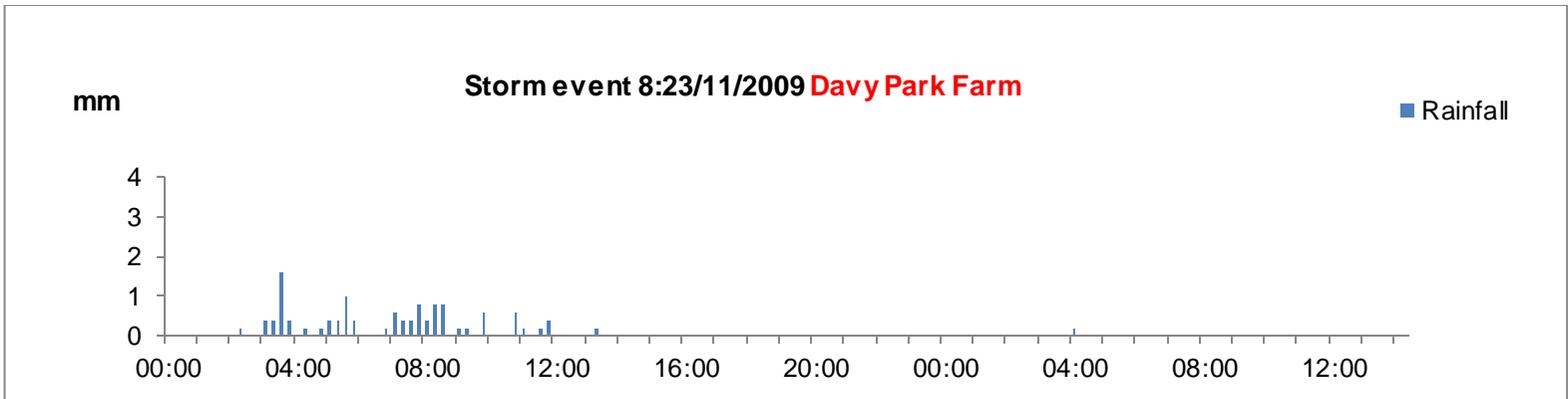


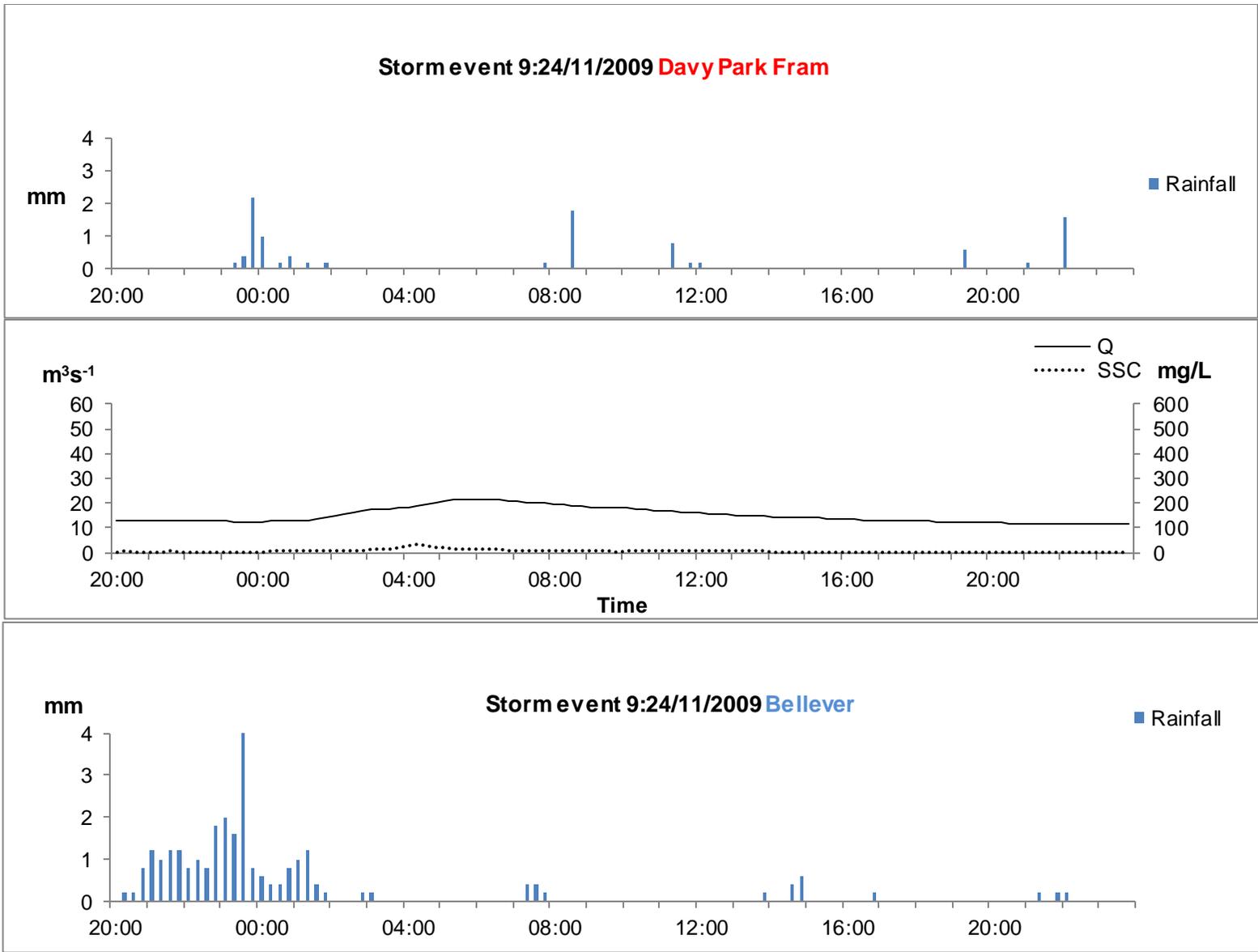


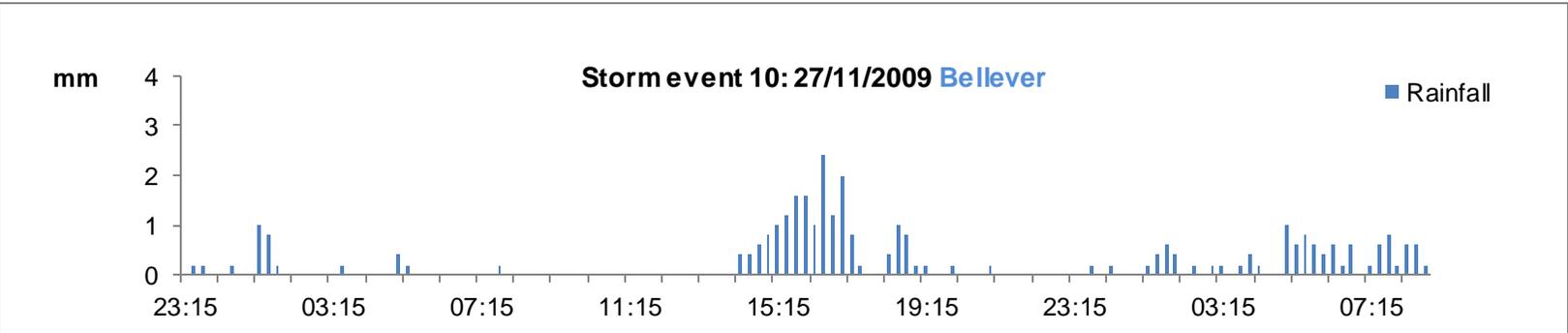
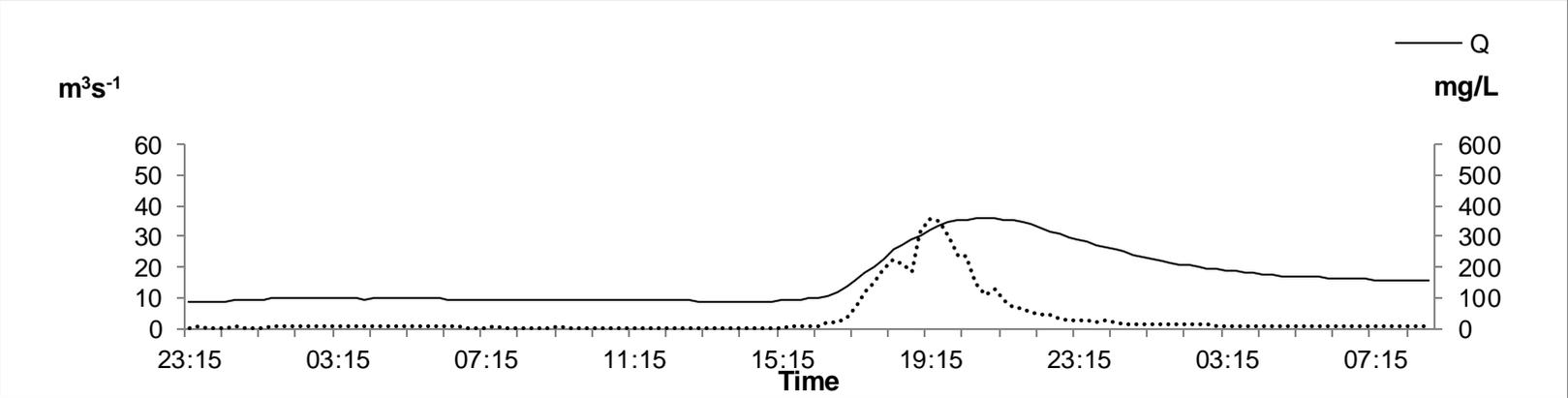
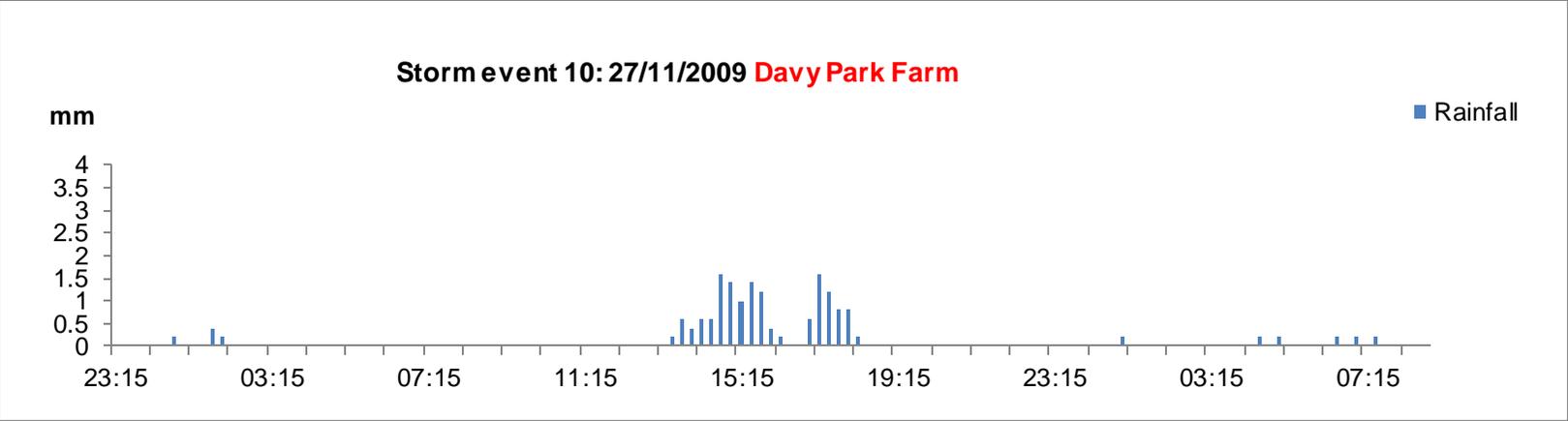


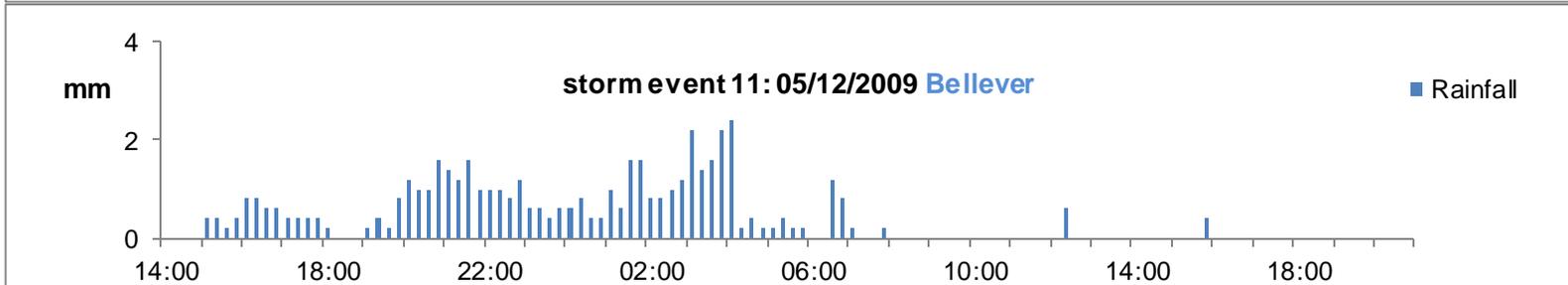
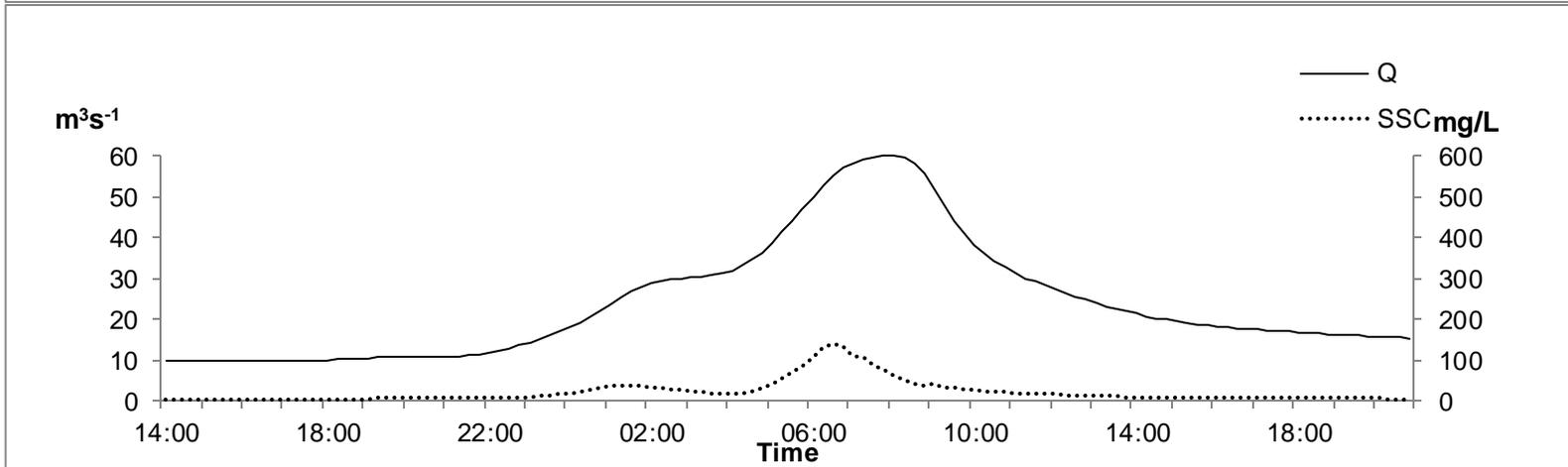
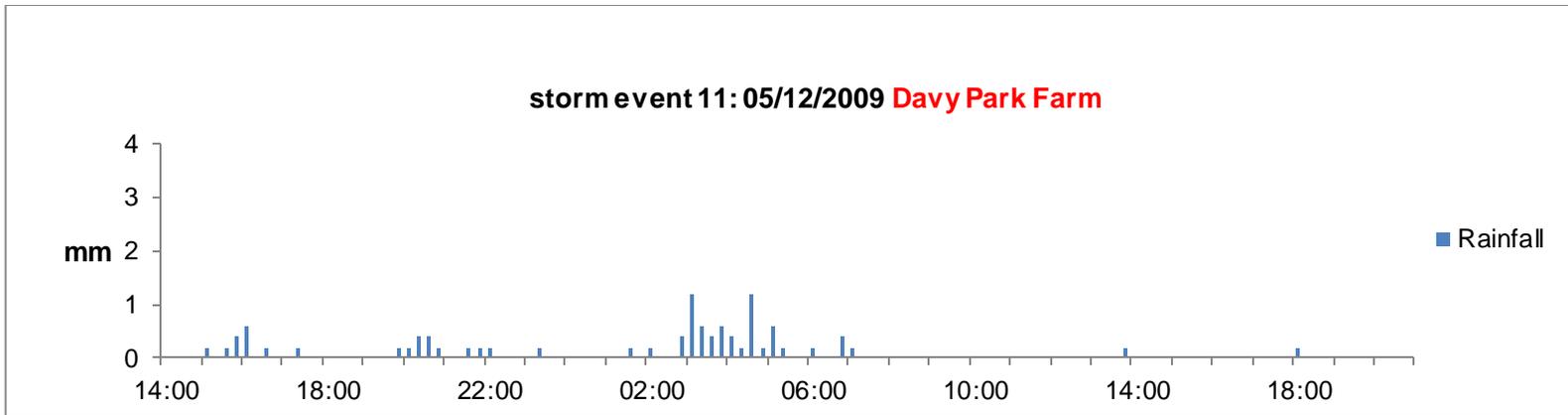


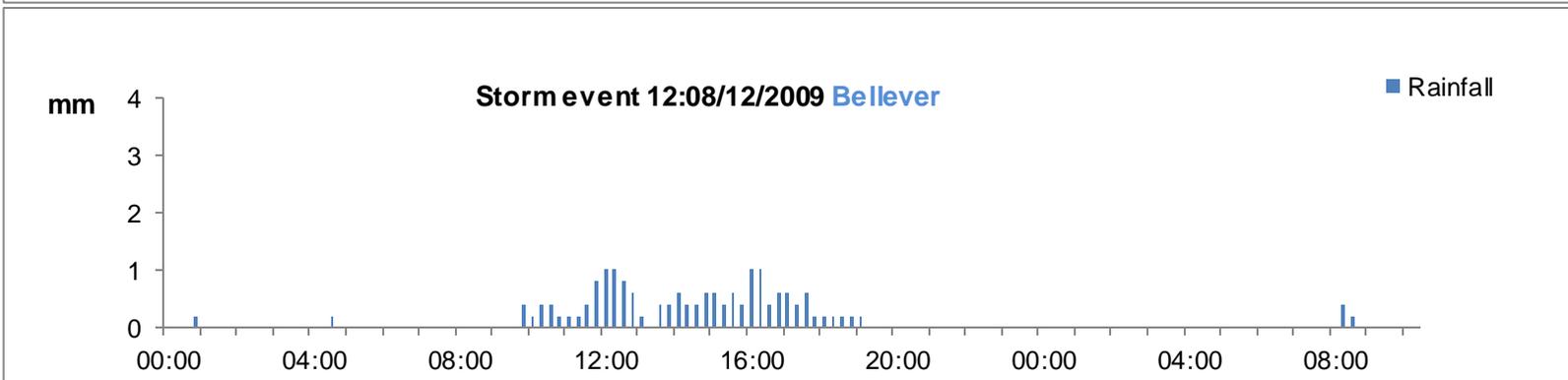
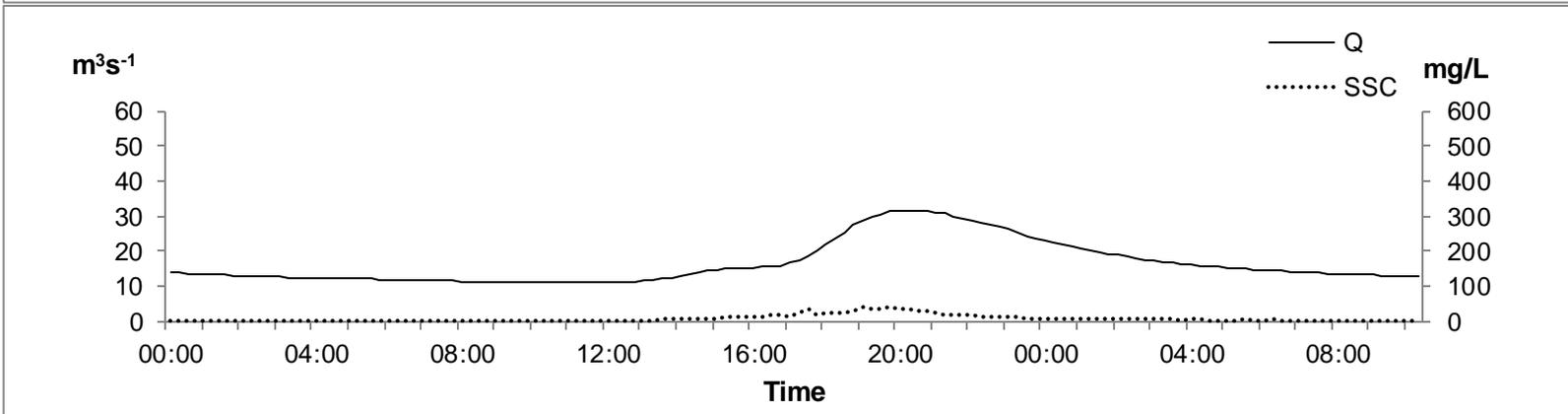
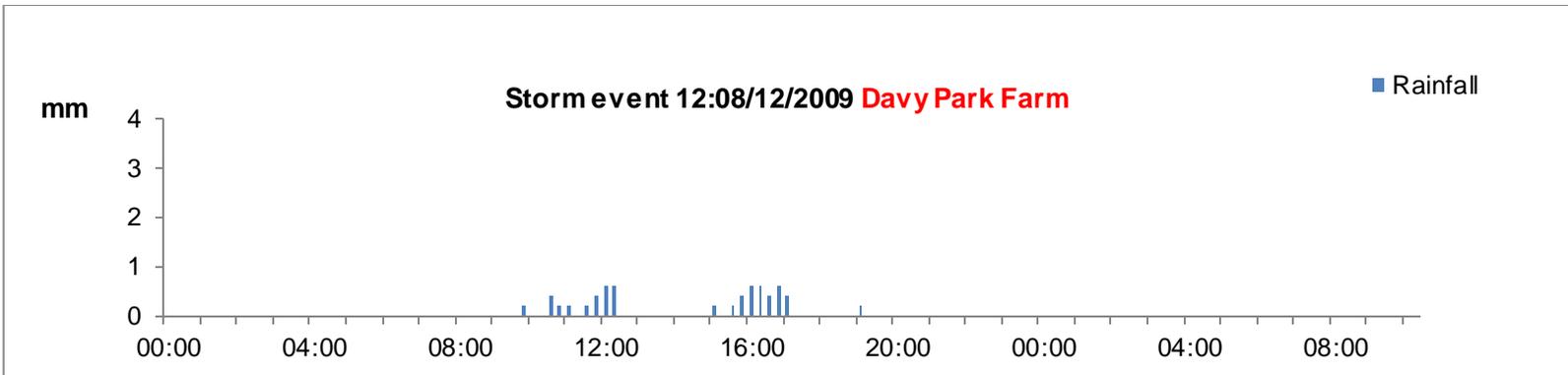


