

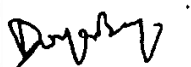
**Modelling the hysteretic patterns of solute concentration-
discharge relationships and their significance for hydrological
pathways at the farm-scale.**

**Submitted by Adebayo Oluwole Eludoyin to the University of Exeter
as a thesis for the degree of Doctor of Philosophy in Geography
In December 2013.**

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Abstract

Recent researches on the effects of environmental degradation on food security suggest that a better understanding of the relationship between agricultural intensification and pollutant transfer is urgently required to support the implementation of sustainable agricultural policies, globally. Poor understanding of the hydrological behaviour of clay-rich soils in intensively managed agricultural regions is highlighted as an important problem. The study therefore evaluated precipitation-soil water chemistry relationships, soil variability and concentration-discharge relationships at the farm-scale based on datasets from the North Wyke Farm Platform between 2011 and 2013. The three main hypotheses were that (1) precipitation and soil water chemistry are significantly related (2) significant relationships exist between the distribution of soil physiochemical characteristics and the managements of the fields, and that (3) hydrological behaviour of fields underlain by certain dominant soils in the study area are different from that of other fields. The basis of this work was to elucidate links between sources of pollutants and water quality, further understanding of the effect that management of the soil may have upon the quality of the water and improve understanding of the pathways of pollutants within intensively managed landscapes.

Precipitation chemistry of the study area was chemically different from that of the other regions in the United Kingdom, and was influenced by contributions from sea salts and terrestrial dusts. The soil chemistry was rich in organic matter which contributed significantly ($r^2 > 0.60$; $p < 0.05$) to the distribution of total carbon and total nitrogen in the fields. Mean total carbon and nitrogen stocks ranged 32.4 - 54.1 t C ha⁻¹, and 4 - 6.2 t N ha⁻¹, respectively in the entire farm platform while runoff coefficient at four selected fields (Pecketsford, Burrows, Middle and Higher Wyke Moor, and Longlands East) varied between 0.1 and 0.28 in January and November, 2013. The study rejected the first and third hypotheses, and concluded that the study area is largely influenced by contributions from the surface runoff mechanisms. The study also noted that sodium and chloride ions were dominant in the precipitation chemistry, and therefore suggests their further investigation as conservative tracers in the soil and runoff chemistry.

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CHAPTER 1

INTRODUCTION

1.1 Background to the Study

Agricultural intensification is widely recognised as one of the most significant human alterations to the global environment because of its on-site and off-site consequences (Matson et al, 1997; Donald et al, 2001; Tscharntke et al, 2005; Tscharntke et al, 2012). Total cultivated area has increased between 1700 and 1980 by 466%, globally (Meyer and Turner, 1992), and although the rate of the increase has slowed down in the last few decades, agricultural intensification through the use of high-yielding farm varieties, chemical fertilisers, irrigation and mechanisation, has increased (Matson et al, 1997; Tilman et al, 2002; Withers and Haygarth, 2007; Cordell et al, 2009; Figure 1.1).

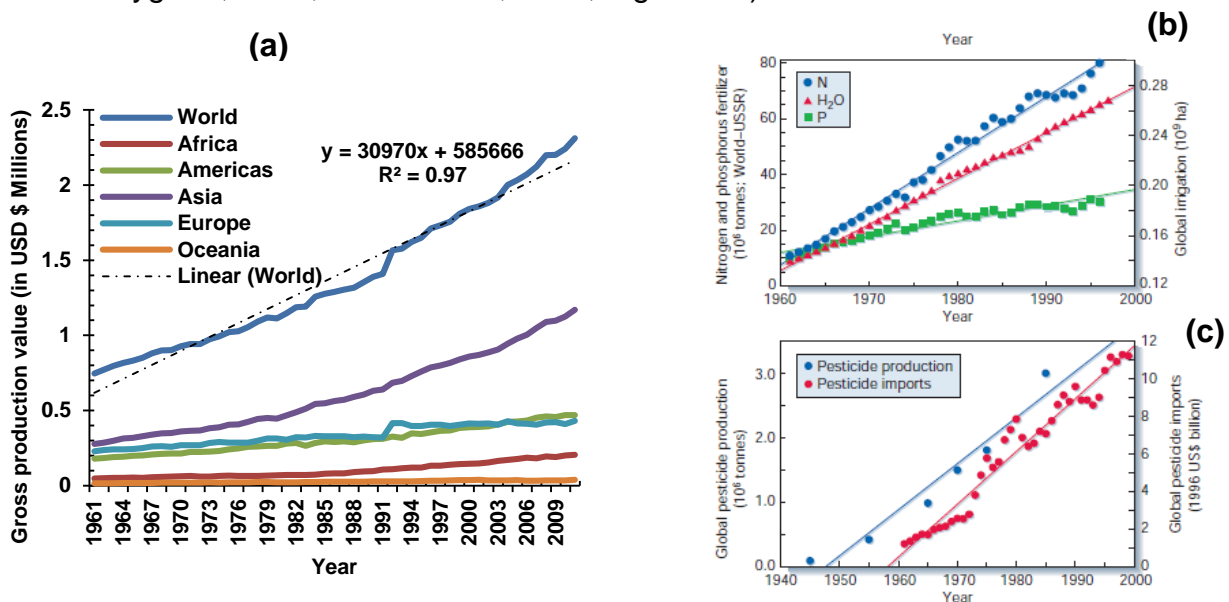


Figure 1.1a-c. Global trends of agricultural intensification; (a) increased gross production value in agriculture at global and continental levels (Data from FAOSTAT (Statistics Division of the Food and Agriculture Organisation) database of the UN Food and Agriculture Organisation). b - c. Increased use of inorganic fertilisers and pesticides, respectively (Tilman et al, 2002).

Agricultural intensification is evident in both developing and developed countries. In developing countries, it occurs under the general perception of ‘the Green Revolution’ which started in most of these countries in the 1960s, involving transfer and dissemination of high-yielding crop seeds (Naylor, 1996). In developed countries, agricultural intensification can be demonstrated (for example) by the 400–500% increase in cotton and wheat yields, in the eastern

Colorado in the United States of America (Matson et al, 1997), the 1947 Agriculture Act in the UK and treaty of Rome for Europe in 1957 (Latacz-Lohmann and Hodge, 2003; Wilson and Rigg, 2003; Martin and Langthaler, 2009). Programmes aimed at promoting agricultural intensification have successfully resulted in increasing agricultural yields in most regions.

Concerns for the long-term sustainability and environmental consequences of agricultural intensification have also increased in recent years (Matson et al, 1997). Studies of the intensive cultivation systems of rice and wheat farms (for example) in Asia have shown serious concerns for decline in crop yield due to loss of soil quality and increased crop health problems (Nambiar, 1994; Yadav et al, 2000). Agricultural intensification has also been linked with increased erosion, reduced soil fertility and reduced biodiversity (Singh, 2000; Tilman et al, 2002; Swift et al, 2004). Across Europe, studies have associated the significant decline in the population of farmland birds since the last quarter of the 20th century to agricultural intensification (e.g. Donald et al, 2002). Donald et al (2002) also reviewed the impact of different provisions of the European Union's Common Agricultural Policy (CAP), and showed that consequences of agricultural intensification when environmental quality is not in the focus of the agricultural development initiatives (Table 1.1). In general, studies have shown that while it is necessary to meet the increasing global food needs (United Nations Population Fund, 2007), it is also important to understand how ecosystems are altered by intensive agriculture, and develop new strategies that take advantage of the ecological interactions within agricultural systems (Latacz-Lohmann and Hodge, 2003; Sutherland et al, 2006; Swinton et al, 2007).

Table 1.1. Some provisions of the Common Agricultural Policy (CAP) and their effects on the environment
(Modified from Donald et al, 2002).

Type of Support	Role under the CAP	Explanation	Effects on the environment
Price support	It is the main form of agricultural support under the CAP. Price support was cut by the 1992 and 1999 CAP reforms, with farmers compensated through direct payments.	Prices of main farm commodities are supported above world market price. Export subsidies, intervention buying, import tariffs, supply controls for maintaining high EU price and dispose of surpluses.	It is the main stimulus for agricultural intensification under CAP, and has encouraged increase in yield, higher use of inputs, use of marginal land, destruction of unfarmed habitats and loss of unfarmed features and land use changes (mainly grassland converted to arable).
Direct area payments	Introduced for cereals, oilseeds and proteins. It is a major part of CAP budget, and of incomes for arable farmers.	Introduced in 1992 for arable crops, to compensate farmers for price cuts. Paid on area basis, linked to previous regional yields, subject to set-aside.	The effect on the environment is not clear. It is however linked to land which were previously used for arable production, and therefore discourages reversion to other habitats. Large subsidy cheques could be used to fund damaging capital projects or environmentally beneficial activities.
Headage livestock payments	It is the main form of subsidy in 'sheepmeat regime', and it became important in beef regime as a compensation for price cuts in 1992 and 1999.	This is paid per ewe or eligible beef animal. It is subject to quota, however, and premium payment on ewe is linked to lamb prices.	This support has substantially encouraged a large increase in stocking rates, especially of sheep, causing environmental damage (soil erosion by overgrazing and degradation of grassland).
Less favoured area payments	It is used to support farming in marginal areas. Reforms now recognise environmental benefits of extensive farming systems.	Before Agenda 2000, this was paid per unit area of livestock or area of arable crops. It is however now paid on an area basis, with attached environmental conditions.	This may have helped to prevent abandonment of margin areas and increase reseeding of pastures, the effect of Headage payment has nullified its significance.
Capital grants	This was introduced under Structures Regulations 1972, and some members of EU still fund agricultural development under structural funds.	Wide range of grants have been available in the past for agricultural development and growth in production.	This has caused direct environmental impacts such as; removal of hedgerows, loss of wetlands by drainage and irrigation of dry habitats.
Afforestation payments	This was introduced in 1992 as an accompanying measure, and it is now included in the rural development regulation.	The payment is made to transfer agricultural land to forestry and to enhance and protect existing woodland.	This is noted to cause direct environmental damage, by influencing afforestation of peat bogs and heather moorland, afforestation on rocky soils and planting of alien species.
Agri-environment schemes	Introduced in 1992 under the Agri-Environment Regulation 2078 and now part of Rural Development Regulation. It is growing in significance but it still has less than 5% of CAP budget.	This schemes pay farmers to implement environmentally beneficial management regimes such as organic farming, habitat restoration and land management of boundary features, and maintaining extensive systems.	This is a beneficial scheme as some have shown to benefit biodiversity. The uptake is however poor in intensive regions with uncompetitive rates of payment, and its benefits are poorly monitored over many parts of Europe.

The negative regional consequences of agricultural intensification include pollution of surface and groundwater, and eutrophication of lakes and rivers systems (Matson et al, 1997; European Environment Agency, 2003). Table 1.2 provides a list of the negative effects of agricultural intensification to water quality and users of water. The recent realisation of the negative effects of agricultural intensification is probably the main reason for the establishment of agri-environment schemes and sustainability policies in many countries, and the continuous agitation for such in the developing countries, where efficient environmental monitoring systems have been a challenge (Li and Zhang, 1999; European Environment Agency, 2003).

In the United Kingdom, efforts have been made to ensure sustainable agricultural practices recently, these are documented in the Catchment Sensitive Farming Programme, CSFP (DEFRA, 2008), Code of Good Agricultural Practice for Farmers, Growers and Land Managers, CGAPF (DEFRA, 2009) and other recommendations on sustainable farming systems (Braden et al, 1989; Agrawal et al, 1999; Pretty et al, 2000; Ewald and Aebischer, 2000; Tilman et al, 2002; Withers and Lords, 2002; European Environment Agency, 2003; Carabias-Martinez et al, 2003; Horsey, 2006). The CSFP, for example, documents direct technical advice to farmers of prioritised or pollution-vulnerable regions, such as Nitrate Vulnerable Zones (Lane et al., 2006). The CGAPF also documents advice to farm users on environmental protection and enhancement of farm quality for sustainable management and development practices. The Code of Good Agricultural Practice (CGAPF) encouraged to farm with the following objectives (DEFRA, 2009):

- i. careful management of livestock to reduce losses of ammonia and other gases to the atmosphere;
- ii. limiting nitrate leaching to groundwater;
- iii. avoiding excessive build-up of nutrients and contaminants in soil,
- iv. preventing micro-organisms from being washed into surface waters and reaching bathing waters;
- v. following a nutrient management plan that will ensure efficient use of fertilisers (and organic manures)
- vi. limit nitrate leaching to surface and groundwater;
- vii. preventing unnecessary accumulation of phosphorus in the soils which will also reduce impact on the water environment; and
- viii. reducing the risk of greenhouse gas emission to the atmosphere.

Table 1.2. Effects of water pollution from agricultural practices.

Farming Component	Problems associated with concentrations higher than recommended limits	References
Farm's organic and inorganic matters	<p>Ecological disruption. This, according to Kapp (1970) is a term still in search of precise definition. Here, it is used to refer to the impairment beyond certain normal threshold levels of the aggregate of all external conditions and influences affecting the life and development of the natural aquatic and terrestrial ecological organisation.</p> <p>Significantly high concentrations of ions such as nitrate (>45 mg l⁻¹) and sulphate (>250 mg l⁻¹) in drinking water are known to cause health hazards, (excess nitrogen causes cyanosis and methamoglobinaemia or blue baby syndrome in infants; excess sulphate causes catharsis, dehydration and gastro-intestinal irritation in humans).</p> <p>Organically polluted beach water can be source of bacteria (e.g. <i>Escherichia coli</i>) contact for beach swimmers and tourists. <i>E. coli</i> and Staphylococci were found to be significantly correlated to skin, respiratory and general illness among beach swimmers in polluted beaches in Hong Kong between 1986 and 1987. Magnesium and calcium cause hardness in water and increase laundry costs.</p> <p>Phosphate with nitrogen cause eutrophication and increase biological oxygen demand (reduce dissolved oxygen) in water bodies, and can endanger aquatic ecosystem and severely impact tourism; it can also encourage epidemic.</p> <p>Sediments pollution is associated with water quality deterioration, reservoir sedimentation and increased turbidity. Sediment pollution can inhibit reproduction of coral reefs in marine region and can trap toxic hydrocarbons in oil spill areas.</p>	<p>Reijnders, 1986; Croll and Hayes, 1988; Kapp, 1970; Rosenberg et al, 2000; Moss, 2008; Chen, 2013; Bowmer, 2013.</p> <p>Bruning-Fann and Kaneene, 1993; Fan and Steinberg, 1996; Carpenter et al, 1998; Bouraoui and Grizzetti, 2014.</p> <p>Cheung et al, 1990; Pruss, 1998; Fujioka, 2001; Carr and Blumenthal, 2004; Amorim et al, 2014; Limayem and Martin, 2014.</p> <p>Turner and Rabalais, 1994; Heathwaite, 1996; Correll, 1998; Sims et al, 1998; Bricker et al, 1999; Blumenthal et al, 2000; Howarth et al, 2002.</p> <p>Lijklema et al, 1983; Guzman and Holst, 1993; Bilotta and Brazier, 2008; Rickson, 2014.</p>
Toxic wastes from farm machinery and input	<p>Toxic substances such as pesticides and herbicides used in agriculture systems can increase the heavy metal concentrations in the ecosystem; cause health hazards to living organism; pollute water bodies and the food web, and can be lethal to vegetation, animal and humans.</p>	<p>Holcombe et al, 1976; Wauchope, 1978; Moore and Ramamoorthy, 1984; Marzadori et al, 1996; Richards and Baker, 1993</p>
Ecosystem management	<p>High cost of pollution control and costs of negative externalities associated with pollution.</p>	<p>Shortle and Dunn, 1986; Pretty et al, 2000; Conway and Pretty, 2013.</p>

1.2. Research Problems

Moss (2008) described the relationship between land-use and water resources, especially surface water, as similar to that of a house and its waste bin. Figure 1.2 is an illustration of a land use-environment relationship; farm additives and by-products of farm activities using machinery are sources of chemical substances which are often mobilised by rainfall. Monitoring of hydrological fluxes of diffuse pollutants has demonstrated severe impacts on adjacent on adjacent water bodies (Van der Weijden and Middelburg, 1989; Eludoyin et al, 2004; Miller and Miller, 2007; Moss, 2008). Agricultural land use changes such as vegetation change, forestry (both deforestation and afforestation), intense grazing, hedgerow removal, fertiliser/pesticide/herbicide inputs and land drainage can affect the soil properties, and influence the rate at which the chemical substances are transferred into the adjacent receiving water bodies, and therefore the rate at which the adjacent water bodies are polluted (Williams et al., 2004; Tsegaye et al., 2006; Arias-Estaevez, 2008; Packett et al., 2009).

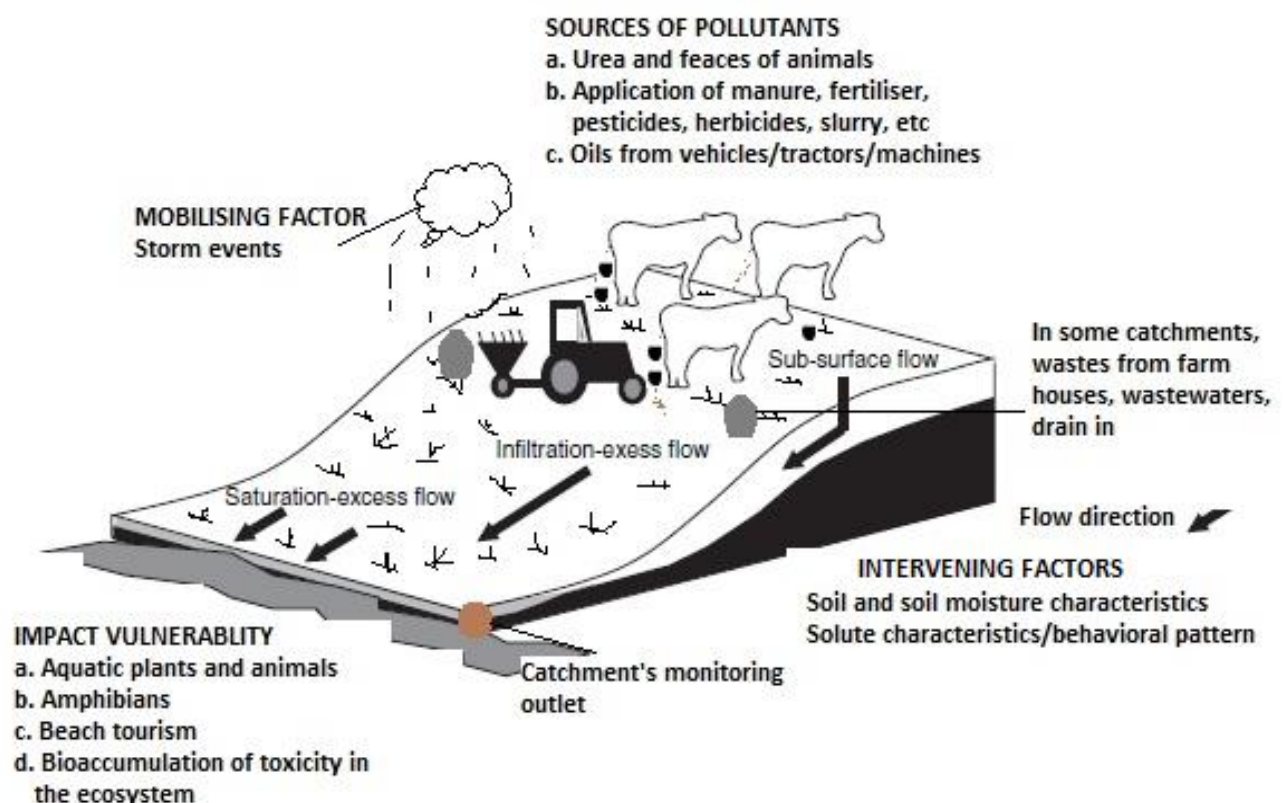


Figure 1.2: Some pollutant-generating activities processes of runoff mobilisation and possible environmental impact of a typical grassland farm (modified from Withers and Haygarth, 2007).

The relationship between agricultural land-use and surface water systems has interested researchers for ages (Biggar and Corey, 1969; Loehr, 2012; Wicke et al, 2012; Conway and Pretty, 2013). Research interests have often borne out of the quests for sustainable development (World Commission Environment and Development, WCED, 1987; Lele, 1991). Sustainable development of agriculture is targeted at meeting the food needs of the present population without compromising the future sustenance needs (WCED, 1987). Research concerns for sustainable agriculture have suggested the need to understand how the chemical substances, which eventually pollute adjacent bodies, are transferred from farmland into water bodies because it is this knowledge of pollutant transfer that can provide clues to how water pollution can be controlled at source (Van der Weijden and Middelburg, 1989; Heathwaite, 1996, Calamari, et al., 1995, Correll, et al., 1999, Di Natale, et al., 2000, Sonneveld, et al., 2006; Yevenes-Burgos and Mannaerts, 2011). Consequently, many studies have evolved to explore the understanding of how chemical substances are transferred from different fields under different climate, soil and topographic conditions, in most parts of the world; and these are discussed in the literature review section (Chapter 2) of this thesis. Despite the increase in research, increased complexity of conceptual and theoretical models, and improved understanding of water and material transfer in catchment systems, a significant amount of grey areas exist, especially in the intensively cultivated clay soil environment (Granger et al, 2010a; Granger et al, 2010b) and as soil, geology, climate and land-use and land cover vary with locations (McDonnell, 1990, 1991, 2003; Jenkins et al, 1994; Sivapalan et al, 2003; Beven et al, 2005; Bilotta et al 2008; McDonnell et al, 2010; Macleod and Haygarth, 2010; Pilgrim et al, 2010).

Hydrologists, biogeochemists and, more broadly, catchment scientists study hydrological losses of macronutrients and sediments from agricultural land (Haygarth et al, 2004; Andrea et al, 2006; Bilotta et al, 2008; Bilotta and Brazier, 2008; Fenicia et al, 2008, 2013). For example, the hydrological question, 'what happens after the catchment caught the storm?' (Penman, 1961; Hewlett and Hibbert, 1967; McDonnell, 2003; Uhlenbrook et al, 2005) is useful for understanding the field- or farm-adjacent water body, hydrological connectivity. The hydrological energy associated with precipitation events has been shown to mobilise particulate (Crawford, 1991; Zeigler et al, 2004; Beven

et al, 2005; Bilotta and Brazier, 2008; Bilotta et al, 2008) and soluble chemical substances (Agrawal et al, 1999; Bishop et al, 2004; Bowes et al, 2005; Biggs et al, 2006; Granger et al, 2010a, Granger et al, 2010b). Flowpaths of mobilised chemical substances are often complex to decipher because of certain uncertainties or complexity, including misapplication of hydrological models as a result poor understanding of the spatial scale, parameterisation and differences in catchments physiography (McDonnell, 2003; Kirchner, 2003; Wallender et al, 2014; Cibin et al, 2014; Singh et al, 2014). The poor understanding of the hydrological flow paths, due to the complexity, especially in the humid climate has been the concerns for many hydrological researchers, who have subsequently recommended the need for more case-specific researches (Hewlett and Hibbert, 1967; Jones and Swanson, 2001; Beven, 2002; McDonnell, 2003; Kirchner, 2003). For example, although many areas occupied by clay soils (Cambisols) are known to favour agriculture intensification and are often grasslands, the hydrology of the clay soils, as well as their transfer of chemical substances under grazing and other agriculture land uses are still poorly understood. Existing studies on the clay soil environment have also shown that it is still unclear if fields underlain with different clay soil series can respond differently to the same storm conditions or how much would the variation in material inputs through rainfall and soil wetness condition and field properties (such as topography and scale) affect the hydrological responses in the clay-soil environment (Gifford and Hawkins, 1978; Neuzi, 1994; McCartney et al, 1998; Bilotta et al, 2008; Granger et al, 2010a; Klaus et al, 2013). Granger et al (2010a) concluded that better understanding of the hydrology of the heavy clay grassland soils was needed, and suggested that the 'current perception of clay soil systems as being event water driven may be wrong'.

Recent research has revisited the use of the hysteretic relationships between concentrations (c) of substances, such as suspended solids (Wood, 1977; William, 1989) and solutes (Whitfield, 1981), and their corresponding discharge (q) rates to decipher hydrological pathways (Evans and Davies, 1998; Rice and Hornberger, 1998; Rice, et al., 2004; Krueger et al, 2010; Burt et al, 2014). Significant inferences about temporal variability, hydrological health status of catchments, source areas of targeted pollutants, flow pathway and resident time of targeted substances have been made from concentration-discharge patterns, and as such, informed land management strategies have

been advised (e.g. Walling and Webb, 1980; Johnson and East, 1982; William, 1989; Davies and Evans, 1998; Chanut et al, 2002; Rose, 2003; Haygarth et al, 2004; Krueger et al, 2010; Murphy et al, 2012). This study will therefore advance knowledge in the scientific field of hydrological modelling, and improve understanding of hydrological behaviour of intensively managed, heavily clayed-drained soils.

1.3. General Aim and Approach

The present study aims at improving the understanding of the hydrologic responses of a humid grassland region that is underlain by heavy clay soils of the *Stagni-vertic* or *Stagni-eutric* Cambisols soil groups (Harrod and Hogan, 1981). Cambisols soil groups are regarded as one of the most widespread soils, covering some 1.57 billion ha or 12.5 % of the earth's land surface, where they have been found to support intensive agriculture (Toth et al, 2008).

Studies have shown that complexity exists in explaining hydrological processes in agricultural fields, across spatio-temporal scales and wetness conditions (Dunne, 1978; Anderson and Burt, 1970; McGuire et al, 2007), mainly due to poor understanding of hydrological connectivity of flow pathways (Bulling et al, 2006; Norberg and Cumming, 2013; Kandziora et al, 2013; Bracken et al, 2013). A novel approach to understanding hydrological connectivity in agricultural fields and other environments (including urban landscapes) is to examine the relationship between the concentration of dissolved and suspended materials, and the rate of transfer of corresponding runoff from the fields (Johnson and East, 1982; Miller and Denver, 1977; Hill, 1993; Rose, 2003; Andrea et al, 2006) with a view to assessing the controlling factors, effects and uncertainties. Subsequently, this study considers the system approach to environmental investigations a relevant framework. The systems approach visualises the ecosystem as containing an integrated components of the atmosphere, lithosphere and hydrosphere (Vemuri and Vemuri, 1970; Kirchner, 2009; Simonovic, 2012). The system approach as used in this study involves an investigation into the rainfall characteristics, land surfaces, land use, and runoff at farm scale. Rainfall characteristics (rainfall type; heavy or light storm, duration of events, antecedent level and chemical properties) are considered to be significant factors for understanding the nature of the runoff from the fields (Figure 1.3).

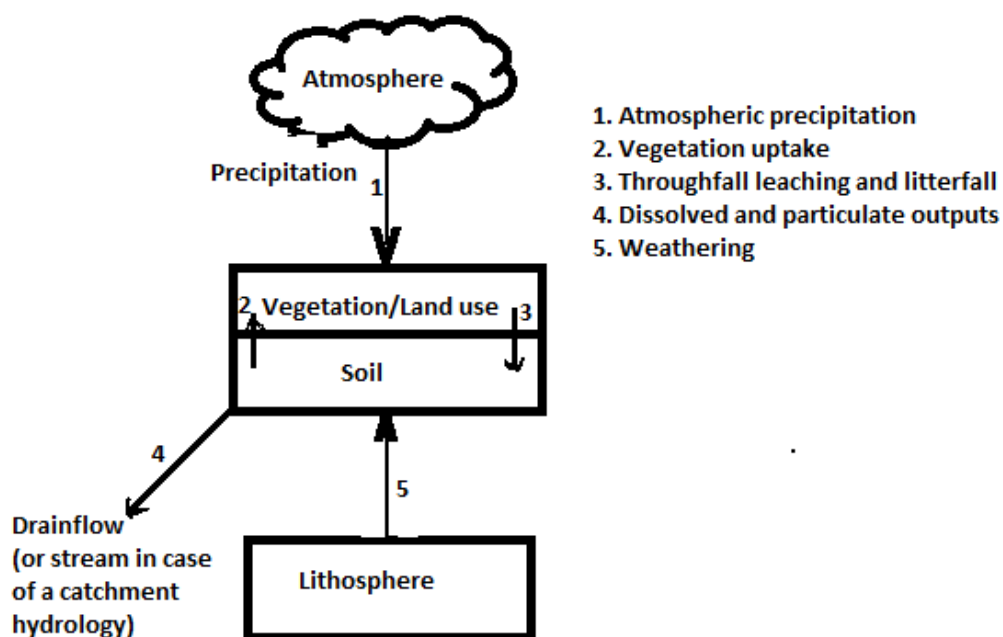


Figure 1.3. A schematic conceptualisation of transfer of chemical constituents at a drained field-scale (modified from Meybeck, 1982).

1.4. Aims and Hypotheses

This study is undertaken to address three aims, to ensure that the rainfall, land surface and runoff components of the system conceptualised in Figure 1.3 are examined. Specific hypotheses investigated under each aim are also presented.

Aim 1: To assess the temporal variability in precipitation chemistry and its contributions to the soil chemistry at the farm-scale. Two hypotheses are tested for this aim: (1) rainfall chemistry does not exhibit significant temporal variability, and (2) the variability in the rainfall chemistry is directly proportional to the variability in the soil chemistry in the farm area. To address these hypotheses, precipitation chemistry data obtained from the Environment Change Network (ECN) platform were analysed, and compared with the soil chemistry (obtained from same source) for the study area. This study was motivated by previous ecohydrological studies (such as Soriano-Soto et al, 1995 and Fraser et al, 2001), which established a significant relationship between rainfall chemistry and biogeochemical cycles.

Aim 2. To quantify the spatial variability of the soil physiochemical properties for hydrological analysis. The main hypothesis to be tested is that the physiochemical characteristics of the soils in the investigated farms reflect the land use systems. To achieve this hypothesis, soil samples were obtained from the

top soil (0-10cm) at the 15 fields of the North Wyke Farm Platform and tested for bulk density, pH, organic matter nitrogen and carbon contents, and nitrogen-15 ($\delta^{15}\text{N}$) and carbon-13 ($\delta^{13}\text{C}$).

Aim 3. To examine the patterns of concentration-discharge (c-q) hysteretic relationships of different chemical constituents at the farm scale. The main hypothesis is that the c-q relationship of same variable under similar land use condition is not significantly different. Hydrological behaviour of different clay soil series can be different, especially with different field size, topography, location and land use (Croft et al, 2013; Berhanu et al, 2013). The study area is covered by at least four major clay soil series, namely the Halstow (Hydrology of Soil Type, HOST 21), Hallsworth (HOST 24), Denbigh (HOST 17) and Fladbury (HOST 9) (Ragg et al, 1984; Boorman et al, 1995; Harrod and Hogan, 2008; White, 2008).

1.5. Structure of the Thesis

This thesis comprises five chapters.

Chapter 1. Introduction: This section provides the background information, justification, aims and research questions for the research. The aims and objectives have been derived after an evaluation of the review of relevant concepts and literature which is later presented in Chapter 2.

Chapter 2: Concepts and Literature Review. The objectives of this chapter are (a) to provide a review of the basic concepts and literature on flow generation and transfer mechanisms within the understanding of catchment hydrology, and (b) to evaluate the different approaches (with emphasis on the concentration-discharge hysteresis approach) for the study of flow transfer mechanisms.

Chapter 3: Study Area and Field Instrumentation. This chapter describes the climate, soil, topography and land cover and land use of the North Wyke Farm Platform (NWFP) in the Southwest England used as a case study. Information of the instrumentation of the fields is also described. The NWFP has been considered as a case study being a major agri-scheme project in the United Kingdom with extensive use of the state-of-the-art field instrumentation. The facilities for monitoring in the field as well as the methodology with which each aim of this study was achieved are reported in the chapter.

Chapter 4: Results and Discussion. In this chapter, the results of the statistical and other inferential analyses of the aims (Aims 1 and 2) are presented and discussed. Aims 1 and 2 are considered to be relevant to the hypothesis of water material transport structures of Lewis et al (2007). The hypothesis considers the spatial arrangement and relative abundance of flow path types within a catchment to influence material retention by the entire catchment, and assumes that the flowpaths are biogeochemically distinct. Aim 3 is focused on the patterns of concentration-discharge relationship for water pH, temperature, conductivity, dissolved oxygen, turbidity and nitrate. Concentration-discharge relationships of the parameters are interpreted to provide information about runoff pathways in the study area.

Chapter 5: A synopsis of the entire research is presented in this short chapter. The chapter also highlighted the limitations of this study and suggest areas requiring further investigations.