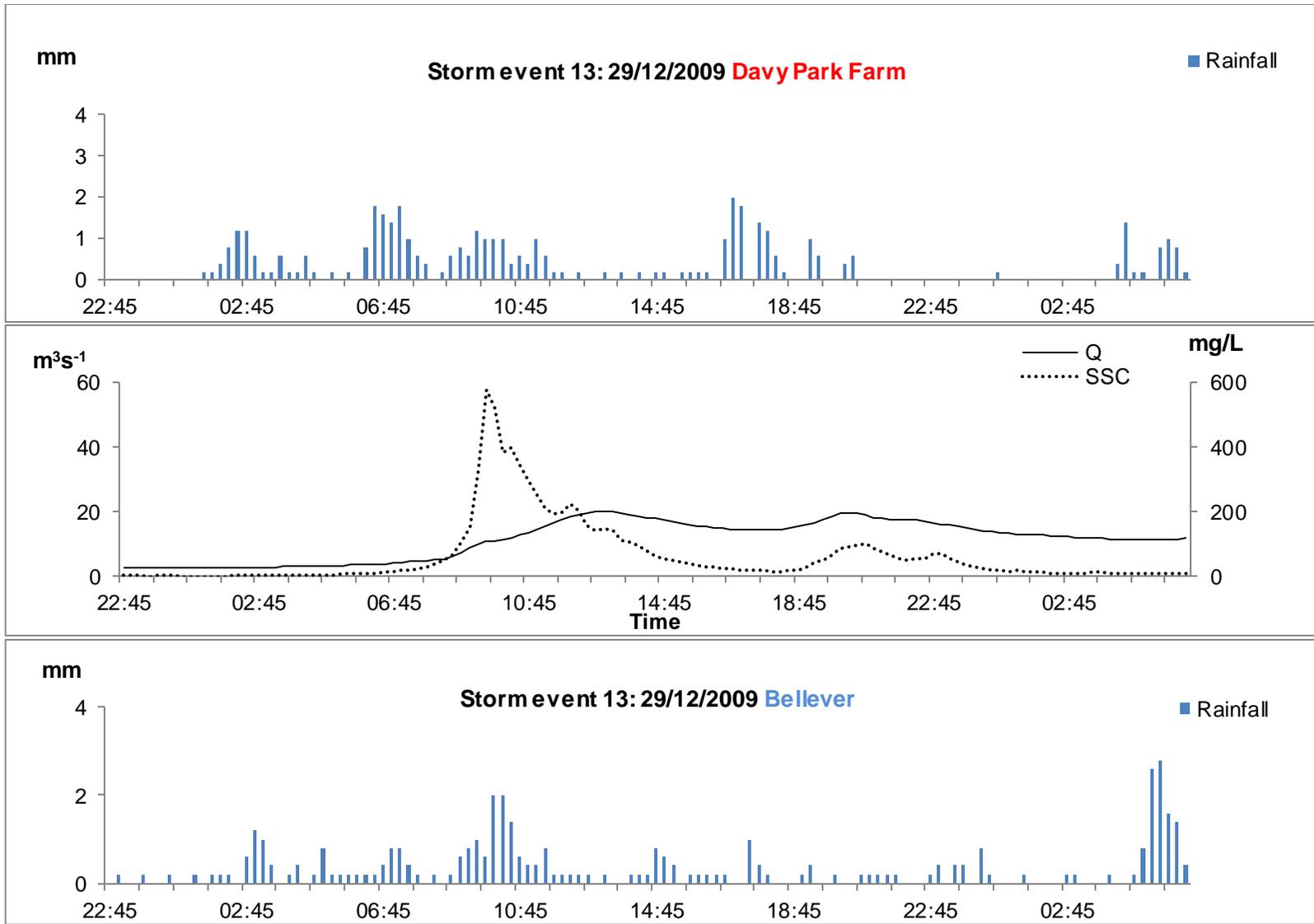


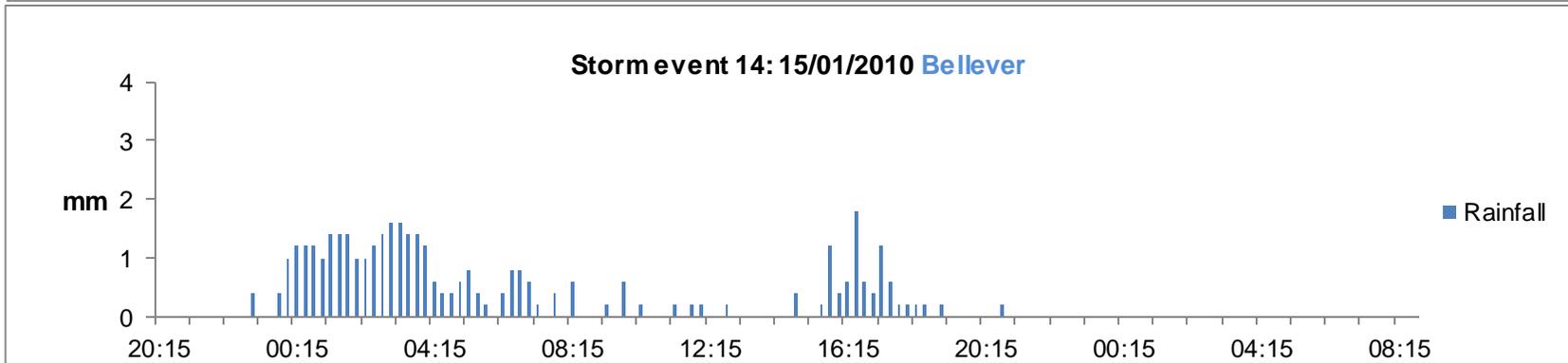
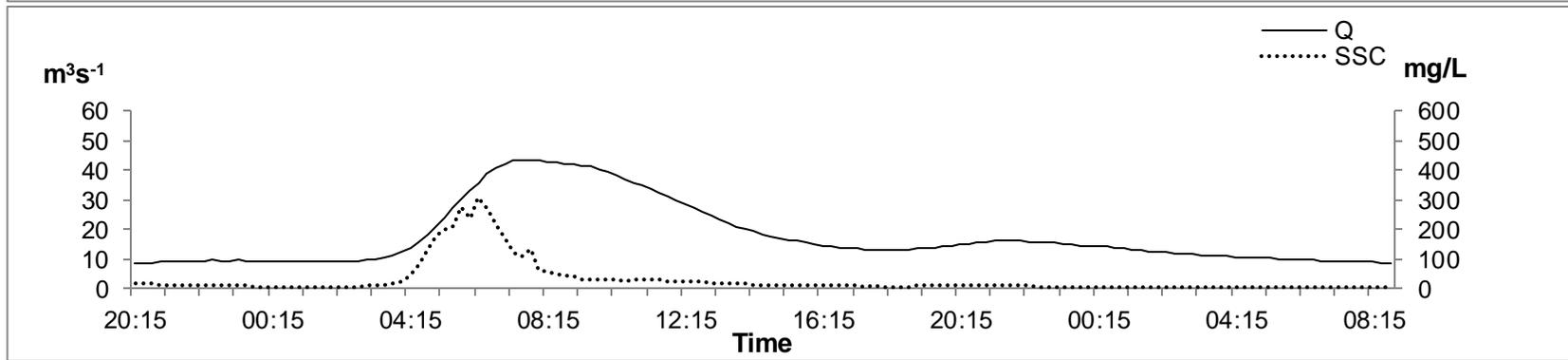
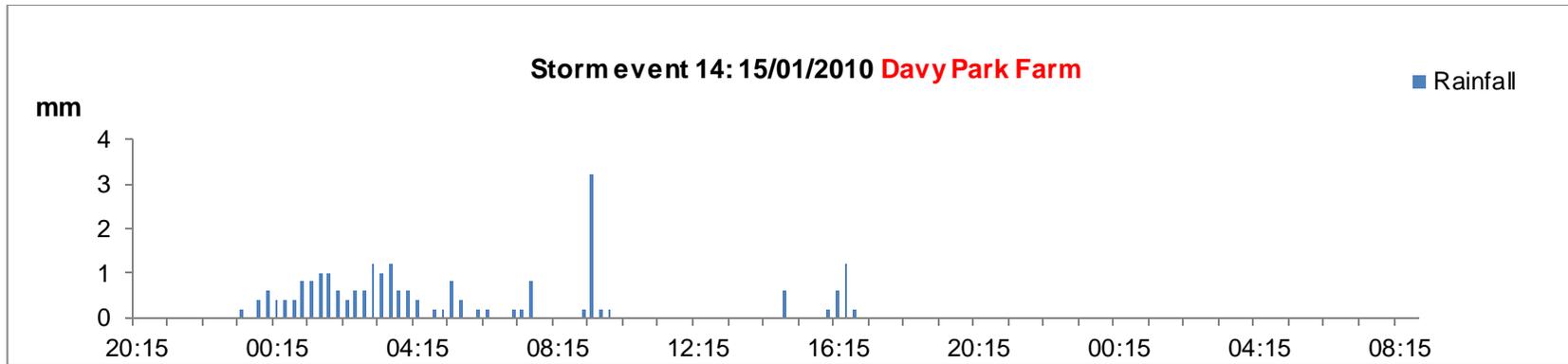


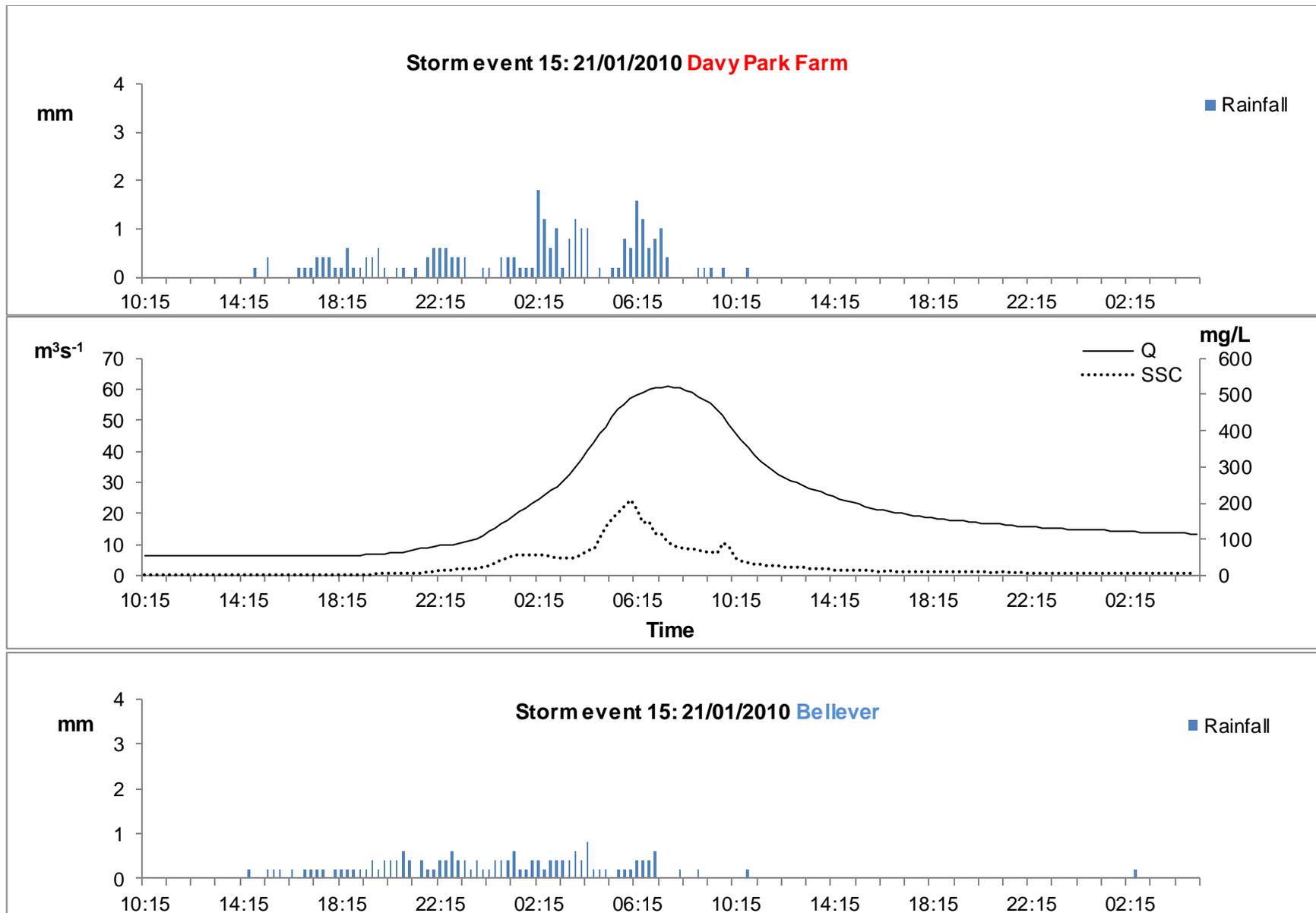


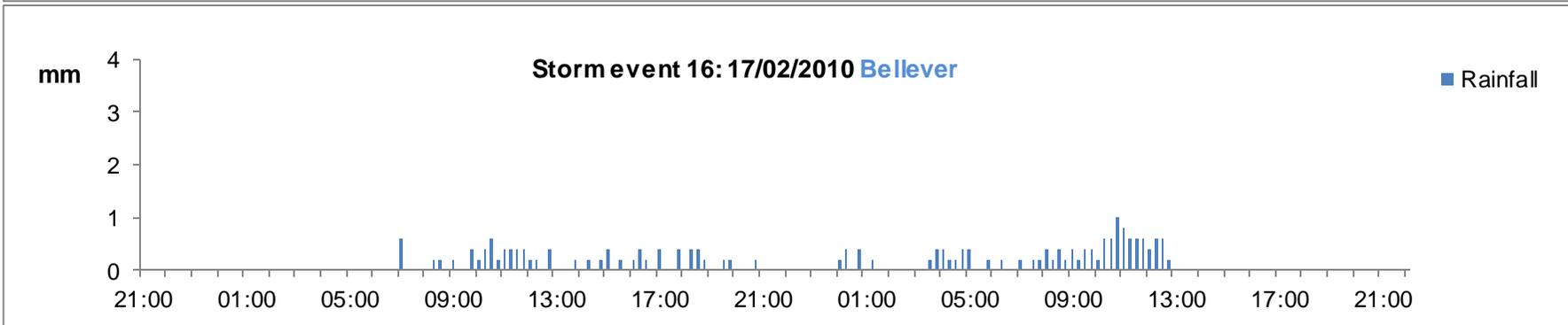
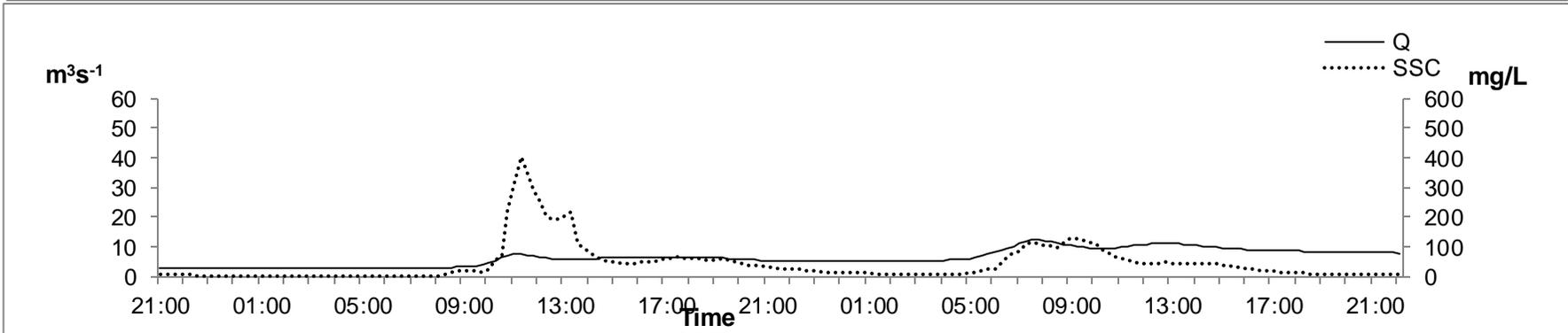
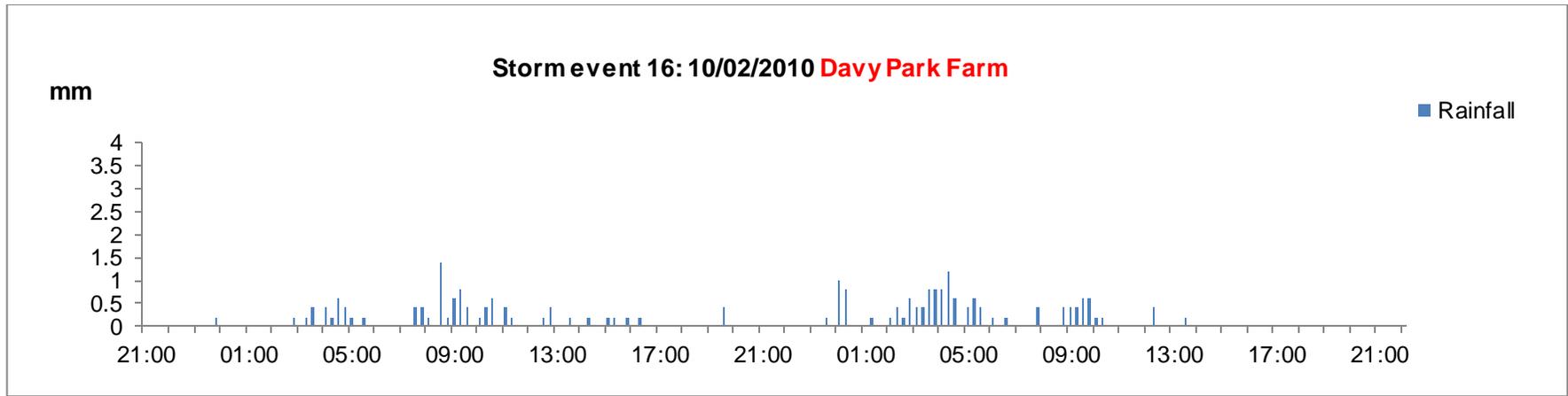