CHAPTER 2

LITERATURE REVIEW AND CONCEPTUAL FRAMEWORK

2.1. Introduction

Investigations into how runoff is generated and how water mobilises and transports chemical substances from different sources into the stream channels have become important to researchers, probably because their understanding can be useful for predicting and controlling aquatic pollution, and for diagnosing the health (quality) of the ecosystem for sources and characteristics of pollution (Christophersen et al, 1993; Elsenbeer et al, 1994; Elsenbeer, 2001; Liu et al, 2004; Sonneveld et al, 2006; Granger et al, 2010 a-b). Many studies (e.g. Penman, 1961; Hewlett and Hibbert, 1967; McDonnell, 2003; Fenicia et al, 2013) have however shown that the investigations into the runoff processes can be daunting because of the many uncertainties that surround the complexity of the hydrological systems. For example, an attempt to conceptualise a simple field-scale hydrological cycle suggested that such conceptualisation can vary with dominant soil, vegetation and land use, precipitation intensity and chemistry, among other factors (Figure 2.1).

For the typical clay-soil rich field, Figure 2.1 indicates that although groundwater can be rare, water can still flow through the hillslope as surface runoff and drain flow, such that the runoff chemistry can be altered. It also suggests that the precipitation chemistry can interact with the vegetation and soil properties, and the consequences of such interactions can be inferred in the runoff chemistry. Studies have shown that consensus about the approach and processes of runoff generation was also made difficult because of differences (and in some regions, complexity) in the dominant climate, topography, vegetation, soil characteristics and the underlying geology across the world (Dunne and Black, 1970; Bonell and Gilmour, 1978; Anderson and Kneale, 1980; Mack, 1989; Church, 1997; Averis, et al., 2004; Bilotta et al., 2007; Kechavarzi, et al., 2010). Other causes of complexity in the understanding of the runoff processes and generation are poor understanding of catchments' hydraulic and hydrologic processes, and the scale of investigations (Hewlett and Hibbert, 1967; Klemes, 1983; Elsenbeer, et al, 1995; Elsenbeer and Vertessy, 2000; Jones and Swanson, 2001; Pringle, 2003; Sivapalan, 2005).

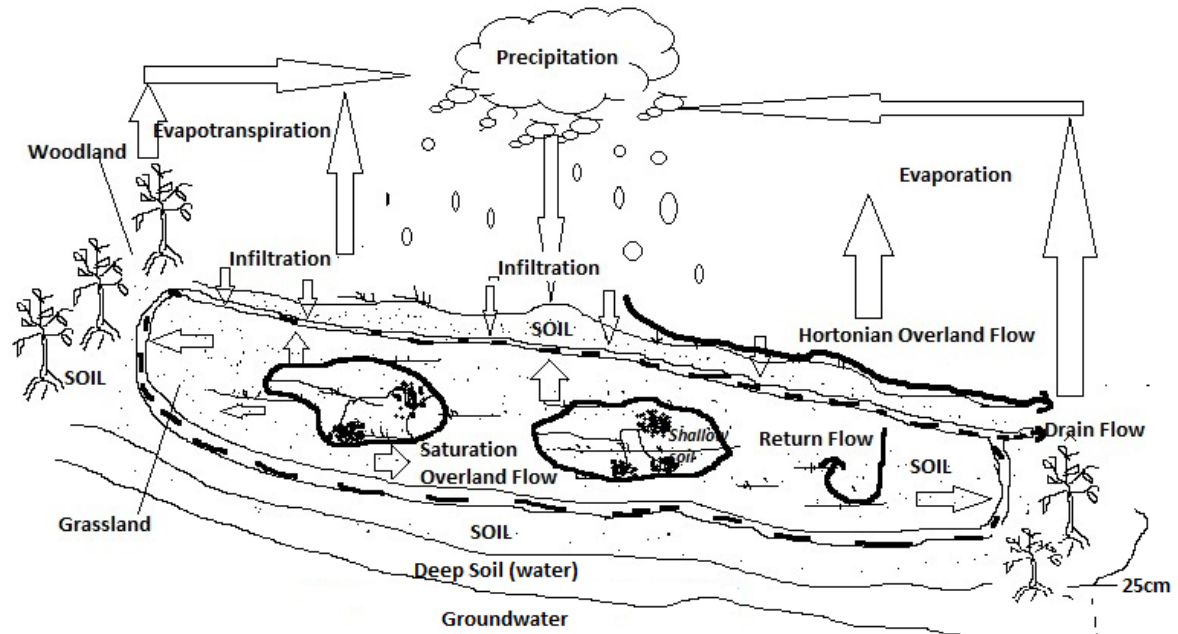


Figure 2.1. A simplified hydrological cycle for a clay-rich grassland farm: surface runoff (Hortonian Overland Flow, Saturation Overland Flow and Return Flow) and drain flow are identified. Unshaded arrow shows direction of flow of water, and shaded arrow indicate direction of runoff flow.

2.2. Flowpaths and the Generating Mechanisms

Runoff mechanisms can generally be grouped into the surface and subsurface processes as explained below:

2.2.1. Surface runoff

Studies generally accept two main hypothesis for explaining the concept of surface runoff, and they are the Hortonian concept of infiltration-excess flow (Horton, 1933) and the Hewlett's hypothesis of saturation-excess flow (Hewlett and Hibbert, 1967) (the other concepts such as the partial-area hypothesis, are not as acceptable as the two are). Both hypotheses are however selectively applicable because a range of processes can generate runoff from specific parts of the field, depending on many factors, including the soil type and relief characteristics, landuse, incident rainfall intensity and antecedent field wetness. In general, surface runoff can occur in either of two broad processes; infiltration-excess overland flow and saturation-excess overland flow. Dominant runoff in a location is usually a factor of physical factors (such as the dominant soil type,

topography, soil permeability and soil wetness) and certain human factors, including land use and management (Verheye, 1991; Al-Khudhairy et al, 1999; Western et al, 2002; Güntner et al, 2004; Liang and Uchida, 2014).

2.2.1.1. Infiltration-excess overland flow

The Hortonian overland flow (HOF) was proposed by R.E. Horton (Horton, 1933) to occur when rainfall intensity exceeds the infiltration capacity of the soil, leading to substantial surface runoff (Figure 2.2). Subsequent studies showed that the HOF can occur in paved and concrete surfaces, cultivated or heavily grazed areas underlain by heavy clayey soils, catchments with extensive rock outcrops and fields with high rate of organic matter decomposition (Pearce, 1976; Dunne, 1978; Anderson and Kneale, 1980, Church, 1997; Bryan, 2000; Ziegler et al, 2001; Kirkby, 2002; Ziegler et al, 2004; Bilotta, et al., 2007; Kechavarzi, et al., 2010). Runoff generated through the HOF mechanism acquires the chemical signature of the top soil only, but can be affected by land use and vegetation (Kirkby, 2002; Ziegler et al, 2004; Bilotta, et al., 2007; Kechavarzi, et al., 2010).

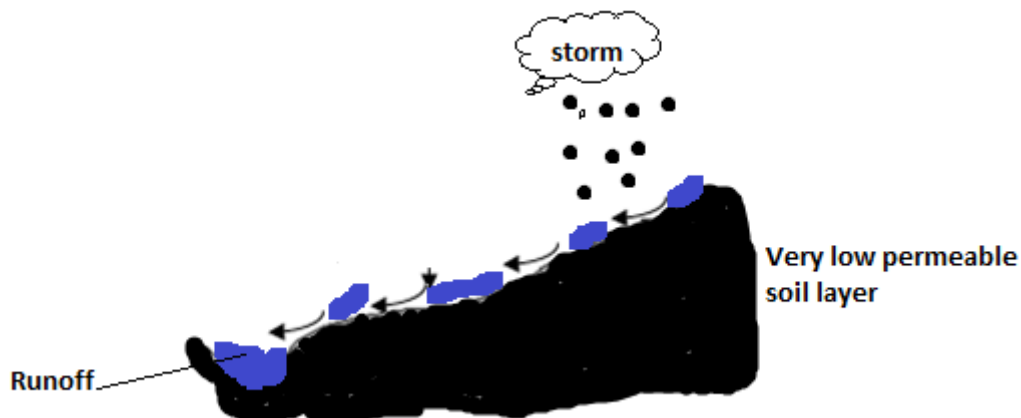


Figure 2.2. The Hortonian infiltration-excess flow occurs where the soil is impermeable and water is forced to flow downslope due to gravity. Water is represented with blue colour, and the impermeable soil with thick black.

Early studies on the partial-area infiltration-excess flow, PAF (Moldenhauer et al, 1960; Amorocho and Orlob, 1961; Betson, 1964) showed that small, localised part of a field may have actually contributed to overland flow (Figure 2.3), as against the notion of the HOF that overland flow is generated as a result of low soil permeability. The partial area is usually a small, but relatively consistent, part of the field that should only vary (expand or shrink) under 'unusual' complex land use change, change in soil's moisture storage

capacity and significant change in rainfall intensity (Beston, 1964). The assumption of the relatively consistent partial area was however challenged by subsequent studies, hence its ambiguity when subsequent studies showed that partial areas can respond to the effect of field wetness, contrasting topography and soil-boring organisms (Hewlett and Hibbert, 1967; Bonell et al, 1984; Van de Griend and Engman, 1985), and to the (Weyman, 1970; Bonell et al 1984). The idea of a 'flexible' partial area led to the development of the variable source area (VSA) concept that has been used to explain the saturation-excess runoff generating mechanism (Hewlet and Hibbert, 1967).

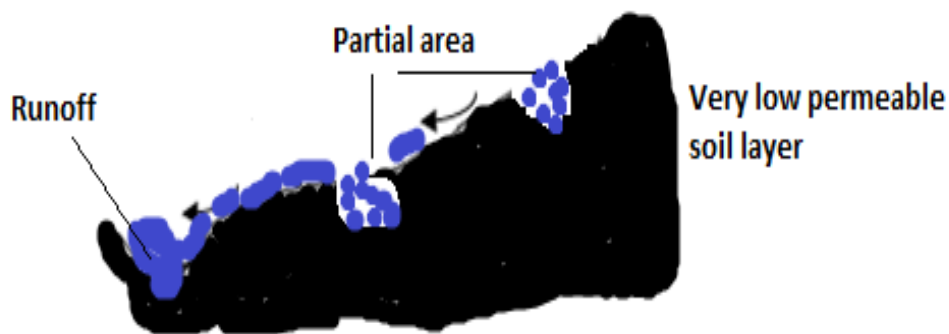


Figure 2.3. Partial area infiltration-excess flow. The partial area is usually a small and relatively consistent, part of the field that should only expand or shrink under 'unusual' complex land use change, change in soil's moisture storage capacity and significant change in rainfall intensity (Beston, 1964). Water is represented with blue colour and the impermeable soil with thick black.

2.2.1.2. Saturation-excess overland flow (SOF)

Investigation by many authors in the humid region (especially Hewlett and Hibbert, 1967; Kirkby, 1969; Dunne and Black, 1970) expanded the Hewlettian concept of the SOF. The SOF is known to occur as excess water after the soil is saturated, probably as a result of antecedent wetness, intense rainfall, near-surface water table or near-stream regions (Loague, 1992; Grady, 2001). As the soil saturates, new water mixes with the pre-event water, and once the soil becomes saturated and the water table reaches the earth surface, additional water flows as SOF. The process of SOF generation is explained by the VSA concept (Hewlett and Hibbert, 1967; Dunne and Black, 1970; Dunne, 1983, Loague, 1992; Grady, 2001; Schneiderman, et al., 2007). The VSA concept explains that runoff is generated by the expansion of small, locally variable water table (known as 'contributing areas') during storm condition (Figure 2.4).

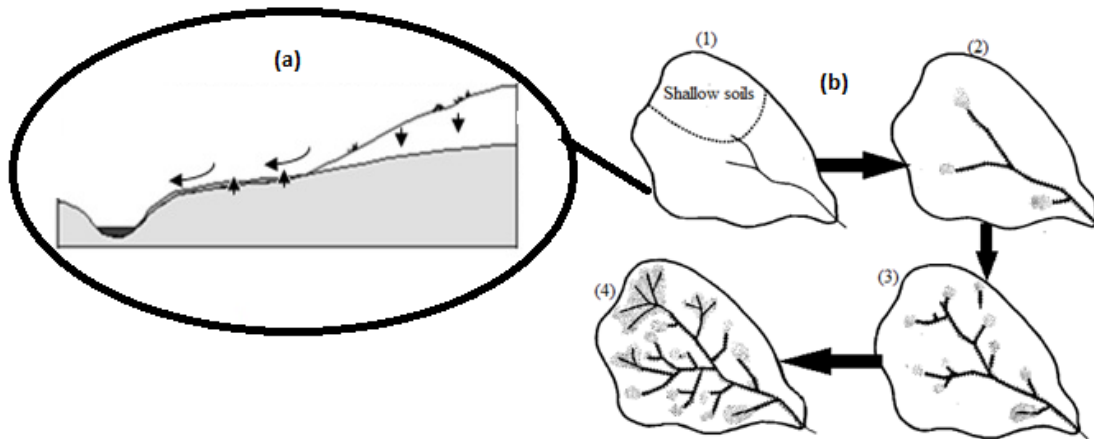


Figure 2.4. Simplified descriptions of saturation-excess overland flow (a) and the variable area concept (b). In (a) the arrow indicates the flow path while (b) shows the growing (expansion of saturated soils) of the contributing areas due to a storm event (1-4). Rate and extent of saturation is a subject of many factors including antecedent soil wetness, storm and field characteristics.

The SOF as runoff generating mechanism also include translatory flow and return flow. Translatory flow is generated when previously stored water in the soil (old or pre-event water) is released due to a push from the event (new) water (Hewlett and Hibbert, 1967). Return flow occurs when infiltrated water re-emerges at the surface before the water flows downslope due to the push by the event water or an encounter with a perched water table or an impermeable layer (Musgrave and Holtan, 1964; Sklash and Farvolden, 1979; Church, 1997; Chappell, et al., 2006). Determination of whether the water that finally emerges at the stream channel is a new water or old water, and therefore its transit time of the water has been major concerns of researchers in hydrochemistry for long (Hewlett and Hibbert, 1967; McDonnell, 1990; McGuire and McDonnell, 2006; McGuire et al, 2007; McDonnell et al, 2010; Soulsby et al, 2014). McGuire and McDonnell (2006) reviewed more than 32 studies on more than 50 catchments and in a conceptualised lumped parameter transit time modeling approach, and indicated that transit time modeling will provide significant advances in catchment hydrology and improvement in understanding physical runoff generation processes and solute transport through catchments. In general, the factors that can determine the dominant runoff mechanisms in any environment are conceptualised in Figure 2.5. These factors range from soil and slope conditions to the intensity of the storm.

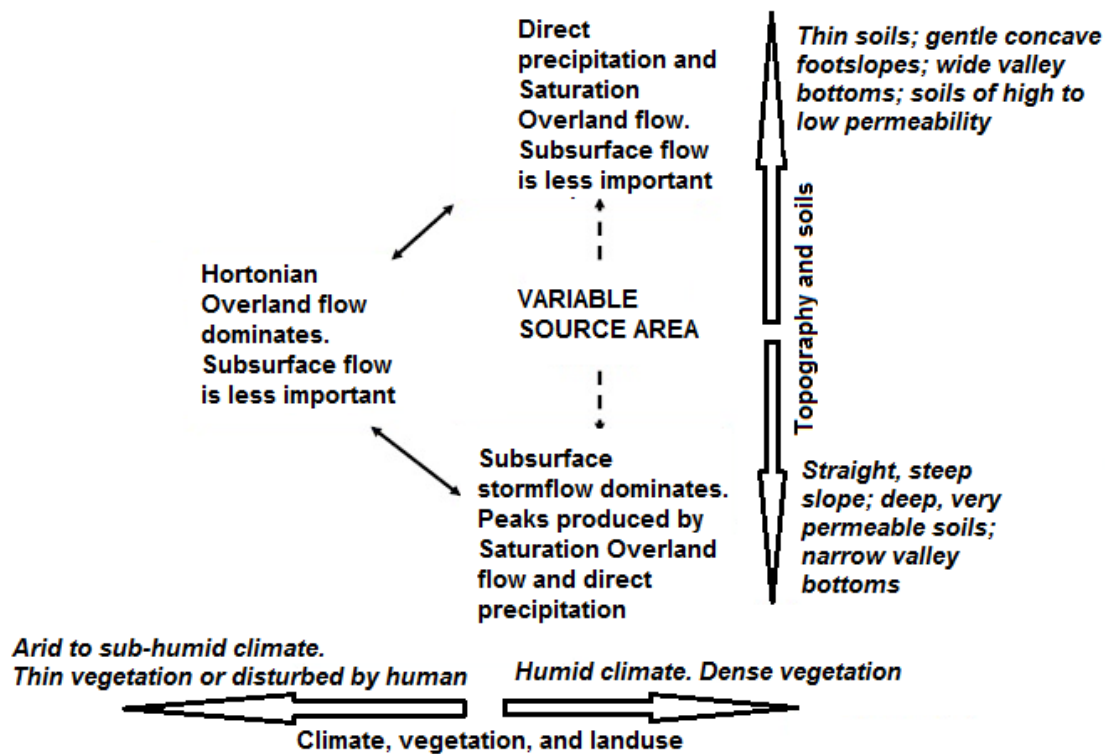


Figure 2.5. Conditions for the surface runoff generation (after Dunne, 1983).

In drained fields as in the present study area, and other regions across the world, the subsurface (including soil flow, drain flow and in some regions, groundwater) can be important. The subsurface flow in the heavy clay region can be mainly the preferential flow, and it is therefore explained below with other kinds of subsurface flow.

2.2.2. Subsurface flow (SSF)

Subsurface flow (SSF) is known to comprise the part of rainwater that infiltrates into the soil and flows underground into a stream channel. This includes the groundwater and soil water. The soil water can flow rapidly as lateral flow, when water encounters a less permeable layer at some depth in the soil or when near-stream water table rises and groundwater increases during a rainfall event (Bear, 1972; Dunne, 1983; Church, 1997; Hagedorn and Bundt, 2002). When SSF occurs in the soil layer, it is often referred to as interflow or throughflow. Hewlett and Hibbert (1967) describe the interflow as the part of the rainwater that moves rapidly as subsurface water into the stream channel. Water can move rapidly through the subsurface layer either as matrix flow or as preferential flow. Matrix flow refers to the relatively slow and even movement of water and solutes through saturated or unsaturated fine soil matrix pores

(Tsuboyama et al, 2010) while the uneven, rapid and saturated flow through a series of connected macropores, soil pipes, fractures and finger flow is referred to as the preferential flow (Beven and Germann, 1982; Dunne, 1983; Haria, et al., 1994; Hagedorn and Bundt, 2002).

The effect of macropores is attributed to the following conditions (Kneale, 1986; Hagedorn and Bundt, 2002; Beven and Germann, 1982; Figure 2.6):

- Pores (usually less than 0.5 mm in size) formed by soil micro fauna within the first 1 m of the soil profile;
- Pores caused by vegetation roots (with sizes varying with type and stage of vegetation growth), dead vegetation, including buried organic matter and rotten wood;
- Naturally occurring macropores caused by varying soil hydraulic conductivity, cracks and fissures (including those caused by desiccation, chemical weathering, soil weathering, drying and wetting of clays, freezing and thawing and pressure release);
- Artificial flowlines such as mole or tile drains which have been used on heavy soils to improve productivity of pastures and crops by removing excess water; underground drainage networks in peat soils (Hallard, 1988; Haria et al, 1994; Averis, et al., 2004, Fraser, et al., 2001, MacEwan, et al., 1992; Simard et al., 2000; Stone and Wilson, 2006).

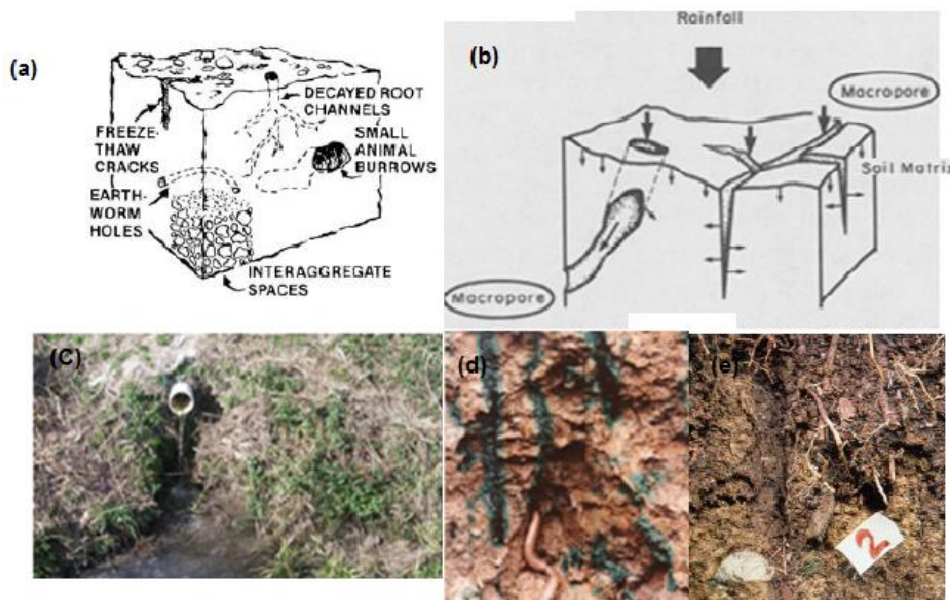


Figure 2.6 a-e. Preferential flow mechanisms (a) and (b): diagrammatic expressions of some preferential pathways. c-d are terrestrial images of a drain flow (c), macropores in a clay soil as traced with a dye (d), and decayed root channel within soil (e). (Source: USGS North Carolina Water Centre).

2.3. Chemical Characteristics of Hydrological Flowpaths

When water passes through and interacts with flowpaths, it is known to acquire chemical characteristics of the flowpaths, and as such can be distinguished (Whitfield and Schreier, 1981; Hooper et al., 1990; Church, 1997; McGlynn et al., 2003; Bishop et al., 2004; Burns et al., 2001; Zhang, et al., 2009; Brown, et al., 2010; Botter et al., 2011). The conditions encountered by water originating from different catchment sources while flowing to the stream control biogeochemical transformations that ultimately determine stream water chemistry (Bishop et al., 1990; Bonell, 1993; Ali et al., 2012). Runoff chemistry is therefore often partitioned by how high or low its chemical constituents are when it emerges at the stream channel or point of sampling to provide insights into its flowpaths and source areas. Water is generally classified as 'old' and 'new' or 'pre-event' and 'event' waters (Sklash and Farvolden, 1979; Dewalle, et al., 1988; Turton et al., 1995; Davies and Evans, 1998; Collins et al., 2000; Lee and Krothe, 2001; Shanley et al., 2002). The old or pre-event water is the soil water (and groundwater, (where it exists)), which is considered to be chemically conservative and makes up the contribution of runoff at baseflow, or water stored in the soil *prior* to a storm-event that is considered to exhibit higher concentration of certain chemical constituents than the new or event water while the new or event water is the most recent water in the catchment, typically water contribution from precipitation or throughfall (Evans and Davies, 1998; Rose, 2003).

Many studies on hydrochemistry have noted that it is important to understand flow sources within a field for adequate understanding of its dominant hydrological pathways (Cirimo and McDonnell, 1997; Holko and Lepisto, 1997; Perakis, 2002; Liu et al., 2004; Freeman et al., 2007; Pringle, 2003; Stieglitz et al., 2003; Bracken et al., 2013; Lofts et al., 2013). Most of these studies (especially Freeman et al., 2007; Stieglitz et al., 2003; Bracken et al., 2013; Lofts et al., 2013) have showed that the link between the precipitation chemistry and soil stores can be significant to the understanding of flow connections. Certain precipitation (such as intensity, rate, volume and chemistry) and soil characteristics (especially the physio-chemical) (invariably accounted for by land use) have been used (explicitly or implicitly as variations in soil moisture or soil rewetting) to provide quantitative explanations to nutrient runoff in the predominantly rain-fed soils (Krueger et al., 2010) of the study area

(North Wyke), in drained fields and some other clayey soil fields in England (Elliott et al, 1990; Heathwaite and Burt, 1991; Armstrong et al, 2005; McDowell et al, 2001; Chatskikh et al, 2005; Morecroft et al, 2009; Blackwell et al, 2009; Blackwell et al, 2013).

2.3.3. Precipitation chemistry

Changes in precipitation chemistry often occur within and between storm events, and runoff chemistry varies frequently with discharge (Cresser et al, 1987; Rees et al, 1989; Reiter et al, 2013; Ulrich et al, 2013). Precipitation chemistry is regarded as significant in hydrochemical studies because precipitation impacts significantly on the mobilisation of chemical ions in the ecosystem and can cause important changes in the water quality of adjacent streams (Reynolds et al, 1984, 1997; Cerny et al., 1994; McDowell et al, 2013; Miller and Zegre, 2014; Evans et al, 2014). Recent studies have attributed the acidification of surface water and decrease in the population of wet heathlands species (*Erica tetralix* by about 10% in a 5-year period) in northern England to the negative effects of precipitation deposition in the area (Damgaard et al, 2014; Evans et al, 2014). Cresser and Edward (1987) also showed (in a study of podzol soils in Scotland) that the runoff pH can be altered during a storm event by the mobilized chemical ions in the field. Previous studies on precipitation chemistry in the United Kingdom showed that rainfall chemistry exhibits spatial variation caused by effects of industrialisation, urbanisation, commercialisation, meteorology and atmospheric transport patterns (Cape and Fowler, 1984; Irwin and Williams, 1988; Reynolds et al, 1984, 1997; Beverland et al., 1998; Avila and Alarion, 1999; Irwin et al., 2002; Fowler et al, 2004, 2009). Some of these studies also showed that the knowledge of the relationship between the rainfall chemistry and runoff chemistry can be useful in the understanding of contributing sources chemical variables in field hydrology (Smart et al., 1998; Hutchins et al, 1999; Curtis et al, 2014).

2.3.4. Soil physio-chemical characteristics

Many reasons have been advanced for determining the spatial variability of the soil's physiochemical properties, and these include seeking to understand the pattern of variations of these properties with change in land use and various effects of different land management (Goovaerts, 1991; Conant et al, 2001;

Kellman and Hillaire-Marcel, 2003; Diekow et al, 2005; Peukert et al, 2012). It is also important to understand the sources of various contaminants under a specified land use (Arnold and Allen, 1996; Arnold et al, 1998; Kellman and Hillaire-Marcel, 2003), and rate of targeted or potential material fluxes from agricultural fields (Glendell and Brazier, 2014; Glendell et al, 2014). In addition, the spatial variability of soil properties is still poorly understood (Bilotta et al, 2007; Peukert et al, 2012), probably because many physiochemical properties vary continuously over space; such that only variability over short distances is low (Marriott et al, 1997). Adequate understanding of contamination sources and solute transfer in agricultural fields therefore requires knowledge of the spatial variability of the material loads, and studies showed that analytical procedures such as geostatistics (Webster and Butler, 1976), multivariate analysis and geoinformation-based descriptive mapping (Goovaerts, 2001) can be useful to achieve this.

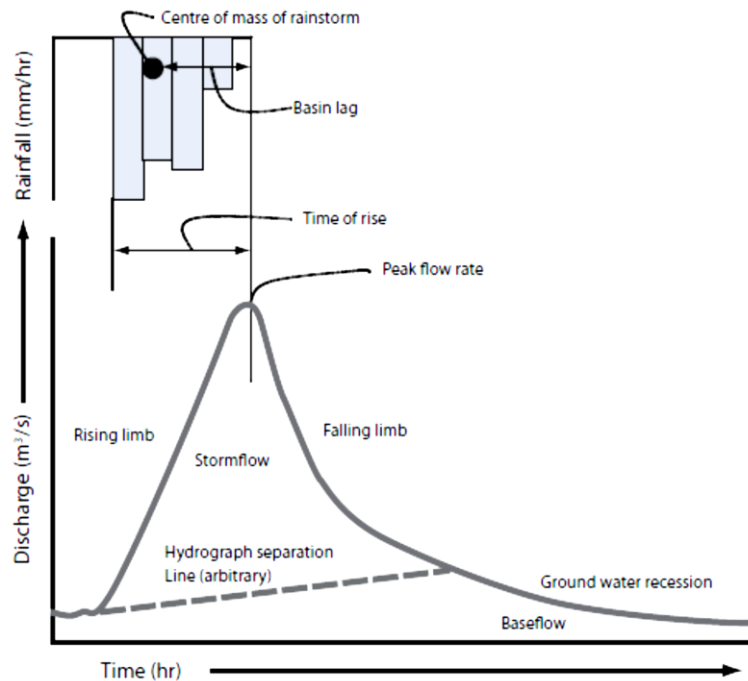
2.4. Development in Hydrograph Separation Techniques

Investigators have adopted the classification of runoff based on its chemical properties as a development over the earlier method of graphical delineation of flow (Sherman, 1932; Singh, 1976) that is fraught with challenges of being arbitrary and significantly subjective (Hewlett and Hibbert, 1967). Studies that have adopted the graphical delineation technique (known as graphical hydrograph separation technique) assumed that the overland flow was dominant in all catchments (Hooper and Shoemaker, 1986) whereas studies under some other catchments where climate is more humid and soil is permeable have shown that water that have been stored in the near-stream region of the catchment *prior* to rainfall get displaced and reach the stream channel first before the overland flow (Hewlett and Hibbert, 1967). While the method of delineating the flow components was immersed in controversies, the principle of the hydrograph as the graphical illustration of the variation of water flow over a period of time and at a particular point of measurement is well accepted in the literature (Information about a hydrograph is presented as Box 2.1). Table 2.1 shows a simple classification of existing approaches to hydrograph separation (including the graphical, chemical and modelling (mathematical) approach), as provided in literature.

Box 2.1. A hydrograph and its structure.

What is a hydrograph?

The hydrograph is a graphical illustration of the variation of water flow over a period of time at a particular point of measurement (Figure 1).



Box 1. A hydrograph. Above (bar graph) is the rainfall intensity graph of the corresponding part of the hydrograph.

A hydrograph shows how flow changes in response to a rainfall event, for single or cumulative events, and can provide information on the integration of climate and catchments' physiographic characteristics. The structure or shape of a hydrograph can reflect the processes and activities within the catchment for which, and as at the time, is recorded (Sherman, 1932; Hewlett and Hibbert, 1967; Robert and Klingeman, 1970; Black, 1997; Jakeman et al, 1990; Yue and Hashino, 1999; Sujono et al, 2004; Tetzlaff et al, 2010; Hoeg et al, 2010). Black (1977) noted that a hydrograph can reflect the size and activities of source area, such as increase or decrease in soil saturation and saturation-excess flow, as well as landuse change within the catchment. In addition, using a laboratory experiment of simulated rainfall, Roberts and Klingeman (1970) had showed that the shape of a hydrograph can be affected by certain hydrologic and geomorphic factors, especially rainfall intensity, rainfall duration, storm movement, permeability and antecedent moisture conditions. In general, basin or catchment's size, soil, vegetation, landuse, topography and drainage characteristics, climate elements and time are factors that can affect the shape of a hydrograph (Robert and Klingeman, 1970).

Table 2.1: Basic hydrograph separation techniques and their descriptions.

Approach		Explanation
Graphical technique		The graphical technique was one of the earliest methods of hydrograph separation techniques and it prevailed between 1930 and 1960s. It involved arbitrarily separating the flow components into quick-response runoff and base flow. The quick-response runoff or quick flow is a mixture of the overland flow and lateral flow or interflow. Hewlett and Hibbert (1967) regarded the graphical technique as 'one of the desperate analysis techniques use in hydrology' and Freeze (1972) argued that the technique 'appears to be a little more than a convenient fiction'. The graphical technique is also limited because the delimitation of quick flow and base flow is often subjective, and can infer very limited water components. The concept of interflow using this graphical technique has also been questioned (Hewlett and Hibbert, 1967; Kuusisto, 1982). The method is still nonetheless used by engineers, and can be a basis for comparing catchments (Burns and Vitvar, 2001).
Mass-balance equation and End-Member Mixing Analysis approaches	Chemical hydrograph separation	Consequent on the inability of the graphical technique to capture most flow components, and its subjective approach to delimiting the one that can be captured, the use of chemical tracers was advanced. This technique is based on the mass-balance equation $Q_t C_t = Q_1 C_1 + Q_2 C_2 \dots Q_n C_n$ (2.1). Where $C_t, C_1 \dots C_n$ are concentrations of solutes or any chemical variable in the total storm runoff and its assumed components, $Q_t, Q_1 \dots Q_n$ are the corresponding discharge rates (Ogunkoya and Jenkins, 1993). The approach assumes that (a) the chemical tracer used is conservative; meaning that tracer does not change its chemical identity during the course of its journey down slope (downstream) and (b) that the tracer must be uniquely attached to a source (atmosphere, soil and groundwater) (Ritchie and McHenry, 1990; Christophersen et al, 1992; 1993). Solute are however, often, not truly conservative- and can at best be 'quasi-conservative' (Richey et al, 1998). Solute can be affected by vegetation influence, evaporation and dilution- and within-storm's flushing effects. Subsequently, the search for truly conservative tracers has resulted to the use of isotopes and artificial tracers.
	Isotope Hydrograph separation	Delimiting flow compositions and providing insights into sources of runoff have made significant progress with the use of isotopes. The use of isotope has made it possible to detect the origin of runoff (Kuusisto, 1982; Payne, 1988). The use of isotope showed that (a) soil water composition can be distinct from the chemistry of groundwater (Ogunkoya and Jenkins, 1983), (b) Isotopes can be combined, complementarily, with solute; such that one can be effective when conditions for the other is uncertain (Hooper and Shoemaker, 1986), and (c) age of water can be determined to infer how long the water has remained in the soil before it is released (Kuusisto, 1982; Richey et al, 1998). However, isotopes can be fractionated by temperature change and vegetation influence, and are therefore not conservative in the real sense (Ball and Trudgill, 1997; Burns et al, 2001). Isotopes can also be expensive to determine in many catchments, especially in developing countries. Both solutes and isotopes have also raised further questions as on how best to conceptualise a catchment's response to rainfall, the effect of stores and reservoirs and implications on the mass-balance equation (input-output response) assumption (McDonnell, 2003). Other issues that have been raised include the Kirchner (2003)'s double paradox questions on the contrasting behaviour of catchment concerning water storage and release during storm event; heterogeneity in catchment properties and location, and effect of model assumptions.
Mathematical models of rainfall-runoff relationship		Many mathematical models of rainfall-runoff relationship have evolved as attempts to understand catchment behaviour improves, especially from runoff hydrographs and as accessibility to computing improve (Todini, 1988; Hromadka, 1990; Singh, 1995; Singh and Woolhiser, 2002). These models are many but the fact that there is currently no universally accepted approach to model catchment behaviour (Hromadka, 1989) or provide a scientific holy grail model (Beven, 2006a) shows that a purely deterministic solution has not been found. Technology employed in the past few decades with computer models have also increased, and the models have become increasingly complex in detail of describing the catchment's hydrologic and hydraulic processes; and in terms of accuracy too (Lischeid, 2008; Beven, 2006b; Krueger et al, 2010).
Coupling of existing models with advances field knowledge offer by improved technology		As a result of the modelling difficulties of the older approaches, it has been suggested that previous approaches can be coupled with advanced knowledge of catchment behaviour that is offered by the current advances in information technologies for better confidence (Hromadka, 1990; Sign and Woolhiser, 2002).

The arrow shows direction of development, sophistication and complexity.

2.4.1. Chemical and isotopic hydrograph separation techniques

The use of the certain chemical and isotopic models to infer information on flowpaths from hysteresis in concentration-discharge relationship for many catchments have suggested that the models can be important to hysteretic modelling (Evans and Davies, 1998; Chanut et al, 2002; Hornberger et al, 2001). The most commonly investigated models are the mass balance and end-member mixing analysis (EMMA), and these are explained below. Many models are also case-specific, and most of these have been classified as mathematical modelling approaches because of their nature.

2.4.1.1. The mass balance model

One of the earlier techniques by which runoff chemistry was investigated was a hydrograph separation based on the mass balance model (Pinder and Jones, 1969). Pinder and Jones (1969) had used a mass balance equation (equations 2.2 and 2.3) to relate total, direct, and groundwater runoff from pre-event and event water samples in three small catchments in Nova Scotia.

$$Q_{total\ water} = Q_{pre-event\ water} + Q_{event\ water} \quad (2.2)$$

$$\frac{Q_{pre-event\ water}}{Q_{total\ water}} = \frac{(C_{total\ water} - C_{event\ water})}{(C_{pre-event\ water} - C_{event\ water})} \quad (2.3)$$

Where Q is discharge and C is the concentration of some tracer.

Using this approach, 'event' water is generally represented by precipitation or throughfall and 'event' water by groundwater assumed equivalent to the resident water prior to an event (Dewalle et al, 1988). The mass balance approach to hydrograph separation was found applicable to many catchment studies (Hooper and Shoemaker, 1986; Caine, 1989; Hendershot et al, 1992; Elsenbeer et al, 1995). The mass balance approach assumes that selected tracers behave conservatively; that is they do not participate in any chemical reactions along their flow paths (Elsenbeer et al, 1995). The mass balance model was also known as a two-component model because it assumes pre-event and event water as the main components of the total water, and combines soil and groundwater into pre-event (or old) water component by assuming that soil water contribution is minor or chemically equivalent to groundwater (Sklash and Farvolden, 1979; Dewalle et al, 1988; Ogunkoya and Jenkins, 1993).

Investigations from a number of catchments encouraged the mass balance approach to be expanded to three or more components, in which either the discharge of one of the components is known or when two tracers are used simultaneously (Dewalle et al, 1988; Ogunkoya and Jenkins, 1991; Hinton et al, 1994; Merot et al, 1995; Richey et al, 1998; Lee and Krothe, 2001). A three-component model distinguishes the water into different sources, such as soil water, groundwater and channel precipitation (equations 2.4 and 2.5).

$$Q_{\text{total water}} = Q_{\text{ch.precipitation}} + Q_{\text{soil}} + Q_{\text{groundwater}} \quad (2.4)$$

$$\frac{Q_{\text{soil}}}{Q_{\text{total water}}} = \frac{(C_{\text{total water}} - C_{\text{groundwater}})}{(C_{\text{total water}} - C_{\text{soil}})} - \frac{Q_{\text{ch.precipitation}}}{Q_{\text{total water}}} \times \frac{(C_{\text{ch.precipitation}} - C_{\text{groundwater}})}{(C_{\text{soil}} - C_{\text{groundwater}})} \quad (2.5)$$

Where Q and C are discharge and chemical concentrations, and *ch.precipitation*, *soil* and *total water* are channel precipitation, soil water and total flow, respectively (Dewalle et al, 1988)

The mass balance approach is capable of identifying the sources of the water in the catchment, but it is known to be limited in the capacity to identify the mechanisms of runoff generation or elucidate the flow paths of the water (Elsenbeer et al, 1995). The limitation apparently led to the credence for another method. The end-member mixing analysis which evolved thereafter is described below:

2.4.1.2. End-member mixing analysis

The end-member mixing analysis (EMMA) technique evolved in the 1990s (Christophersen et al, 1990; Hooper et al, 1990) to predict proportions of contributing sources (Elsenbeer et al, 1995; Ali et al, 2012). The EMMA assumes a mixing model, which suggests the stream water is a mixture of sources, such as soil water from various depths and groundwater. The contributing sources that eventually mix to constitute the stream water chemistry are called the 'end-members' (Elsenbeer et al, 1995). The mixing model assumes that chemical signatures of end-members are time-invariant; that is, the output does not explicitly depend on time (Hooper, 2001; James and Roulet, 2006).

Unlike the mass balance approach, EMMA relies on the solution of a constrained linear least squares estimation problem, and its estimation is based on the principle of the principal component analysis (PCA) (Christophersen et

al, 1990). The PCA was primarily formulated by Pearson (Pearson, 1901) to find 'lines and planes of closest fit to systems of points in space', and has for a long time been found useful to provide approximation of multivariate datasets (Wold et al, 1987; Abdi and Williams, 2010). The PCA has also been found applicable to water quality analysis, and the proponents of EMMA approach have found it applicable to analyse their data (Hooper and Shoemaker, 1986; Hooper, 2003). Hooper (2003) provided a diagnostic tool for EMMA for a general mathematical formulation in which eigenvector and residual analyses of observed stream water chemistry can be used to estimate the appropriate number of contributing end-members. The diagnostic EMMA tool therefore enables end-members, sampled in the field, to be screened for their ability to fit into the PCA mixing space (the multidimensional space obtained from the PCA of observed stream water chemistry) (Hooper, 2003; James and Roulet, 2006).

Both mass balance and EMMA approaches share the assumption that selected tracers are conservative. Other known assumptions of the EMMA are that the chemistry of different end-member are distinguishable; and that the chemical identity of each water course is maintained throughout an event (in transit from the source to the discharge point), but is only altered during mixing in the channel (Hooper and Shoemaker, 1986; Gremillion et al, 2000; Ladouche et al, 2001). Studies have also shown that both mass balance and mixing model approaches are useful in catchment hydrology, because as they allow the relative contributions of different sources to streamflow to be inferred and quantified by using small-scale, internal catchment measurements (e.g. groundwater and soil water chemistry) to explain complex catchment responses (Ogunkoya and Jenkins, 1993; Elsenbeer et al, 1995; Genereux and Hooper, 1998; Hooper, 2001, 2003; James and Roulet, 2006; Ali et al, 2010).

Nonetheless, the mass balance and EMMA approaches are at best described as 'black-box' models which do not require explicit understanding of the internal conditions of the catchment (Todini, 1988; Elsenbeer et al, 1995). On the other hand, the internal system of a catchment can be complex, and the complexity may cause sufficient heterogeneity in what can happen to water after rainfall or the mechanisms of water flow in the catchment (Hromadka, 1990; Beven, 2001, Kirchner 2003; Krueger, et al., 2012).

2.4.1.3. Mathematical modelling approaches

A number of models have evolved over the years to explain the rainfall-runoff relationship in catchments. These are well documented in literature, including Singh, 1995; Arnold et al, 1998; Singh and Woolhiser, 2002; Hromadka, 1990). A number of criteria have been used to classify the models; these include complexity (difficulty or reliability of model calibration; Beard and Chang, 1979; Hromadka, 1990), assumptions of linearity (or non-linearity), scale of application and amount of data required for model calibration (Hromadka, 1990; Singh and Woolhiser, 2002).

While models can vary in their complexity in terms of parameters, Hromadka (1990) noted that it is not well established whether complex models provide an increase in accuracy or not. A study of six models and three variants of two of the models in an urban catchment in California, USA concluded that 'the more complex models did not produce better results than the simple models...' (Abbott, 1978; Krueger et al, 2010). In addition, the tendency to increase uncertainties with too small or too large parameters in models have been a subject of focus in Bayesian statistics (Reichert and Omlin, 1997). It has been noted that over-parameterisation of models does not guarantee their success or better performance than the models that are not over-parameterised, but much information can be lost when the number of parameters is too few (Gaume and Gosset, 2003; Kirchner, 2006). In addition, Pilgrim (1986) argued that 'simple nonlinear models fitted by data from events covering the whole range of flow may give gross errors when used to estimate large events' and that 'only relatively high flows are generally considered in the derivation of unit hydrographs or other response parameters, and this is the region of approximate linearity'.

In summary, the problems associated with the poor understanding of catchment behaviour have been addressed by trying to understand the complexity of the catchment system. The catchment system is a complex one, and this complexity has undermined the ability to conceptualise it appropriately or find an all-emcompassing model ('scientific Holy Grail'; Beven, 2006 a-b) for predicting its behaviour (Bloschl, 2006, Tetzlaff et al, 2008; Fenicia et al, 2013). The space- and time-scales in which investigations are carried out in catchment hydrology are also diverse. Tetzlaff et al (2008) described the catchment as a bio-physical system with a history of constantly evolving and

changing transient features in the landscape. The catchment has also been regarded as a complex adaptive system, which can exhibit self-organising structures. The structure of the catchment can be influenced by the flows of water and state of its storage (Sivapalan, 2005; Wagener et al, 2007). In addition, the methodological challenges to modelling the catchment are still not sufficiently met, especially because of the aforementioned problems of complexity and diverse timescales of investigations (Hewlett and Hibbert, 1966; Todini, 1988; Arnold et al, 1998; Beven et al, 1995; Beven, 1997; Singh and Woolhiser, 2002; Sivapalan, 2009; Fenicia et al, 2013).

2.4.2. Hysteresis modelling

Hysteresis occurs when the state of an ecosystem depends strongly on its previous history, such that the critical condition under which a system switches from one stable state to another is different from the condition that will allow the system to return to the original state (Prowse, 1984; Andrea et al, 2006; O'Kane, 2005; Moravcová et al, 2009; Eder et al, 2010). It is important in the analysis of concentration-discharge (c-q) relationships because such relationships are rarely linear, and any form or pattern the relationship exhibit can also provide information about the prevailing hydrological processes and flowpaths (Johnson and East, 1982; Prowse, 1985; William, 1989; Evans and Davies, 1998; House and Warwick, 1998; Blackwood et al, 2012). Hysteresis has been long noted in concentration-discharge (c-q) relationship when solute and sediments concentrations vary systematically with respect to rising and falling limb discharge on the storm hydrograph (Toler, 1965; Arnborg et al, 1967; Johnson and East, 1982; Prowse, 1985). It results to an occurrence of a non-unique solute concentration for a given value of discharge, often due to factors, including variation in rain intensity, nature of runoff, nature of targeted transported (physical or chemical) materials, interactions between the targeted material, precipitation, soil, vegetation and other components of the environment (William, 1989; Evans and Davies, 1998; House and Warwick, 1998; Rose, 2003; Bowes et al, 2005; Andrea et al, 2006; Krueger et al, 2010; Eder et al, 2010; Jiang et al, 2012).

2.4.2.1. Applications of concentration-discharge hysteresis models

Hysteresis loop patterns have been used, often in conjunction with supporting evidence, to delineate source area contributions of dissolved and solid materials to stream flow, to infer geochemical processes that affect storm water quality, to discern mixing processes as they occur before, during, and after storm events, assess field or catchment's hydrological behaviour and examine different runoff processes, among other applications (Prowse, 1984; William, 1989; Evans and Davies, 1998; House and Warwick, 1998; Rose, 2003; Haygarth et al, 2004; Hornberger et al, 2001; Andrea et al, 2006; Eder et al, 2010; Krueger et al, 2012). Ebel et al (2010) from a study of the 3D variably saturated subsurface flow simulation of the Coos Bay 1 experimental catchment in the Oregon Coast Range, USA examined hysteretic effects on hydrologic response along a slope and showed that hysteresis occurred as a result of wetting and drying of the soil water. Ebel et al (2010) concluded that slope conditions and prediction of slope stability can be underestimated without considering hysteresis. Ivanov et al (2010) provides an extensive review of hysteresis in soil water response, and investigated soil moisture spatial variability resulting from varying topography and vegetation using the Biosphere 2 facility (a large-scale Earth science facility with a variety of opportunities for in situ experiments at Tucson in the USA). Their study showed that hysteresis is inherent in mean state of the soil moisture distribution system, and that variability in soil properties caused by variation in the soil hydraulic property may account for a significant proportion of the spatial heterogeneity of soil moisture and hydrological response. Ivanov et al (2010) attributed the occurrence of hysteresis in the temporal variability of soil moisture to the soil's initial state of wetness, rainfall magnitude, wetting and drying controls. In addition, Bowes et al (2005) studied the phosphorus (phosphorus, particulate phosphorus and soluble reactive phosphorus) concentration–discharge hysteresis from 10 storm events at 3-h intervals for three points along the River Swale in North Yorkshire, UK. Bowes et al (2005) showed that most phosphorus-discharge hysteresis changed down the river continuum, with the upland catchment producing 'anticlockwise hysteresis' and the downstream producing 'clockwise hysteresis', and attributed this pattern to the effect of intensifying land use and reduced sediment particle and change in phosphorous source, downstream.

Earlier studies (such as Walling and Foster, 1975; Walling and Webb, 1980; Hill, 1990) also showed that a 'lag effect' (where changes in solute concentrations do not directly coincide with the dilution effects of storm runoff) can produce anticlockwise hysteresis loops. Walling and Webb (1980) explained the clockwise pattern of the specific conductance-discharge hysteresis in the River Exe in England in terms of variable source area contributions during the course of a storm, and inferred that 'clockwise hysteresis' was the result of groundwater contributions from distal tributaries. In general, most published studies on concentration-discharge hysteresis have either focused on suspended solid concentrations (Wood, 1977; Walling and Webb, 1982; Klein, 1984; Williams, 1989; Asselman, 1999; Lenzi and Marchi, 2000; Jansson, 2002) or on solutes in streams (Bond, 1979; Walling and Webb, 1980; McDiffett et al., 1989; House and Warwick, 1998; Evans and Davies, 1998; Andrea et al, 2006), while only a few have been undertaken at farm scale level (Kronvang et al, 1997; Krueger et al, 2009; Krueger et al, 2012).

2.4.2.1. Hysteresis models and interpretations

Hysteresis modelling has been approached with different methods by many authors. For example, studies (e.g. Ebel et al, 2010; Ivanov et al, 2010) have assessed retention curves of soil water at different wetting and drying stage to examine hysteresis while some others (e.g. Foster, 1978; Walling and Webb, 1980, 1986) have used derived regression relationships (power functions) between solute concentration and discharge, and sometimes distinguished seasonal trends. Some of these approaches, especially the use of regression, have been challenged, especially that it is generally recognised that different hydrological responses occur because of variations in storm characteristics (rainfall amount and intensity) and antecedent soil moisture conditions (O'Connor, 1979; Muscutt et al., 1990; Avila et al., 1992; Jenkins et al., 1994; Soulsby, 1995; Biron et al, 1999; Brown et al, 1999; Welsch et al, 2001; Weiler and McDonnell, 2006), which often occur with different storm event conditions. Johnson and East (1982) identified other causes of variations in concentration-discharge hysteresis to include variations in the antecedent accumulation of dissolved materials, dissolved materials in precipitation, meteorological conditions and conditions affecting the hydrological flow (also Taylor and Pierson, 1985; McDonnell et al, 1991; Wheeler et al, 1991; Coulthard et al,

2005; Fryirs et al, 2009; Sorriso-Valvo et al, 1995; Garcia-Ruiz et al, 2005; Luce, 2003; Lewin et al, 2005; Van der Velde et al, 2010; van Balen et al, 2010).

Review of studies published since year 1998 suggests that studies on concentration-discharge hysteresis are often hypothesised based on hydrograph separations and mixing model assumption (Evans and Davies, 1998's hypothesis) (e.g. Evans et al, 1999; Hornberger et al, 2001; Rose, 2003; Andrea et al, 2006), mathematical modelling-based mass-balance equations (House and Warwick, 1998 hypothesis) and its modified form with analysis of data uncertainties (Krueger et al, 2009; Krueger et al, 2010; Eder et al, 2010) or farm-focused concentration-discharge relationship based on a simple decision tree (Haygarth et al, 2004). Although these concentration-discharge hypotheses were formulated on specific dissolved or solid loads (phosphorus; Haygarth et al (2004); phosphorus, Krueger et al (2009); sediments and phosphorus, Davies and Evans (1998); dissolved solids), their applications are not limited to these variables. Evans and Davies (1998)'s hypothesis 'benchmarked' (Rose, 2003) the interpretation of concentration-discharge plots by modeling variable contributions of ideal two-component ('pre-event' and 'event' water) and three component (ground water, soil water and event water, where applicable) mixtures and devised a nomenclature describing the rotation, curvature, and trend of the resulting hysteresis loops (Figure 2.7).

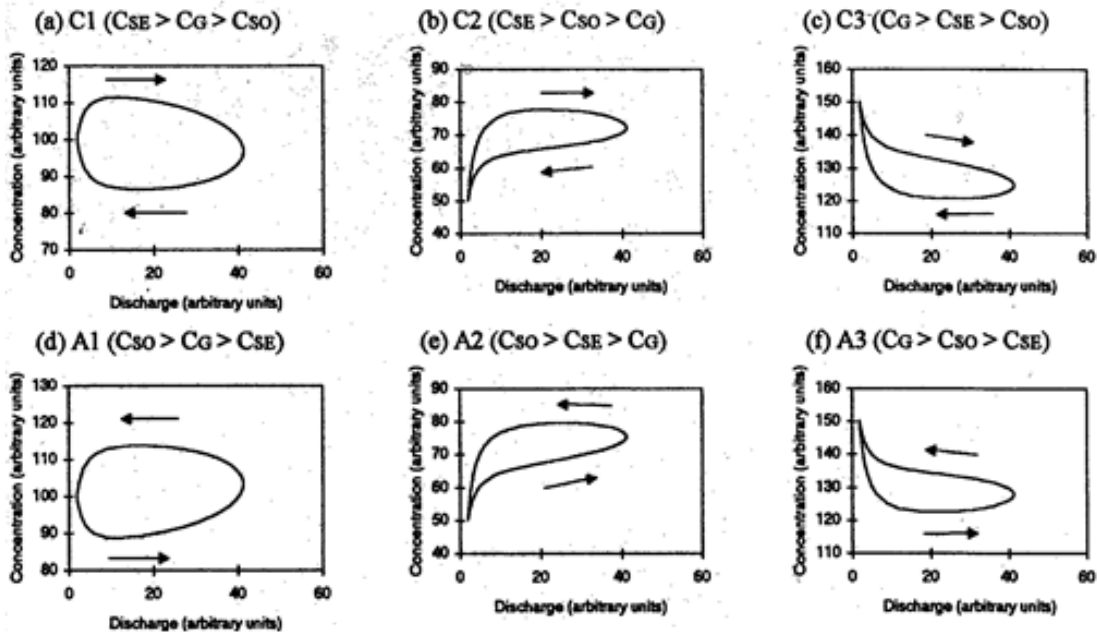
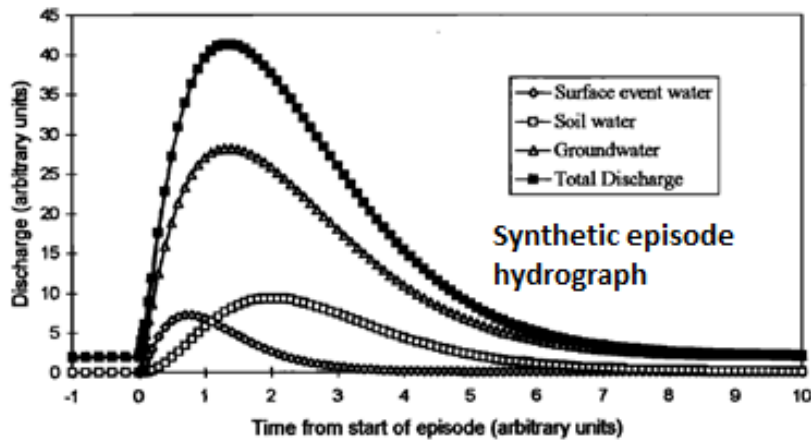


Figure 2.7. Concentration-discharge hysteresis plots (below) and its episodic hydrograph (above). C_{so} represents concentration in soil water, C_{SE} represents concentration in surface event and C_G represents concentration in groundwater (where applicable). In terms of variations in plot patterns, C represents 'Clockwise direction' while A represents 'anticlockwise direction'. In terms of plot' slope, C1, C3 and A1 exhibit convex slope while C2, C3, A2 and A3 exhibit concave slope (Evans and Davies, 1998).

Concentration-discharge relationships based on Figure 2.7 accept the assumptions of concepts of the mixing model and mass balance equation for chemical and isotope hydrograph separation technique (see Table 2.1). assumptions of the mixing model as provided in studies (e.g. Sklash et al, 1976; Sklash and Farvolden, 1979; Moore, 1989; Buttle,1994; Klaus and McDonnell, 2013) are that (i) the chemical or isotopic content of the event and the pre-event water are significantly different, (ii) the event water maintains a constant chemical or isotopic signature in space and time, or any variations can be

accounted for, (iii) the chemical or isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for, (iv) contributions from the vadose zone must be negligible, or the chemical or isotopic signature of the soil water must be similar to that of groundwater, and (v) surface storage contributes minimally to the streamflow. Klaus and McDonnell (2013) provides a critical examination of the isotope hydrograph separation studies, the mixing model and the various studies on them since 1960 to their publication, and showed that at least three of the aforementioned assumptions of the mixing models (assumptions ii-iv) have been vigorously challenged by recent studies.

Krueger et al (2009) introduced an empirical hysteresis concept (equations 2.1-2.3) to estimate sediment-discharge relationship. Equations 2.1-2.3 were previously explored by House and Warwick (1998) to describe solute dynamics in rivers (Eder et al, 2010).

$$y = f_1(x) + f_2(x') \quad (2.1)$$

Where y is the function of x and of the rate of change of x (e.g. over time). To describe the hysteresis between concentration (C) and discharge (Q) observed, Krueger et al (2009) developed equation 2.2.

$$C = \theta_1 Q^{\theta_2} + \theta_3 \frac{dQ}{dt} \quad (2.2)$$

with the local slope of the hydrograph $\frac{dQ}{dt}$ and parameters θ_1 , θ_2 , and θ_3 . All variables in equation 2.2 were treated as uncertainty intervals, with the Q intervals for slope at timestep i as equation 2.3.

$$\frac{dQ}{dt} \left[\frac{(\inf(Q_{i+\Delta t}) - \inf(Q_{i-\Delta t}))/2\Delta t, (\sup(Q_{i+\Delta t}) - \sup(Q_{i-\Delta t}))/2\Delta t} \right] \quad (2.3)$$

$\inf()$ and $\sup()$ are lower and upper interval bounds, respectively, and $\Delta t = 1$ for data.

The importance of Krueger et al (2009)'s approach can be attributed to the increasing recognition of uncertainty in modelling, especially since the study by Beven and Binley (1992) on the Generalized Likelihood Uncertainty Estimation (GLUE) (Krueger et al, 2010; Beven and Binley, 2013). Beven and Binley (2013) noted that there is still no agreement on the solution to the problem of epistemic uncertainties other than adequate knowledge of the nature of the sources of uncertainties.

In addition, Haygarth et al (2004) estimated and classified the (phosphorus) concentration-discharge relationship using a simple decision tree shown in Figure 2.8.

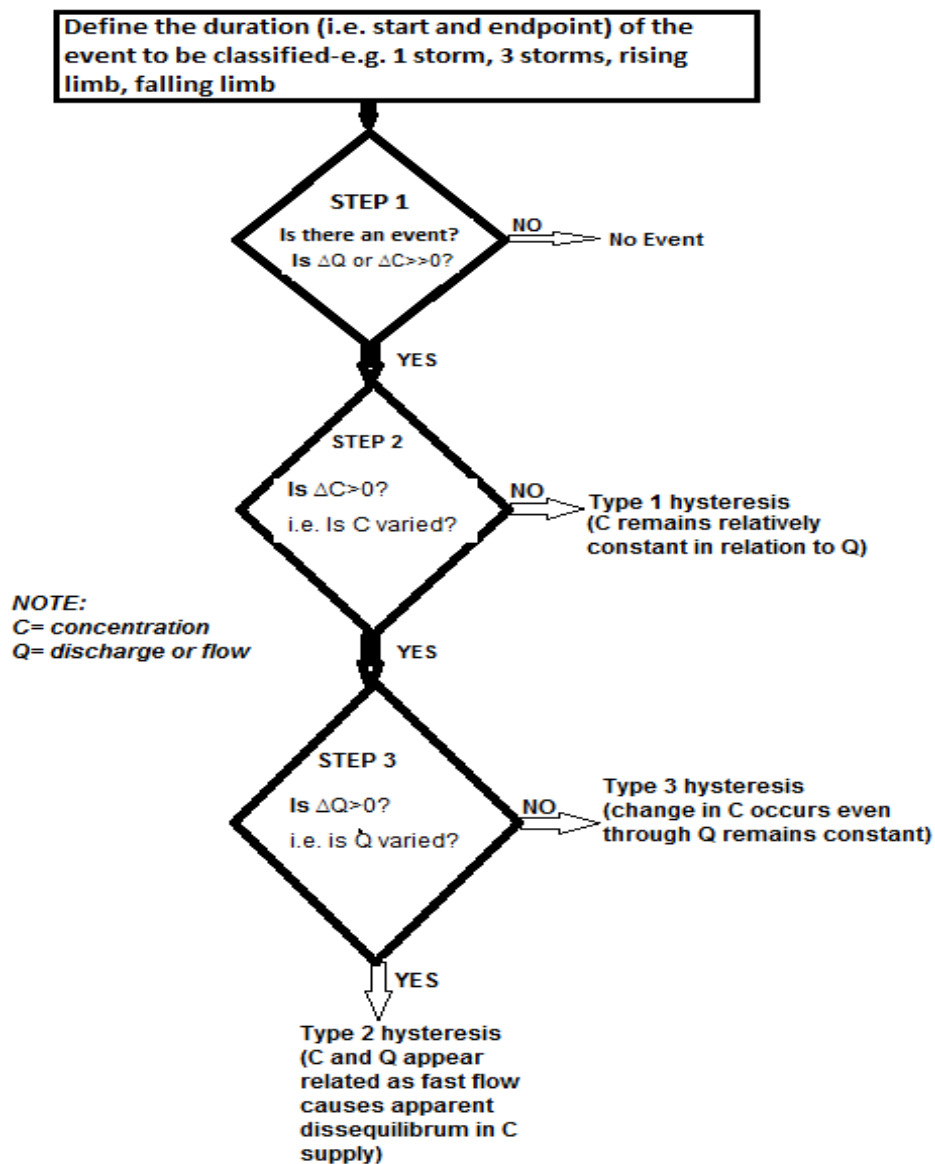


Figure 2.8. Decision tree for classifying the concentration-discharge hysteresis proposed by Haygarth et al (2004).

According to Haygarth et al (2004), 'Type 1' hysteresis can occur from a steady-state situation between the dissolution kinetics of a relatively homogenous soil and discharge, and in areas with not so fast drainage to prevent ions exchange between the soil and solution. 'Type 2' hysteresis can occur where rapid water discharge results in physical entrainment of particulate and colloidal matters, or when solute pathway is different from the normal route during saturated base flow, or due to the alternating soil drying and wetting due to fluctuation in soil

moisture, or as a result dilution and depletion of material source. Type 3 hysteresis, on the other hand reflects enriched material supply to the system. In general, concentration-discharge relationships are known to exhibit various forms (Johnson and East, 1982; Stall and Fok, 1967; Webb and Walling, 1986; Evans and Davies, 1998; Evans et al, 1999; Chanut et al, 2002; Haygarth et al, 2004; Krueger et al, 2009; Eder et al, 2010; Murphy et al, 2012), which can be different due to the effects of different components of the chemical-transfer system earlier conceptualised (Figure 1.3).

2.4.2.2. Concentration-discharge patterns and attributes

Most studies on concentration-discharge relationships showed that hysteresis plots are usually cyclical and they follow either a clockwise or an anticlockwise direction, or both as in a 'figure-of-eight' (8) plot. Concentration-discharge relationships can also exhibit a straight line, or in combination with a loop (which may be clockwise or anti-clockwise) or just in a complicated random form (Stall and Fok, 1967; Foster, 1978; Foster and Grieve, 1982; Prowse, 1984; Olive and Rieger, 1985; Webb and Walling, 1986; William, 1989; Evans and Davies, 1998; Evans et al, 1999; Chanut et al, 2002; Haygarth et al, 2004; Krueger et al, 2009; Eder et al, 2010).

A number of explanations have been offered for the different patterns observed in many studies, and generalised perceptions on them are documented in Table 2.2. Most of these studies have explained that clockwise pattern hysteresis occur when the concentration peaks prior to peak discharge, and associated anti-clockwise patterns to when concentration peaks in the falling limb of the hydrograph.