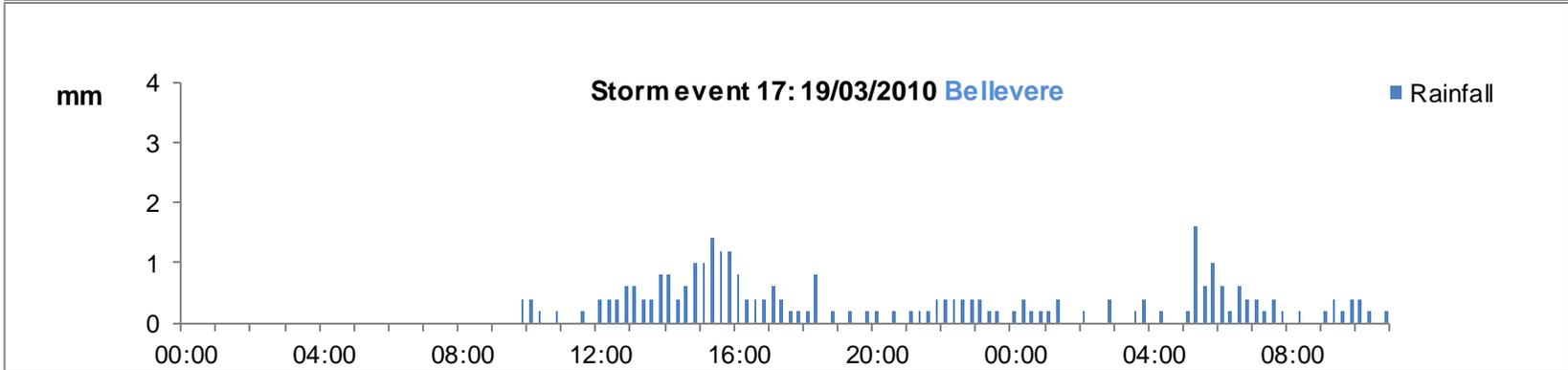
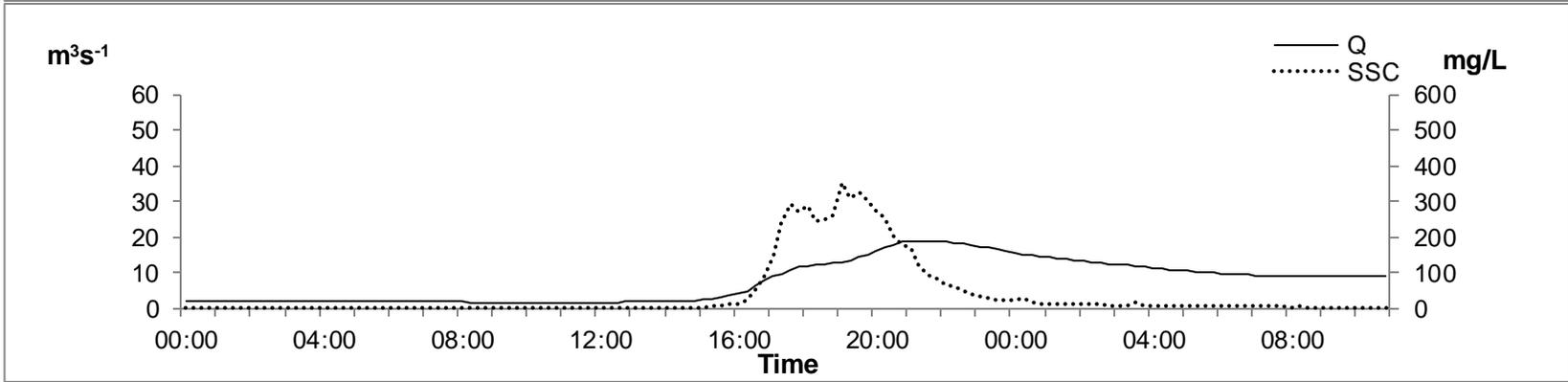
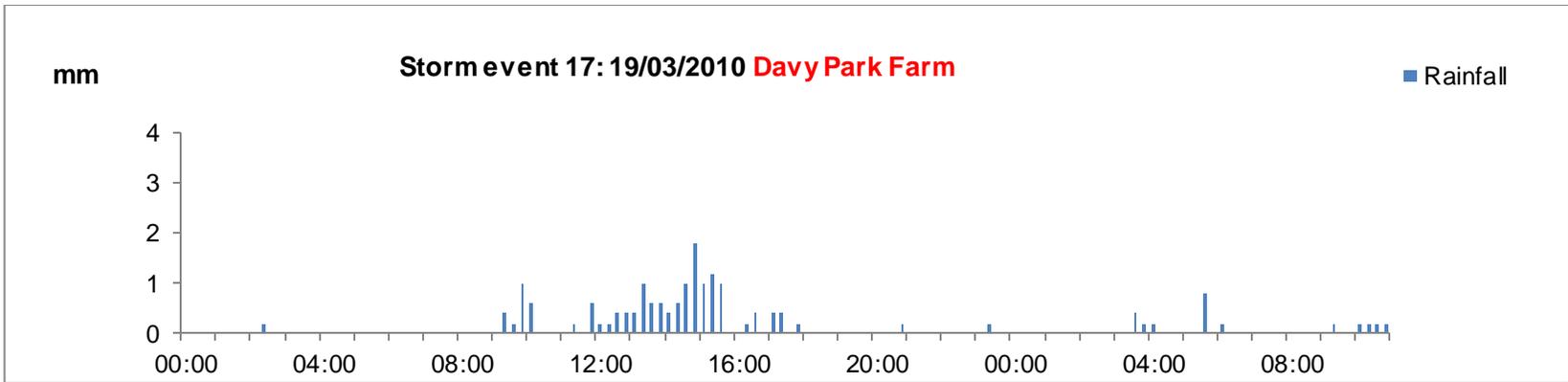


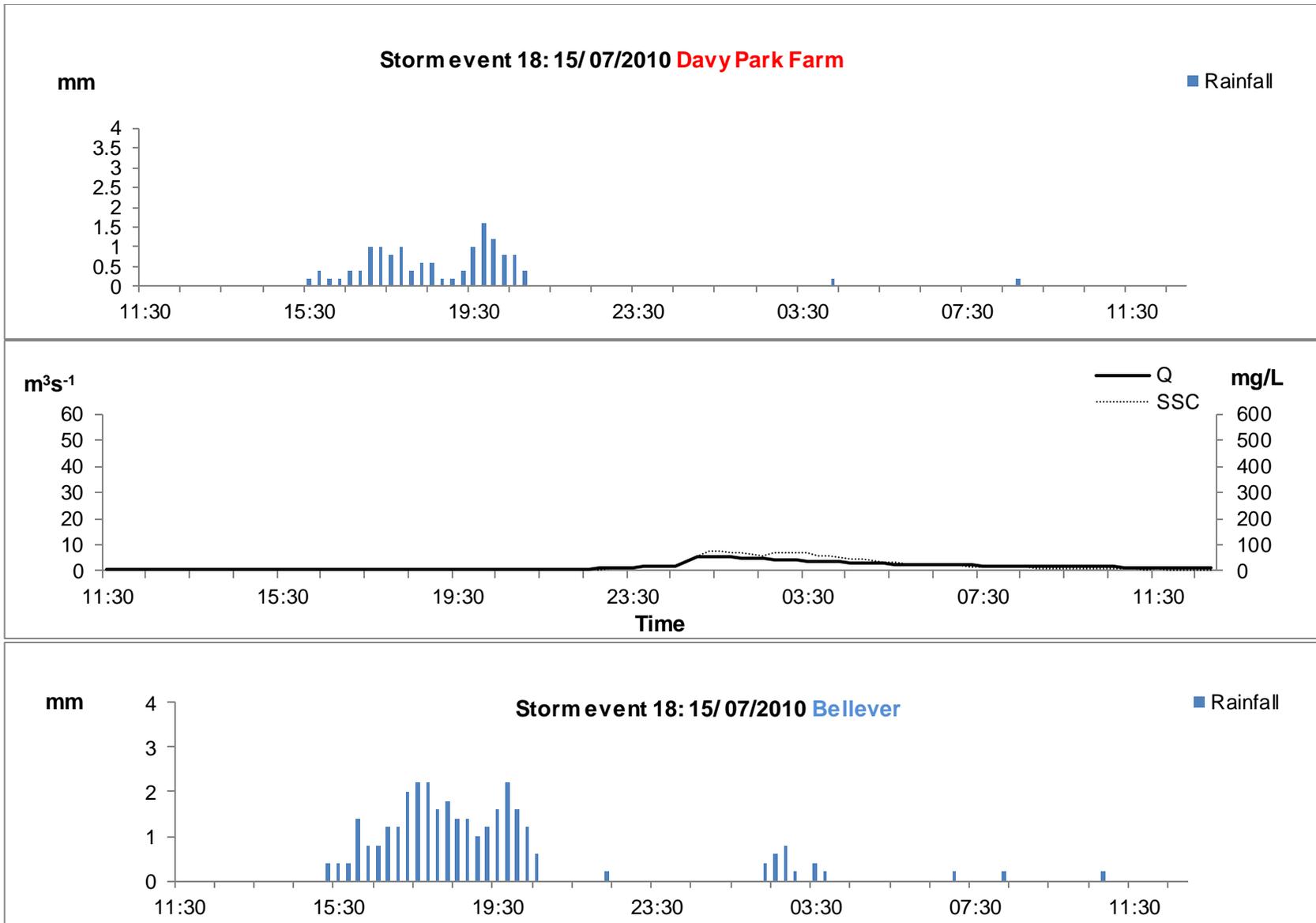


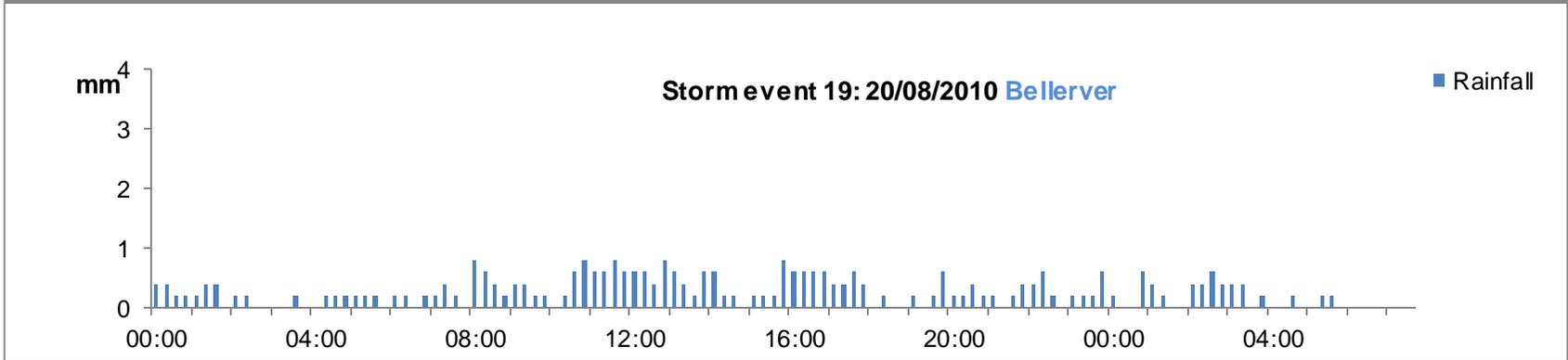
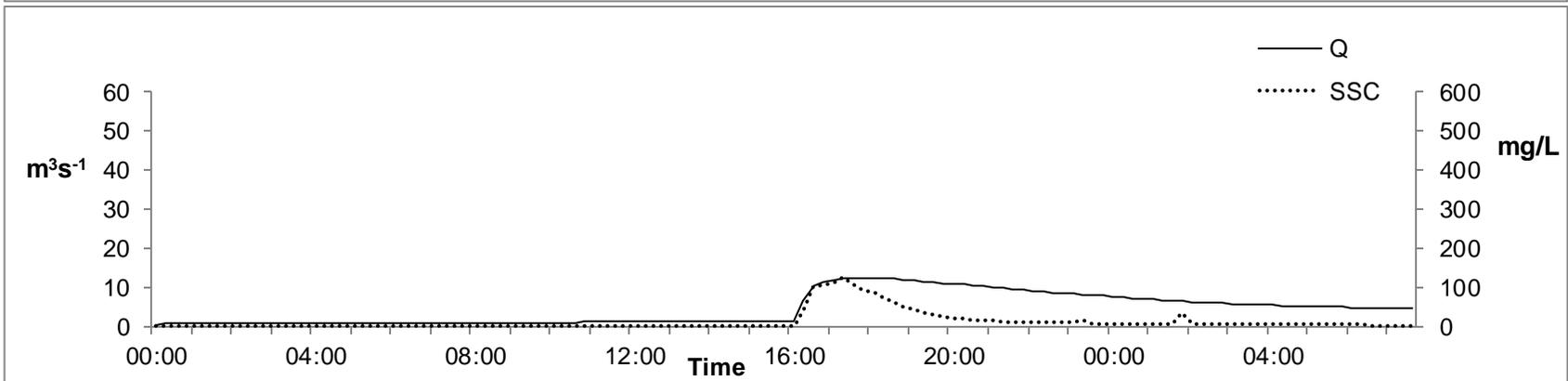
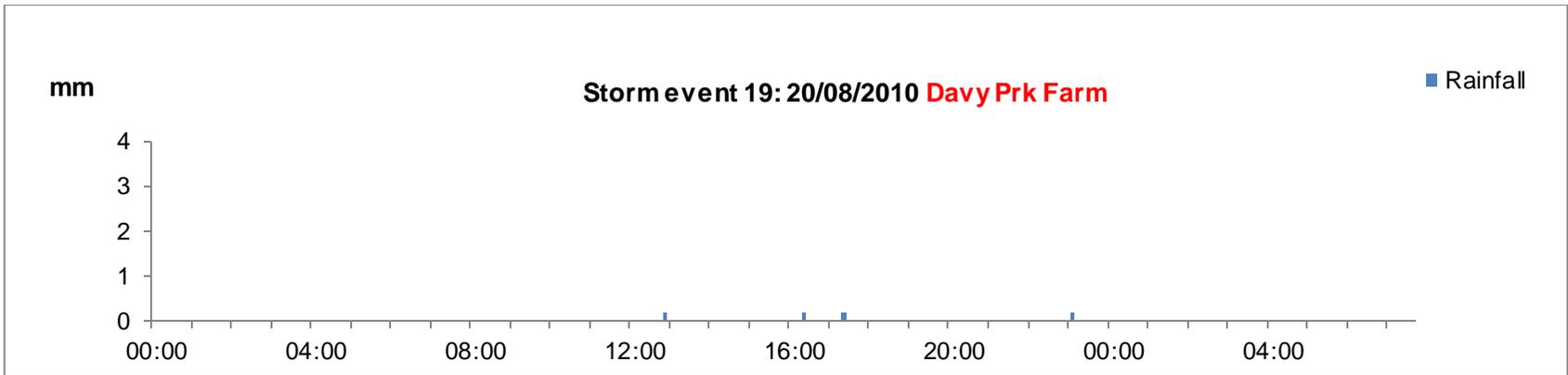




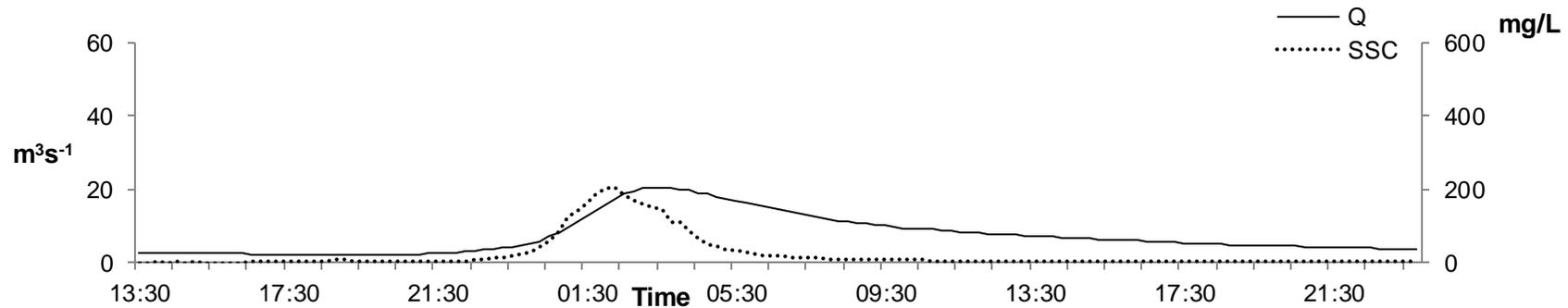
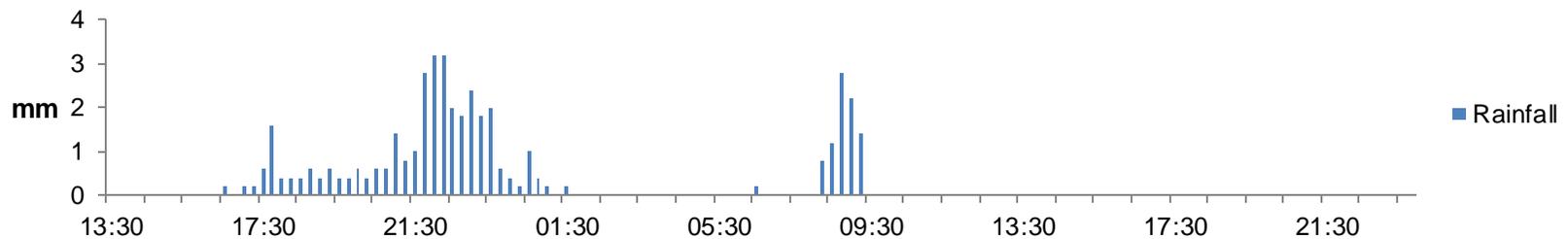




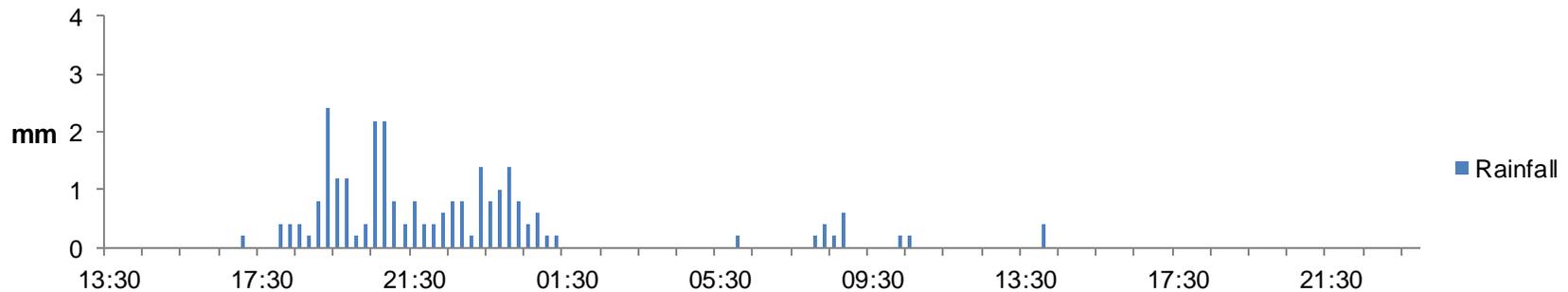


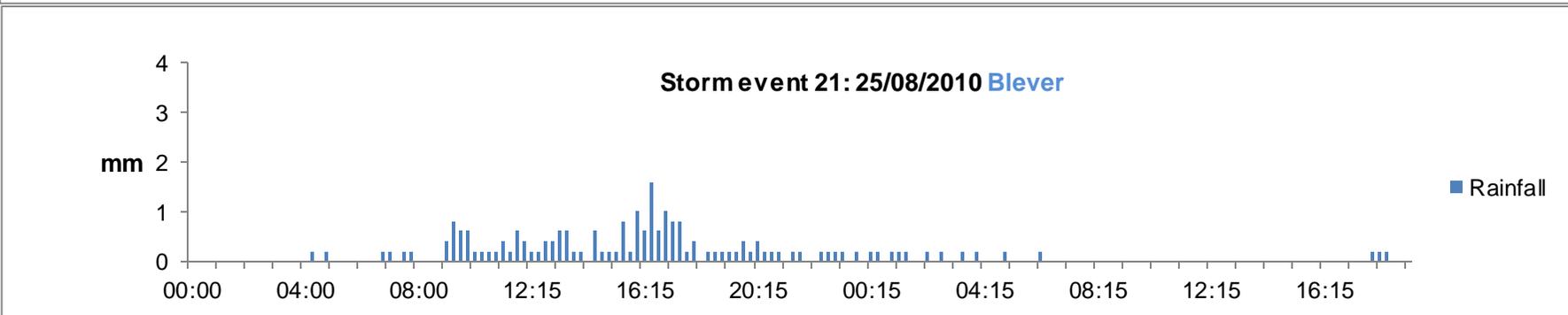
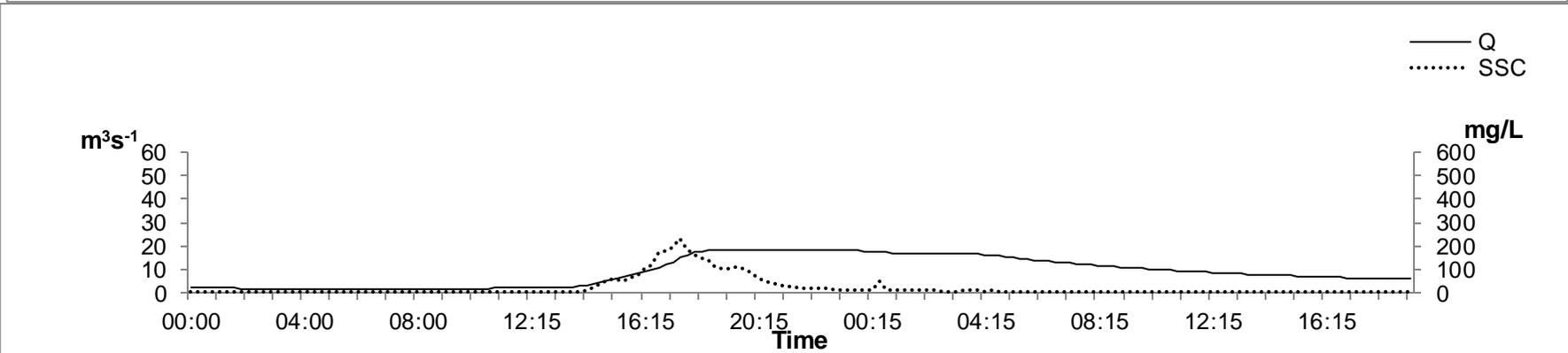
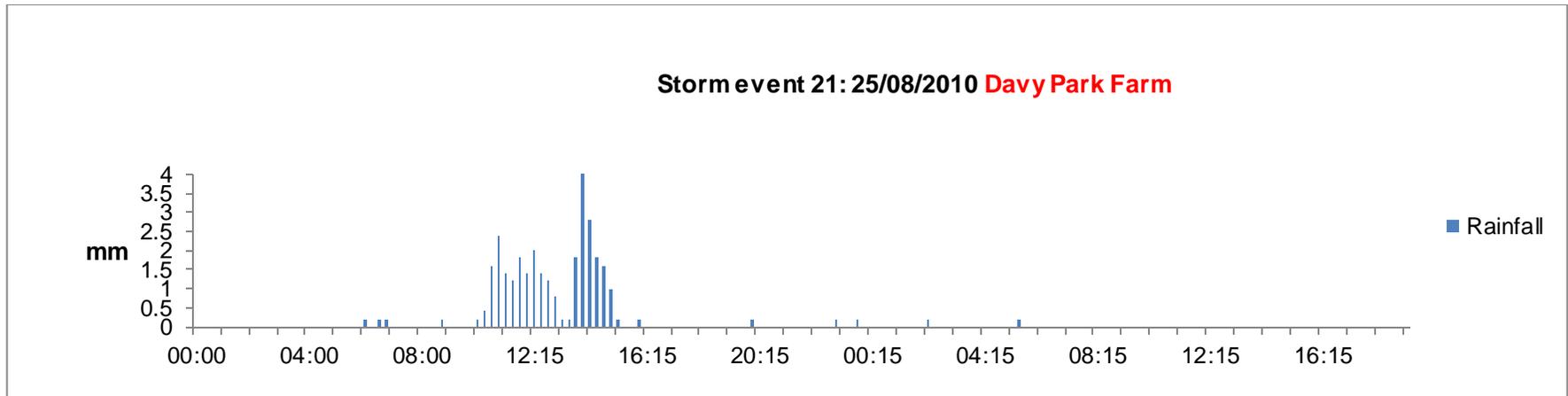