Table 2.2. Basic patterns of solute concentration-discharge hysteresis, their interpretations and causes

Shape of C–Q plot	Explanation of occurrence	Cause	Reference
Clockwise	When the concentration is higher on the rising limb of the storm hydrograph compared with the falling limb.	Flushing of materials from ground and vegetation surfaces at the start of storm event.	Holden, 2005
	Concentration peaks prior to peak discharge and rapidly fall during rainfall cessation or snow melt decline.	Lateral flushing of ready availability of excess nutrients in the near surface soil horizons.	Bishop et al, 2004
		Transmissivity feedback flushing. Nutrients are leached from near-surface layers by a rising water followed by a quick lateral transport of these leached nutrients via near-surface subsurface storm flow on the hillslope or surface, saturation excess runoff in the riparian zone.	Hornberger et al, 2004; Weiler and McDonnell, 2006
Anti-clockwise (Counter-clockwise)	When the concentration is higher on the falling limb of the storm hydrograph compared with the rising limb.	Antecedent soil content; quick displacement by infiltrating rainwater.	McHale et al, 2002
		Lateral displacement of the soil (pre-event) by water infiltrating rainfall.	Holden, 2005
		Flushing by the vertical-lateral preferential flow.	Weiler and McDonnell, 2006
		High concentrations in the O-horizon soil waters.	Brown, 1999
Straight line	Concentration and discharge increase and peak simultaneously.	Time lag associated with the onset of streamflow, which displaced solute-rich waters via macropores.	Hangen et al, 2001
		Uninterrupted supply of materials throughout a storm event.	Wood, 1977
Straight line plus loop	Combines the straight line with either clockwise or anticlockwise loop.	Causes are same for both straight line and either clockwise or anticlockwise loop, in sequence.	William, 1989
'Figure-eight', 'figure of 8' or Cross-over	This combines parts of the clockwise and anticlockwise loops, which sequentially go in opposite directions.	Causes are same for a clockwise loop at high flows and an anticlockwise loop at low flow.	Arnborg et al, 1967; William, 1989
Random, Complicated or indeterminate	This occurs when rotation or shape of C–Q plot does not vary systematically with flow.	Spatial variability of solute concentrations along the flow channel reach.	Jeje et al, 1991; Krueger et al, 2010; Murphy et al, 2012

Clockwise hysteresis pattern is associated with flushing of dissolved or sediment materials in the rising limb of the hydrograph, and can therefore be characterised as a more rapid flow of materials from the ground, vegetal and near surface regions (Bishop et al, 2004; Hornberger et al, 2004; Holden, 2005; Weiler and McDonnell, 2006) or as a result of quick displacement of previously held water in the soil by the infiltrating rainwater (McHale et al, 2002). Anti-clockwise hysteresis pattern can be attributed to the prevalence of preferential flow such as caused by the lateral displacement of the soil (pre-event) water by infiltrating rainfall or flushing by the vertical-lateral preferential flow (Klein, 1984;

Holden, 2005; Weiler and McDonnell, 2006). Prowse (1984) showed that complexities, however, occurred in the interpretations of the clockwise and anti-clockwise hysteresis observed in some of the early studies. For example, Figure 2.9 shows that the clockwise concentration-discharge relationships may be difficult to interpret based on whether there is lag (Figure 2.9 ai-ii), lead (Figure 2.9 ci-cii) or neither lag nor lead response (Figure 2.9 bi-ii). Late flush is often associated with a lead response (Figure 2.9 di-ii). Klein (1984), while studying the Holbeck catchment, Yorkshire, United Kingdom established a relationship between the travelling time, location of solute or sediment materials and type of hysteresis formed (Figure 2.10). According to Klein (1984) clockwise hysteresis patterns can occur in the concentration-discharge relationship, when the solute or sediment material load travel a short to medium distance and the discharge is relatively low while anti-clockwise hysteresis occurs when material transported arrived from farther distance and the flow velocity is high (Figure 2.10). In between the two main hysteresis patterns (clockwise and anticlockwise) are other forms of concentrations relationships, including straight line (which can occur when there is uninterrupted supply of solute or sediment loads throughout an event (Figure 2.11 ai-bii)), straight line plus loop (2.11 ci-ii), 'figure-of-8' (2.11 di-ii) and random, complicated or just indeterminate (Arnborg et al, 1967; William, 1989; Krueger et al, 2010; Murphy et al, 2012).

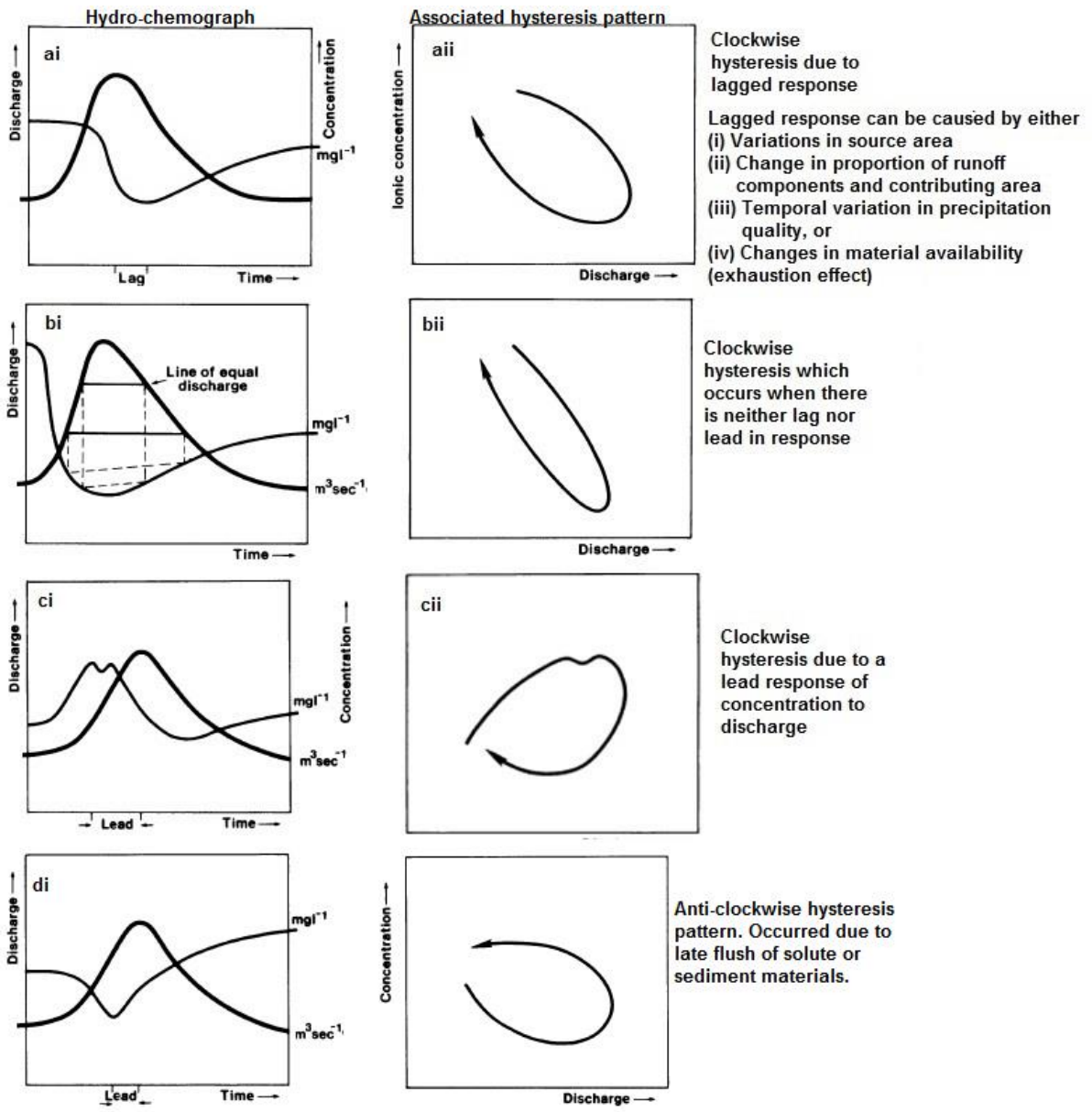


Figure 2.9. Main causes of clockwise and anti-clockwise concentration-discharge hysteresis, and associated hydro-chemographs (modified after Prowse, 1984).

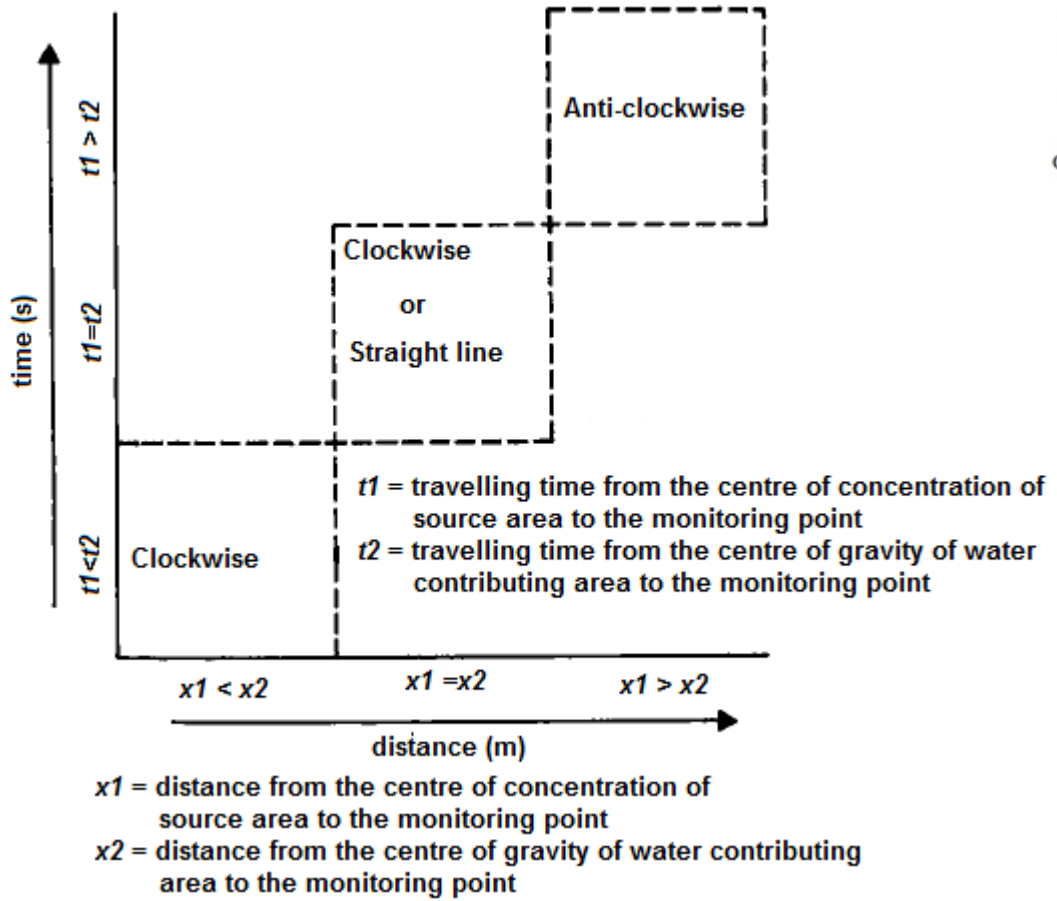


Figure 2.10. Hysteresis pattern as a function of travelling time and location of material (solute or sediment) (modified after Klein, 1984).

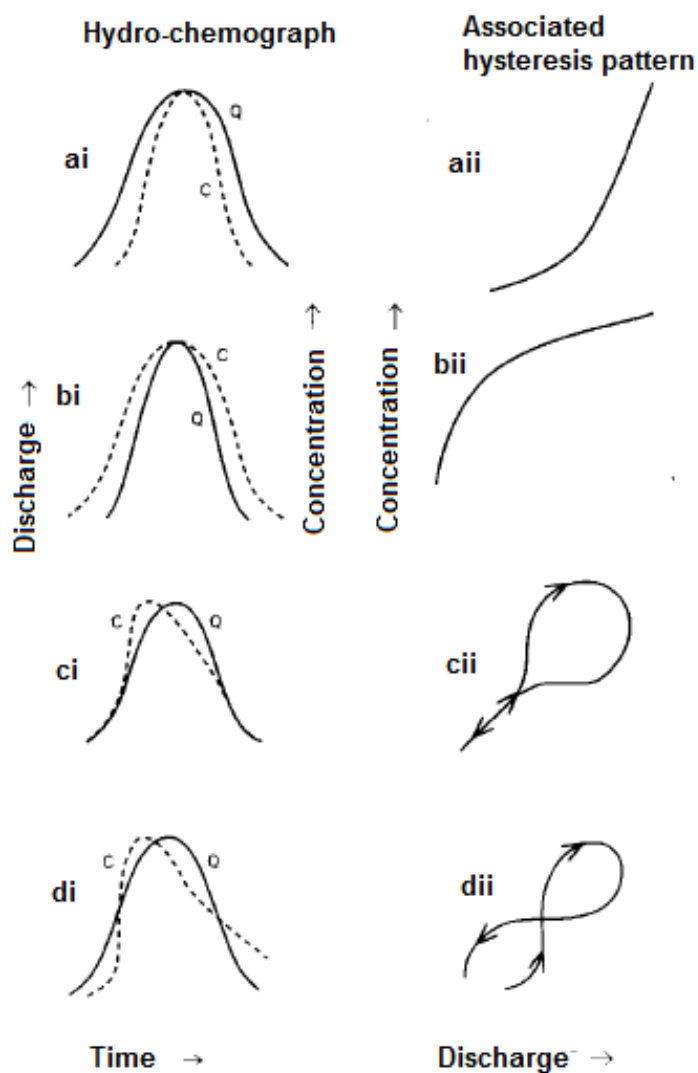


Figure 2.11. Other patterns of concentration-discharge hysteresis in-between the clockwise and anticlockwise patterns' formation region in Figure 2.10.

2.4.2.3. Uncertainties in concentration-discharge (c-q) relationships as elucidators of hydrological pathways

There is generally little or no agreement among scholars on the nature of the materials and nutrients whose c-q relationships exhibit clockwise or anticlockwise loops. Whilst studies (such as Klein, 1984, House and Warwick, 1998; Steegen et al, 2000) have argued that anticlockwise hysteresis observed in some solutes (such as phosphorus, nitrate and ammonium) and suspended solids occurred as a result of the mobilization of loosely bound materials by surface runoff in fields, other studies (including Walling and Foster, 1975; Walling and Webb, 1980; Hill, 1993; Rose 2003) observed that clockwise c-q hysteresis may also result from such mobilization of materials. Materials whose

concentrations typically increase at high discharge have been mobilized by surface runoff from topsoil, where they had been stored prior to rainfall events or snow melt conditions (McDiffett et al, 1989; House and Warwick, 1998; Rose, 2003; Inamdar et al, 2004; Andreas et al, 2006; Bowes et al, 2005; Rusjan et al, 2008; Kopáček et al, 2014). Materials that are mobilized at high discharge may rapidly decline when rain ceases or soon after the melt declines when they have been exhausted from their sources in the fields, and thereby result in c-q relationships that exhibit clockwise hysteresis loops (Hornberger et al, 1994; Creed and Band, 1998; Inamdar et al, 2004; Rusjan et al, 2008). The concentrations of the majority of mobilized materials which exhibit anticlockwise hysteresis are increased after discharge has peaked (McDiffett et al, 1989; William, 1989; House and Warwick, 1998; McHale et al., 2002). Materials which exhibit anticlockwise c-q relationship are those whose concentrations are delayed with peak discharge, probably because their concentrations in the soil surface are low or they are derived from a source that is mobilized slowly (such as a subsoil layer) or they are distant from the sampling point (McDiffett et al, 1989; William, 1989; House and Warwick, 1998; McHale et al., 2002; Bowes et al, 2005).

Differences in the prevailing climate conditions, basin characteristics, soil wetness and land use are some of the factors that have been identified to cause variations in c-q relationships. Studies (such as Johnson and East, 1982; Prowse, 1984; Olive and Rieger, 1985; Walling and Foster, 1995; Rose, 2003) have indicated that clockwise and anticlockwise c-q relationships may occur whether or not discharge peaks before concentrations. Concentration-q relationships can also be linear, irregular, complex (such as 'figure of 8', straight line with a loop) or just complicated (Arnborg et al, 1967; Wood, 1977; William, 1989; Krueger et al, 2010; Murphy et al, 2012), all of which can be used to infer hydrological behaviour in fields. Similarly, except for the studies of Granger et al (2010 a-b), Krueger et al (2010), Haygarth et al (2012), few studies have investigated c-q relationships in heavily clay soils used for intensive agriculture in temperate regions.

2.5. Conclusions

Basic runoff generating models in hillslope hydrology and relevant methodological approaches for hydrochemical studies have been reviewed in this chapter. The review showed that investigations into hydrologic flow paths are diverse in scope and approaches. Research efforts are still continuous to understand adequate way of correctly interpreting hydrologic pathways and understanding hydrological behaviour. Uncertainties in this were linked to the natural complexity of a field and catchment system, as well as the integrating biogeochemical principles of the field ecosystem (Fahle et al, 2013; Perks et al, 2013). The review of the concentration-discharge relationships shows that the hysteresis approach can provide useful information about the internal workings of the catchment. Hysteresis can provide information on changes in flow and occurrences within the catchment such as variable sources, redox and sorption/desorption, soil wetting and drying, vegetation, slope, as well as an alteration in the dominant hydrologic paths during storm events. Comparison of the causes of different hysteresis patterns can however be complex (and contradictory) to make because they can vary with location, season, and antecedent field condition on the biogeochemical complexity. The rest of this study is devoted to explanations on the study area and research methodology (Chapter 3), and the presentation of the results of this study, as well as the discussion of the results.

CHAPTER 3

STUDY AREA, FIELD INSTRUMENTATION AND RESEARCH METHODOLOGY

3.1. Study Area

3.1.1. Location and details of the North Wyke Farm Platform (NWFP)

The Rothamsted Research-NWFP Project is a 67.27 ha experimental farm of 15 hydrologically separated fields situated in the county of Devon in south west England, United Kingdom. The NWFP is funded by the Biotechnology and Biological Science Research Council (BBSRC) to address grassland agriculture's most pressing challenges, including the protection of natural resources and sustenance of the rural economy, especially in grassland regions (<http://www.northwyke.bbsrc.ac.uk/>), using the Code of Good Agricultural Practice (Granger, et al., 2010 a-b; Naden et al, 2010; Orr et al. 2011; Hatch et al. 2011). The farm platform is located on 50.77°N, 3.90°W (Figure 3.1).

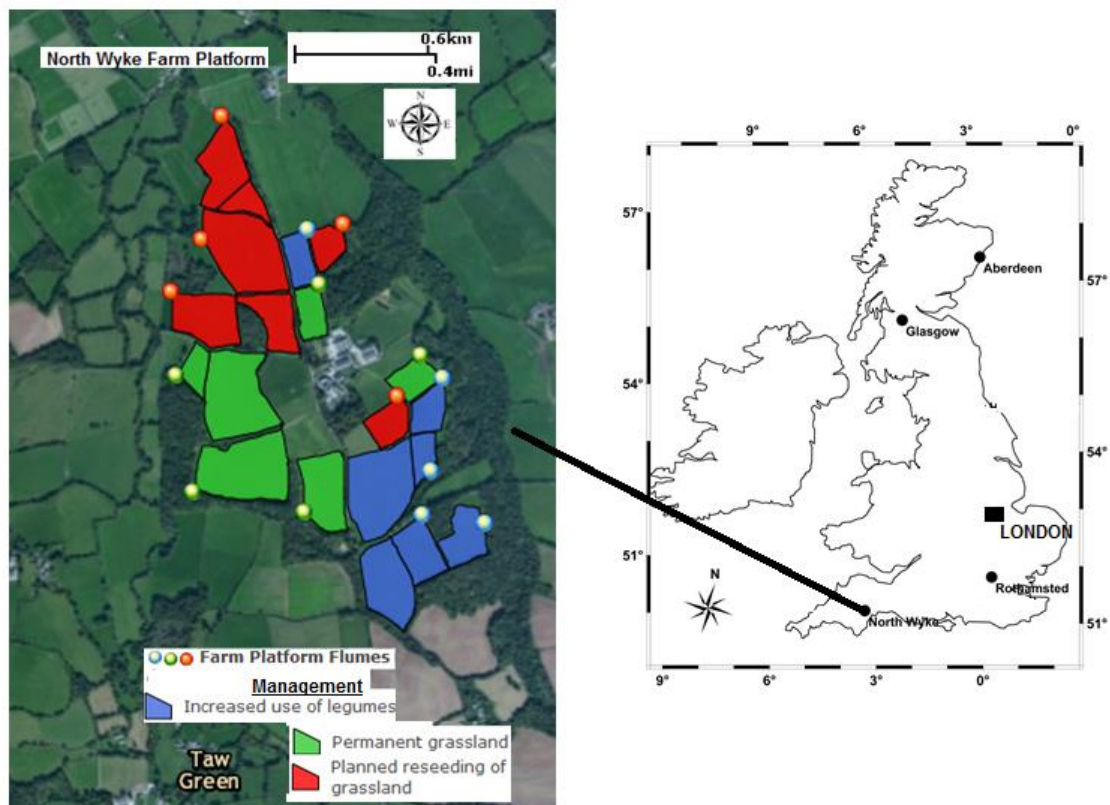
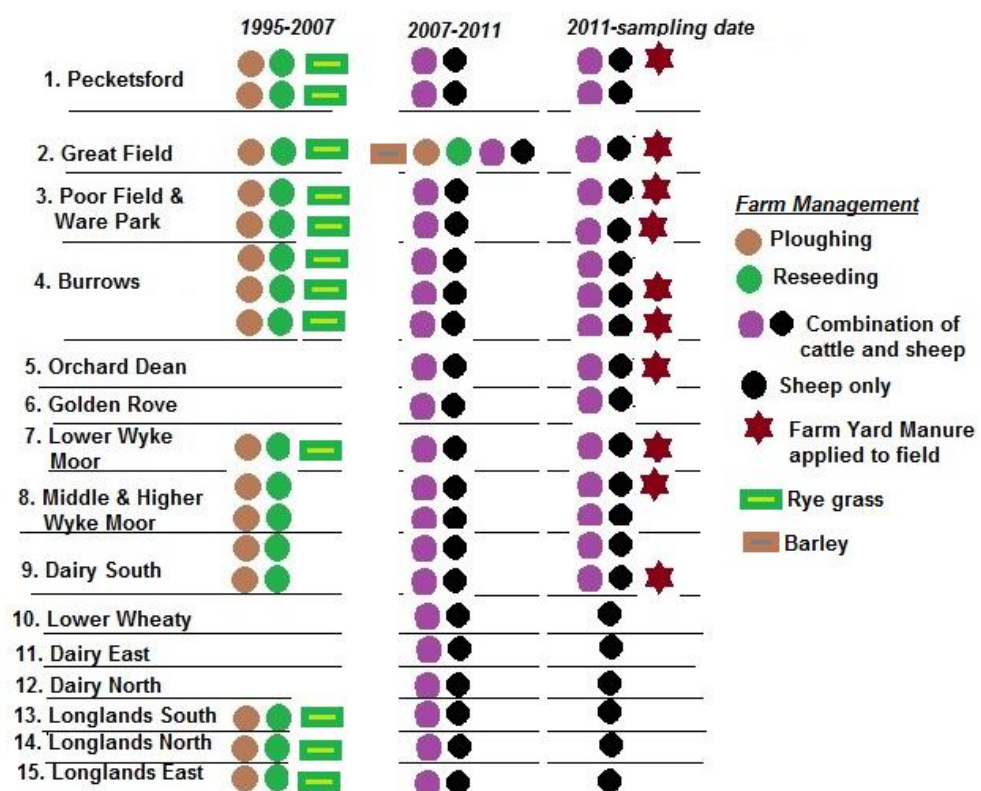


Figure 3.1. North Wyke Farm Platform in the southwest England. The colour (red, green and blue) of the fields are to distinguish them into different land use experiments as noted in the legend. Red, green and blues field occupy about 21, 24.7 and 20.5 ha, respectively.

3.1.2. Land use history and future farm management strategies

The fields of the NWFP have undergone different uses which can affect their physiochemical properties (Table 3.1). The management history of the fields is considered to be representative of normal management cycles of intensive grassland (Peukert et al, 2012). Five large fields (Pecketsford (1), Poor Field and Ware Park (3), Burrows (4), Middle and Higher Wyke Moor (8) and Dairy South (9)) have been subdivided into at least two subfields, and separately managed before the present use. For example, while the southern Great Field region was cultivated with barley, the northern region was grazed. Burrows, on the other hand, was previously managed as three distinct fields. The fields were also managed differently between 1995 and 2011 after which they were all treated to lime and fertilisers to improve soil nutrients levels to a targeted level (such as pH between 6 and 6.5).

Table 3.1. Field management prior sampling. Fields (1, 3, 4, 8 and 9) with more than one symbolised columns were divided into 2 or more regions before the present management (Information used were obtained from the Farm Platform records).



*Fields not ploughed and reseeded in 1995-2007 were cut for silage at the period

The soil tests conducted by the farm management revealed that the fields were subsequently characterised by pH (mean±standard deviation, minimum-maximum in parenthesis) values 5.9 ± 0.3 (5.7-6.1). Lime and fertilisers applications in grasslands are known to impart both long and short term effects on the soil structure and mineralogy. Lime-induced increases in productivity will enhance build-up of soil organic matter and soil biological activity that can improve aggregate stability and increase soil porosity (Haynes and Naidu, 1998). Haynes and Naidu (1998) summarised the short and long-terms effects of lime and fertiliser applications in a conceptual framework described in Figure 3.2.

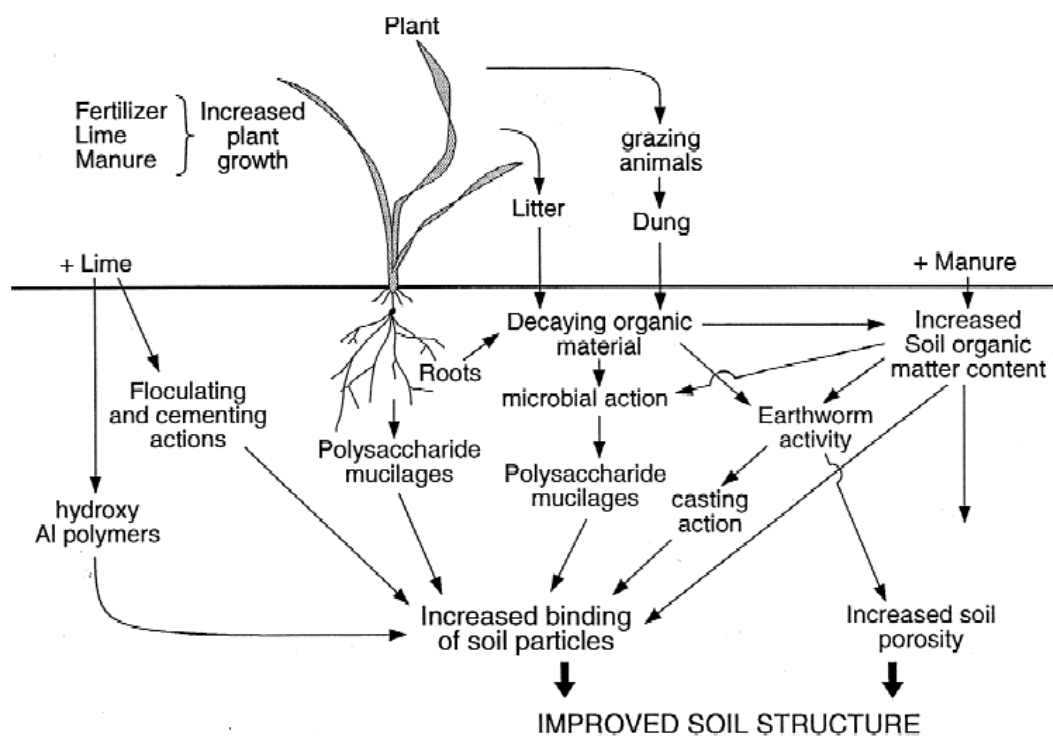


Figure 3.2. A framework to describe the major effects of lime and fertiliser applications, and how they can improve soil aggregation and structural conditions (Haynes and Naidu, 1998).

The fields were managed similarly from 2012 as permanent pastures predominately used for grazing. While smaller fields (< 2 ha i.e. Fields 10, 11, 12, 13, 14 and 15 were grazed with sheep (about 40 ewes and 3 rams on rotational grazing), the larger fields were grazed on a rotational basis between sheep (average of 110 ewes and 3 rams) and cattle (an average of 32 cattle). Farm management from 2012 is intended to focus on the three plans of permanent grassland, planned reseeding and increased use of legumes (Table 3.2).

Table 3.2. Proposed (and emerging) field management at the North Wyke Farm Platform (Sources: Orr et al, 2011; Griffith et al, 2013).

Farmlet	Field			Area (ha)	Planned farm use and management
	Code	Previous local name	Name in this study		
Red	FP 1	Pecketsford Barn Field/Peck	Pecketsford	4.8	Sustainable intensification of permanent grassland. This, according to the Rothamsted Research Bulletin on the North Wyke Farm Platform, involves sward improvement through increased fertilisation. The approach includes the use of industrially produced fertiliser and a corresponding increase of the carrying capacity of grazed animals.
	FP 2	Barn Field/ Great Field Great Field	Great Field	6.5	
	FP 3	Poor field Ware park	Poor Field/Ware Park	6.5	
	FP10	Lower Wheaty	Lower Wheaty	1.8	
	FP15	Longlands East	Longlands East	1.5	
	Total area of Red Farmlets			21.0	
Green	FP 4	Bottom Burrows (Middle) Burrows Top Burrows	Burrows	10.9	Planned reseeding; a landuse management approach that involves sward improvement through reseeding. Reseeding on the Farm Platform is expected to involve collaborations with industrial partners and cultivation of cereals.
	FP 5	Orchard Dean	Orchard Dean	6.5	
	FP 6	Golden Rove	Golden Rove	3.8	
	FP12	Dairy North	Dairy North	1.7	
	FP13	Longlands South	Longland South	1.7	
	Total area of Green Farmlets			24.7	
Blue	FP 7	Lower Wyke Moor	Lower Wyke Moor	2.6	Increased use of legumes, involving sward improvement through introduction of legumes. Clover based systems will be supplemented with manures and low level use of inorganic fertilisers.
	FP 8	Higher Wyke Moor Middle Wyke Moor	Higher and Middle Wyke Moor	6.9	
	FP 9	Dairy South	Dairy South	7.7	
	FP11	Dairy East	Dairy East	1.7	
	FP14	Longlands North	Longland North	1.7	
	Total area of Blue Farmlets			20.5	
Total area of Farm Platform				66.2	

When not grazed, the grasses in the fields were usually cut for silage twice a year. All the sheep and cattle were removed from the land and housed in winter to protect them from weather hazards and to prevent damage to the soil structure.

3.2. Physical Characteristics of the North Wyke Farm Platform

3.2.1. Climate

Harrod and Hogan (2008) gave the 1961-2000 mean annual rainfall total as 1055.7mm. Data from a meteorological station sited by the Ecological Change Network (ECN) at North Wyke showed that the 1982-2011 mean annual rainfall is 1041.7mm. The summary statistics of daily rainfall, sunshine, temperature wind speed and relative humidity measured between 1982 and 2011 at the North Wyke station are shown in Table 3.2. Daily mean temperature range is between 5.97 and 12.16 °C. Daily mean wind speed, rainfall, sunshine and relative humidity are 4.69 m s⁻¹, 4.30 mm, 4.43 hours and 77.33%, respectively (Table 3.3).

Table 3.3. Summary of some climate elements at North Wyke (1982-2011).

Statistics	Sunshine (hours)	Rainfall (mm)	Temperature (°C)		Wind Speed (m s ⁻¹)	Relative Humidity (%)
			Minimum	Maximum		
Mean	4.43	4.30	5.97	12.16	4.69	77.33
Coefficient of Variation	0.82	1.35	0.78	0.53	0.75	0.33
Minimum	0.10	0.10	-11.30	-6.20	0.13	1.0
1st quartile	1.40	0.50	2.10	7.75	2.23	77.25
Median	3.69	2.0	5.93	12.68	3.77	85.35
3rd quartile	6.67	5.70	9.30	16.78	6.13	91.83
Maximum	23.0	73.70	38.50	138.0	29.28	99.96
Standard deviation	3.61	5.81	4.66	6.48	3.53	25.45

(Data source: Meteorological data archive at the North Wyke Station).

Table 3.3 also shows that rainfall was the most varied (as determined by the values of the coefficient of variation) of the climatic elements shown, exhibiting more than 100% coefficient variation; relative humidity (with 33% percentage coefficient of variation) was the lowest. The average temperature and rainfall at North Wyke also exhibited significant seasonal differences. Seasonal variations also occur, with average temperatures of 4.9 ± 0.6°C (winter), 8.2 ± 2.3°C (spring), 14.8 ± 1.1°C (summer) and 10.5 ± 3.0°C (autumn) while rainfall varied

seasonally as 119.3 ± 21.1 , 101.0 ± 18.3 , 72.0 ± 10.6 and 59.7 ± 7.64 mm in winter, autumn, spring and summer, respectively. Daily rainfall distribution from 1982 to 2010 indicated extreme rainfall events in the study area (largest rainfall extreme between these years occurred in October 2000, with 74 mm rain event in a day (Figure 3.3).

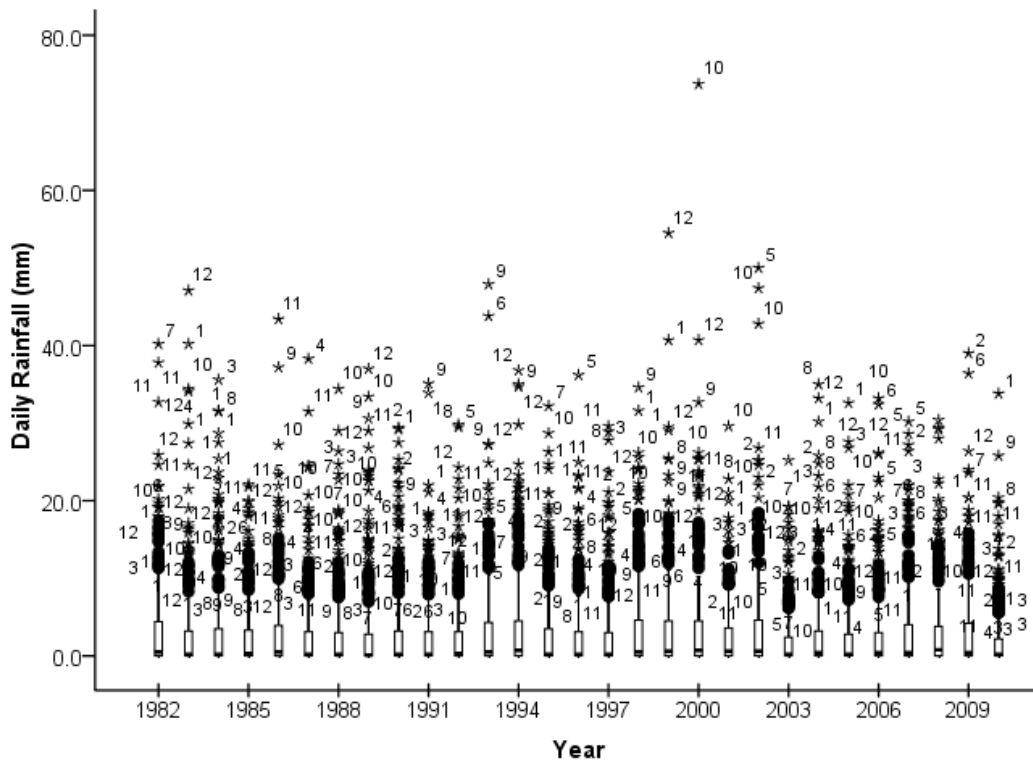


Figure 3.3. Boxplots of daily rainfall events at North Wyke between 1982 and 2000. Months with daily extreme rain events are labelled (1-12 as January-December).

The summary of the rain event and records of dry days in the study area indicated high summer rain events in May and June (50 and 44 mm, respectively) despite low rainfall as shown in 2000 and 2011 (in the 30 year means) (Table 3.4). More number of years in the 2000s years also exhibited shortest (between 1982 and 2011; 2000, 2003, 2007, 2008) number of dry days (day will less than 0.2mm of rainfall), than the number of years with the longest number of dry days since for same period. In general, Table 3.4 suggests a significant temporal variation in the rainfall of the study area, which may influence the hydrology of the study area.

Table 3.4. Lengths of dry days, range of rain events and 30 year (1982-2011) means, median and peaks of rain events at the North Wyke Farm Platform (dry days are defined as days without at least 0.2mm of rainfall) (Data was obtained from the North Wyke Meteorological records).

Month	Longest dry days (number of dry days in parenthesis*)	Shortest dry days (number of days in parenthesis)	Highest rain events	Lowest rain events	1982-2011 mean (mm)	1982-2011 median (mm)	1982-2011 Peak rain events (mm)
January	1987 (28)	1988 (8)	1999	1987	3.86	1.10	41
February	1986 (27)	1995 (9)	2009	1986	3.17	0.60	39
March	1993 (29)	2001 (11)	1984	1995	2.60	0.40	36
April	1984, 2007 (29 each)	2000, 2001 (14 each)	1987	2006, 2007	2.18	0.20	38
May	1989 (29)	1983 (14)	2002	2011	2.16	0.1	50
June	1996 (29)	1991, 2007 (16)	1993	2000	1.90	0.10	44
July	1996 (29)	2003 (13)	1982	1996	1.89	0.2	40
August	1995 (29)	1986 (13)	2004	1996	2.11	0.2	35
September	2003 (27)	1998 (15)	1993	1996,2003	2.42	0.2	48
October	2007 (27)	1987, 2007 (11)	2000	2006	3.77	0.9	74
November	1983 (26)	2008 (4)	1986	1985	3.97	1.30	43
December	1996 (26)	1993 (8)	1999	1987, 1991, 2001	4.17	1.05	55

3.2.2. Geology

The region occupied by the Farm Platform is underlain by the Carboniferous Crackington Formation, which is part of the 'Culm Measures' geology (Harrod and Hogan, 2008). The 'Culm Measures' is a geologic term for the sandstone and shale sequence of the extensive outcrop of Carboniferous strata (Laming and Roche, 2006) in the Millstone Grit (Warrington et al, 2012). The Millstone Grit is characterised by small fragments of plants that have been washed into the river deltas (Page and Chamberlin, 1996). The Carboniferous strata in the region (and other part of the southwest England) were deposited around 360-300 million years ago, but its succession is dominated by marine shales and sandstones (Laming and Roche, 2006). Soils produced from this geology (Crackington Formation) are usually clay-rich (Lestlie at al., 2007) with dark grey, black or weathered pale shales and thin subsidiary sandstone bands. The soils characteristically would readily breakdown to form clay, when waterlogged. They include deposits of grey or black fine-grained sandstones and sandy alluvium in stream valleys (Harrod and Hogan, 2008).

3.2.3. Soils

Table 3.5 shows the classifications and properties of the soil series in the North Wyke Farm Platform. The soils in the Farm Platform is generally the heavy clay soils of the Cambisols soil group containing the Stagni-vertic Cambisols (Halstow and Hallsworth soil series) and Stagni-eutric Cambisols (Denbigh series) of the Halstow Association, as well as the Fladbury soils (Gleyi-eutri fluvisol or pelo-alluvial gley) series of the Fladbury 1 Association (Avery, 1980; Harrod and Hogan, 2008; Farewell, 2008). The Halstow soil association covers 280 km² of England and Wales and accounts for 0.19% of the landmass in the region (Farewell, 2008). Soil series in the association are slowly permeable clayey soils that have developed over carboniferous shale. Halstow soil series can also include some well-drained loamy soils but the overall potential groundwater movement is low (Hogan and Harrod, 2008). The Fladbury soil series are generally described as clayey river alluvium found in places that are calcareous and can be variably affected by groundwater (Farewell, 2008). About 821 km² or 0.54% of the entire landmass of England and Wales is covered by Fladbury 1 association (Farewell, 2008).

Table 3.5: Some characteristics of soils series at the North Wyke Farm Platform.

Soil Properties	Halstow soil	Hallsworth soil	Denbigh soil	Fladbury soil
Classification	Stagni-vertic Cambisols or typical non-calcareous Pelosols.		Stagni-eutric Cambisols or typical brown earths.	Gleyi-eutri fluvisol or pelo-alluvial gley soils.
Description	Slowly permeable clayey soils often over shale. The major land use is defined as permanent and short term grassland with dairying and stock rearing.	It is a soil series within the Halstow soil association. It is described as clayey pelostagnogley soil in head from clay shale.	A fine loamy, typical brown earth soil, and often occur in mixture with Cherubeer soil series.	Clayey river alluvium; stony, pelo-alluvial gley soils.
Profile	Topsoil is clay, silty-clay loam or clay loam. Immediate subsoil is more clayey, with clay content declining below about 60 cm as weathering decreases.	It is characterised by mottled greyish-coloured mottled clayey throughout.	Topsoil is silty-clay loam with fine macropores. Subsoil is characterised by micaceous sandstone and shale stones. Entire profile is brown, brightly coloured subsoil can be a field indicator of a podzolic B horizon.	Top soil is dark grey-brown clay loam with reddish yellow; yellow-red mottles along root channels. Subsoil is clay to silty- clay; bouldery gravel, fine-grained dark grey siliceous sediments with roots concentration around stones.
Hydrology of Soil Type (HOST)	'HOST 21', 'slowly permeable soils with slight seasonal water-logging and low storage capacity over slowly permeable substrates and negligible storage capacity.	'HOST'24', 'slowly permeable, seasonally waterlogged, and overlain by slowly permeable substrates with negligible storage capacity.	'HOST 17', free draining permeable soil on hard (slate and shale) substrates with relatively low permeability and low storage capacity.	'HOST 9', slowly permeable and seasonally waterlogged, occurring in unconsolidated clays with groundwater at less than 40cm from the surface.
Particle size information (above 15cm)	22% Sand, 31% Clay and 47% Silt, pH is 5.0.	31% Sand, 26% Clay and 43% Silt, pH is 6.8.	18% Sand, 32% Clay and 50% Silt, pH is 5.0.	19% Sand, 32% Clay and 42% Silt, pH is 5.6.
Bulk density	1.04 -1.51 gcm ⁻³ .	0.99-1.55 gcm ⁻³ .	0.91-1.29 gcm ⁻³ .	Information is not available.

(Sources: Avery, 1980; Boorman et al, 1995; Harrod and Hogan, 2008; Farewell, 2008)

The NWFP relationship distribution of the soils on the Culm shales geological underlain is shown in Figure 3.4. Figure 3.4 shows that soil series varies with difference in elevation, with the Halstow soil occupying the relatively higher altitude than the Denbigh and Hallsworth. The distribution suggests that fields with greater proportions of Halstow, Denbigh and Hallsworth soil series may have different hydrological responses.

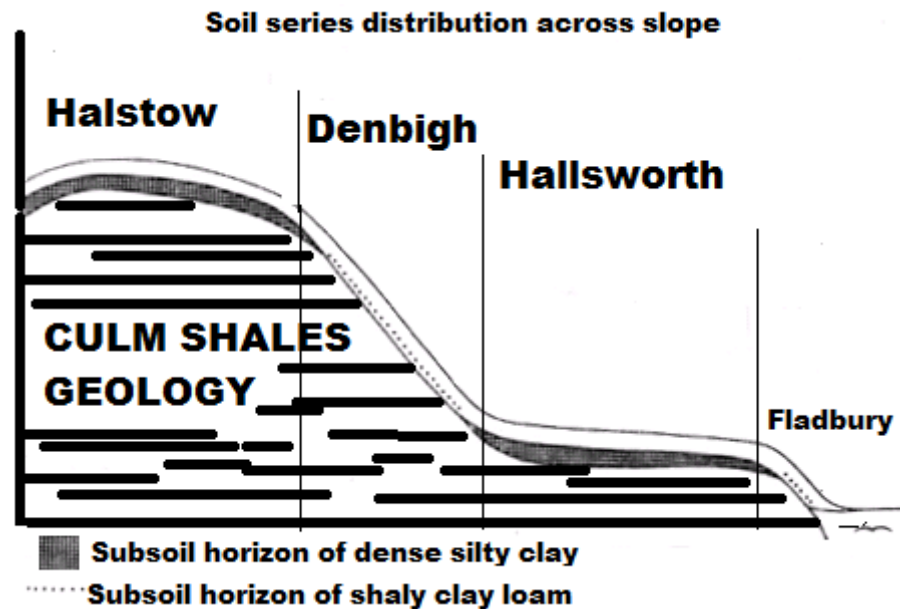


Figure 3.4. Distribution of the Halstow, Hallsworth, Denbigh and Fladbury soil series across the slope at the North Wyke Farm Platform (modified from Harrod and Hogan, 1981).

The Halstow soil series is the most extensive on the Farm Platform, and it occupies 12 of the 15 fields of the Farm Platform, although in different proportions (Figure 3.5). The next abundant soil series is the Hallsworth soil series, found in most fields in the southern and western part of the Farm Platform. The Fladbury soil series covers the western edge of the Fields 1 and 3, along the River Taw flood plain (not shown in Figure 3.5), and in association with other soil series. The Denbigh soil series also occupies parts of the western and southern fields. In all, only the small fields (Fields 10–15) are homogeneously covered by the Halstow series, and only Field 8 is homogeneously covered by the Hallsworth series. Fields 1–9 are large fields and are covered by at least two of the soil series (Figure 3.5). The specific characteristics of the identified four soils series across their profiles are compared in Figure 3.5. Figure 3.6 shows that the soils series are different, but these differences can be difficult to observe with small scale study, it therefore

will be interesting to see if the differences can be revealed with the semi-qualitative approach use by this study.

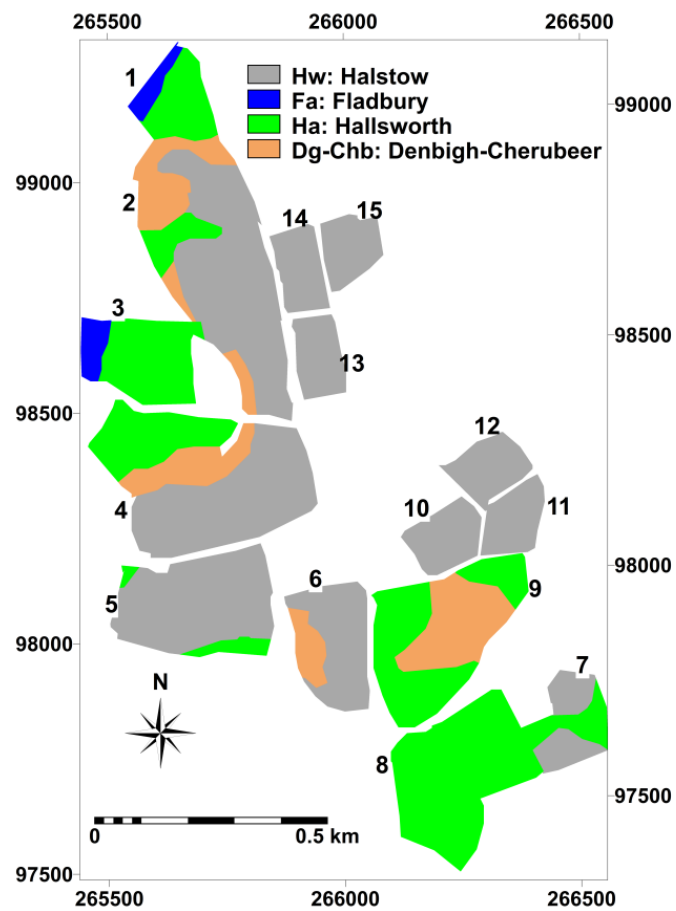
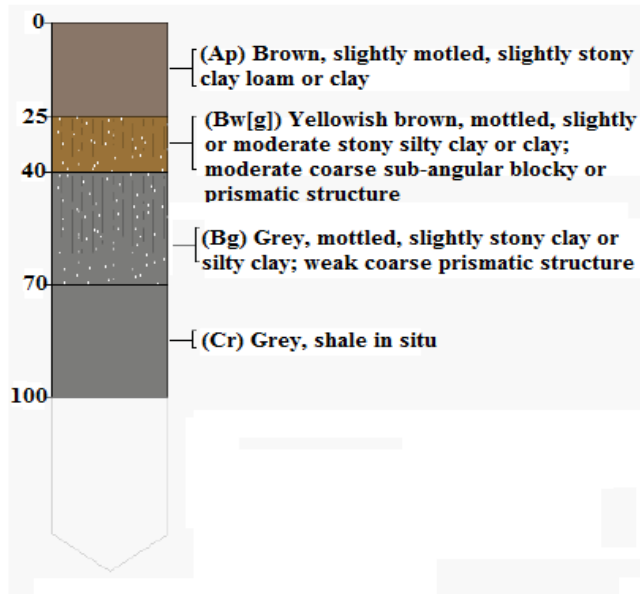
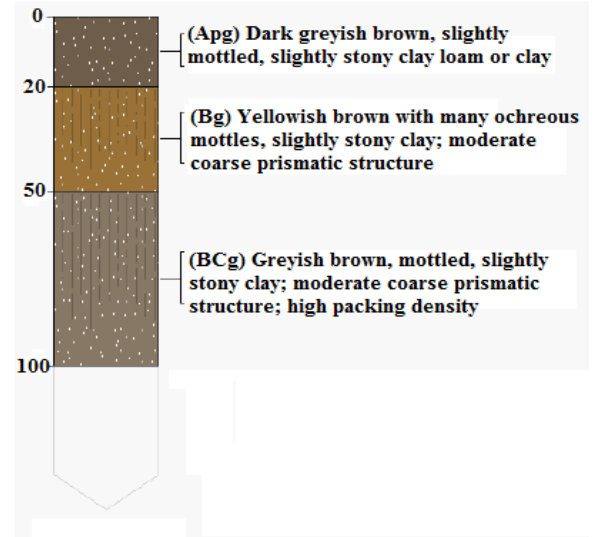


Figure 3.5. Distribution of soil series across the farm platform (modified from Harrod and Hogan, 2008).

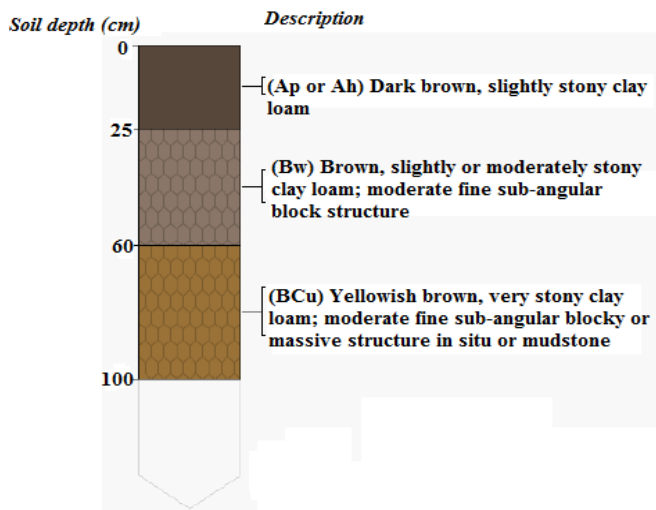
HALSTOW (Hw)



HALLSWORTH (Hk)



DENBIGH (Dg)



FLADBURY (Fa)

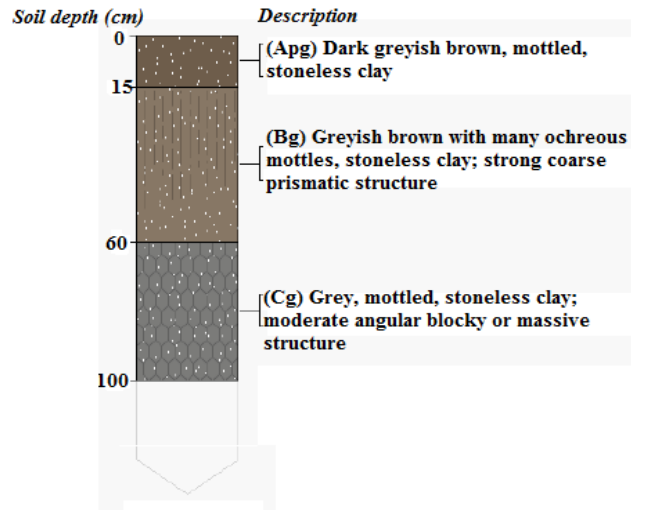


Figure 3.6. Cross-sections of dominant soil series in the North Wyke Farm Platform (Modified after White, 2008).

3.2.4. Elevation and Slope

Based on the Global Positioning System (GPS) surveys conducted on the farm platform, the elevation range of the entire fields is 128 - 189.1 m above sea level (Ordnance Survey, OS) (Figure 3.7a). Altitude increases from the northwest towards the south-eastern part of farm platform, and the slope varied between 0 and 25%; highest slope occurs in Fields 4 and 9 (Figure 3.7 a-b). The small fields expectedly exhibit relatively more homogeneity than most large fields.

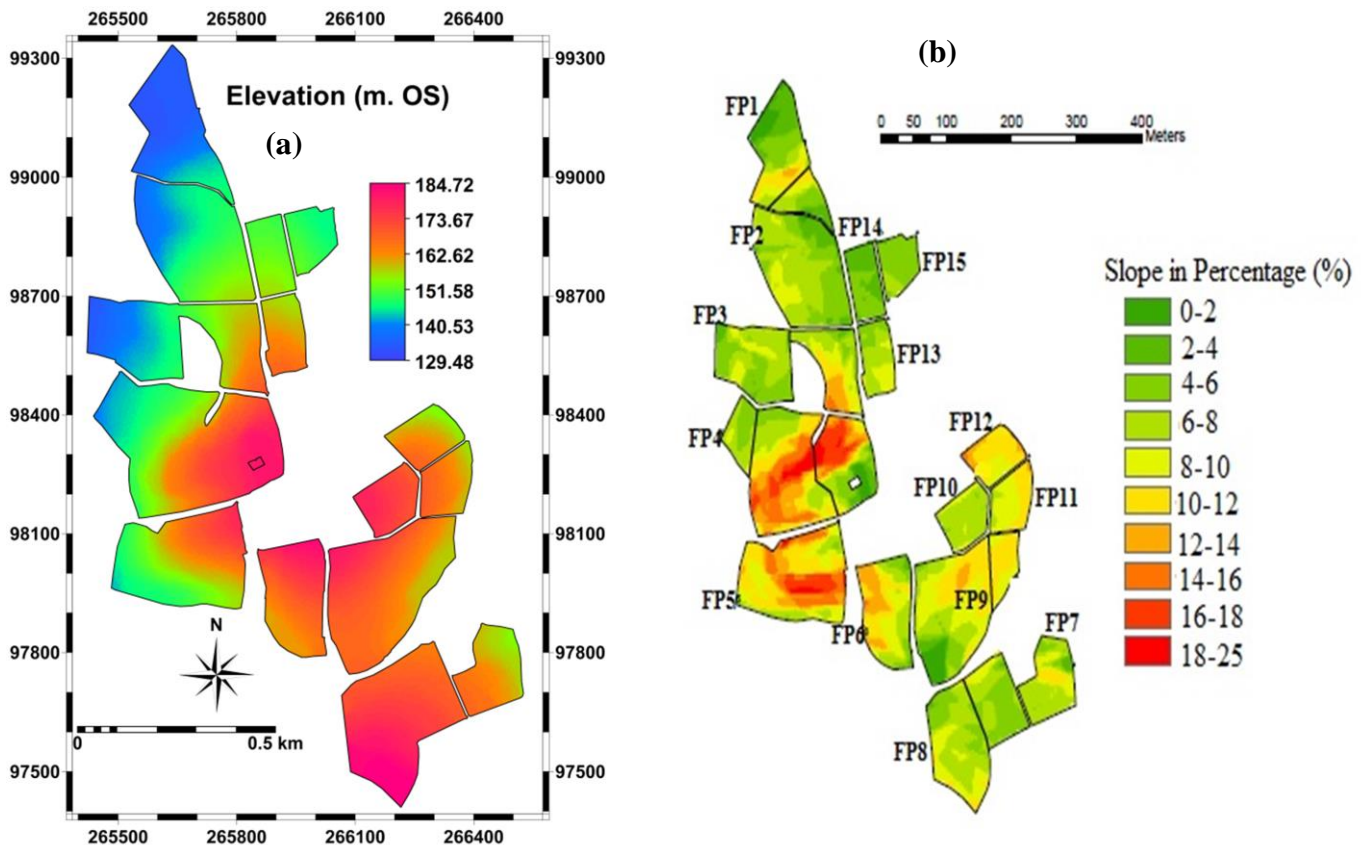
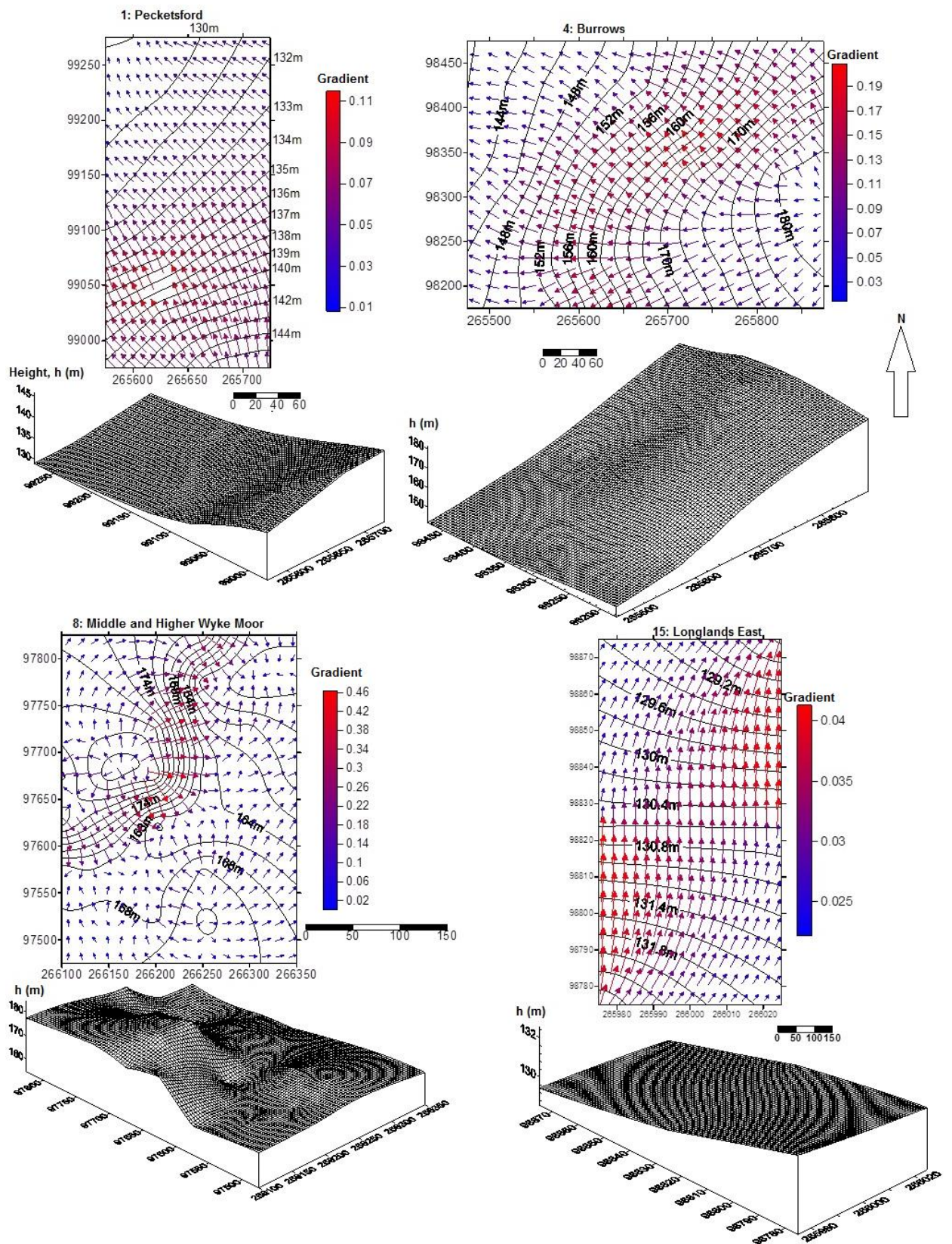


Figure 3.7 a-b. Elevation (a) and slope (b) characteristics of the North Wyke Farm Platform: (a) was produced with spherical kriging model; range = 698.1, nugget = 210.6, sill = 17.44, accounting for 99.1% variance estimate as computed from a variogram estimate before kriging was achieved. (b) was produced by Bruce Griffiths (North Wyke Farm Platform).

Since four fields (1, 4, 8 and 15) are selected for hydrological investigations under Aim 3, it is considered necessary to describe their topography in this section. Figures 3.8, which shows the relief (overlaid with vector grid diagram) and corresponding 3 dimensional (3D) frame for each field, indicate that the four fields that have been selected for hydrological investigation under Aim 3 are different in terms of their sizes, gradient and altitude. The most expansive is the Burrows (Field 4) with about 11 ha, and the largest of the entire fields in the Farm Platform (refer to Table 3.1). Burrows is also characterised by elevation ranging from about 143 to 180 m, and gradient value of 0.3-0.19. The Middle and Higher Wyke Moor (8) exhibited a relatively more complex terrain structure, because of its undulating pattern in about the middle of the field. Its elevation varied from 148 to 184 m. Pecketsford (1) and Longland East exhibit fairly similar gentle sloping landscape (129 - 145 m and 128.6 - 132.4 m, respectively), Pecketsford also exhibits more range of gradient than obtained with the Longlands East (Figure 3.8).



3.2.5. Land cover and landuse

A compilation of the British Plant Communities (Rodwell, 1992) classified the plant community at North Wyke as 'MG7', which consists of *Lolium perenne* leys and related grasslands. MG7 plant community includes 'highly productive short term agricultural grassland for grazing or mowing in rotation with arable farming and permanent amenity and recreational swards developed for heavy use' (Rodwell, 1992). *Lolium perenne* may occur dominantly or in association with *L. multiflorum* or *L. hybridum* (Stace, 1997). Dominant vegetative land cover of the North Wyke Farm Platform is the perennial ryegrass (*Lolium perenne*) pasture and some fields in association with buttercup (*Ranunculus repens*) and white clover (*Trifolium repens*). Identified vegetation at the period of this study includes the following:

- *Lolium perenne* (Ryegrass) pasture: a species of tufted grasses, important for grazing and hay because of its highly nutritious stock feed (Bond et al., 2007).
- *Trifolium repens* (White clover): a procumbent perennial grass in clay soils environment preferred for its nitrogen fixing ability (Mosquera-Losada et al, 2005).
- *Holcus lanalus* (Yorkshire fog), *Agrostis stoloniforaum* (Brown Bent), *Poa trivialis* (Royal Meadow grass) and *Phleum pratense* (in Great Field, Field 2).
- Stretches of woodland around some fields.
- *Ranunculus repens* (creeping buttercup): an invasive species, usually avoided by animals because they produce bitter taste and cause mouth blistering if eaten (Rutter, 2006)
- *Cirsium vulgare* (spear tissue), a common invasive weed (Bond and Turner, 2004) (Figure 3.9).

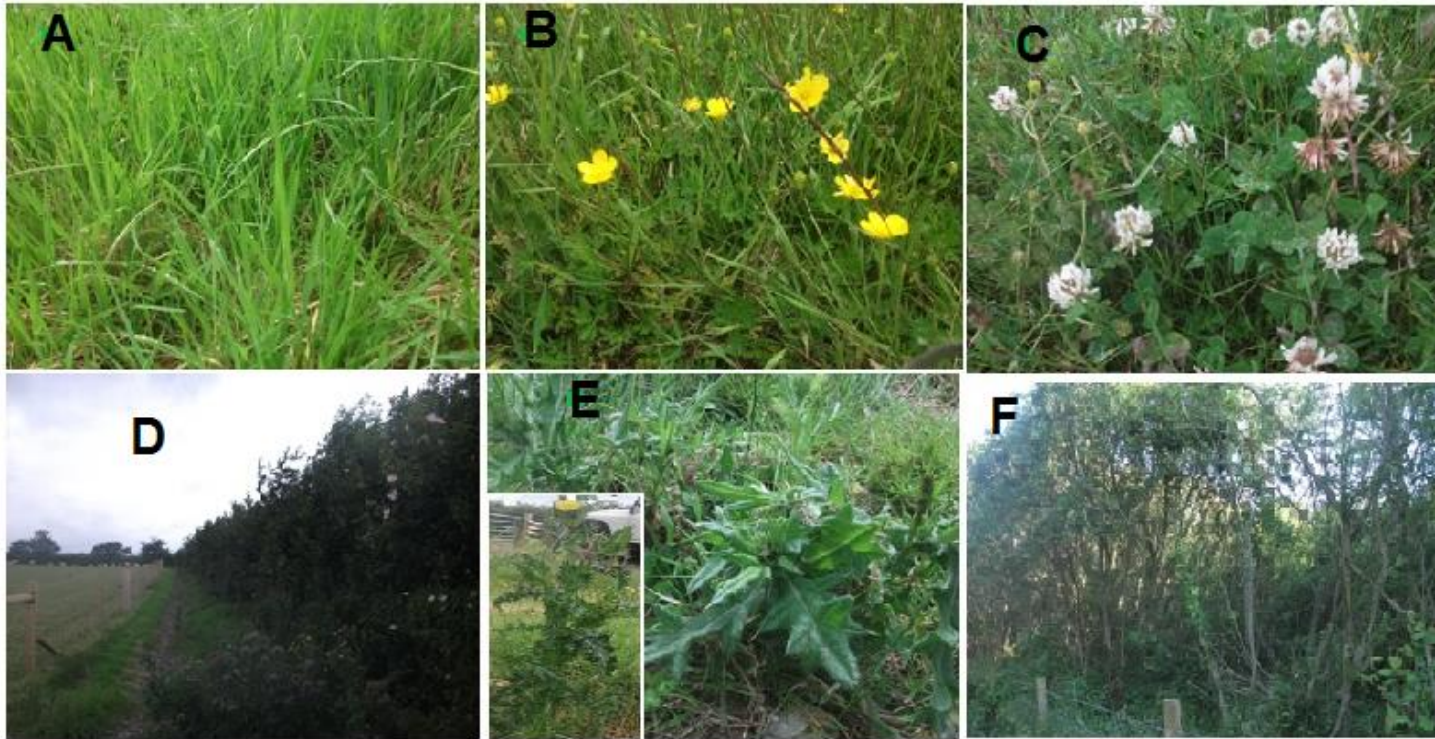


Figure 3.9: Some identified land cover plants on the North Wyke Farm Platform; *Lolium perenne* (A) is the most dominant but sometimes occur in a mixture with other grass species such as *Ranunculus repens* (B) and *Trifolium repens* (C). *Ranunculus repens* and *Cirsium vulgare* (E) are invasive species. Hedges (D) separate some of the fields. Areas occupied by woodland (F) are outside the Farm Platform.