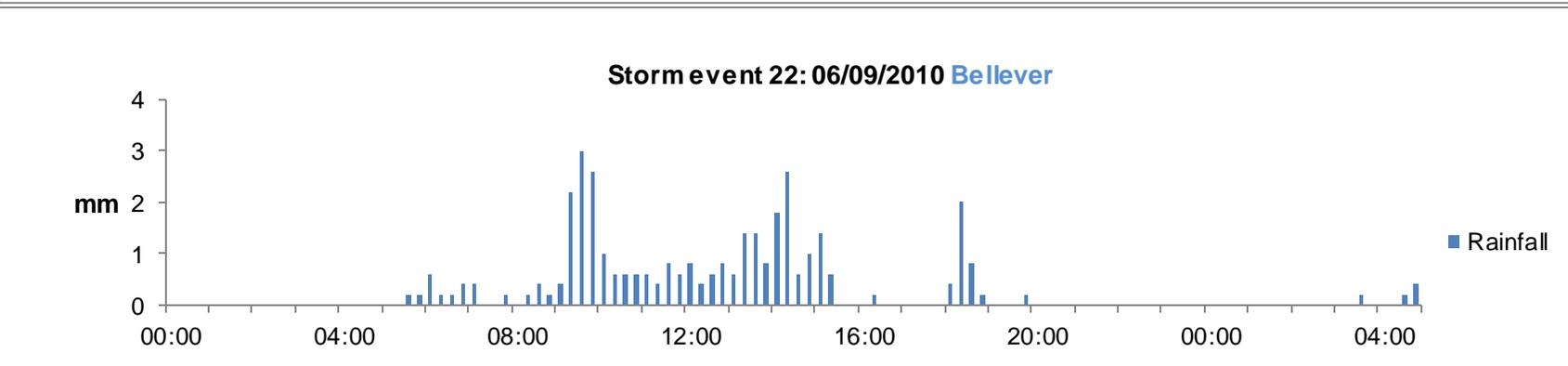
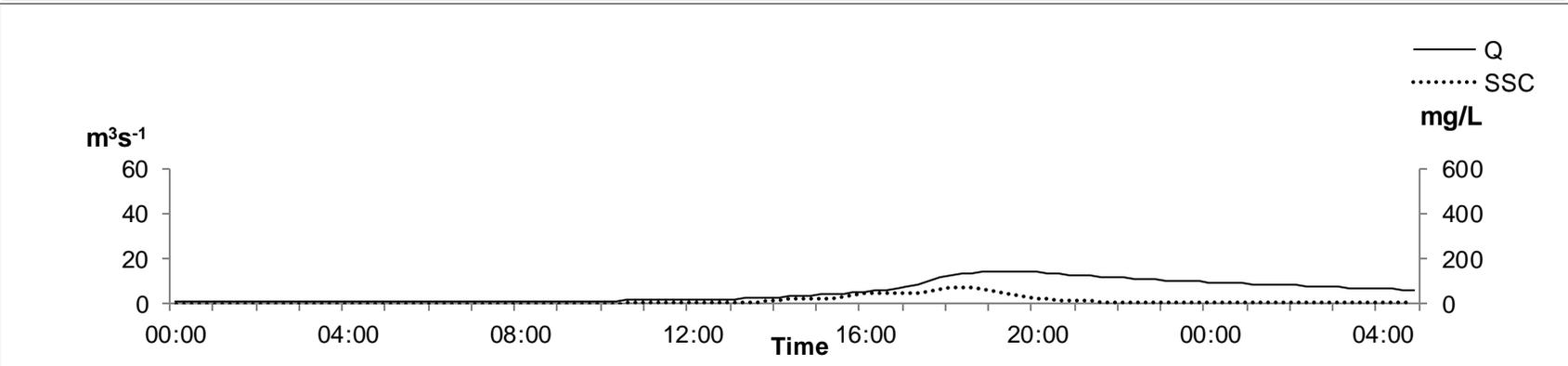
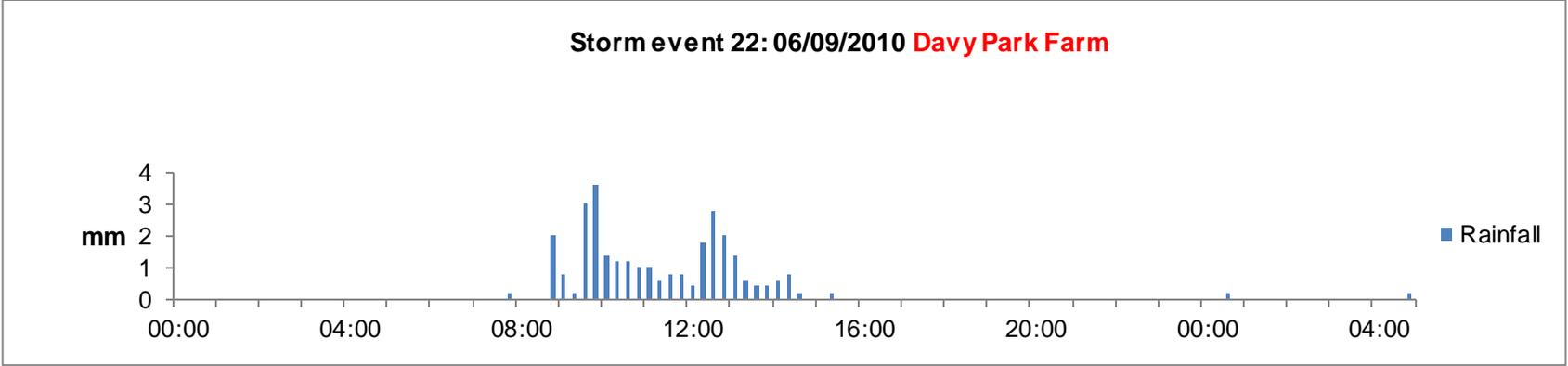
Storm event 20: 22/08/2010 Davy Park Farm

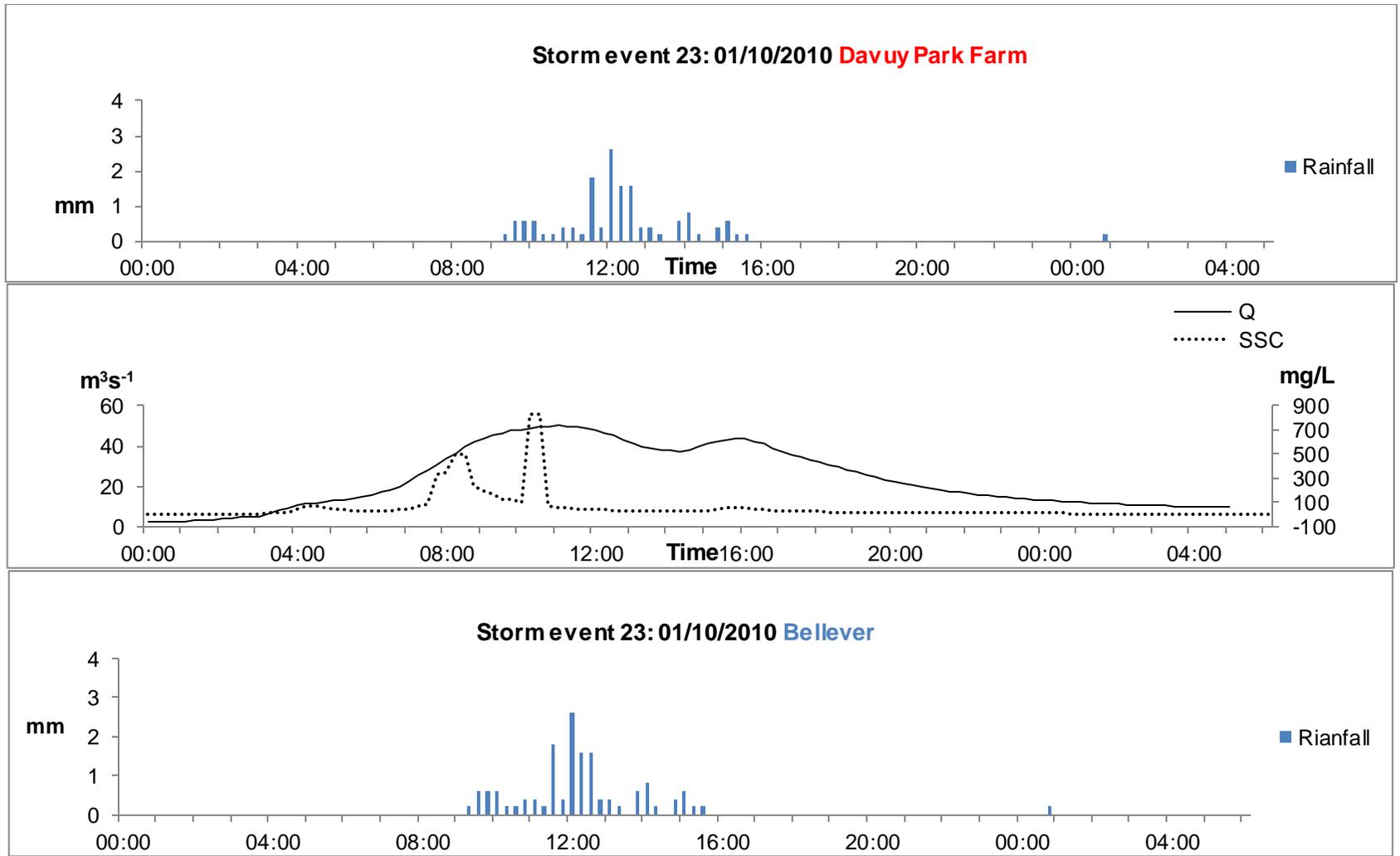


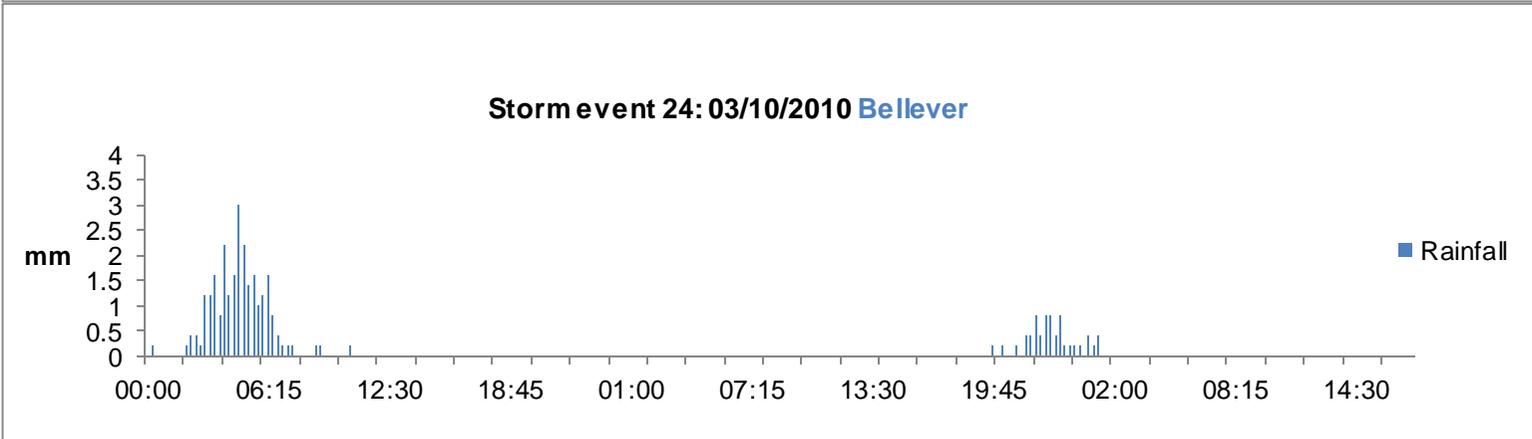
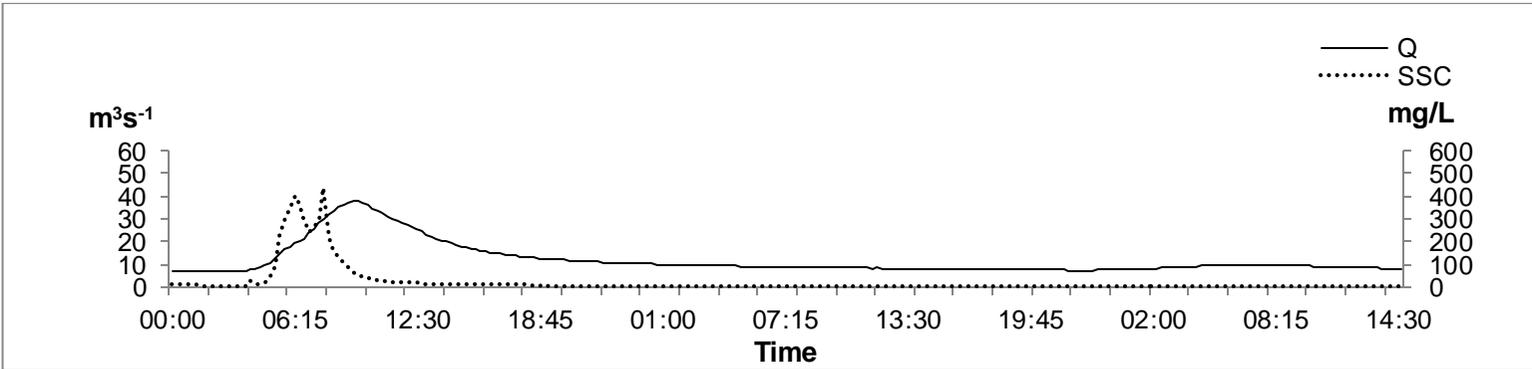
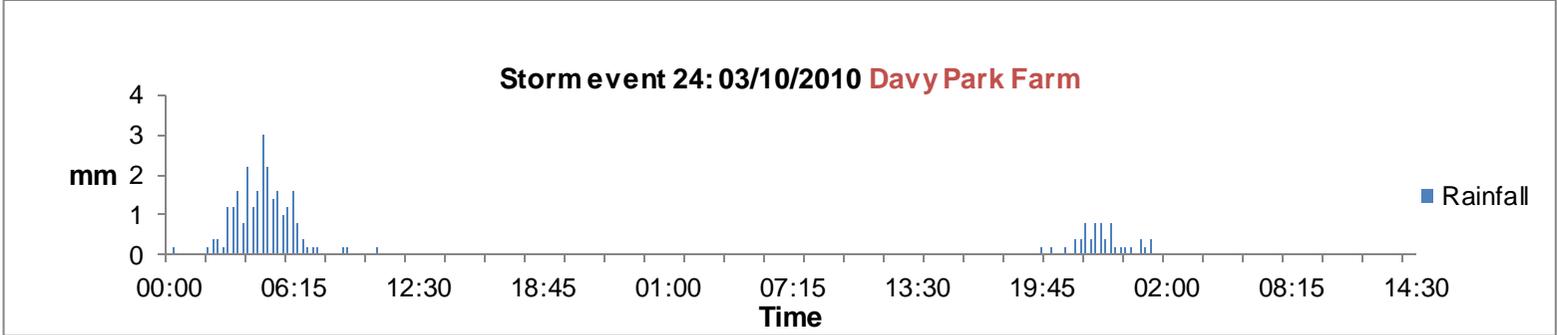
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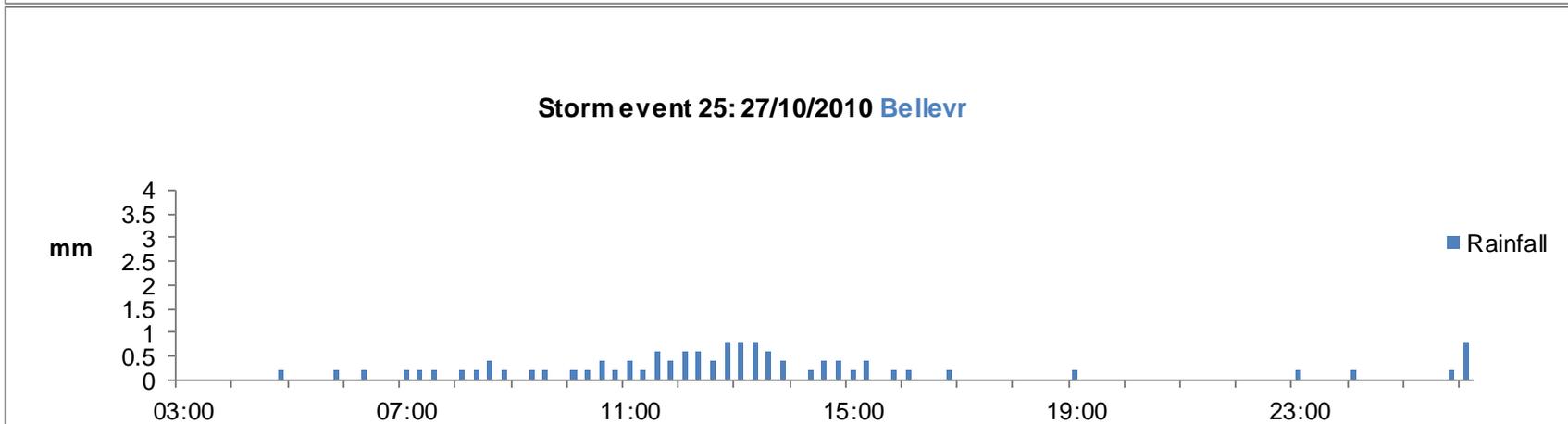
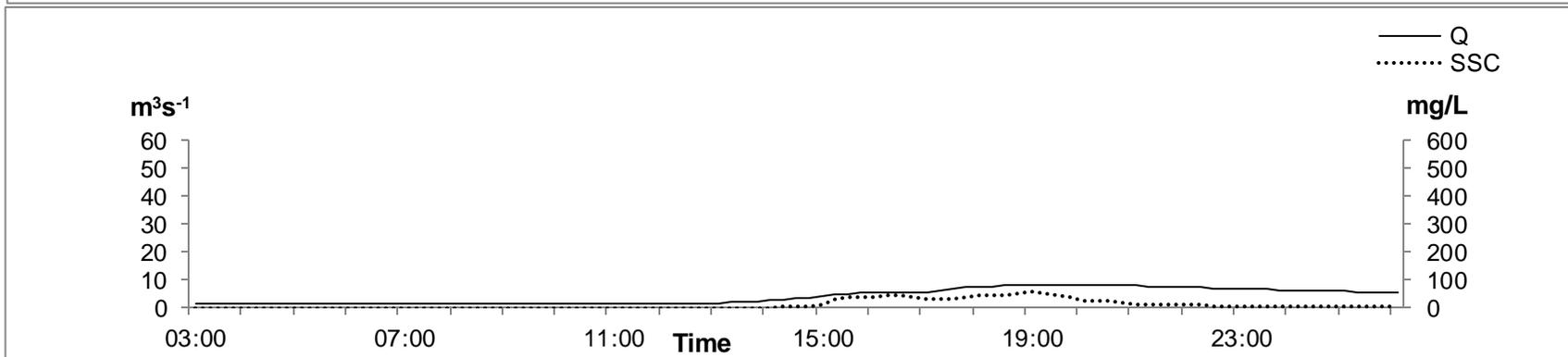
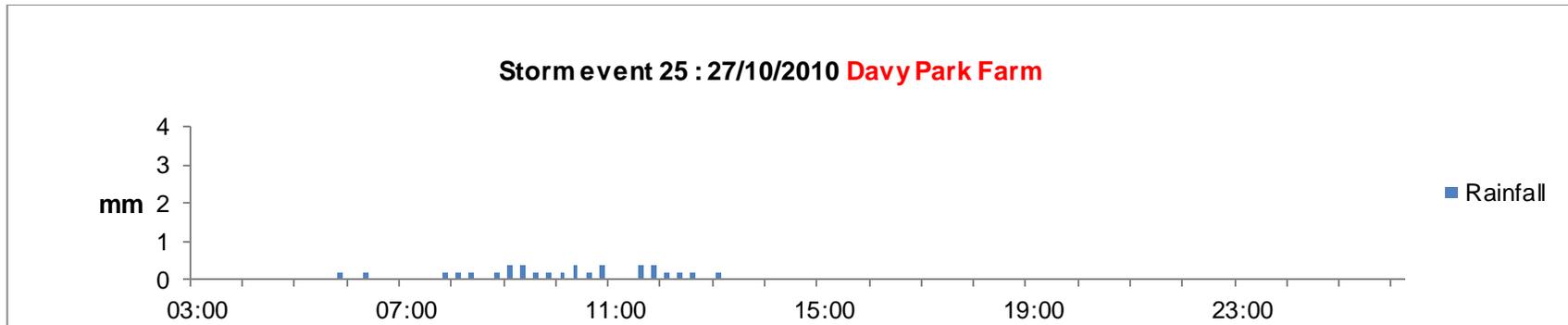