Dominant landuse in the farm platform is sheep and cattle grazing. The planned management options require that the farmlets are grazed by yearling male and female beef cattle, ewes, rams and lambs at differently planned periods, especially during the baseline year (April 2012 - March 2013). In each of the fields is a 'drinking trough' where the animals (cattle, sheep) usually congregate, excete and physically alter the soil texture (Figure 3.10).

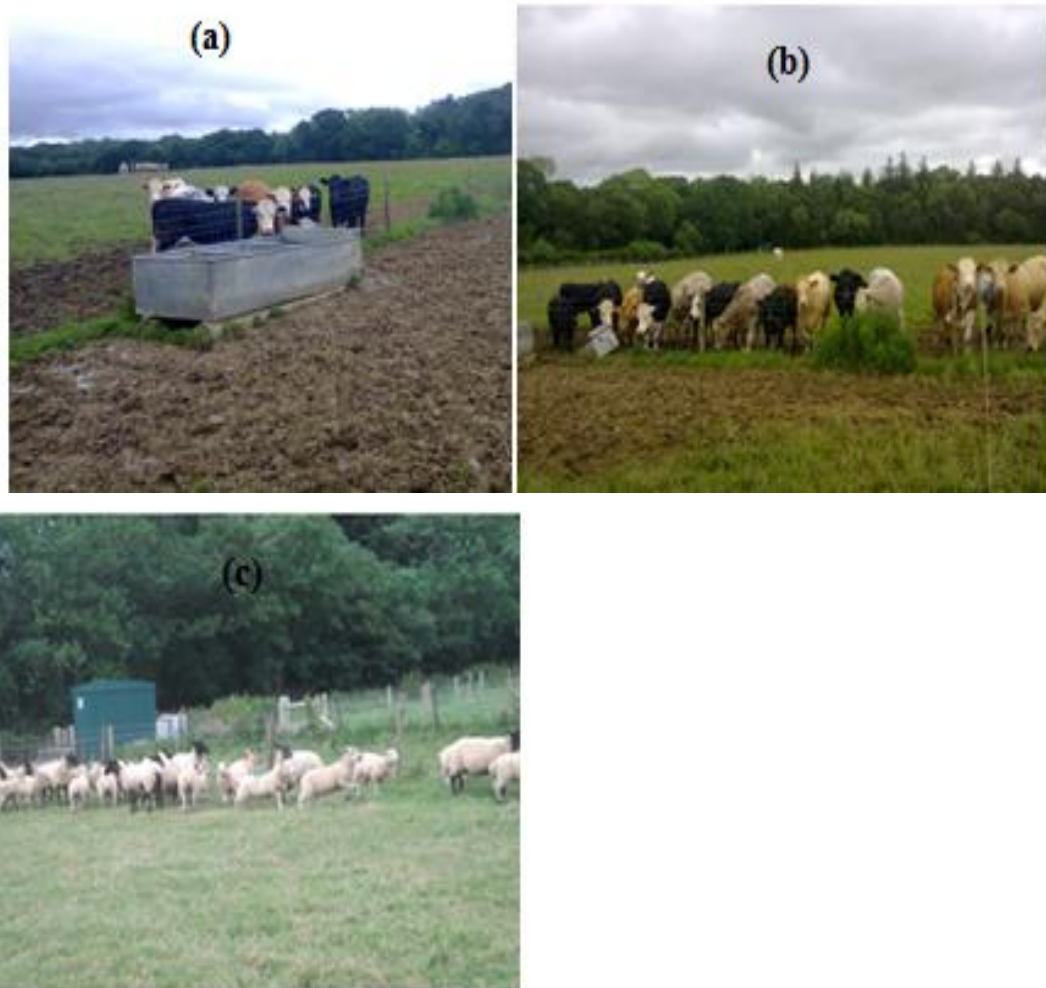


Figure 3.10 a-c: Grazing activities at the North Wyke Farm Platform (a, b) cattle drinking from a water trough- sited in all the fields, and the altered soil structure as a result of their congregation (c) sheep in one of the smaller fields. Grazed cattle and sheep exhibit different impact on the soil of the fields; soil structure is more altered where sheep are grazed.

Water pollution, eutrophication, sedimentation and bacterial contamination, as well as increased runoff have been linked to the level of grazing by animals or stock density (Bilotta et al, 2007). Specifically, activities of animals, such as treading, feeding and excretion during grazing produce negative effects on the fields, and many of these have been reported in literature (e.g. Milchunas et al, 1988; Bilotta et al, 2008; Zhou et al, 2010). Some of the effects are summarised in Table 3.6.

Table 3.6. Some effects of animal grazing on field ecosystem (The significance of the effect can vary with stock density, age of animals, soil and climate of an area).

Animals activities	Description	References
Treading and trampling.	Facilitate crushing, bruising and shearing of plant tissues and vegetative cover. Deformation of soil structure through soil compaction, soil pugging and poaching by the hoofs of grazed animals can increase the bulk density, reduce porosity and infiltration capacity. Causes decline of fauna biodiversity and pasture productivity.	Liddle, 1975; Duncan and Holdaway, 1989; Bilotta et al, 2008.
Feeding	The rumen and digestive track of agricultural livestock contains microflora which are pathogenic, and could pose threat to health, especially during regurgitation.	Andrew, 1988; Schulz and Leininger, 1990; Jeffries and Klopatek, 1987; Rickard, 1985; Belsky, 1987; Milchunas et al, 1988.
Excretion	Livestock wastes are a rich source of nutrients especially N and P, which if abnormally high can cause enrich adjacent water bodies and cause eutrophication. Livestock wastes are sources of pathogenic (bacteria, e.g. <i>E. coli</i> , <i>Salmonella</i> spp; viruses, e.g. <i>Rotavirus</i> spp; and protozoa, e.g. <i>Cryptosporidium</i> spp contamination which is capable of impairing adjacent water bodies, including recreational surface waters. These could be of grave consequences to humans and animals.	
Overall grazing activity	Grazing facilitates increases soil carbon storage. Invasion of exotics in areas around watering tanks and heavily grazed and trampled areas. Causes disturbance or changes in ecosystem community structure and diversity.	Milchunas and Lauenroth, 1993; McSherry and Ritchie, 2013; Raiesi and Riahi, 2014; Newton et al, 2014.

3.2.6. Previous studies on the North Wyke fields

Many studies have been conducted on the soils, farm management, hydrochemistry and transformation of nutrients, especially phosphorus and nitrogen, in the North Wyke. Most of these studies have indicated that losses and transformation of nutrients from soil in this area are influenced by a number of factors, including land use (whether intensively grazing, arable cropping or

less intensive grazing is practiced), drying and rewetting of soils, rate of application of N fertilizers and farmyard manure (pig or cattle slurry) among others (Jarvis and Barrachough, 1991; Scholfield et al, 1991; Scholefield and Stone, 1995; Hatch et al, 2000; Bhogal et al, 1999; 2000; Brown et al, 2001; Webb et al, 2004; Smith et al, 2012; Blackwell et al, 2012, 2013). These studies have noted that intensively grazed soils tend to release more leachates than the less intensively managed fields because the less grazed fields are often characterised by richer fungal communities that are capable of retaining the nutrients under drying and wetting stress (e.g. Blackwell et al, 2013). The experiment by Scholefield and Stone (1995) indicated that although nitrate loss varied with the intensity of storm events, they were released in small proportions, relative to the amount applied because of the fine texture of the heavy clayey soils in the area.

Other studies (including Granger et al, 2010a, 2010b; Old et al, 2012) have also investigated the hydrological processes in the study area using isotopes, such as deuterium ($\delta^2\text{H}$), oxygen 18 (^{18}O) and carbon-13 ($\delta^{13}\text{C}$), and natural fluorescence. Their results indicated that hydrological process in the study area is influenced by the contributions from the surface flow.

3.3. Field Instrumentation

3.3.1. The NWFP drainage system

All the fields of the NWFP are drained because of the heavy clay soils and characteristically poor drainage (Granger et al, 2010a). Around each field is a network of French drains to collect runoff from the entire circumference of the field and release it into a flume at a monitoring station in the field (Total length of drainage = approximately 9203 m). A French drain (named after the designer of the earliest version, Robert French) is a trench covered with gravel or rock or containing a perforated pipe that redirects surface and groundwater away from an area (Orser Jr, 1997). The French drain used in the fields can collect runoff from within the first 0.6m of the soil profile across the field, and the velocity of the runoff and water chemistry can be determined before it is released to the environment, outside the field (Figure 3.11).

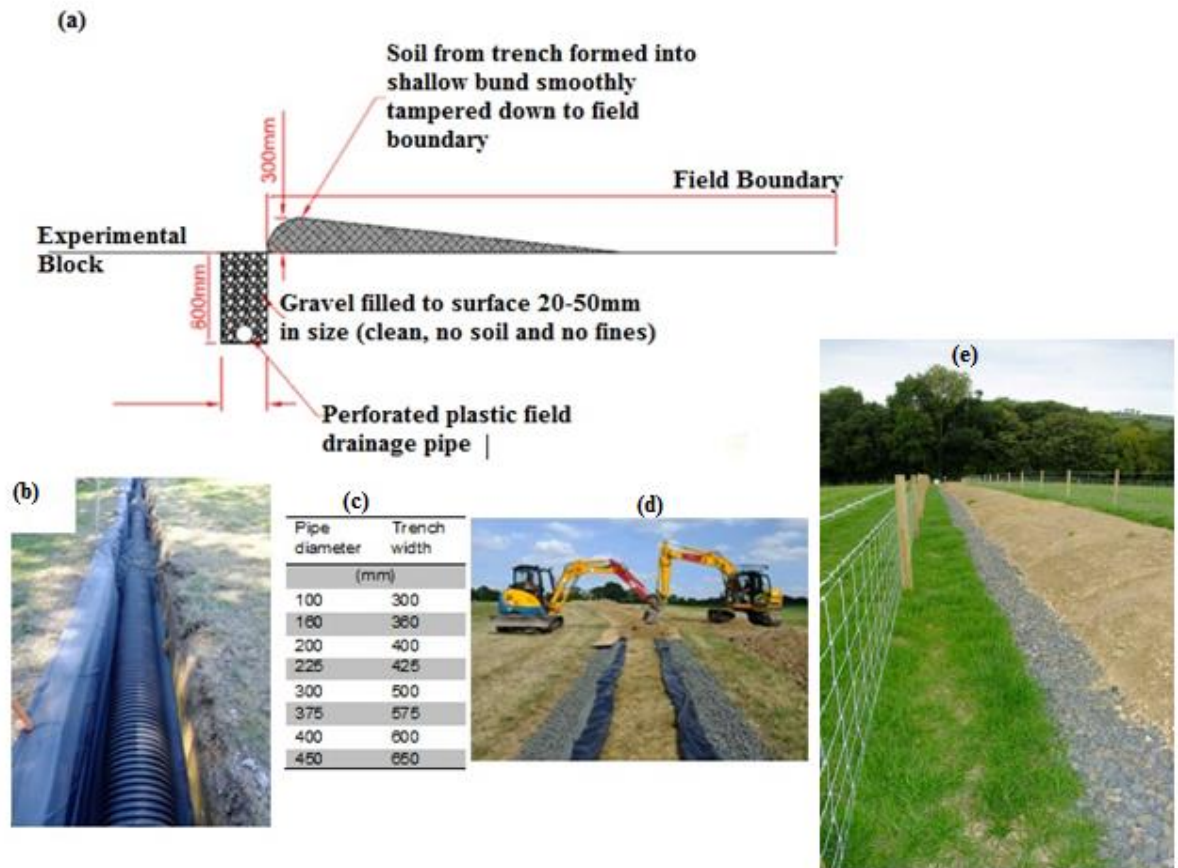


Figure 3.11 a-e. French drains layout at the North Wyke Farm Platform: a and c shows the dimension of the drain and soil trench; b, d-e are the various stages of the drain installation.

The sizes of the drain for a particular field can vary (Figure 3.11c), depending on the engineering estimates of predicted runoff established at the beginning of the entire project. Each drain network was cautiously constructed to prevent runoff escape and groundwater (in case there is any when water table rises) ingress by lining the trench with polyethylene drape. Blockage of the drains is also avoided by first covering the plastic drains with gravels, before drape and sand were added to cover (protect from exposure) the drains (Figure 3.11d-e).

In each field, the drain network finishes with an H-Flume in which the probes for water quality and runoff velocity measurements are inserted for continuous reading at a pre-determined time-step (15 minutes) (Figure 3.12). There is a standby universal power system (UPS) to ensure uninterrupted measurement and data- logging.

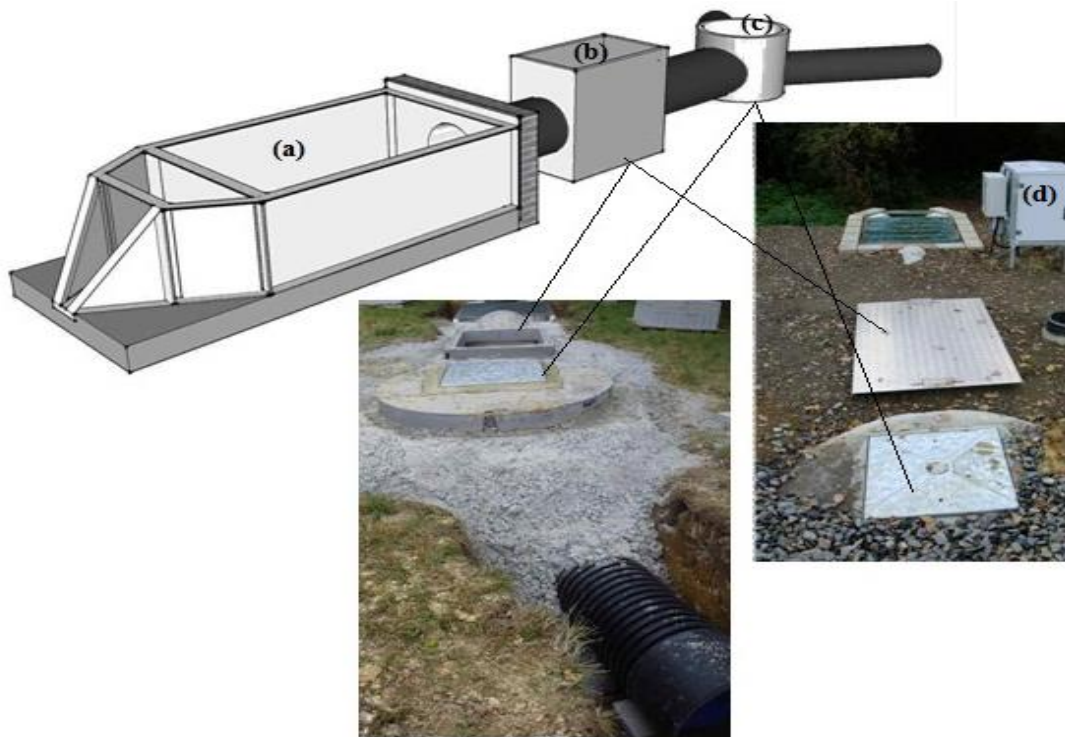


Figure 3.12 a-d: Images of the H-Flume and the mixing chambers in each field: a. is the water (effluent) space where runoff is collected before it is discharged through the H-notched weir at the outlet, b. is where the probes for runoff chemistry are, c. is the 'elbow joint' where drains from different parts of a field are intersected (the point of intersection are well protected against leakage).

3.3.2. Determination of runoff parameters (chemistry and discharge)

Indicators of water quality assessed in the runoff from each field at the North Wyke Farm Platform are managed using the sensor-based technology that was provided by Adcon Advantage (Adcon, 2013) Water temperature, pH, turbidity and dissolved oxygen are measured in all the fields using Multi-parameter water quality sonde (6600 V2 model; accuracy: $\pm 0.15^{\circ}\text{C}$ (water temperature), $\pm 0.3\text{NTU}$ (turbidity) and ± 0.2 unit (pH)). Nitrate-nitrogen is determined with 'Nitratax plus sc' (accuracy = $\pm 3\%$), and dissolved organic carbon, DOC (mg l^{-1}) is measured with ProPS-UV process (photometer Zeiss, Germany; accuracy = 0.05 mg l^{-1}). Runoff velocity or discharge is measured at the V-notch part of the ceramic weir of the H-Flume in each field with a Teledyne ISCO 4230 bubbler flow meter (Figure 3.13 a-g). All the monitoring instruments are protected from weather effects in spacious metallic (green) chambers located close to the outlet of each field (Figure 3.13h) and are monitored to prevent theft, animal interaction or measurement errors, when

necessary. In addition, rainfall, soil temperature and moisture are measured on the farm platform as described in the next section.



Figure 3.13 a-g: Sensors for monitoring the runoff chemistry and flow in each field of the North Wyke Farm Platform: **(a)**. is the Nitratax plus sc' for nitrate determination, **(b)**. is the Multi-parameter water quality sonde for determination of temperature, pH, turbidity, dissolved oxygen and conductivity; it is fixed in the flow cell **(i)**, **(c)** and **(d)** are Phosphax Phosphate analysers for Ortho-P and Total-P, respectively. Phosphate analyser is installed in FP2, FP5 and FP8 only but their data were not used in this study; **(e)** is ProPS-UV process photometer for determination of dissolved organic carbon; **(f)** is a sequential or composite sampler for event-based grab samples; **(g)** is the Bubbler flow meter for discharge measurement; and **(h)** is the chamber that houses the monitoring equipment.

3.3.3. Measurement of rainfall

Rainfall is measured by a tipping bucket automated rain gauge (Adcon RG1 model). The Adcon RG1 rain gauge is a double tipping bucket system designed as a universal rain gauge, capable of measuring to $\pm 5\%$ accuracy level per mm. It consists of a funnel with an orifice of 200 cm² and operates with 0.2 mm resolution. Figure 3.14 shows the Adcon RG1 rain gauge and the protective metallic bar emplaced to prevent animal invasion. In each catchment, the rain gauge is mounted on 1 m pipe. The funnel is attached to the body (of the rain gauge) with a bayonet-style lock, which prevents the funnel from being shaken off in heavy winds. It is protected from leaves and bird droppings by a removable and cleanable aluminium filter. The gauge (except the container) is constructed from anodised aluminium. Anodizing increases corrosion resistance and wear- resistance, and provides better adhesion for paint primers and glues than bare metal (Adcon, 2013).



Figure 3.14 a-b: Adcon RG1 double tipping bucket system rain gauge; (b) shows the protective metallic housing from animals' attacks .

Additionally, an automatic weather station (AWS) of the United Kingdom Environmental Change Network (ECN) (<http://www.ecn.ac.uk/>) is sited in one of the fields (Field 4 or Burrows) to provide longer (from 1980) term data on rainfall and its chemistry. The weather station is managed by a Protocol of the United

Kingdom Joint Code for research for data quality assessment and maintenance of weather instruments (<http://www.ecn.ac.uk/technicalnotes/AWS.pdf>). Rainfall is measured with a tipping bucket rain gauge while water samples for chemical analysis (bulk precipitation) is collected at the station using continuously open funnel bulk collector (NERC, 1996). Samples of both dry and wet deposition are therefore collected from this site, fortnightly, for laboratory analysis.

The bulk collector is designed and constructed as described by Hall (1986) (Adamson, 1996a), consisting a conical polythene funnel that rests on a polythene collecting bottle. The funnel is made up a 63° cone with 115 or 152 mm diameter. The upper surface of the collector is 1.75 m above the ground level (Figure 3.15).



Figure 3.15. The UK Environmental Change Network's bulk precipitation collector in Field 4 (Burrows) of the North Wyke Farm Platform.

The collecting bottle is protected, from coarse debris and leaves falling into it, with a removable filter of 1 mm mesh Teflon which is surrounded by a jacket of polished steel; from which it is also separated by a 25 mm gap. The collector is bird deterrent, and problems with birds have not been recorded since the station has become operational. Local sources of contamination are also avoided by placing the collector upwind of any of such sources, apart from being situated

away from vehicle tracks, animal house and obstructions such as a building or tree. It is also firmly secured to the ground. Water sample is collected at 0900 GMT Wednesdays of every week, by removing the bottle containing the precipitation sample (Beaumont, 2012, *pers comm*; Adamson, 1996a). The bottle and the sample are labelled and subsequently taken to the laboratory, where the volume of precipitation is first determined to the nearest 1 ml. The used funnel is subsequently cleaned with de-ionised water and shaken to remove any droplets or replaced with another funnel that has been cleaned in the laboratory. The bottled that contained the precipitation is also replaced by a clean bottle fitted with a clean filter.

The UK Environmental Change Network's laboratory at North Wyke determines conductivity and pH of the unfiltered water samples within 7 hours of collection with pH/conductivity meter (Jenway Model 3320) while dissolved Na^+ , K^+ , Mg^{2+} , Fe^{2+} , Al^{3+} , $\text{NH}_4^+\text{-N}$, Cl^- , $\text{NO}_3^-\text{-N}$, $\text{SO}_4^{2-}\text{-S}$, $\text{PO}_4^{3-}\text{-P}$ and alkalinity are determined in filtered samples, using the procedure itemised in Table 3.7 (Adamson and Sykes, 1996). When not immediately analysed, samples were stored in freezer at $1\text{-}4^\circ\text{C}$ (Beaumont, 2012, *pers comm.*; Adamson, 1996a).

Table 3.7: List of variables and associated procedure for the analysis of bulk precipitation water samples.

Variable	Sample condition	Procedure	Reference
pH	Unfiltered	Combination electrode.	HMSO, 1988.
Conductivity		Platinum electrodes.	
Alkalinity	Filtered	Discrete analyser.	Heyes et al, 1985.
Sodium		Induction-coupled plasma emission spectroscopy.	
Potassium			
Calcium			
Magnesium			
Iron			
Aluminium			
Phosphate		Discrete analyser.	
Nitrate			
Ammonium			
Chloride			
Sulphate		Combustion and infrared detection of CO ₂ .	
Dissolved organic carbon			
Total nitrogen	Segmented flow auto analyser.		

(Source: UK Environmental Change Network).

3.3.4. Soil Water Chemistry

Soil water (solution) chemistry data for 0-10 cm and 10-20 cm soil depths was examined in relation to the precipitation chemistry in Aim 1 because the relationships (and with that of land use discussed in Aim 2) can affect important ecosystem processes and be affected by the physical and chemical changes in the environment (Adamson, 1996b). The soil solution chemistry data were the results of the soil water samples at the Environment Change Network (ECN) station at North Wyke (in the same field (4: Burrows) that the bulk precipitation collector is also sited). Soil solution samples were collected at this site (targeted sampling site, TSS) using the Prenart 'super quartz' soil water suction samplers. The TSS is a paddock of old bio-diverse permanent grassland, which receives no nitrogen fertilizer input but are since 1984 been under controlled grazing (Tyson, 1995; Adamson, 1996b). Sykes and Lane (1996) provides the detailed protocol for soil water sampling and analysis in the entire ECN sites, and this is included as appendix 3.1. The Prenart 'super quartz' soil water samplers are cylindrical, 21 mm in diameter and 95 mm in length, conical at one end and with a tube attachment at the other. The tubing links the sampler to a 1 L glass

collecting bottle with a Prenart screw cap. The collecting bottles are placed in an insulated box to protect the samples from extremes of temperature and are evacuated using a portable pump. Samplers are located within a 6 m by 6 m plot (which is itself located within a 10 m by 10 m plot) in the Field 4 (Burrows) at North Wyke (Figure 3.16). Samplers are usually emptied into plastic bottles where water volumes are recorded before samples for chemical analysis are taken.

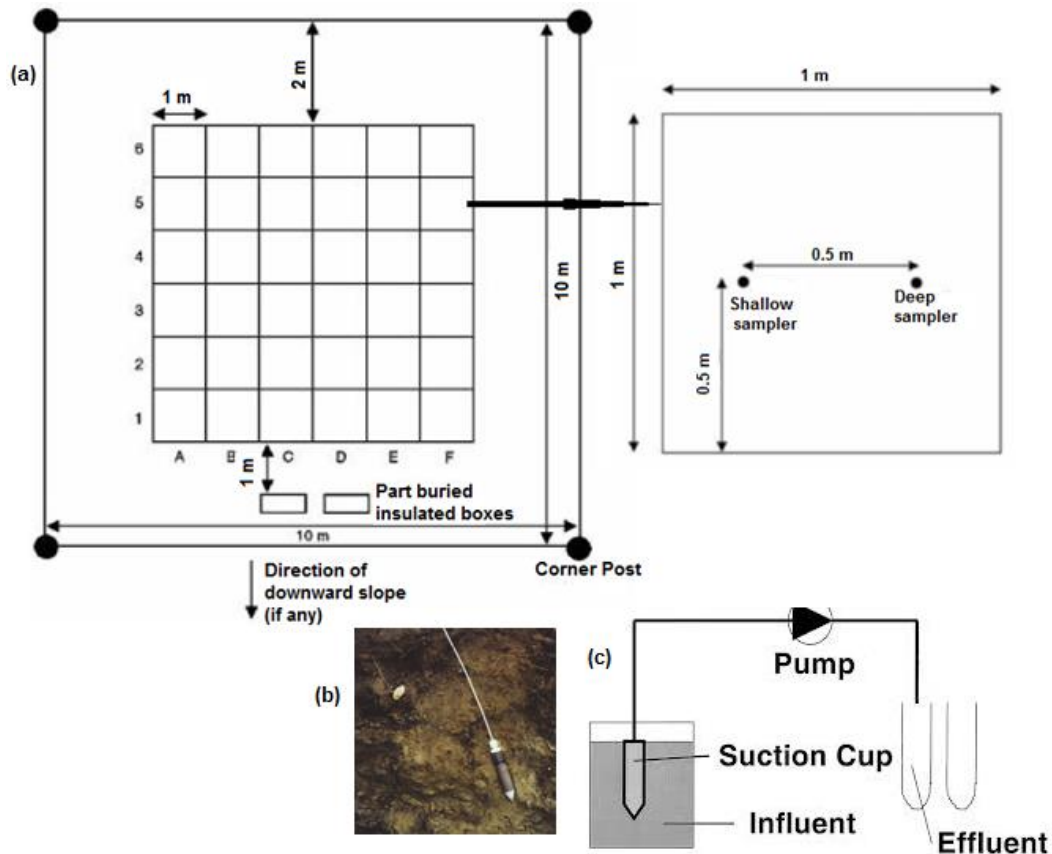


Figure 3.16. Soil water sampling procedure of the Environment Change Network. (a) shows the setting for the installation of the Prenart 'super quartz' soil water suction samplers (Cells in which samplers are installed are systematically selected within a 5-year period based on the condition of the sampler), (b) image of a typical Prenart 'super quartz' soil water suction sampler in the soil, (c) shows the operation of a suction sampler.

3.3.5. Measurement of the soil temperature and moisture

Soil temperature and moisture are determined at each field at 15 cm (for soil temperature) and 10, 20 and 30 cm depths (for soil moisture), respectively, probably because the top soil temperature and moisture are considered more significant to grassland farming than the deep soil layer, especially in thick

clayey soil as the study area. Soil temperature and moisture are measured by an Adcon SM1 model of a soil moisture and temperature sensor (Figure 3.17).



Figure 3.17. Adcon SM1 soil temperature and moisture sensor (calibrated to measure soil temperature at 15cm and soil moisture at 10, 20 and 30 cm in the study area).

The sensor integrates the measurement of both soil temperature and moisture, and determines the values of these parameters at the differently calibrated soil profiles (15cm for soil temperature and 10, 20 and 30 cm for soil moisture). The sensor is made up of a capacitance probe, with two sensor boards; a 30cm long with 3 sensors or 50cm long with 5 sensors, and a centrally located temperature sensor for 0-100% soil moisture and minus 20 to 60°C soil temperature (Adcon, 2013).

3.3.6. Data management and quality assurance

All the farm monitoring components are linked remotely by Adcon advantage Pro 6.1 software. The Adcon Advantage software is a sensor-based technology which requires conventional radio transmitters, government license (for use of the radio frequency), and extensive cabling, and managed by an administrator who provides guided access to users to minimise potential corruption of the databases (Adcon, 2013). All the instruments are checked for malfunctions and calibrations problems weekly by a dedicated member of the North Wyke Farm Platform (Bruce Griffiths). All data were first subjected to the quality assurance with an in-house program, DISCREPANCY-FLUMES. The soil moisture, rainfall

and soil temperature data were also treated with DISCREPANCY-PROBES, an in-house quality assurance program, and those that are approved are made available for use through the Rothamsted archive at <http://www.era.rothamsted.ac.uk>. Only approved datasets were used in this study. The entire ECN data used in this study were the approved ones (received after completed paperwork between the researcher and the ECN contacts).

3.4. Research Methodology

The different aims of this research are approached in differently, for simplicity. The approaches are described as follows:

3.4.1. Methodology for Research Aim 1

3.4.1.1. *Data sourcing*

Two sets of data were used to accomplish this aim. The first set comprises 16 (1993-2011) years' monthly rainfall chemistry, daily rainfall, humidity and temperature data, and the second is the biweekly (once in 2 weeks) precipitation and soil water chemistry (for 0 - 10 cm and below 10 cm soil depth) for the ECN (<http://www.ecn.ac.uk/>) terrestrial site on the Field 4 (Burrows) in the North Wyke Farm Platform. The quality of the data records were assured by the managers of the ECN data and North Wyke Centre (Lorna Sherrin, Centre for Ecology and Hydrology, Lancaster; Deborah Beaumont, Rothamsted Research–North Wyke, and Anita Shepherd, North Wyke Farm Platform) before use.

The protocol for quality control for water chemistry during data collection is documented in www.ecn.ac.uk/measurements/terrestrial/pc.

3.4.1.2. *Statistics and inferential analysis*

Both temporal variations and precipitation-soil chemistry relationship were investigated in this aim. Consequently, time series statistics including linear regression and correlation analyses were used to investigate the variations over time and examine the relationships of parameters in both the precipitation and soil chemistry (at 0 - 10 cm and below 10 cm soil depths), respectively. Principal Component Analysis (PCA) and the percentage contributions of the investigated parameters was examined for precipitation,

topsoil (0 - 10 cm depth) and subsoil (below 10 cm depth) to establish a relationship between the contributions of the chemical ions among the three end members (precipitation, topsoil and subsoil). The PCA explains the variance-covariance structure of data, using a choice rotational model (Kaiser's Varimax rotation) to maximally group variables into distinct clusters (Kaiser, 1958; Wold et al, 1987; Bengraine and Marhaba, 2003; Xu et al, 2008).

Data quality assessment using the ion-balance equations (equations 3.1 - 3.2) indicated that the balance estimate for the water samples was less than 10% (see appendix 3.1). Ion balance analysis doubles as is used to for quality assessment (Kulshrestha et al, 2003, 2014; Jawad et al., 2006), and acceptable limit is usually fixed for less than 15% (Lara et al, 2001; Irwin et al, 2002).

$$X \text{ mgl}^{-1} \text{ of ion } Y = \frac{X}{\text{equivalent weight of ion } Y} \text{ meql}^{-1} \quad (3.1)$$

$$\% \text{ difference} = 100 \frac{|\sum \text{cations} - \sum \text{anions}|}{\sum \text{cations} + \sum \text{anions}} \quad (3.2)$$

Where X is the concentration of an ion Y

3.4.2. Methodology for Research Aim 2

3.4.2.1. Data sourcing

Two hundred and sixty four soil samples obtained on a regular interval of 50 by 50 m (Figure 3.18) between June and July 2012 from the North Wyke Farm Platform were analysed. The entire farm platform was sampled at 25 by 25 m interval by five students (refer to Box 3.1 for the specific role of the author in the sampling and analysis) from the Universities of Exeter and Bristol but only samples obtained from 50 by 50 m grids were analysed because of the significantly high time and cost implications.

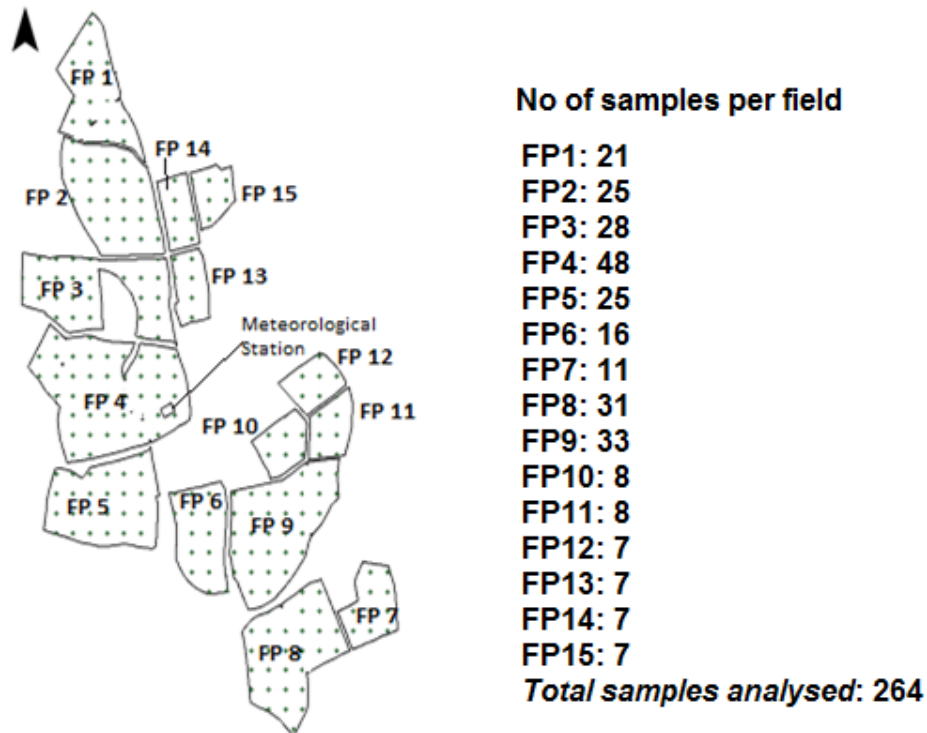


Figure 3.18: Locations (50 x 50m) of soil samples, and number of samples analysed in each field. Sample sites were obtained from a gridded map of the farm platform with a Global Positioning System (GPS) (Source: North Wyke Farm Platform Group at Rothamsted Research).

Box 3.1. Direct contribution of the author to data used in this Aim (Aim 2)

As a participant in the sampling and analysis procedures, I was involved in the sampling of the entire 15 fields, an activity that was completed in about 3 weeks. As a result of my previous knowledge of the use of GPS, I was fixing the positions to sample (after the farm manager had demonstrated it), and my first responsibility was to fix pegs on sited positions and record their coordinates (x, y, z) on the GPS, while the remaining students took samples for either bulk density administration or soil chemical analysis from the fixed points (these activities were shared on our agreements). We interchanged these roles to make sure everyone partook in all of them. We also prepared the samples together for subsequent laboratory analysis (refer to Appendix 3.2 for some photographs showing my involvement).

Sampling positions or points were pre-determined by overlaying a 25 by 25 m interval grid on a 1:50m map of the farm platform on a Global Positioning System (GPS, Trimble R6 model). The positions were physically fixed on the fields with the GPS using a detachable precision antenna and radio receiver that was radio-linked in Real-Time Kinematic (RTK) geodetic surveying mode to a base station as described in Trimble (2003) (Figure 3.19 a-b). Two sample-sets were obtained from each location; the first (Set A) was for bulk density analysis, and was collected by hammering the cutting head of a 5.5 cm (diameter) by 10 cm (height) cylindrical core (Figure 3.19c) into the soil as described by many studies (Black and Hartge, 1986; Rogers and Carter, 1987). Set B samples were obtained in 10 replicates with a 2 cm (diameter) by 10 cm (immersed depth) grass plot sampler (Figure 3.19d). All the samples were taken to the Soil and Herbage Laboratory (SHL) in the Rothamsted Research, North Wyke (www.rothamsted.ac.uk/northwyke/Facilities.php) for storage, until analysed.



Figure 3.19 a-d. Equipment used for soil sampling. a) Antennae with the detachable receiver Trimble GPS for siting where sample should be taken, b) the GPS base station which is radio-linked with the receiver for the real time kinematic site location (survey). c) A 5.5 by 10 cm cylindrical core and sample for bulk density determination, and d) 2 by 10 cm grass plot samplers.

3.4.2.2. Laboratory analysis

Samples were stored in the SHL at 5 - 7°C immediately they were returned from the fields, after each sampling session (morning or evening) for a maximum of 24 hours before they were prepared for analysis. All samples were weighed. The pH of the soil samples was determined by STM 219 method of the Rothamsted Research Laboratory Protocol, RRLP) using pH meter (Jenway 3320 Model). The RRLP analyses a sample pH as equation 3.3.

$$pH_{sample} = pH_{standard} + \frac{(E_{sample} - E_{standard})}{kT} \quad (3.3)$$

Where k = constant, T = absolute temperature (°K), and E = measured 'emf' output of the electrochemical cell used for the test.

The process of determination of bulk density and the organic matter content in the soil samples is summarised in Figure 3.20 a-c. Bulk density (in Set A) was determined as described by the International Organisation for Standardisation, ISO 11272 (ISO, 1998) as the ratio of oven-dried (after 24 hours at 105°C) soil samples to volume of the core (after the volume of materials greater than 2 mm and other organics that were removed had been subtracted) (equation 3.4):

$$BD_d = \frac{\text{Mass of oven-dry soil (Ms in grams)}}{\text{Total volume of core (Vt) - (volume of solids greater >2mm and vegetation), (Wt)}} \quad (3.4)$$

Where Wt was determined by water displacement method, such that volume of materials larger than 2 mm and removed organics were estimated from the volume of water displaced, in a water cylinder as described in Throop et al (2012).

Set B samples were also crumbled on a polyethylene spread supported by a foil during which organics and stones were removed (Figure 3.20 b), before they were sieved to 2 mm particle size, re-labelled and divided into three (about 10 g, each) polyethylene as Subsets B1, B2 and B3 for different chemical analysis. Subset B1 was meant for determination of total nitrogen (TN) and total carbon (TC), and were finely ground in a clean and deionised mortar mill (Retsch RM200 model) before taken to an Elemental Analyser (NA2000, Carlo Erba model) where the concentrations of TN and TC were determined. Subset B2 was also finely ground and were analysed for Nitrogen-15 ($\delta^{15}\text{N}$) and Carbon-13 ($\delta^{13}\text{C}$) isotopes with an Isotope Ratio Spectrometer (SerCon 20-22 model) linked to the Elemental Analyser used for the analysis of Subset B1 (The

structure and procedure of operation of an elemental analyser is documented in Thomson, 2008). Only subset B3 was later oven-dried as required for the determination of the soil organic matter content by the loss-of-weight-on-ignition (or loss on ignition, LOI) method described by Motsara and Roy (2008).



(a) Soil samples kept at 5 - 7 degree Celcius



(b) Sample being crumbled on a polyethylene spread and re-labelled



(c) Crumbled and sieved samples in the oven at 105 degree celcius for 24 hours (for bulk density determination) and less number of hours for loss on ignition method for organic matter determination.

Figure 3.20 a-c: Storage and laboratory preparation of soil samples. All materials were cleaned with deionised water before use for a new sample. Transparent hand gloves were worn before samples were handled.

3.4.2.3. Statistics and inferential analysis

The entire data were first examined with different semi-variogram models in Genstat software (Discovery version, Rothamsted Research, Harpenden, UK), and the model which accounted for the highest percentage of variance in the distribution of data along with the positions (x, y) was selected for the spatial analysis of each variable. The parameters of the variogram models and the percentage variance are explained with the results. The derived values of nugget, sill and range effects for each variable were considered (substituted for the default values) in the generation of the kriging interpolation maps in the Integrated Land and Water Information System (ILWIS, 3.3 version, ITC, Eschende, Netherlands) software. Kriging interpolation is known to be efficient for soil evaluation, and the 'ordinary kriging' which is often preferred because of its assumption of constant localised neighbourhood, rather than the constant overall neighbourhood assumption of most other variants of kriging (Hendrikse, 2000; Mueller et al, 2001; Bohling, 2005), and is adopted for this study. The assumption of constant localised neighbourhood suggests that close regions

can be correlated but tendency for variation occurs with distances away from a point. Carbon and nitrogen stocks were derived as described by Kiely et al (2010) with equations 3.5 and 3.6:

$$C_d = BD_d \times \%TC_d \times d_d \quad (3.5)$$

$$N_d = BD_d \times \%TN_d \times d_d \quad (3.6)$$

Where

C_d and N_d = soil carbon and nitrogen stock, respectively (t C ha⁻¹, t N ha⁻¹, respectively) for depth interval d (m)

$\%C_d$ and $\%N_d$ = percentage of carbon and nitrogen content, respectively, for depth interval d (m)

BD_d = Bulk density (kg m⁻³) at depth interval d (m)

d_d = soil depth (0.1 m was used in this study)

Effects of soil organic matter, elevation and bulk density on the distribution of total nitrogen, total carbon, carbon-to-nitrogen ratio (C: N), as well as carbon and nitrogen stocks, were assessed with regression models. Many measures of variability exist, and among the common ones is the Coefficient of variation (CV), which is used in this study to evaluate the variations among the fields. The CV can however be meaningless for data whose mean or standard deviation is close to zero (0), and negative values, thus the Gini coefficient of inequality and Lorenz curve is used in this study to evaluate the homogeneity of heterogeneity in the soil characteristics across the fields. The Gini coefficient of inequality, and Lorenz curve was proposed by Weiner and Solbrig (1984) to overcome the inadequacies of statistical descriptors of dispersion in plant population, but have more recently been found adequate in soil mapping, classification and general pedo-diversity (Shepherd and Walsh, 2002; Wiegand et al, 2005; McBratney and Minasny, 2007; Stahr et al, 2013) (The original Gini coefficient had originated from Gini, 1912). The Gini coefficient G quantifies the area between the Lorenz curve and the line of perfect equality expressed as a fraction of the area under the $y = x$ line (Sadras and Bongiovanni, 2004). The G coefficient ranges 0–1 (G=1 if there is absolute heterogeneity, and G=0 in case of absolute homogeneity; the range between 0 and 1 indicates varying level of heterogeneity) (e.g. Weiner and Solbrig, 1984).

3.4.3. Methodology for Research Aim 3

3.4.3.1. Data sourcing

The objectives of this Aim (Aim 3) are to (1) examine the spatial and temporal variations in discharge and chemical effluents from selected fields in

the North Wyke Farm Platform; and (2) examine the patterns of concentration-discharge (c-q) hysteretic relationships of different chemical constituents at the farm-scale. Selected chemical constituents are; water temperature, pH, dissolved oxygen (DO), conductivity, turbidity and nitrate (NO_3^-). The chemical parameters have been selected because of their importance in water monitoring (Chapman, 1992). Conductivity and turbidity have been extensively used as surrogates for dissolved and suspended solids (Packman et al, 1999; Pellerin et al, 2008; Kim and Furumai, 2013; Viviano et al, 2014) while water temperature, pH and dissolved oxygen are known to provide insights into water quality and solute behavioural patterns (Foster, 1978; Shanley and Peters, 1988; Chapman, 1992; Rose, 1994; Webb and Nobilis, 1994; Cirimo and McDonnell, 1997; Packman et al, 1999; Chapman, 1992; Davies-Colley and Smith, 2001; Webb et al, 2003; Pavanelli and Bigi 2005; Gippel, 2006; Bilotta and Brazier, 2008; Minella et al, 2008; Oeurng et al, 2010; Siwek et al, 2011). Nitrate is also an important limiting nutrient, and is an important element since the study area is within the nitrate-vulnerable zone in the United Kingdom (Figure 3.21).

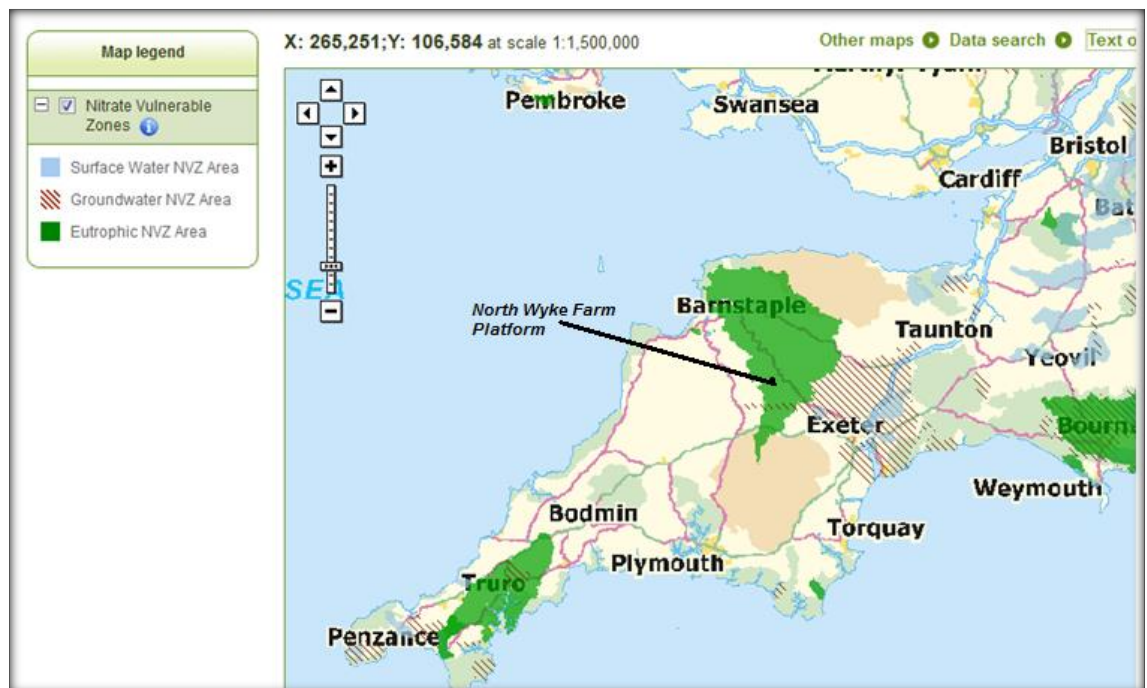


Figure 3.21. North Wyke Farm Platform in the area classified as nitrate vulnerable zone in the United Kingdom.
(Source: environment-agency.gov.uk)

3.4.3.2. Selected fields and their characteristics

Four fields (Pecketsford (Field 1)), Burrows (Field 4), Middle and Higher Wyke Moor (Field 8), and Longlands East (Field 15)) were selected for the investigation of the concentration-discharge that this aim proposed. The fields have been selected because of their varying attributes (Table 3.8 and Figure 3.22 a-b). Selected fields were all ploughed and grazed in 1995-2005 (except for southern Pecketsford which was cultivated with rye grass within the period). Three of the fields (except Longlands East) were also fertilized with farm yard manure (FYM) in 2011. The three fertilized fields (except Longlands East) have also been grazed with both cattle and sheep on a rotational pattern since 2005. Only sheep has been grazed on Longlands East since 2005.

Average proportions of areas occupied by the dominant soil series and the sizes of the fields showed that Burrows contains four different soil series; Pecketsford has three while Middle and Higher Wyke Moor and Longlands East are relatively homogenous (Hallsworth soil series dominates the Middle and Higher Wyke Moor while Longlands East is covered by Halstow soil series) (Figure 3.22 a). Burrows is the largest of the selected fields (Figure 3.22 b), and its average slope varies between 0 and 25% while the smallest field is the Longlands East with average slope varying between 2-6%. Pecketsford and Middle and Higher Wyke Moor are 0-12% and 2-8%.

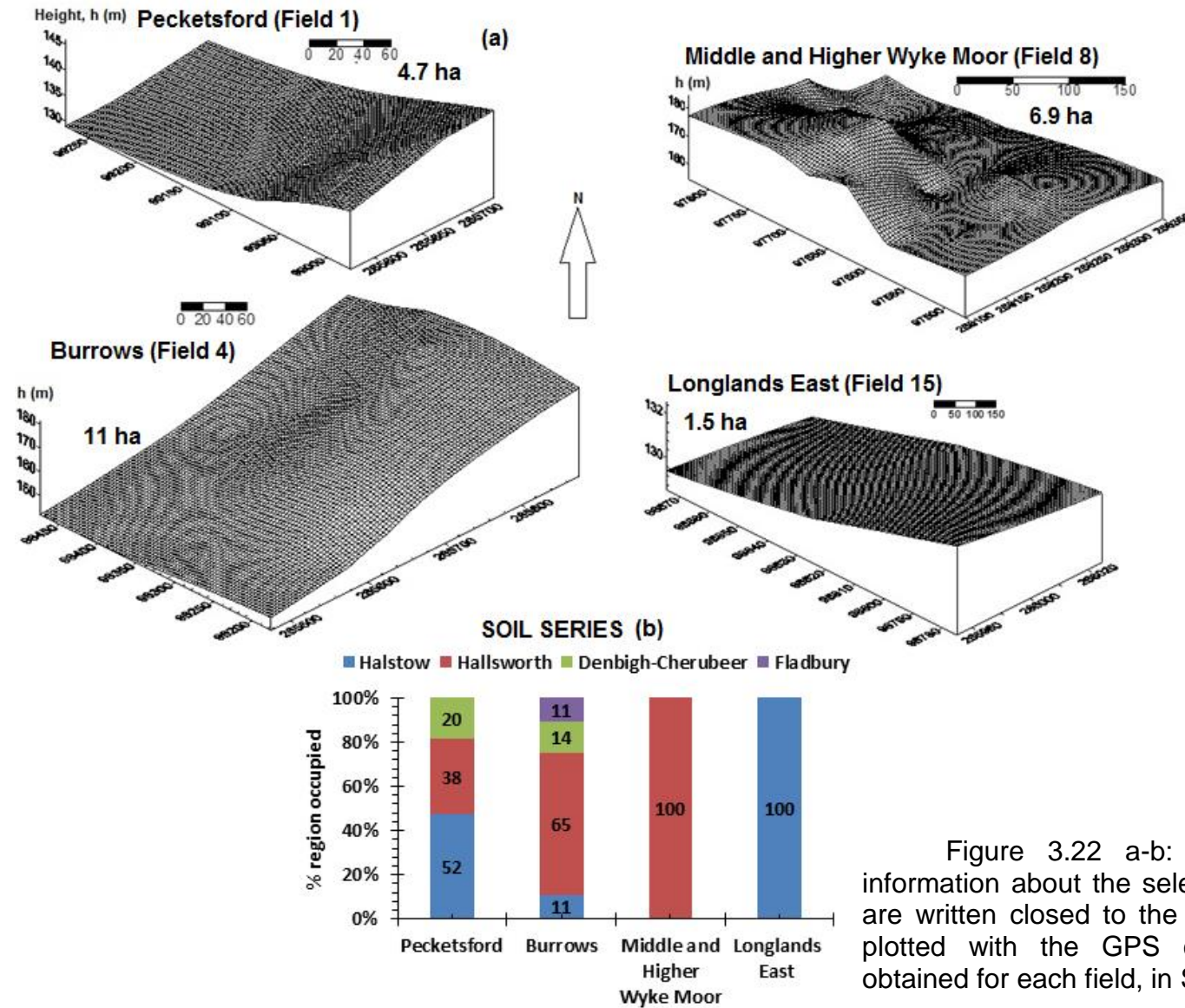


Figure 3.22 a-b: Elevation (a) and soil series (b) information about the selected fields. The values of their sizes are written closed to the elevation map. Elevation maps were plotted with the GPS coordinates and respective heights obtained for each field, in Surfer software.

Table 3.8. Some attributes of selected fields for investigation on concentration-discharge relationships (Aim 3).

Field No	Field Name	Soil Series distribution	Field size (ha)	Land management		Average slope (%)
				1995-2005	2005-2011	
1	Pecketsford	52% Halstow 28% Hallsworth, and 20% Denbigh-Cherubeer.	4.7	Ploughed, reseeded and cultivated with rye grass.	Grazing of sheep and cattle. Farm yard manure (FYM) was added to the southern section part of the field in 2011.	0-12.
4	Burrows	65% Hallsworth, 14% Denbigh-Cherubeer 11% Halstow and 11% Fladbury.	11.0	Ploughed, reseeded and grazed.	Grazing of sheep and cattle. FYM was added, except the northern section (top Burrow) of the field in 2011.	0-25%.
8	Middle & Higher Wyke Moor	100% Hallsworth.	6.9	Ploughed, reseeded and grazed	Grazing of sheep and cattle. FYM was added to part (Middle Wyke Moor) in 2011.	2-8%.
15	Longland East	100% Halstow.	1.5	Ploughed, reseeded and grazed.	The field was grazed with sheep since 2011, and unlike other fields, FYM was not added to this field in 2011.	2-6%.

3.4.3.3. Event sampling

Selected storm events occurred in the 2013 hydrological year (January and November, 2013, which are typical winter and autumn period of a hydrological year were selected). January 2013 was characterised by a mild weather and little rainfall in most parts of England, and average temperature (3.3 -12 °C) was significantly above average for the time of year, until 18th of the month (UK Met Office, 2013). Significant snowfalls (around 25 cm in some locations) however began on 18th January as frontal systems attempted to push across the UK from the west. Rapid thaw and heavy rains also occurred in this month, causing flood and disruptions to the transport network. November (2013) was characterised by westerly weather type with mean temperature of about 5.5 °C, across the United Kingdom and a maximum of about 16.5 °C around Exeter (Airport). January and November receive an average (1981-2010) of 110 mm of rainfall and maximum temperature of 7 °C (more rainfall and less temperature in January) (Appendix 3.3).

An event, as used in this study, starts when runoff begins to increase after the start of a rainfall event that triggers it (or when runoff is increasing after a rainfall event), and it ends when the flow rescinds to its initial pre-event level. If runoff does not return to its initial level, however, the event is assumed to end when the runoff reaches the lowest value before it again increases (Deasy et al., 2006). Thirteen events were selected in both January and November (8 in January and 5 in November) out of the 17 events that were observed. Selected events include low and high, single and multiple peaks events, and are considered to be representatives of the entire events in the study period. Events were selected by with the steps indicated in the flow chart presented as Figure 3.23.

Event-based hydrographs, chemographs and corresponding concentration-discharge (c–q) plots were plotted with the Microsoft Excel, and patterns of both single and multiple events were observed. Event based temporal and spatial variations (across the four selected fields-Pecketsford (Field 1), Burrows (Field 4), Middle and Higher Wyke Moor (Field 8) and Longlands East (Field 15)) in the concentrations of targeted chemical parameters were investigated with analysis of variance. The linearity of the peak discharge, runoff coefficient and runoff chemistry (in terms of selected chemical parameters) was investigated with logarithmic and linear regression analysis. Runoff coefficient, the ratio of total streamflow volume to the total precipitation over a certain area and time was estimated in this study from

the Rational Method (Kadioglu and Sen, 2001), and compare across fields. Patterns of c-q relationship observed in the investigated events were visually compared for inferences about the slope and direction before they were classified into different types.

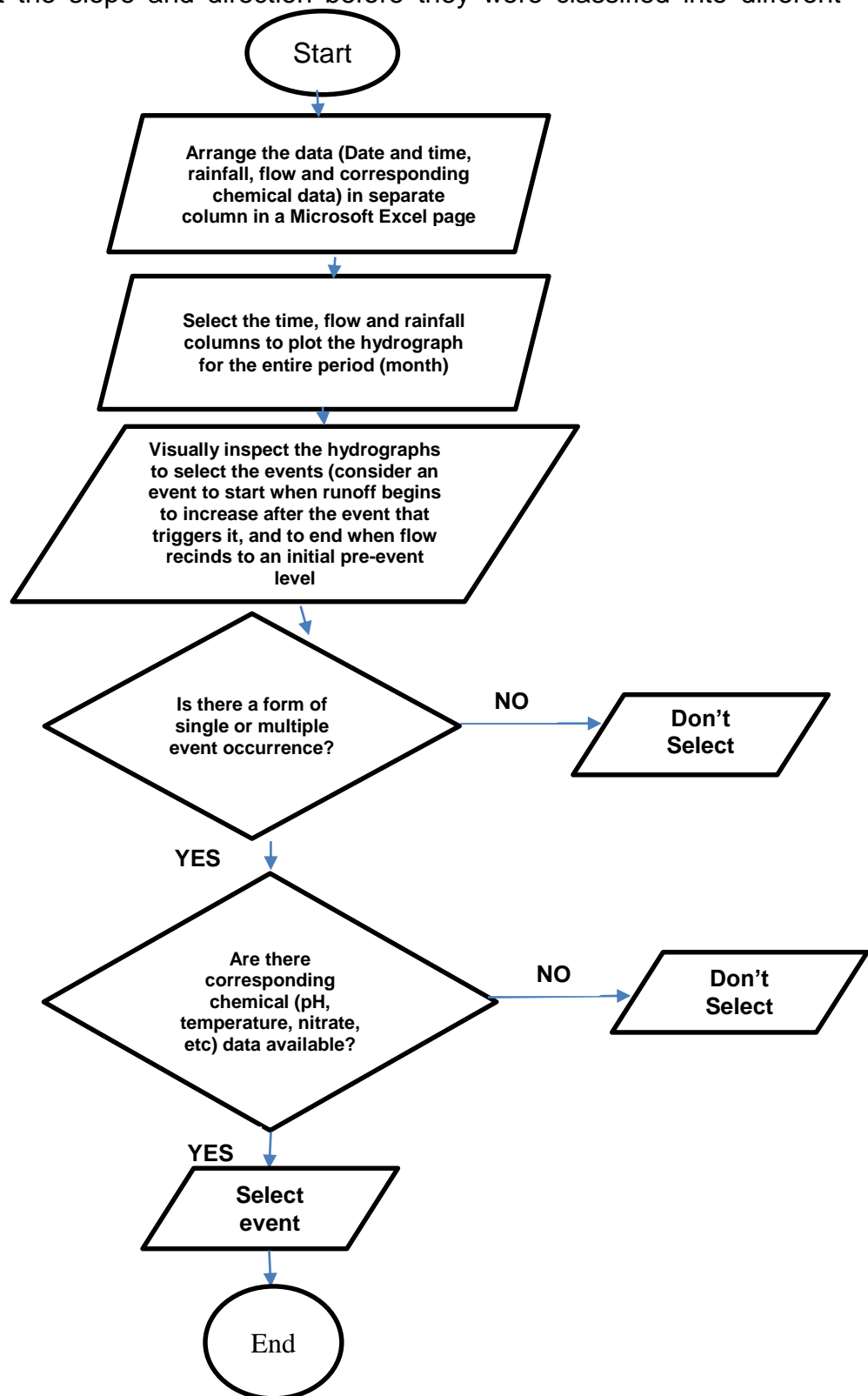


Figure 3.23. Flow chart of the procedure used for selecting the rainfall-runoff events in this study.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. AIM 1: Temporal variability in precipitation and soil water chemistry

4.1.1 Introduction

This section of the thesis (Aim 1) is focused on the interaction of atmospheric deposition, through rainfall events, with the soil in the study area. Specific objectives are to examine (i) the temporal variations in the precipitation and soil water chemistry, and (ii) relationships between the precipitation and soil chemistry. The main hypothesis is that the precipitation chemistry and soil chemistry are directly related in the study area. Two sets of data were analysed based on their availability, and they include (i) a 16 (1993-2011) year monthly precipitation chemistry dataset which was analysed for the relatively long term temporal variability, and (ii) a 2010-2012 biweekly (once in 2 weeks) precipitation and soil chemistry dataset, used in this study to establish whether there are relationships between the chemical variables observed in the two sources (i.e. precipitation and soil). The soil chemistry data comprises those of 0-10cm and below 10cm (depth) water solution, and these are subsequently referred to as topsoil and lower soil layers.

4.1.2. Summary of precipitation and soil water chemistry distribution

A summary of chemical variables in the bulk precipitation and soil solution (topsoil and lower soil layer) samples between 2010 and 2012 (and 1993-2011 for bulk precipitation) at the North Wyke Farm Platform (NWFP) (North Wyke station of the Environment Change Network) is presented in Table 4.1. Mean values of the chemical variables in the 1993-2011 precipitation samples were not statistically different from those of 2010-2012 (Table 4.1), suggesting relative stability in the atmospheric chemistry since 1993, despite the larger variability in the longer term (1993-2010) data. The summary for the 2010-2012 biweekly data showed that both soil water and precipitation were slightly acidic (mean pH is 5.2 - 6.4). The concentrations of cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+ and NH_4^+) were generally low, and except from Na^+ (mean concentration in precipitation was 2.3 mg l^{-1} , and was 6.1 and 6.7 in top and below soils, respectively) they were all below 1 mg l^{-1} . Most anionic concentrations (NO_3^- , PO_4^{3-} and SO_4^{2-}) were also generally low, being less than 1 mg l^{-1} , except the SO_4^{2-} in the soil waters, and Cl^- . Mean concentration of dissolved organic carbon (DOC) was fairly equally distributed, varying $2.1\text{-}2.4 \text{ mg l}^{-1}$ in both

precipitation and soil waters (Table 4.1). The dominant ionic components of the precipitation and soil waters are illustrated in Figure 4.1. Except for K⁺, NH₄⁺ and NO₃⁻, the mean concentrations of the investigated chemical variables were higher in the precipitation than the soil waters.

Table 4.1. Mean concentrations ± standard deviation, and range of the concentrations (in parentheses) of investigated chemical variables in the bulk precipitation and soil water at the North Wyke Farm Platform in Devon County, United Kingdom (Data were sourced from the Environment Change Network).

Chemical Variable	Bulk Precipitation ^a		Soil water solution	
	1993-2011	2010-2012	Topsoil (2010-2012)	Lower soil layer (2010-2012)
pH	5.4±0.57 (4.3-7.3)	5.2±0.35 (4.5-6.0)	6.3±0.24 (5.5-6.7)	6.4±0.26 (5.4-6.8)
Alkalinity (mg l ⁻¹)	3.8±4.12 (0-28.9)	4.3±3.51 (0.1-12.4)	6.3±4.42 (1.0-19.2)	8.3±5.67 (0-21.6)
Conductivity (µScm ⁻¹)	27.8±14.21 (6.5-103.4)	23.0±9.65 (9.3-49.6)	58.4±8.88 (40.7-74.1)	56.1±7.18 (41.8-69.4)
Na ⁺ (mg l ⁻¹)	3.3±1.91 (0.5-17.3)	2.3±1.36 (0.5-6.6)	6.1±0.51 (5.3-7.4)	6.6±0.48 (5.7-7.8)
K ⁺ (mg l ⁻¹)	0.6±0.75 (0-9.4)	0.3±0.28 (0.01-1.3)	0.2±0.28 (0.01-1.2)	0.2±0.20 (0-0.8)
Mg ²⁺ (mg l ⁻¹)	0.4±0.4 (0-5.1)	0.3±0.18 (0.1-0.8)	1.1±0.29 (0.4-1.6)	1.1±0.20 (0.6-1.4)
Ca ²⁺ (mg l ⁻¹)	0.6±1.21 (0-6.51)	0.4±0.49 (0.1-2.7)	3.0±1.01 (1.1-4.9)	2.1±0.59 (0.9-3.4)
NH ₄ ⁺ (mg l ⁻¹)	0.3±0.89 (0-4.9)	0.3±0.27 (0.1-1.54)	0.04±0.13 (0-0.6)	0.01±0.01 (0.001-0.03)
NO ₃ ⁻ (mg l ⁻¹)	0.3±0.61 (0-2.1)	0.3±0.17 (0.1-1.1)	0.1±0.06 (0-0.3)	0.1±0.05 (0.0-0.3)
Cl ⁻ (mg l ⁻¹)	5.5±3.21 (0.6-25.7)	4.4±2.47 (0.7-12.1)	8.0±1.4 (4.5-9.9)	9.6±1.11 (6.3-11.7)
PO ₄ ³⁻ (mg l ⁻¹)	0.02±0.04 (0-0.3)	0.02±0.03 (0-0.2)	0.01±0.02 (0-0.09)	0.02±0.04 (0.001-0.27)
SO ₄ ²⁻ (mg l ⁻¹)	0.3±0.81 (0-7.9)	0.3±0.22 (0.01-1.2)	2.1±0.46 (0.2-2.8)	1.9±0.40 (0.3-2.4)
DOC (mg l ⁻¹)	*2.3±1.81 (0.5-12.1)	2.1±1.26 (1.3-4.4)	2.4±0.72 (1.7-3.9)	2.1±0.54 (1.4-3.2)

*Asterisked value was only for 2006-2011. ^a the monthly (2010-2012) and biweekly (1993-2009) did not exhibit significant difference (Pearson $r \geq 0.62$)

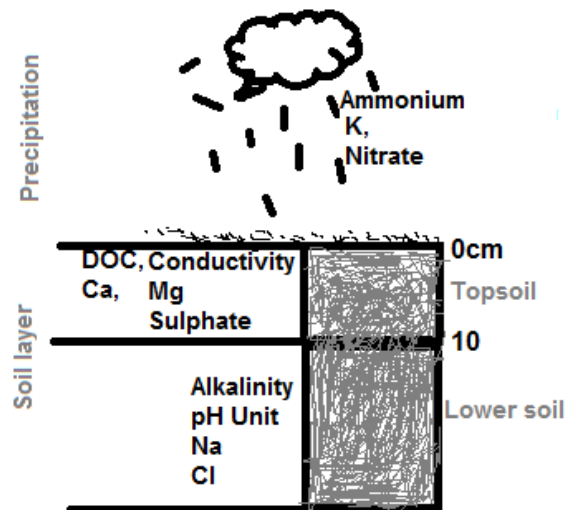


Figure 4.1. Distribution of the chemical variables based on their relative dominant mean concentrations in the precipitation and soil waters. Note that mean distributions is based on Table 4.1.