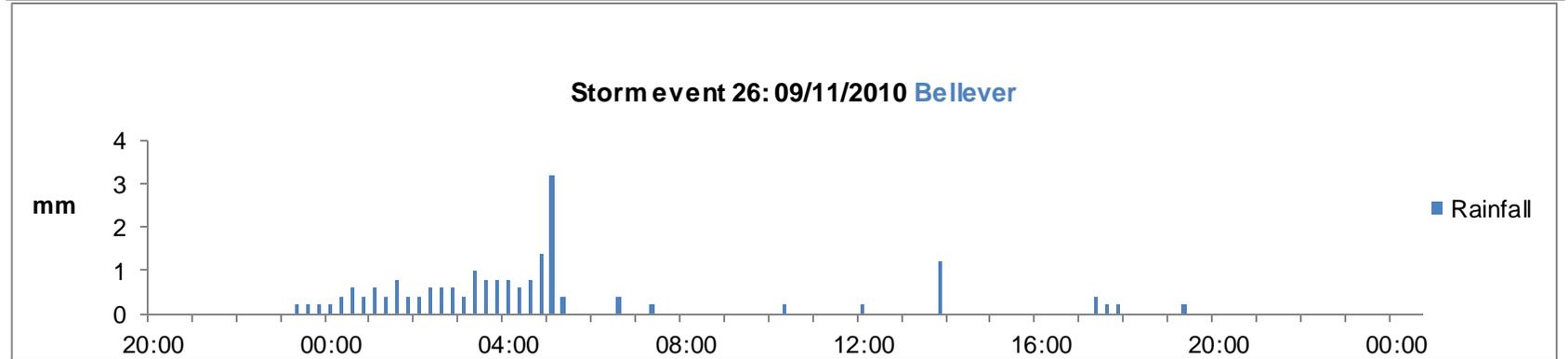
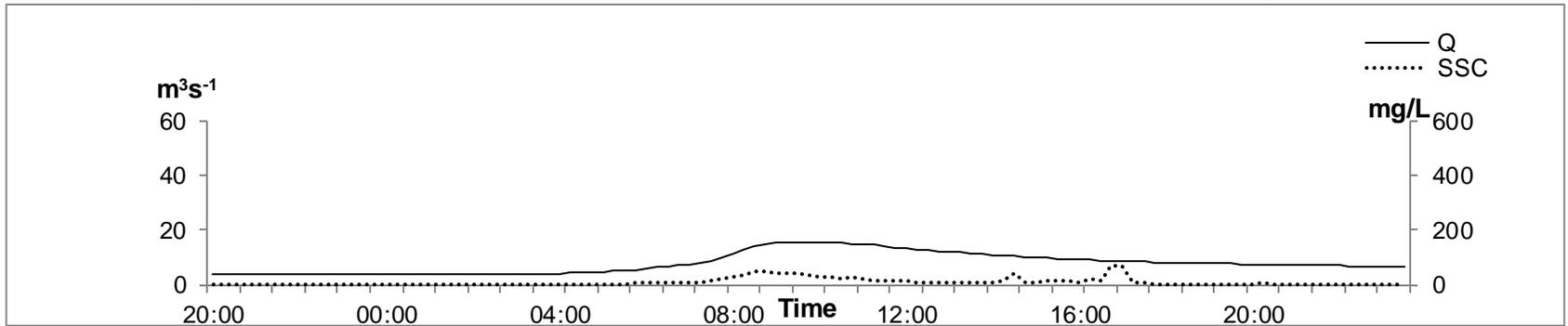
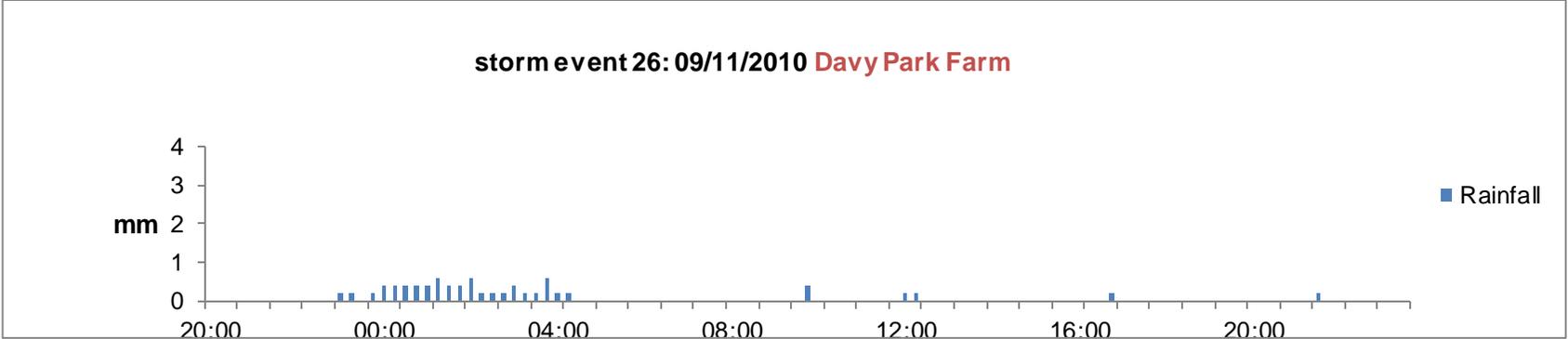


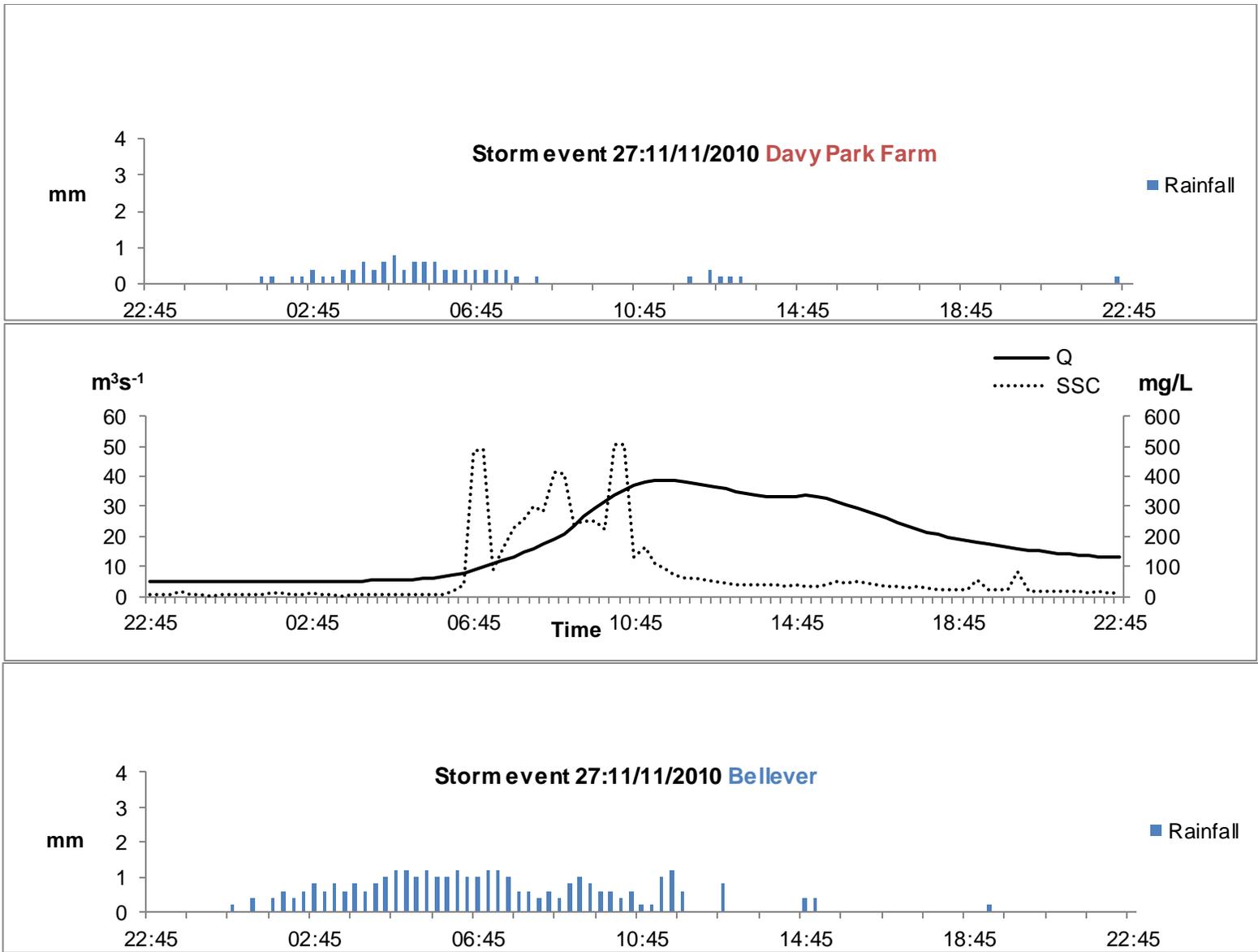


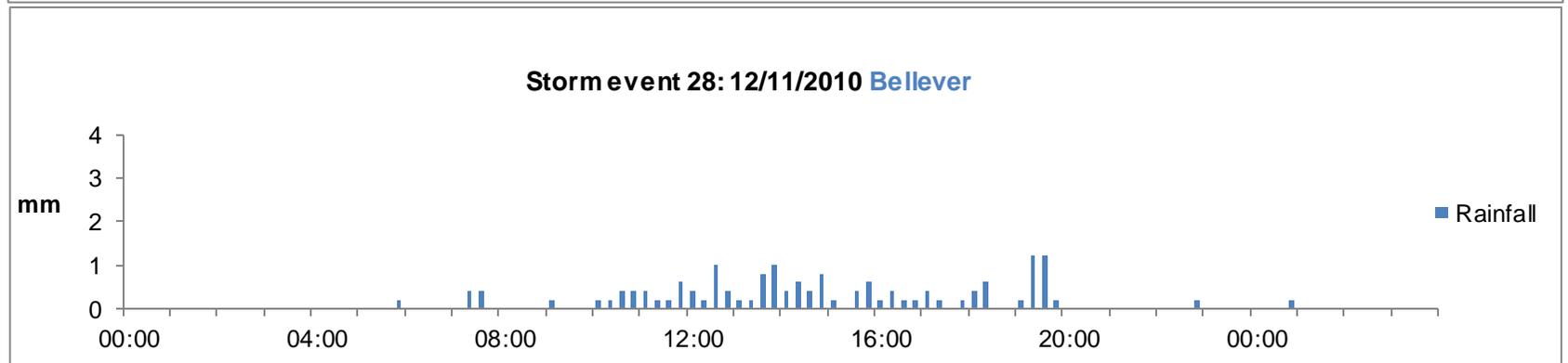
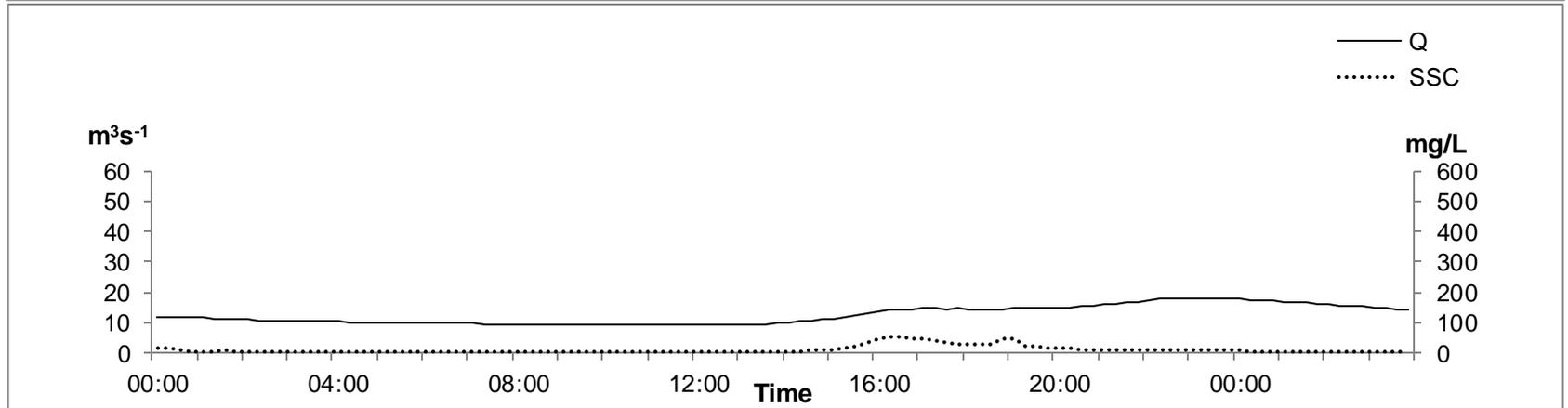
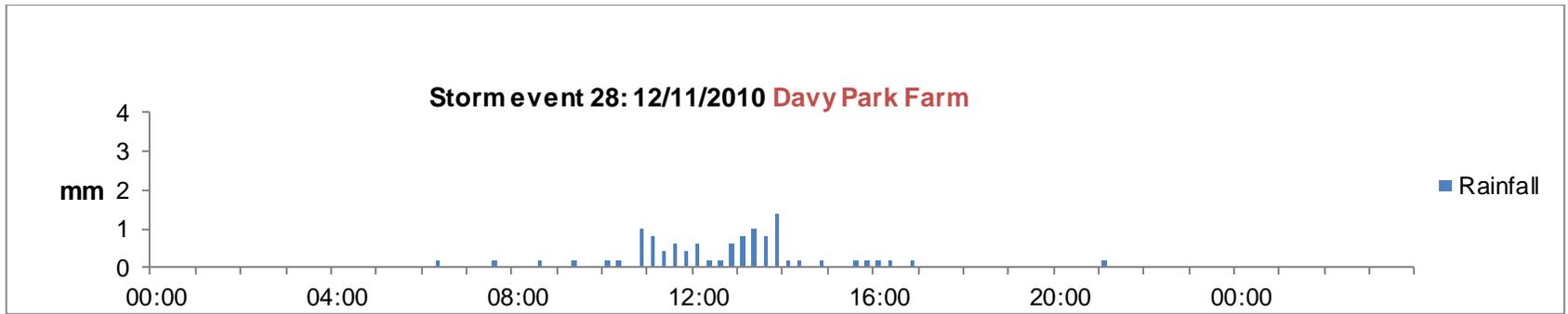


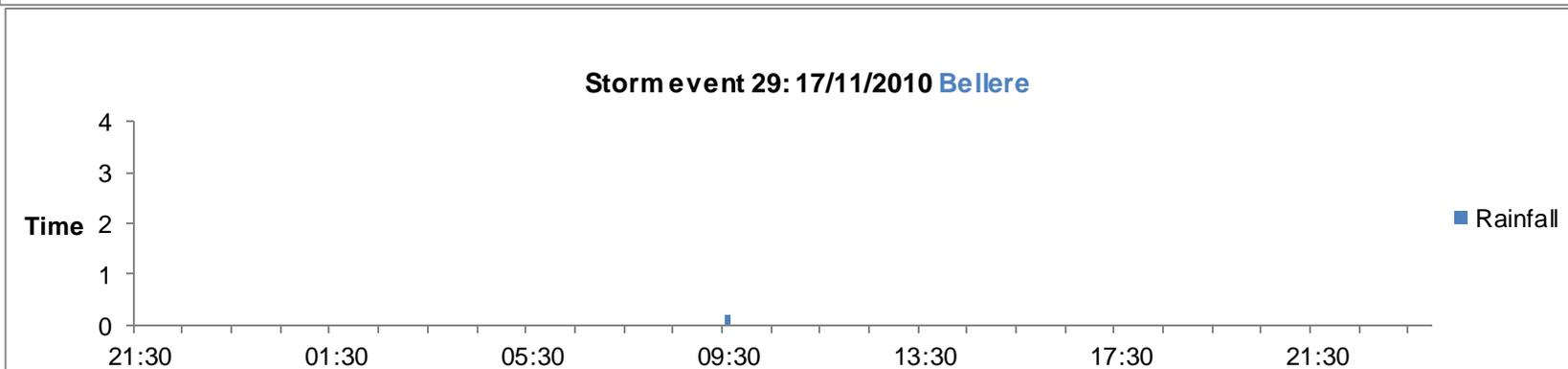
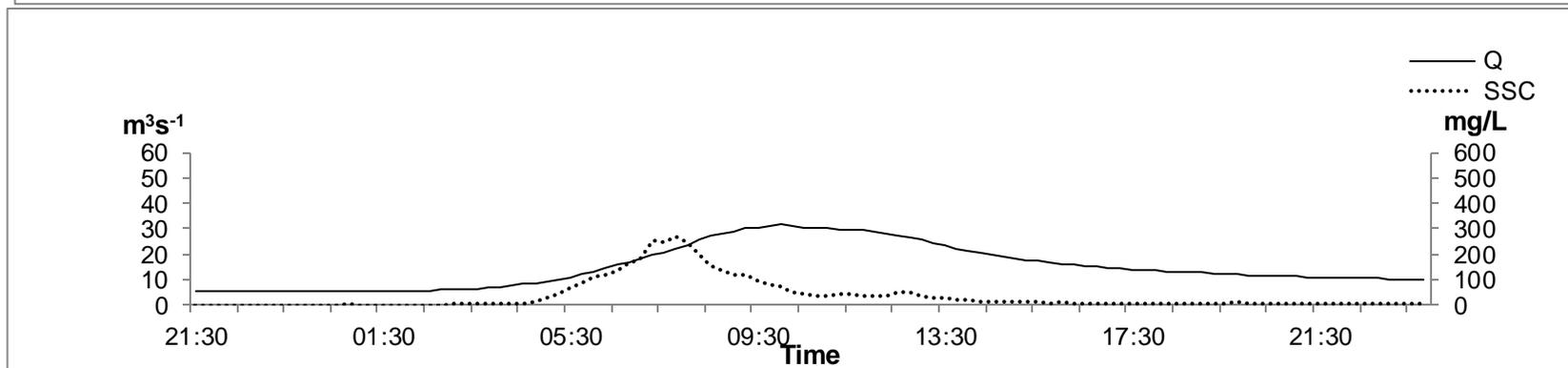
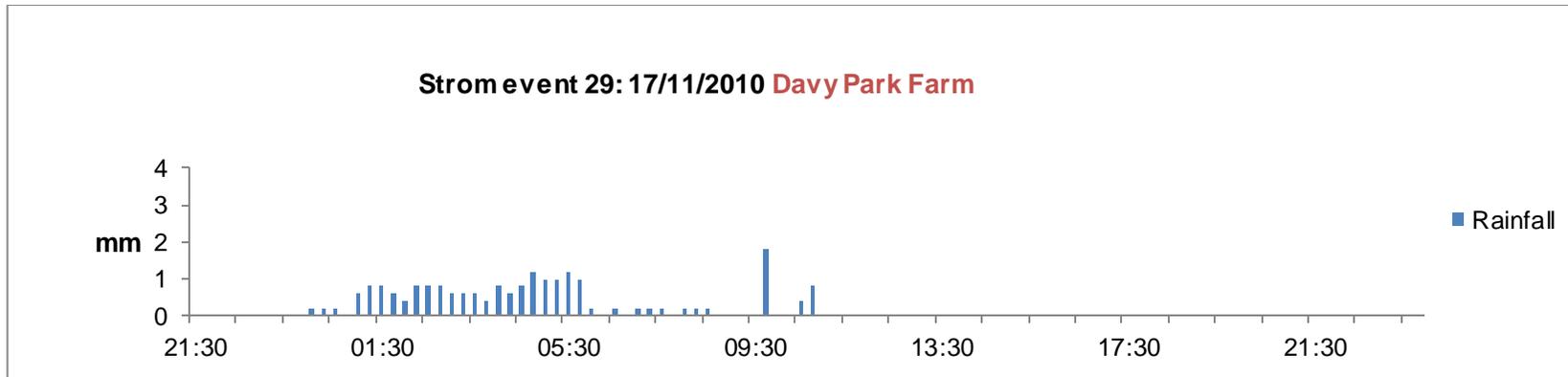


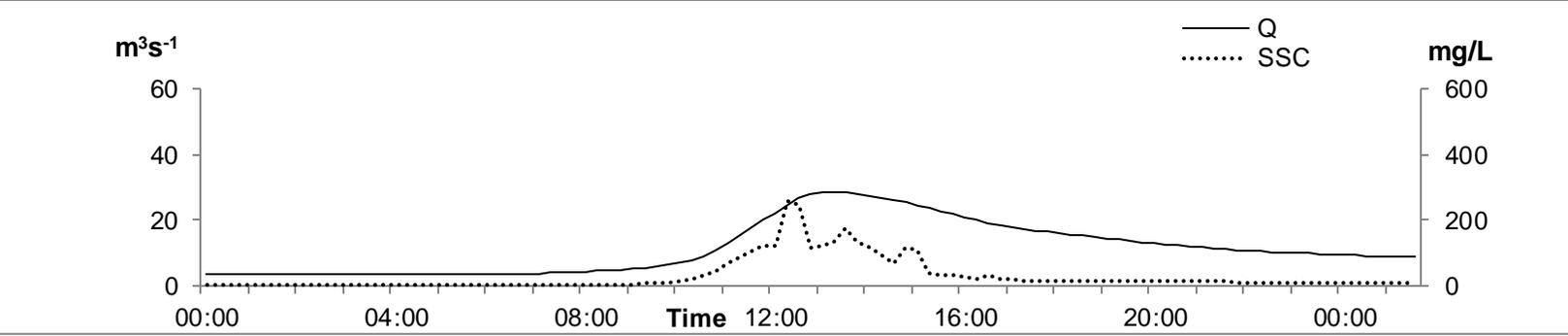
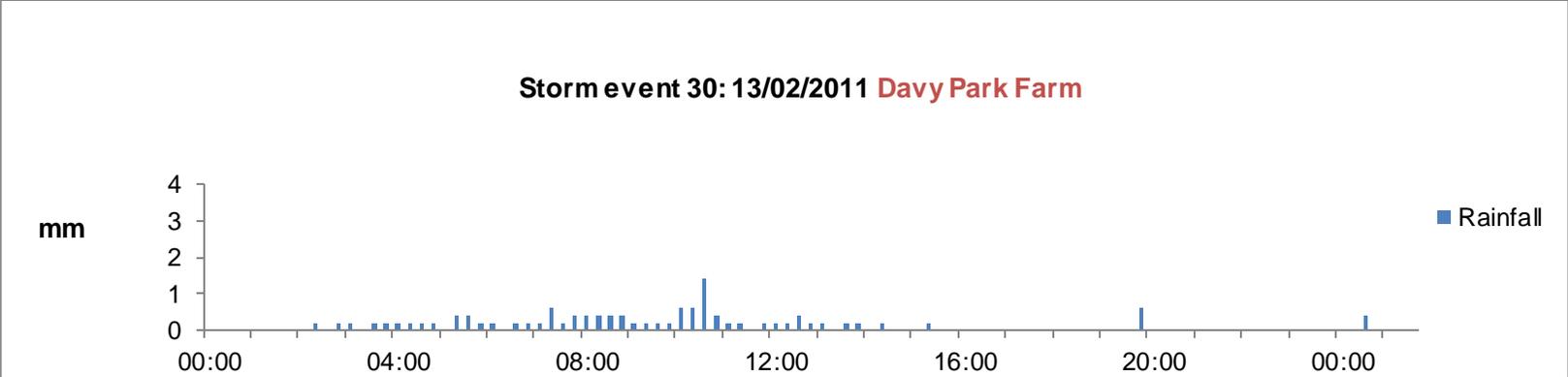


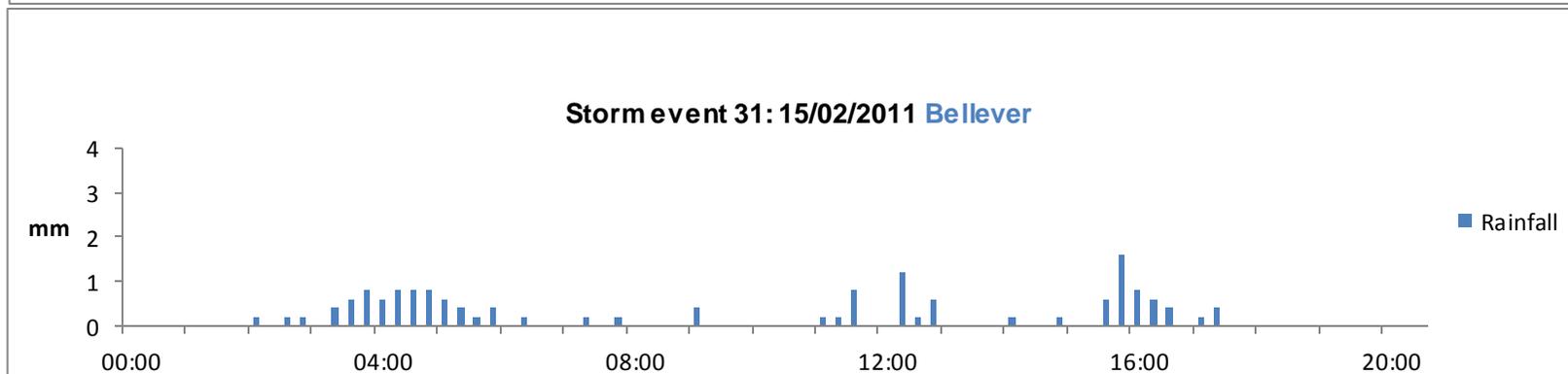
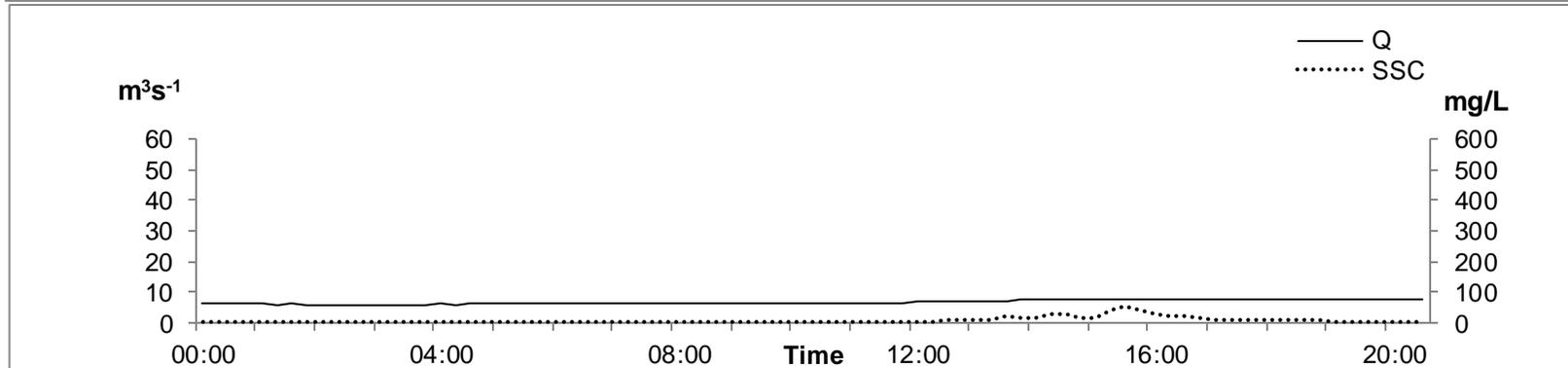
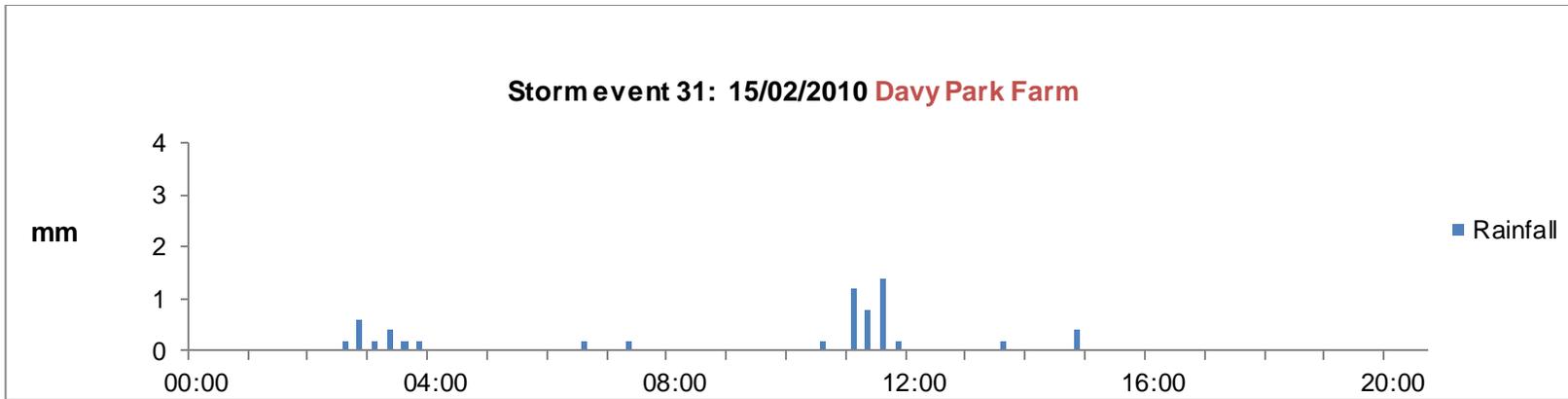


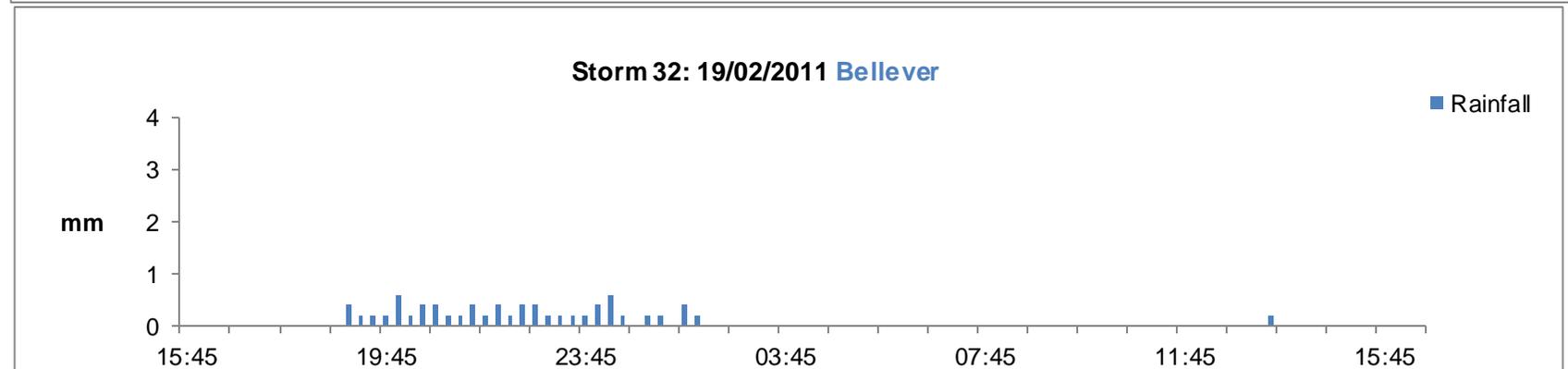
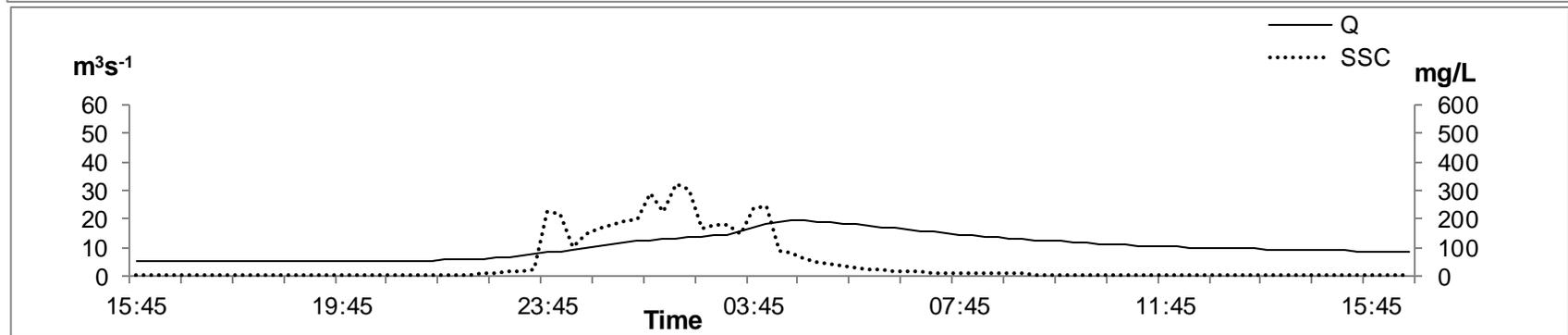
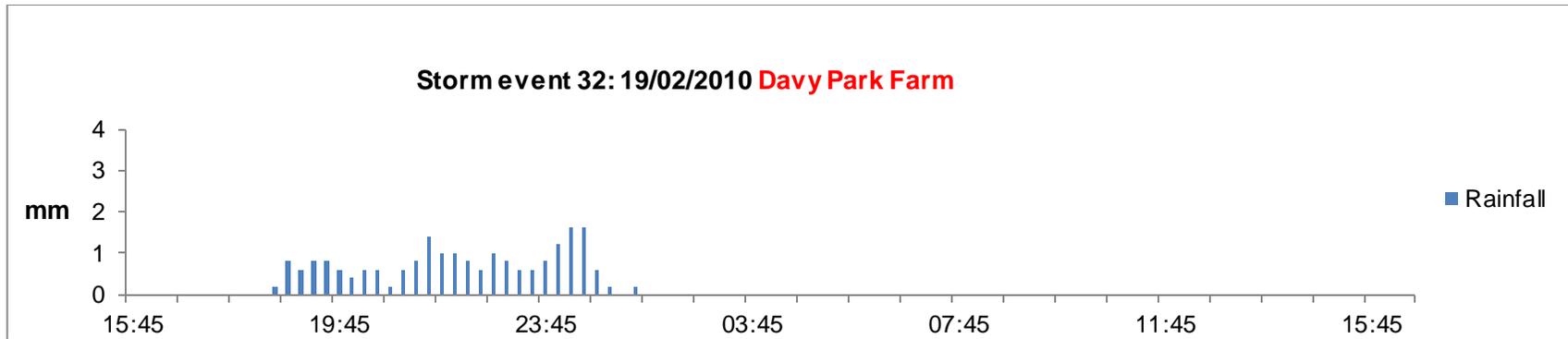


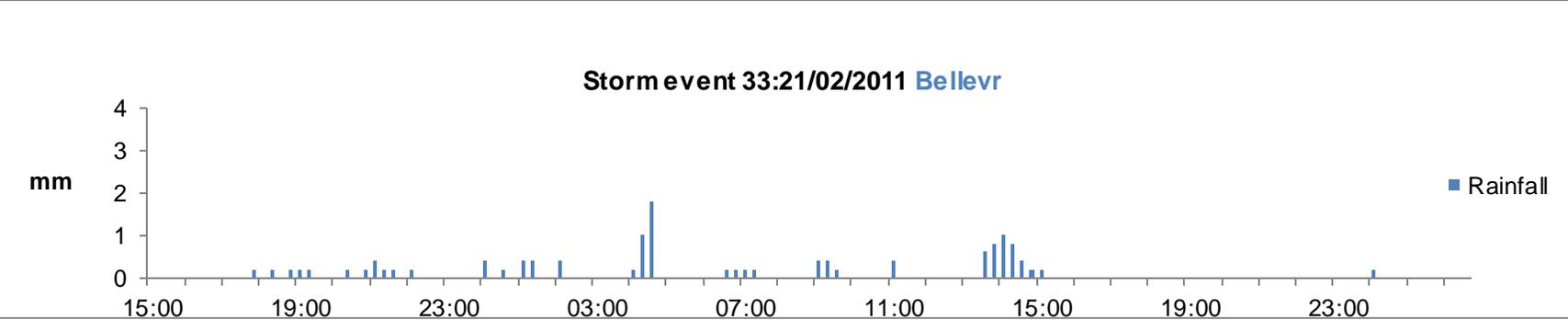
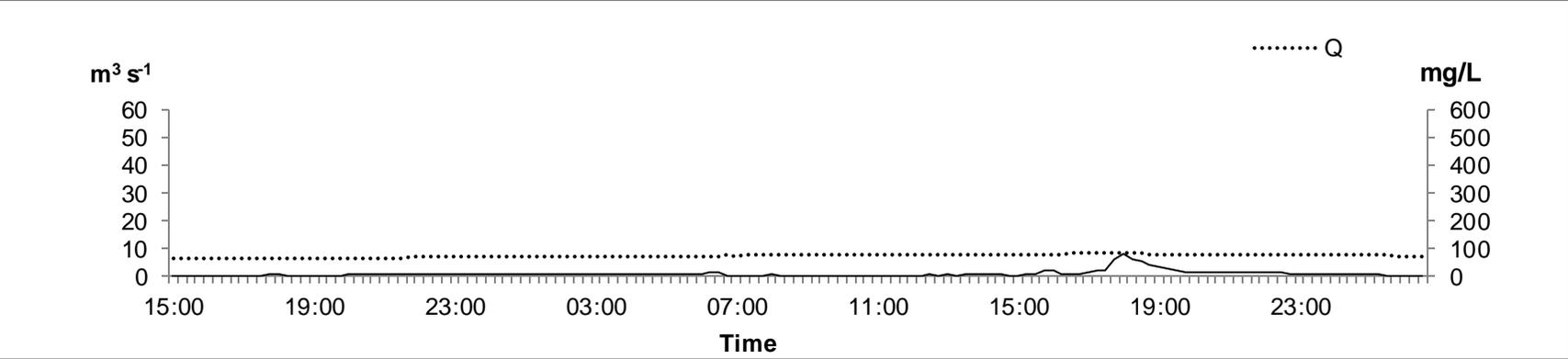
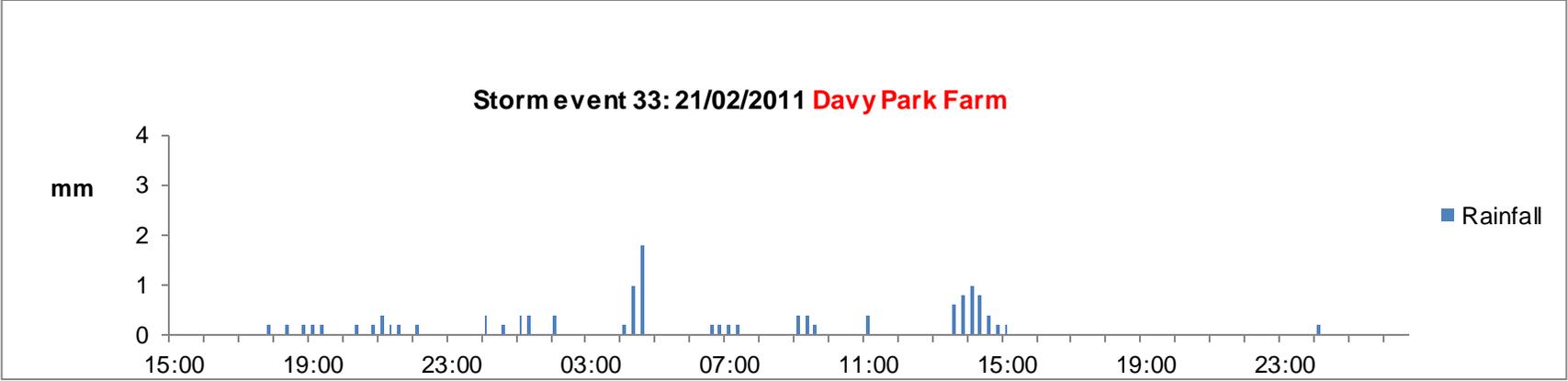


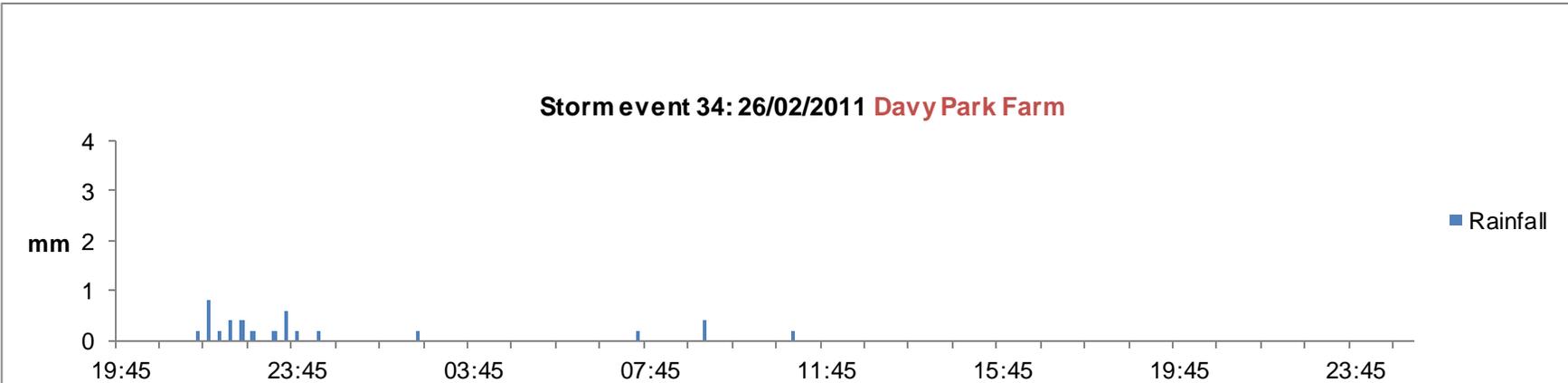
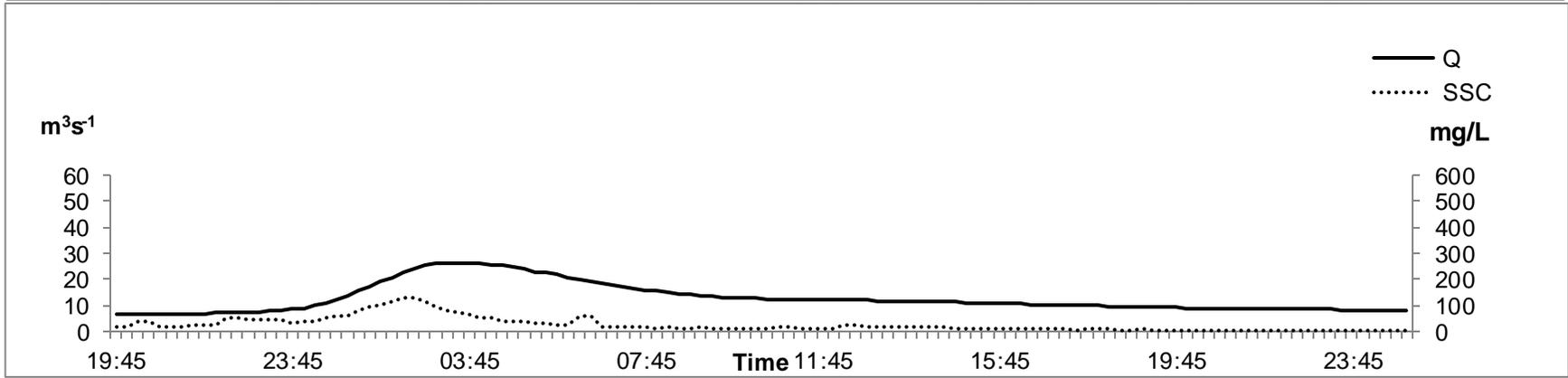
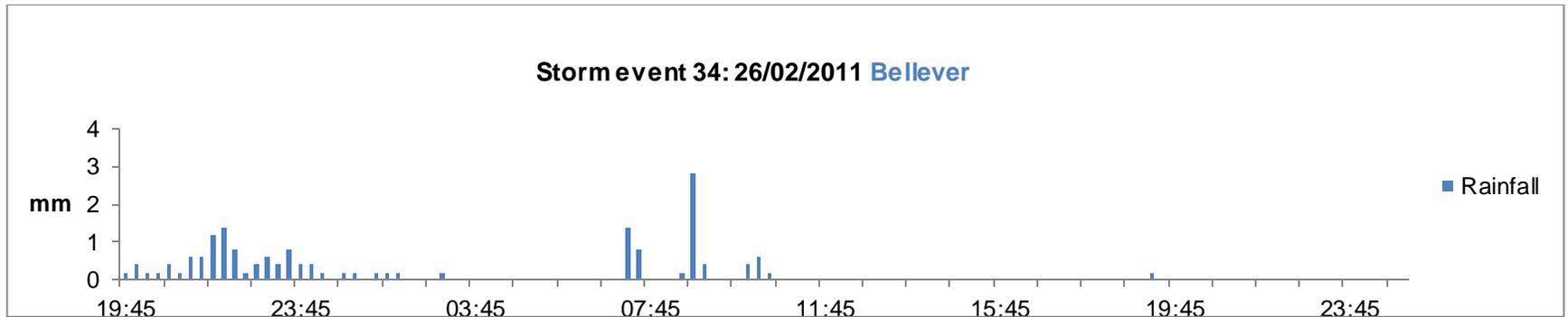


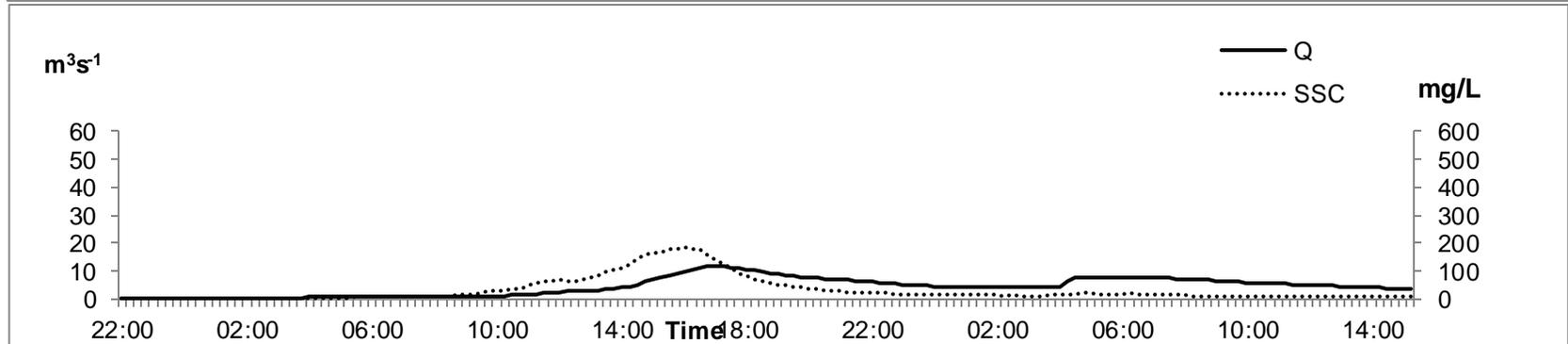
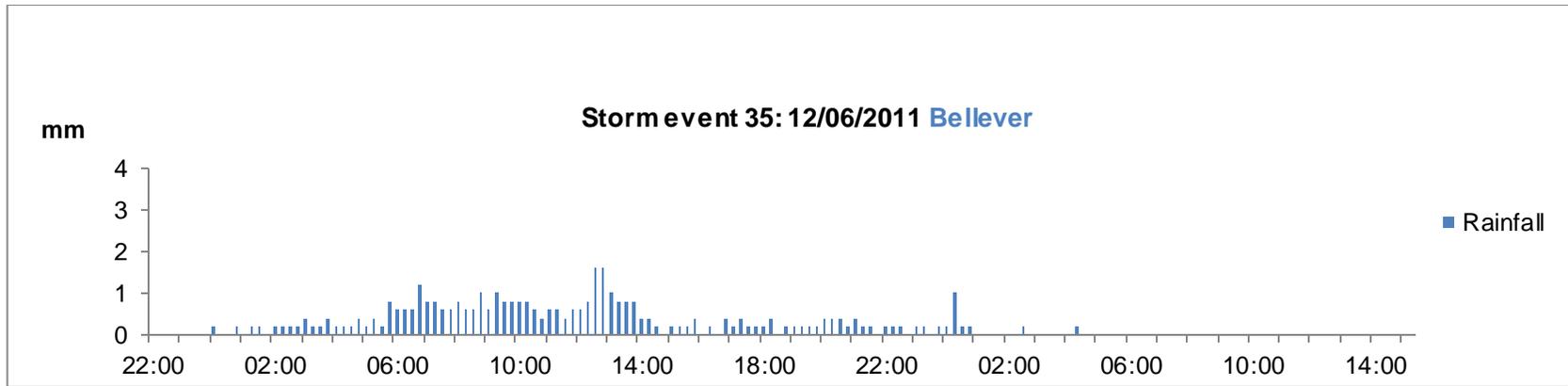












Appendix II: Data Analysis (TP,TOC,clay,silt,sand, and SSA)

Mudflat <63 micron fine sediment								
ID	Weight	P extract	mudflat<63μ m	Sand%	Silt%	Clay%	SSA	TOC
	kg	mg l ⁻¹	mgkg ⁻¹	%	%	%	%	g m ⁻²
S5-1	0.0005	21.064	2046	12	86	2	0.179	
S5-2	0.0005	10.554	1012	10	88	2	0.187	
S5-2	0.0005	11.324	1122					
S5-2	0.0005	10.907	994					4
S5-3	0.0005	21.034	1981	22	77	1	0.139	5
S7-1	0.0005	13.024	1264	15	83	2	0.143	
S7-1	0.0005	12.302	1193					
S7-1	0.0006	15.032	1326					4
S7-2	0.0005	9.975	981	18	81	2	0.146	3
S7-3	0.0005	11.703	1158	21	77	1	0.139	5
S7-4	0.0005	14.65	1443	14	84	2	0.185	5
S8-1	0.0005	6.618	653	13	86	2	0.168	
S8-1	0.0005	6.716	663					
S8-1	0.0005	9.599	903					3
S8-2	0.0005	11.498	1114	14	84	2	0.163	3
S8-3	0.0005	13.182	1274	14	84	2	0.159	3
S9-1	0.0005	10.176	1015	12	86	2	0.216	2
S9-2	0.0005	9.142	893	10	88	2	0.184	4
S9-3	0.0005	12.01	1139	11	86	2	0.208	4
S9-4	0.0006	13.564	1170	16	83	2	0.192	3
S9-4	0.0005	14.147	1334					
S9-4	0.0005	11.542	1086					
S9-5	0.0006	15.422	1370	17	81	1	0.147	4
S10-1	0.0006	13.209	1109	11	87	2	0.187	
S10-1	0.0006	9.893	890					
S10-1	0.0005	9.23	900					3
S10-2	0.0006	12.675	1124	10	88	2	0.164	1
S10-3	0.0005	14.352	1389	12	86	2	0.205	2
S10-4	0.0006	15.415	1361	15	83	2	0.178	2
S10-5	0.0005	16.875	1582	14	84	2	0.191	2
S10-6	0.0005	12.185	1120	14	85	2	0.159	1
S11-1	0.0005	10.18	957	16	82	2	0.170	
S11-1	0.0006	13.233	1188					
S11-1	0.0005	12.421	1147					2
S11-2	0.0005	14.173	1375	7	90	3	0.253	3
S11-3	0.0005	14.503	1360	9	88	2	0.227	2

S11-4	0.0005	13.469	1239	9	89	2	0.198	2
S11-5	0.0006	15.88	1437	12	86	2	0.180	1
S11-6	0.0005	15.166	1447	15	83	2	0.181	1
S12-1	0.0006	13.876	1241	14	85	2	0.166	
S12-1	0.0005	11.727	1124					
S12-1	0.0005	11.294	1067					2
S12-2	0.0005	10.972	1079	16	83	2	0.195	2
S12-3	0.0006	11.422	1002	17	81	2	0.166	2
S12-4	0.0005	12.269	1216	10	88	2	0.211	2
S12-5	0.0005	12.069	1134	8	90	2	0.260	2
S12-6	0.0005	10.404	1027	19	79	2	0.172	2
S13-1	0.0005	11.909	1175	5	92	3	0.250	
S13-1	0.0005	9.863	978					
S13-1	0.0005	12.201	1181					2
S13-2	0.0005	16.138	1594	14	84	2	0.186	2
S13-3	0.0005	13.343	1274	12	86	2	0.191	0
S13-4	0.0006	10.969	951	16	83	2	0.178	2
S13-5	0.0006	13.358	1147	9	89	2	0.200	2
S13-6	0.0005	9.342	879	15	83	2	0.184	1
S14-1	0.0005	22.186	2172	6	91	3	0.229	
S14-1	0.0005	24.117	2313					
S14-1	0.0005	24.217	2342					5
S14-2	0.0005	20.205	1860	19	79	2	0.166	1
S14-3	0.0005	21.596	2107	15	83	2	0.169	4
S14-4	0.0005	15.75	1517	10	88	2	0.183	5
S14-5	0.0005	18.048	1668	14	85	2	0.173	3
S14-6	0.0005	16.743	1630	15	83	2	0.204	3

Samples	latitude	longitude							
W-MF1			Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.30586	-3.85032	31	68	2	0.16348	7.35	685	3.0
S2	50.30939	-3.83868	46	53	1	0.12508	4.37	432	2.0
S3	50.30833	-3.83985	41	58	1	0.12316	4.57	442	2.0
S4	50.30719	-3.84563	36	63	1	0.14924	3.63	360	3.0
Mean			38	60	1	0.14	5	480	2.0
SD			6	6	0	0.02		142	0.6
E-MF2 samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.3037	-3.84929	48	51	1	0.22385	1.33	112	2.4
S2	50.30395	-3.84904	59	40	1	0.16408	10.27	943	2.9
S3	50.30411	-3.84879	62	38	1	0.13052	2.06	206	2.0
S4	50.30439	-3.84852	57	42	1	0.20784	1.27	124	2.9
S5	50.30445	-3.84813	51	48	1	0.27744	5.37	532	2.6
S6	50.3045	-3.84796	59	40	1	0.291789	1.30	121	2.5
S7	50.30461	-3.84766	57	42	1	0.1234	8.78	830	2.4
S8	50.30478	-3.84735	54	45	1	0.25356	9.46	834	2.2
S9	50.30492	-3.84693	46	53	1	0.13256	8.40	836	2.1
S10	50.30511	-3.84671	46	53	1	0.12752	9.67	915	2.3
S11	50.30534	-3.84671	46	53	1	0.12236	7.25	724	2.1
S12	50.30556	-3.84607	51	48	1	0.12744	7.90	765	2.6
S13	50.30575	-3.84582	30	68	2	0.138	1.13	112	2.4
S14	50.30603	-3.84543	21	77	2	0.12388	1.19	118	2.5
S15	50.3065	-3.84479	43	56	1	0.1446	1.29	124	2.5
S16	50.30675	-3.84452	40	59	1	0.12472	2.76	258	2.4
S17	50.30706	-3.84413	38	62	1	0.11748	9.08	788	2.7
S18	50.30728	-3.84363	47	52	1	0.12808	9.56	866	2.5
S19	50.30761	-3.84296	41	58	1	0.11068	9.83	905	3.3
S20	50.30795	-3.84221	45	54	1	0.13256	8.47	739	2.9

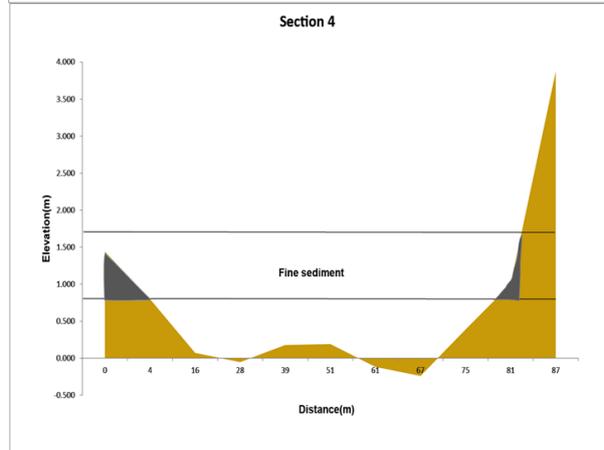
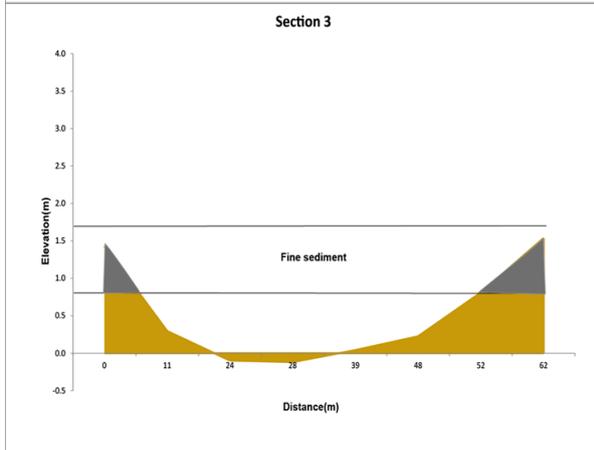
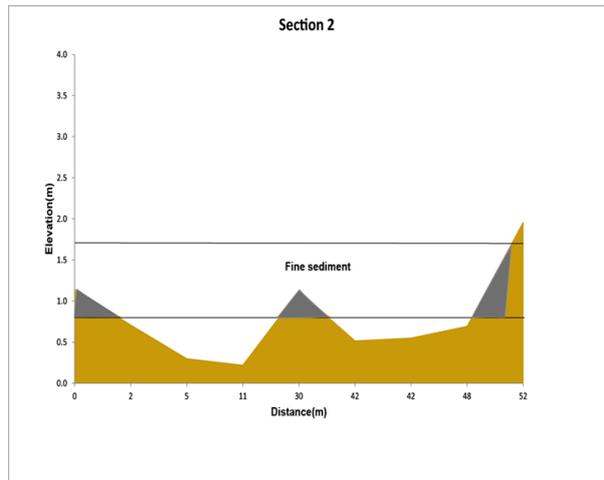
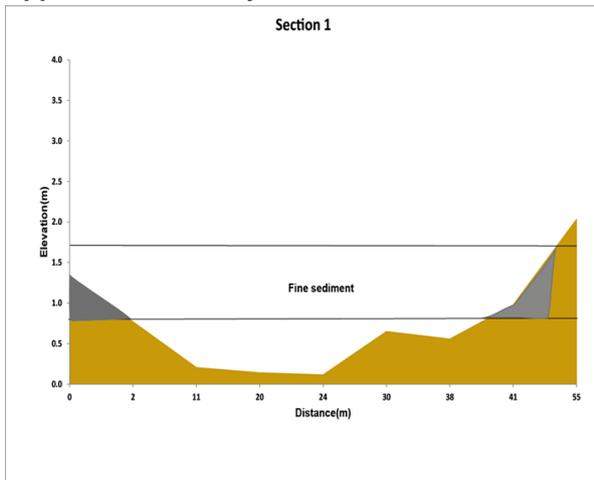
S21	50.30817	-3.84149	50	49	1	0.12752	8.10	799	2.6
S22	50.30853	-3.84096	43	56	1	0.12236	9.69	862	2.7
Mean			47	52	1	0.16	6	569	2.5
SD			10	9	0	0.06		338	0.3
W-SM1 samples									
Samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.30004	-3.85823	40	59	1	0.1426	1.40	124	2.7
S2	50.29997	-3.8583	64	36	1	0.08912	8.50	825	2.6
S3	50.30045	-3.85675	32	67	1	0.1592	10.23	908	2.9
S4	50.30109	-3.85511	35	64	1	0.1628	1.38	125	3.1
S4B	50.3009	-3.85491	41	58	1	0.1396	8.61	831	1.9
S5A	50.30155	-3.85376	39	60	2	0.15275	1.82	176	2.2
S5B	50.30147	-3.85369	16	82	2	0.254	2.45	206	4.0
S5C	50.30127	-3.85342	18	80	2	0.238	12.31	1198	3.6
S6A	50.30347	-3.85217	26	72	2	0.1792	10.29	1011	2.2
S6B	50.30307	-3.85196	12	85	3	0.302	10	915	3.0
Mean			32	66	2	0.18	7	632	2.8
SD			15	15	1	0.06		422	0.7
W-SM2 samples			Sand	Silt	Clay	SSA gm ²	TP mg l ⁻¹		TC
Samples	latitude	longitude							
S1	50.3052	-3.84959	34	65	1	0.184	5.50	536	3.6
S2	50.30604	-3.85036	22	76	2	0.2054	2.57	223	3.1
S3	50.30707	-3.85162	13	85	2	0.253	8.99	774	4.7
S4	50.30744	-3.85162	13	85	3	0.2896		714	5.0
S5	50.3056	-3.84996	16	82	2	0.264	2.27	214	5.6
Mean			19	79	2	0.24	5	492	4.4
SD			9	8	0	0.04		265	1.0
E-SM3 samples									

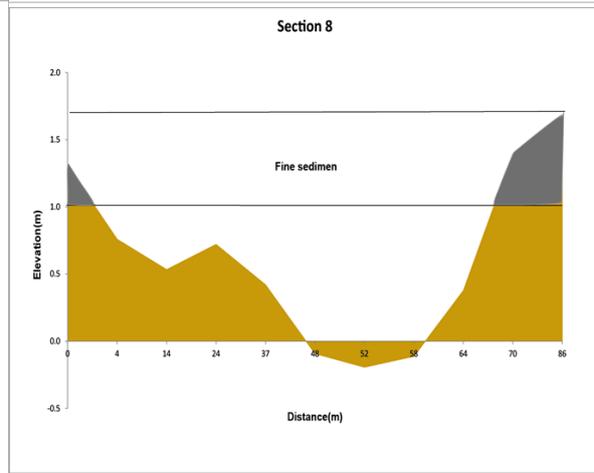
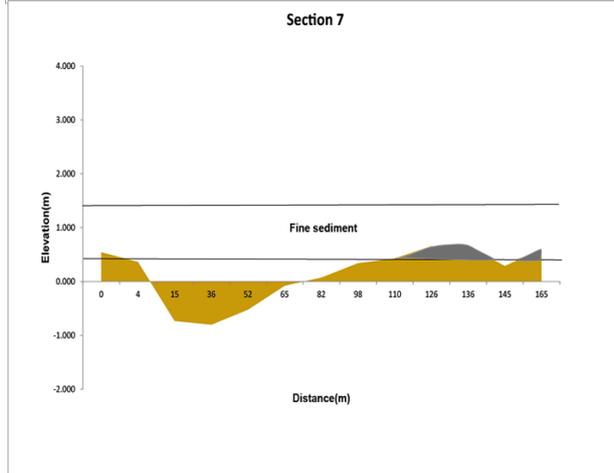
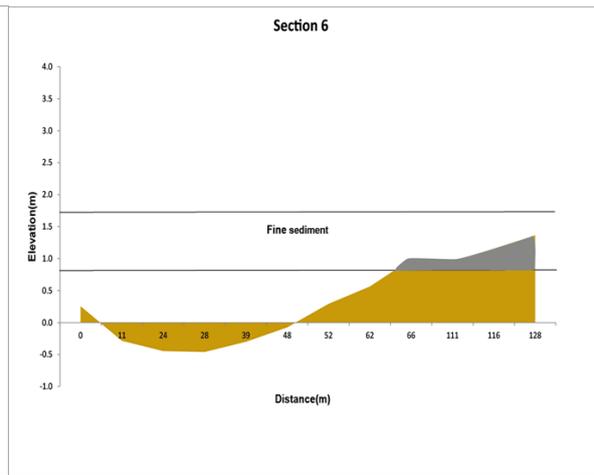
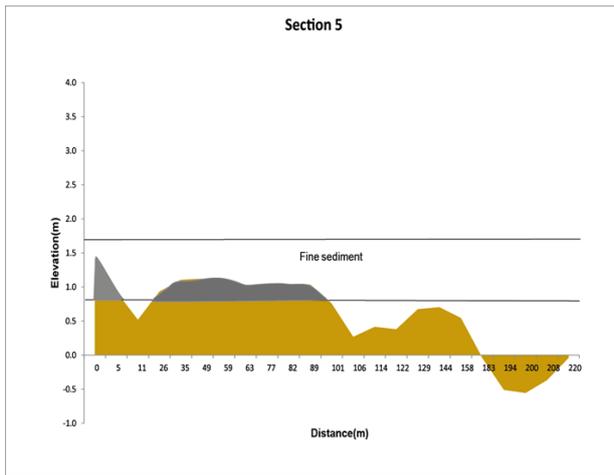
Samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.30319	-3.84897	20	78	2	0.2292	2.05	194	4.6
S2	50.30307	-3.84894	17	81	3	0.2538	4.03	383	4.1
S3	50.302	-3.84894	13	84	3	0.287	4.30	429	7.5
S4	50.30167	-3.84956	13	85	2	0.2848	15.56	1524	6.4
S5	50.30154	-3.85019	29	70	1	0.175	1.71	151	2.2
Mean			18	80	2	0.25	6	536	5.0
SD			6	5	0	0.05		505	1.9
E-MF3									
Samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.30037	-3.8516	47	52	1	0.16348	6.75	669	1.8
S2	50.30042	-3.85153	31	68	1	0.12508	7.18	708	1.5
S3	50.30105	-3.85148	29	70	1	0.12316	8.67	843	2.5
S4	50.30223	-3.85118	39	60	1	0.14924	9.62	821	5.6
Mean			37	63	1	0.14	8	760	2.8
SD			8	8	0	0.02		85	1.9
E-MF 4									
Samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.28998	-3.85808	45	54	1	0.09832	6.53	612	2.6
S2	50.2916	-3.85663	34	65	1	0.115	7.33	729	0.0
S3	50.29075	-3.8569	34	65	1	0.162	7.69	738	2.2
S4	50.29105	-3.85522	26	73	1	0.1284	9.47	824	2.1
S5	50.2917	-3.85343	33	66	1	0.1402	9.42	911	
S6	50.29165	-3.85368	40	59	1	0.125	2.13	197	2.3
S7	50.2916	-3.85845	90	10	0	0.03246	6.91	606	2.8
S8	50.29275	-3.85885	67	33	0	0.07512	7.42	698	2.4
S9	50.29352	-3.85927	80	20	0	0.0507	7.12	670	2.3
S10	50.29455	-3.85988	85	15	0	0.04122	7.47	738	2.1
S11	50.29587	-3.86052	93	7	0	0.03038	10.05	846	2.3

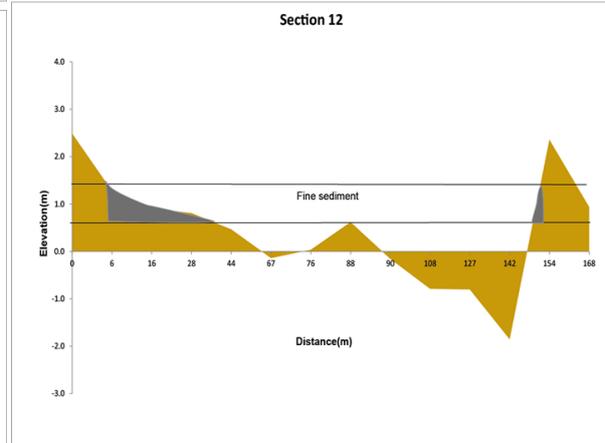
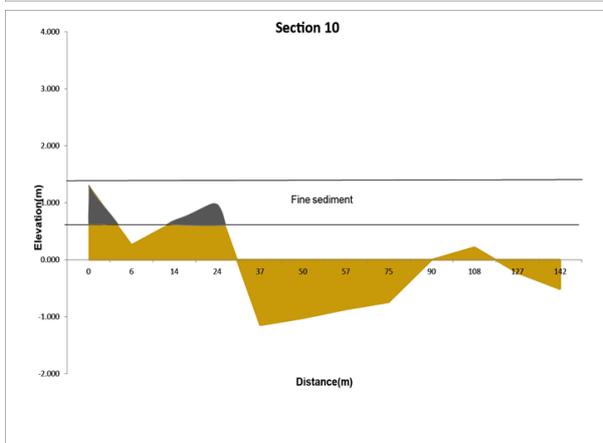
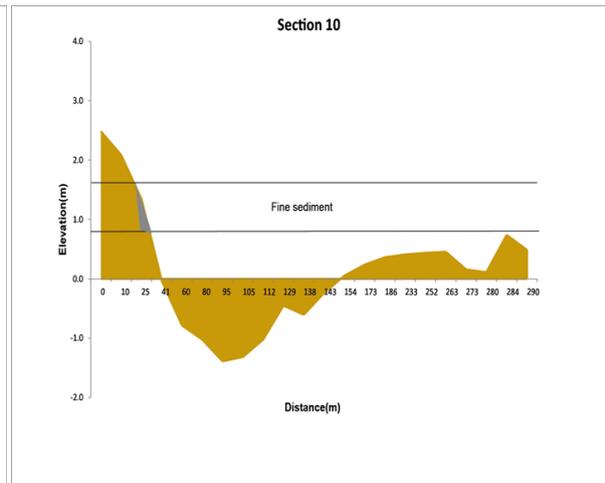
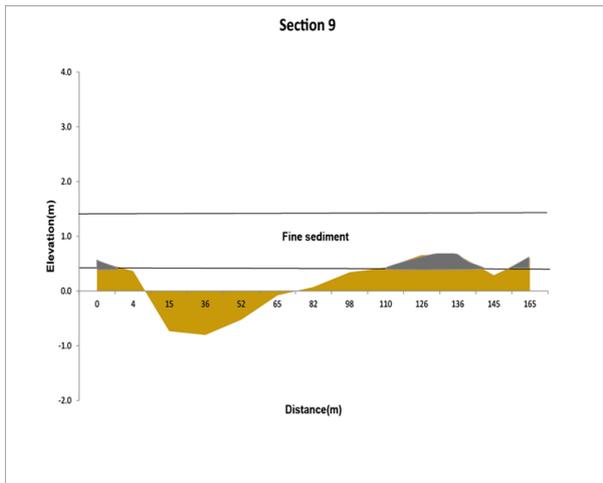
Mean			57	42	1	0.09	7	688	2.1
SD			26	26	1	0.05		188	0.8
W-MF 5									
Samples	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.28815	-3.86623	56	43	1	0.08824	8.00	0	3.0
S2	50.28948	-3.86623	43	56	1	0.1266	8.12	778	2.8
S3	50.28887	-3.86553	41	58	1	0.129	7.43	706	2.7
S4	50.28932	-3.86492	91	9	0	0.1124	8.27	752	2.6
S5	50.28988	-3.86318	91	9	0	0.03404	6.83	632	1.9
S6	50.29022	-3.86248	97	3	0	0.01754	6.57		2.8
S7A	50.2904	-3.86198	72	28	0	0.06944	8.73	776	2.6
S7B	50.29028	-3.86183	82	18	0	0.05334	1.25	110	2.0
S7C	50.29037	-3.86195	100	0	0	0.01004	0.00	0	0.0
Mean			75	25	0	0.07	6	469	2.3
SD			23	22	0	0.05		363	0.9
W-shoal 1	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
Samples	latitude	longitude							
S1	50.28072	-3.87573	100	0	0	0.00757	1.21	110	1.0
S2A	50.28057	-3.87518	100	0	0	0.02504	1.25	120	0.0
S2B	50.28068	-3.87523	100	0	0	0.00718	1.69	157	1.5
S3A	50.28052	-3.87428	90	10	0	0.00720	6.03	545	2.2
S3B	50.28067	-3.87425	100	0	0	0.00716	6.03	562	2.0
S3C	50.28088	-3.87425	100	0	0	0.00700	4.65	573	1.0
S4A	50.2805	-3.87097	100	0	0	0.006568	6.95	659	2.0
S4B	50.28088	-3.87107	86	14	0	0.03416	1.69	163	2.8
S4C	50.28117	-3.8712	95	5	0	0.0173	2.00	0	0.0
S5	50.28103	-3.87045	90	10	0	0.02246	6.74	606	2.3
S6	50.28173	-3.86953	90	10	0	0.03416	0.00	0	0.0

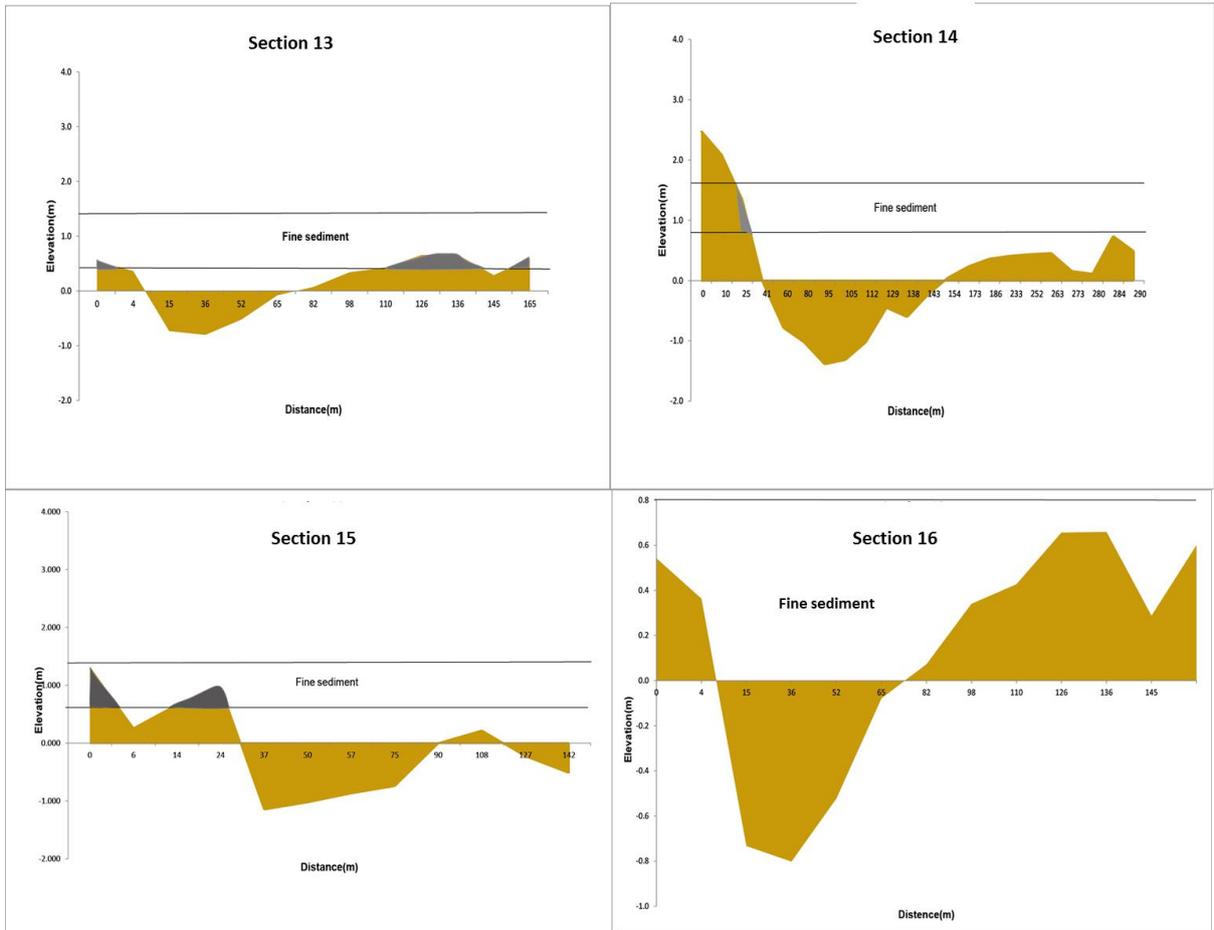
Mean			96	4	0	0.02	3	318	1.3
SD			23	22	0	0.01		254	0.6
E-shoal 2	latitude	longitude	Sand%	Silt%	Clay%	SSA gm ²	TP mg l ⁻¹	TP mg kg ⁻¹	TC%
S1	50.28148	-3.8337	87	13	0	0.03836	0.89	80	0.0
S2	50.28685	-3.8647	92	8	0	0.02814	1.39	129	0.0
S3	50.28575	-3.8653	86	14	0	0.03844	1.00	84	0.0
S4	50.28292	-3.8666	94	6	0	0.0223	0.85	79	0.0
S5	50.28758	-3.8638	98	2	0	0.02	0.76	74	0.0
S6	50.28438	-3.8658	98	2	0	0.01066	0.72	68	0.0
Mean			93	7	0	0.03	1	86	0.0
SD			5	6	0	0.01		22	0.0

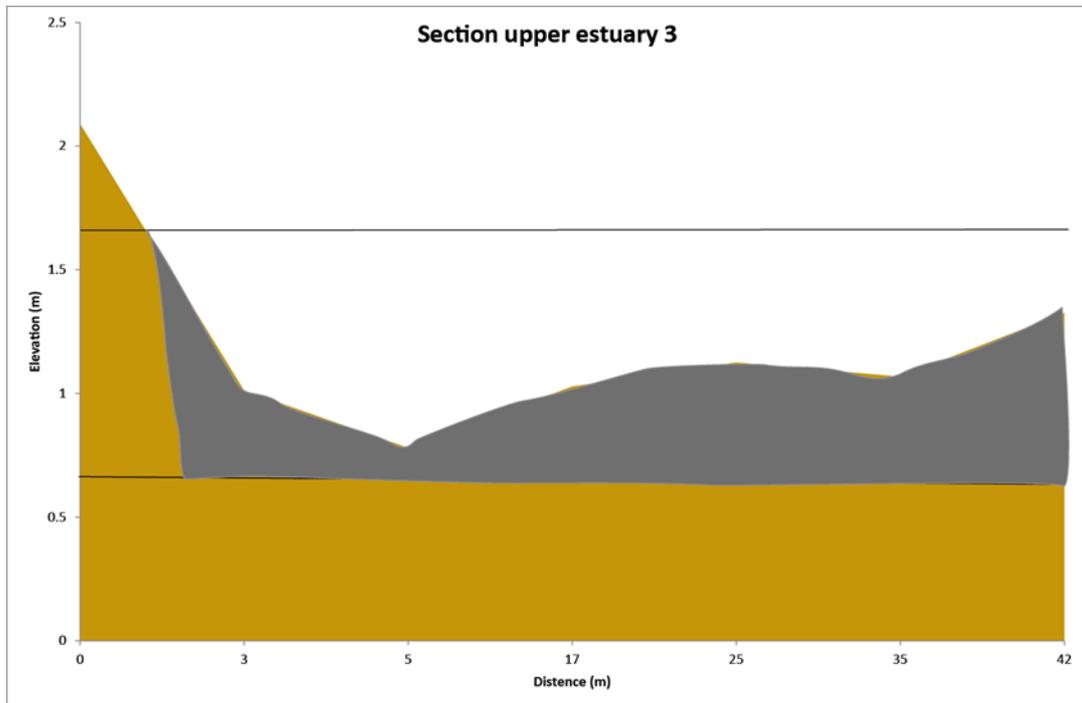
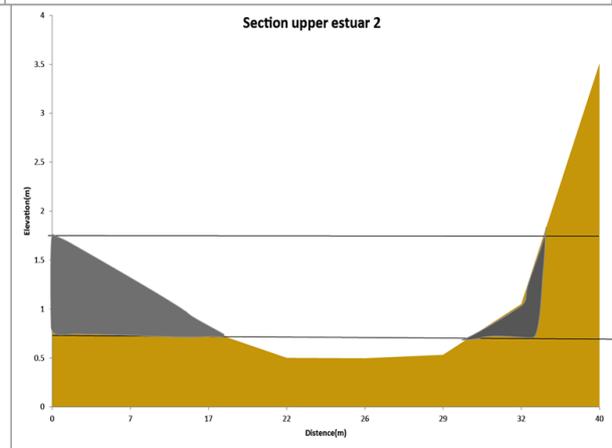
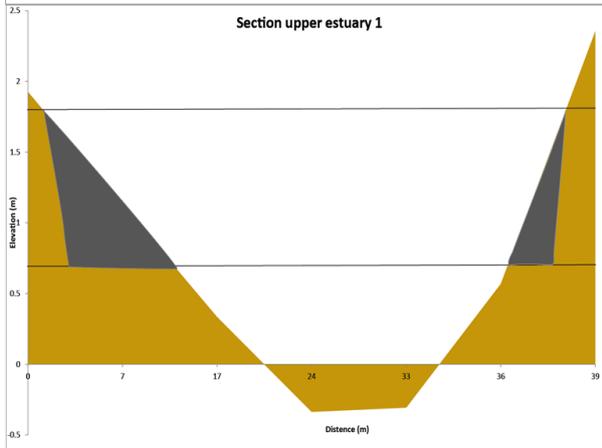
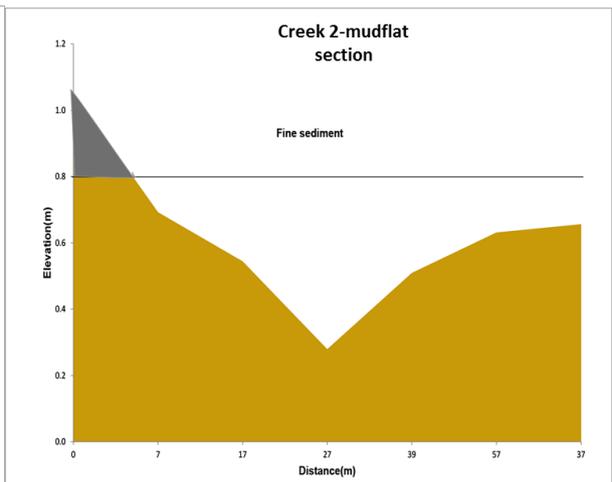
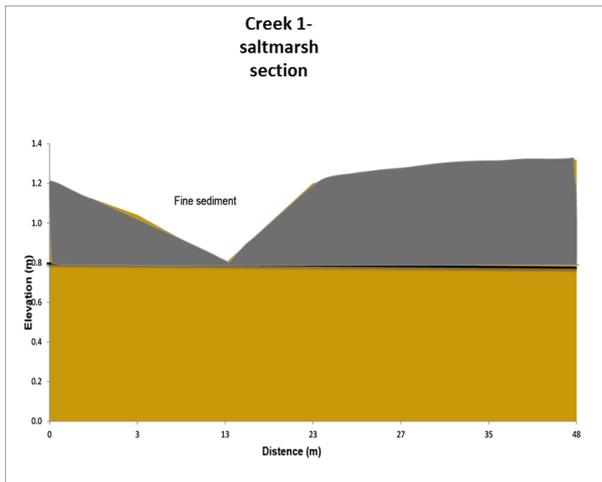
Appendix III: estuayr channel cross-section











Suspended sediment sampler data:

Samples	Sand%	Silt%	Clay%	SSA gm ⁻²	TP mg l ⁻¹	TP mg kg ⁻¹
S1	5.47	91.75	2.78	0.294	4.655	465