4.1.3. Temporal Variations in precipitation and soil chemistry

Most of the chemical variables exhibited smaller variability (except NH_4^+) in the soil water than in the precipitation (Figure 4.2). Conductivity, Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{3-} and DOC chemical variables exhibited smaller (<50%) variability in the soil water than observed in the precipitation, and NH_4^+ , PO_4^{3-} and K^+ exhibited relatively larger variability than other chemical variables in the soil water. In general, both the earlier results (Table 4.1) and Figure 4.2 showed that the longer time series of precipitation chemistry (1993-2011) revealed larger variation than the shorter dataset. When the solute variability in the same time-scale precipitation and soil data (2010-2012) were compared, PO_4^{3-} , NH_4^+ , K^+ and alkalinity exhibited the largest variability ($\geq 100\%$ in both precipitation and soil waters) while pH was the least varied in all the waters. Conductivity, Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} and DOC were less varied (<50%) in the soil waters than the rest variables.

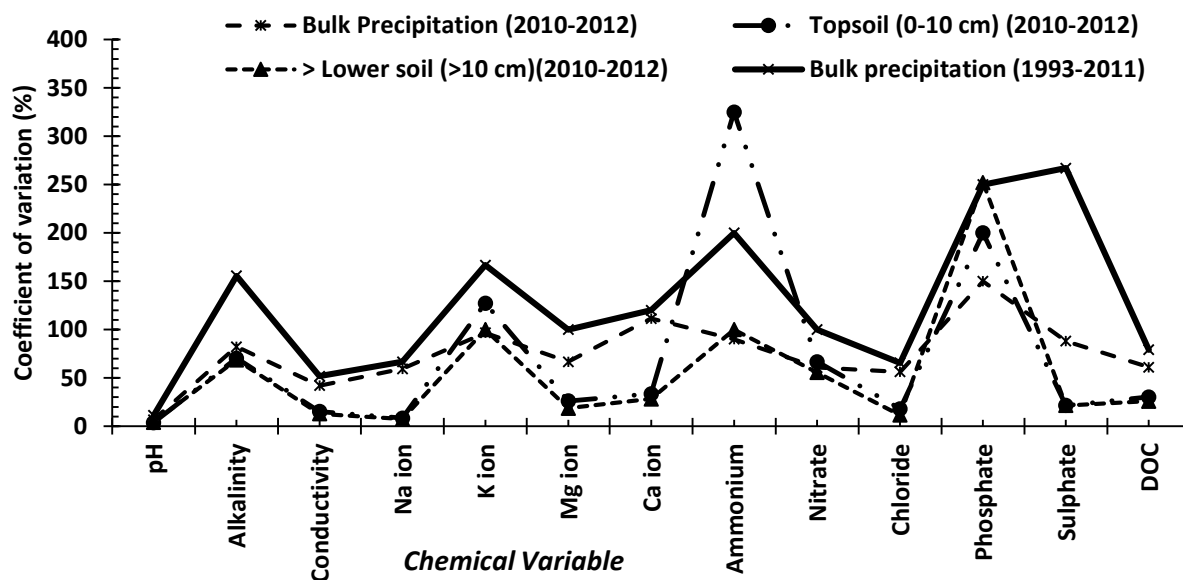


Figure 4.2. Coefficients of variations of the investigated chemical variables in the bulk precipitation and soil water solution at the North Wyke Farm Platform (Note that bulk precipitation is in two sets; 1993-2011 and 2010-2012. Segregation into these sets is to compare same chemical variable for soil solution for same period of dataset).

One of the values of the 1993-2011 data in the study is in the examination of the annual and monthly variations in the precipitation chemistry over time. All the chemical variables showed significant temporal variation, both annually and monthly (Figure 4.3a and 4.3b). The range (minimum-maximum) in both the annual and monthly distribution graphs suggests that variability was larger at one period than the other. For example, extreme concentrations of K^+ in the bulk precipitation samples occurred in 2010 (Figure 4.3a) in October (Figure 4.3b) while the high concentrations in conductivity, PO_4^{3-} and Cl^- (in year 2011), and Na^+ , NH_4^+ and Mg^{2+} (2002-2004) also showed extreme concentrations in the precipitation (Figure 4.3a). Figure 4.13b showed that Mg^{2+} , conductivity, Na^+ , Ca^{2+} and pH were generally higher in October-February while NO_3^- , SO_4^{2-} , DOC, PO_4^- and alkalinity showed extreme cases in March-September.

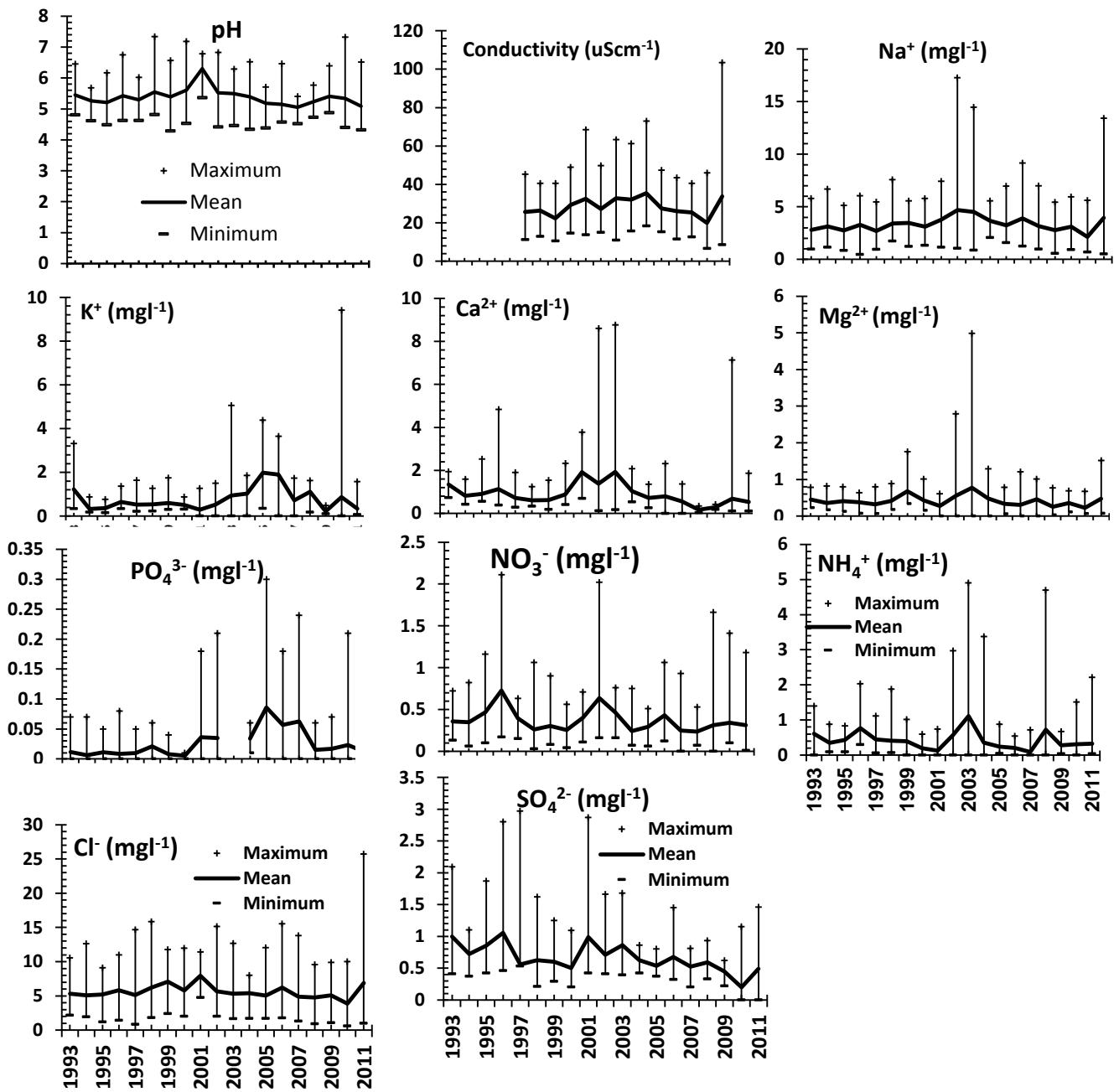


Figure 4.3 a: Annual (1993–2011) mean and range (minimum–maximum) of investigated chemical variables in the bulk precipitation at North Wyke Farm Platform. Note that annual variation in DOC is not presented here because of its 1993-2005 missing data gap.

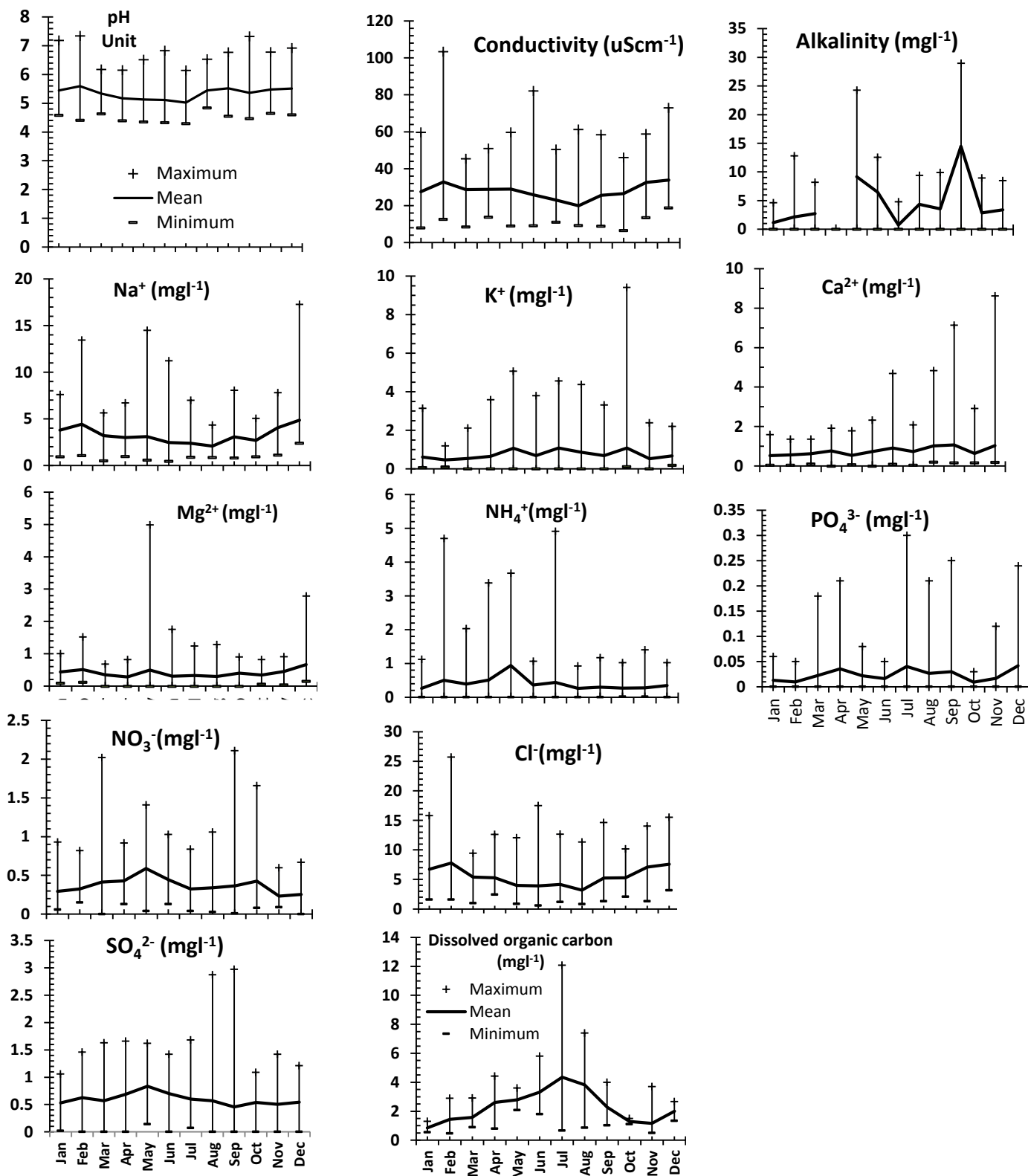


Figure 4.3 b: Monthly (1993–2011) mean and range (minimum–maximum) of investigated chemical variables in the bulk precipitation at North Wyke Farm Platform. Note that the mean monthly variation for conductivity and DOC is for 1998–2011 and 2005–2011, respectively.

4.1.4 Relationship between the bulk precipitation, topsoil water and the lower soil water chemistry

The results of the Pearson correlation and regression analyses that were used to relate each of the investigated chemical variables in the precipitation and soil (top and lower soil layers) chemistry in the study area with the biweekly (2010-2012) datasets are presented in Table 4.2. Fairly strong and significant ($p \leq 0.05$) correlations between the precipitation and topsoil chemistry occurred only with pH ($r = -0.45$), alkalinity ($r = 0.54$), Ca^{2+} ($r = -0.45$) and NH_4^+ ($r = 0.46$). The coefficient of determination (R^2) for the linear regression of the relationships between these two sources (precipitation and soil) showed that less than 30% of the variance in the chemistry of the topsoil solution was explained by the variance in the precipitation chemistry (Table 4.2). The relationship between precipitation and the lower soil layer's solution also showed fairly strong relationship with alkalinity, ($r = 0.54$), Ca^{2+} ($r = -0.45$) and DOC ($r = 0.43$), and about 16-30% ($R^2 = 0.16-0.30$; $p < 0.05$) variance of the total variance of these variables in the lower soil were only explained by their variations in the precipitation. In general, approximately 30% (or less) of the variance in the distribution of the investigated chemical variables in the soil water solution were explained by their variance in the precipitation in the study period. The relationship between the chemistry of the top and lower soil solution was stronger (than either of the soil layers with precipitation) for most of the investigated variables ($r = 0.47-0.80$; $p < 0.05$), except for chloride and phosphate. Neither chloride nor phosphate exhibited significant correlation with any of the identified sources (Table 4.2). Variance in the distribution of alkalinity, conductivity, Mg^{2+} , Ca^{2+} and SO_4^{2-} in the topsoil explained at least 60% ($R^2 = 0.60-0.65$; $p < 0.05$) of the total variations of same variables in the in the lower soil layer, and other variables, except DOC , PO_4^{3-} and Cl^- explained between 36 and 49% ($R^2 = 0.36-0.49$; $p < 0.05$) of their variance in the lower soil layer.

Table 4.2: Results of the Pearson correlation (r) and regression of the concentration of each chemical variable in bulk precipitation and soil (top soil and lower layer) water (the coefficient of determination R² is in parenthesis in the 'regression' column). Corresponding graphs are provided in Appendix 4.1.

Chemical Parameter	Bulk Precipitation						Topsoil (< 10cm depth)		
	< Top soil 10cm depth)			Lower soil layer (> 10 cm depth)			Lower soil layer (< 10cm depth)		
	r	Slope (b)	R ²	r	Slope (b)	R ²	r	Slope (b)	R ²
pH	-0.5	-3.5	0.2	-0.2	-1.4	0.02	0.65	5.1	0.4
Alkalinity (mg l ⁻¹)*	0.5	0.3	0.2	0.5	0.4	0.3	0.79	1.0	0.6
Conductivity (µS cm ⁻¹)	0.4	0.2	0.03	0.2	11.3	0.04	0.78	36.2	0.7
Na ⁺ (mg l ⁻¹)	0.2	3.6	0.03	0.3	4.3	0.1	0.67	4.0	0.5
K ⁺ (mg l ⁻¹)*	0.2	0.2	0.03	-0.01	0.02	0.02	0.54	0.1	0.5
Mg ²⁺ (mg l ⁻¹)	0.1	0.1	0.02	0.2	0.13	0.1	0.79	0.6	0.6
Ca ²⁺ (mg l ⁻¹)	-0.5	-0.9	0.3	-0.5	-0.7	0.3	0.79	1.3	0.6
NH ₄ ⁺ (mg l ⁻¹)*	0.5	15.9	0.2	0.03	0.1	0.001	0.62	0.3	0.4
NO ₃ ⁻ (mg l ⁻¹)*	0.2	0.6	0.04	0.2	0.5	0.03	0.60	0.6	0.4
Cl ⁻ (mg l ⁻¹)	-0.2	-0.7	0.001	0.1	1.5	0.01	0.23	1.3	0.1
PO ₄ ³⁻ (mg l ⁻¹)*	0.2	0.1	0.04	0.1	0.1	0.01	0.02	0.1	0.0004
SO ₄ ²⁻ (mg l ⁻¹)	0.3	0.2	0.06	0.3	0.1	0.1	0.80	0.7	0.6
Dissolved organic carbon (mg l ⁻¹)	0.1	0.1	0.0004	0.4	2.1	0.2	0.47	1.3	0.2

4.1.5. Relationships among chemical variables in the different source areas

Relationships among the chemical variables in the precipitation, topsoil and lower soil solution investigated via the Principal Component Analysis (PCA) showed significant differences in the relative distribution of the chemical variables around a Varimax rotated scale (Figure 4.3ai-cii). Whilst Cl, Na⁺, Mg²⁺, conductivity, alkalinity and Ca²⁺ were similarly distributed in the precipitation and lower soil water, SO₄²⁻ was similarly relatively positioned as with the topsoil. In addition, PO₄³⁻, NO₃⁻, NH₄⁺, K⁺ and DOC were similarly rotated in the topsoil and lower soil waters (Figure 4.3ai-ci). In general, all the investigated variables exhibited closer relationship in the precipitation than observed in the soil solutions. The percentage contributions of each chemical variable in the sources suggests NO₃⁻ was the least (of all the investigated variables) contributor to the overall water chemistry in the lower soil layer, and DOC was also comparatively less significant in the soil solution from both top and lower soil layers (Figure 4.3bii-cii).

In addition, the results of the Pearson correlation coefficient of the relationship among the chemical variables are presented in Table 4.3a-c. More variables exhibit strong and significant relationship in the precipitation samples more than either the topsoil or lower soil solution. For example while conductivity in the precipitation chemistry showed strong and positive correlation ($r \geq 0.60$; $p < 0.05$) with all other variables, except alkalinity and DOC, conductivity in the soil waters correlated positively with only K⁺ ($r = 0.93$) and Na⁺ ($r = 0.78$) in the topsoil and only fairly strongly with pH ($r = 0.60$) and DOC ($r = 0.48$) in the lower soil water (Table 4.3c). Na⁺ and Cl⁻ were also strongly correlated in all the sources, although the ions were most strongly correlated in the precipitation ($r = 0.97$ in precipitation; $r = 0.53$ in the topsoil and $r = 0.68$ in the lower soil layer). The anions were more significantly correlated in the precipitation than in either of the soil waters (Table 4.3a-c).

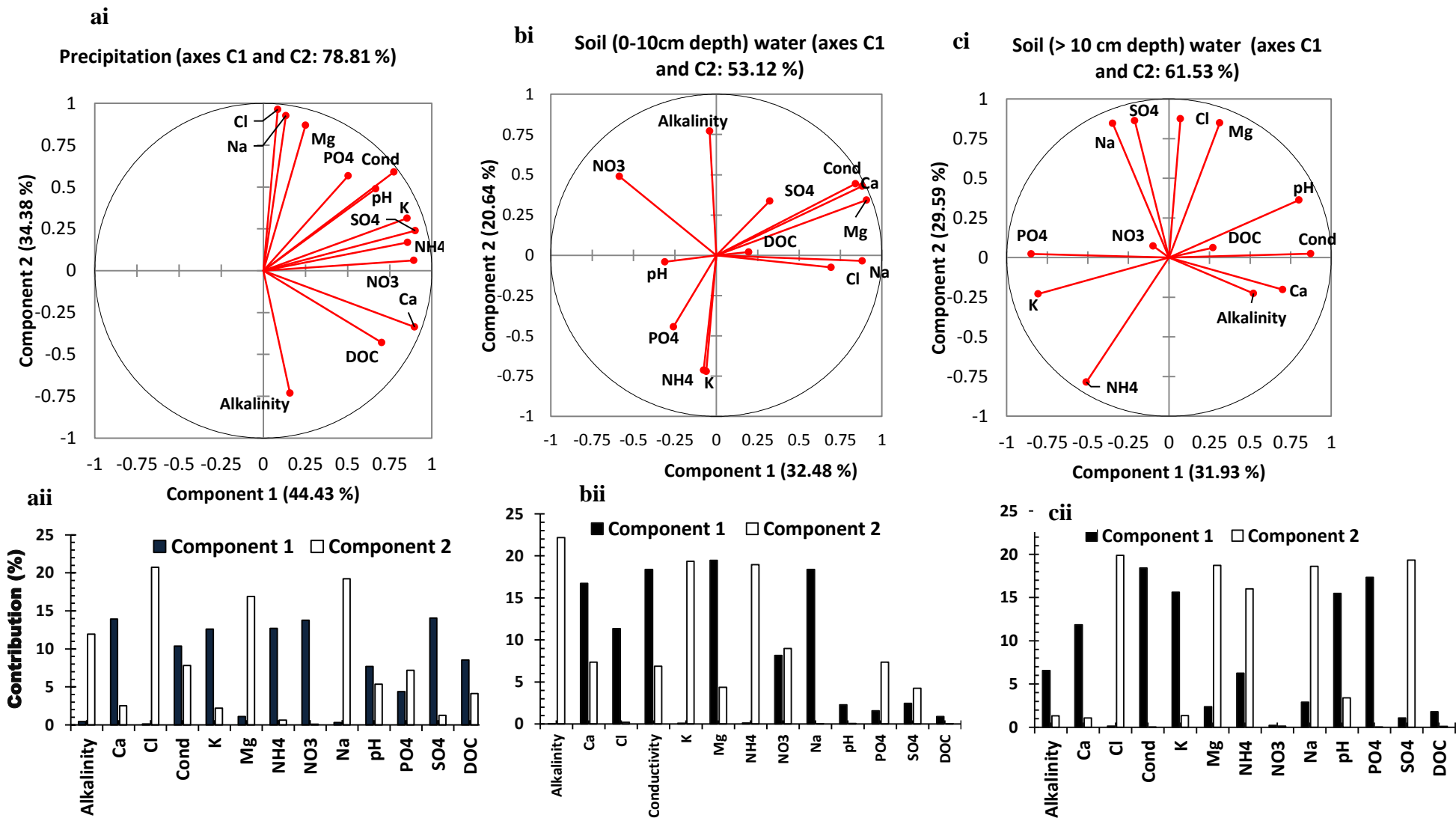


Figure 4.4 ai-cii. Principal components' distributions and the corresponding percentage contributions of the investigated chemical variables in the precipitation and soil (0-10cm and below 10cm depths) water at North Wyke from 2010-2012 (bimonthly data). Results presented have all been rotated by Varimax rotation and Kaiser Normalisation procedures in XLSTAT. The correlation matrix for each spatial result is presented as Appendix 4.2 a-c.

Table 4.3 a: Correlation matrix of the investigated chemical parameters in the bulk precipitation at North Wyke.

Variables	Alkalinity	Ca ²⁺	Cl ⁻	Cond.	K ⁺	Mg ²⁺	NH ₄ ⁻	NO ₃ ⁻	Na ⁺	pH	PO ₄ ³⁻	SO ₄ ²⁻	DOC
<i>Alkalinity</i>	1												
<i>Ca²⁺</i>	0.328	1											
<i>Cl⁻</i>	-0.573	-0.232	1										
<i>Cond.</i>	-0.296	0.520	0.662	1									
<i>K⁺</i>	0.004	0.649	0.373	0.778	1								
<i>Mg²⁺</i>	-0.416	-0.027	0.941	0.779	0.444	1							
<i>NH₄⁺</i>	-0.236	0.723	0.177	0.802	0.663	0.287	1						
<i>NO₃⁻</i>	-0.160	0.814	0.080	0.767	0.645	0.224	0.977	1					
<i>Na⁺</i>	-0.455	-0.199	0.968	0.651	0.493	0.912	0.161	0.047	1				
<i>pH</i>	-0.248	0.378	0.496	0.723	0.757	0.510	0.518	0.550	0.491	1			
<i>PO₄³⁻</i>	-0.339	0.174	0.495	0.583	0.814	0.426	0.429	0.366	0.605	0.791	1		
<i>SO₄²⁻</i>	-0.010	0.697	0.321	0.901	0.723	0.495	0.892	0.884	0.320	0.644	0.435	1	
<i>DOC</i>	0.749	0.746	-0.258	0.254	0.614	-0.108	0.272	0.353	-0.134	0.346	0.198	0.453	1

Values in bold are significant at $p=0.05$.

Table 4.3 b. Correlation matrix of the investigated chemical parameters in the topsoil (0-10cm) water solution at North Wyke.

Variables	Alkalinity	Ca ²⁺	Cl ⁻	Cond.	K ⁺	Mg ²⁺	NH ₄ ⁻	NO ₃ ⁻	Na ⁺	pH	PO ₄ ³⁻	SO ₄ ²⁻	DOC
Alkalinity	1												
Ca²⁺	0.196	1											
Cl⁻	0.232	0.487	1										
Cond.	0.227	0.950	0.522	1									
K⁺	-0.474	-0.356	-0.156	-0.343	1								
Mg²⁺	0.331	0.902	0.658	0.934	-0.219	1							
NH₄⁺	-0.372	-0.445	0.270	-0.430	0.304	-0.358	1						
NO₃⁻	0.545	-0.308	-0.313	-0.308	-0.242	-0.367	-0.010	1					
Na⁺	-0.055	0.719	0.537	0.779	0.033	0.765	0.093	-0.286	1				
pH	-0.206	-0.136	-0.224	-0.172	-0.031	-0.294	-0.068	0.112	-0.271	1			
PO₄³⁻	-0.031	-0.588	0.048	-0.482	0.219	-0.267	0.365	-0.102	-0.250	-0.087	1		
SO₄²⁻	0.237	0.272	-0.039	0.364	-0.309	0.403	-0.229	-0.117	0.279	-0.546	0.116	1	
DOC	-0.120	0.097	0.058	0.279	-0.159	0.113	-0.029	-0.074	0.255	0.456	-0.086	0.047	1

Values in bold are significant at $p=0.05$.

Table 4.3 c. Correlation matrix of the investigated chemical parameters in the below 10cm soil (depth) water solution at North Wyke.

Variables	Alkalinity	Ca ²⁺	Cl ⁻	Cond.	K ⁺	Mg ²⁺	NH ₄ ⁻	NO ₃ ⁻	Na ⁺	pH	PO ₄ ³⁻	SO ₄ ²⁻	DOC
Alkalinity	1												
Ca²⁺	0.311	1											
Cl⁻	-0.336	-0.119	1										
Cond.	0.340	0.632	0.150	1									
K⁺	-0.527	-0.189	-0.181	-0.616	1								
Mg²⁺	0.055	0.173	0.684	0.229	-0.348	1							
NH₄⁺	-0.099	-0.072	-0.717	-0.529	0.679	-0.732	1						
NO₃⁻	0.523	-0.235	-0.107	-0.358	-0.238	0.020	0.072	1					
Na⁺	-0.334	-0.287	0.684	-0.147	0.208	0.628	-0.494	-0.019	1				
pH	0.275	0.474	0.402	0.597	-0.785	0.514	-0.607	0.182	-0.046	1			
PO₄³⁻	-0.370	-0.729	0.037	-0.632	0.590	-0.392	0.385	0.275	0.357	-0.593	1		
SO₄²⁻	-0.139	-0.254	0.574	-0.312	-0.076	0.754	-0.537	0.324	0.759	0.152	0.078	1	
DOC	-0.281	-0.042	0.373	0.483	-0.260	-0.085	-0.201	-0.258	-0.059	0.374	0.107	-0.364	1

Values in bold are significant at $p=0.05$.

4.1.6. Discussion

The objectives of this study are to examine the temporal variations in the precipitation and soil water chemistry, as well as the relationship between the precipitation and soil chemistry. The main hypothesis was that precipitation and soil chemistry in the study area are significantly related. Results of the analysis showed significant temporal variations in the precipitation of the study area. The mean pH of the precipitation samples were fairly acidic (5.2-5.4), and slightly more acidic than those of the soils (topsoil and lower soil layer) solution (6.3-6.4). Whilst the precipitation samples contained more NH_4^+ , K^+ and NO_3^- in the study period (2010-2012) than existed in the soil solutions, the topsoil was comparatively richer in the dissolved organic carbons, Ca^{2+} , Mg^{2+} , conductivity and SO_4^{2-} , alkalinity, pH unit, Na^+ and Cl^- occurred in comparatively higher concentrations in the lower soil solution. In addition, the coefficient of determination (R^2) of the relationship between the tested chemical variables in the precipitation and soil solutions were less than 30%, and there were only fairly strong correlations ($r = \pm 0.45 - \pm 0.54$) between both the precipitation chemistry and the topsoil solution or and the lower soil solution. Relationships among the investigated variables were also different in the precipitation from the soil sources.

4.1.6.1 Temporal variations in the precipitation and soil water chemistry

The mean pH obtained in this study is considered to be fairly representative of the study area because it is fairly close to the median pH reported (5.6) by Porteous and Barratt (1989) for the Devon County area in which the present study is situated. The pH value is also within the range (4.5-5.6) described by Charlson and Rodhe (1982) that cannot be attributed to acid rain but to be a consequent of the removal of some naturally occurring acids (such as H_2SO_4) from the air by rainfall (Bravo et al, 2000). Naturally occurring acids such as H_2SO_4 are often introduced into the earth's biogeochemical cycles through the sea or ocean bodies as a result of the activities of sulphate-reducing bacteria otherwise known as sea-salt sulphates, and non-sea salt sources (Redfield, 1958; Irwin et al, 2002). Irwin et al (2002) in a study of the trends in sulphate and nitrate wet deposition over the United Kingdom associated sulphate wet deposition with westerly or cyclonic flow because the

sulphate concentration gradient often reflects the origin of cloud-forming air masses.

The effect of climate in the present study cannot be overestimated, especially when the time-series analysis of the 1993-2011 period of chemical variables in the precipitation exhibited significant temporal variations. This effect was also established when the correlation between common meteorological element (rainfall, temperature and relative humidity) and the investigated precipitation chemistry produced significant trends with different levels and directions of association of major chemical variables, as presented in Figure 4.5. Many studies (Eriksson, 1960; Stevenson, 1968; Reid et al, 1981; Irwin et al, 2002) have also linked the distribution of conductivity, Mg^{2+} , Cl^- , Na^+ and SO_4^{2-} to sea spray enrichment, especially in regions under the influence of maritime climate as the present study area.

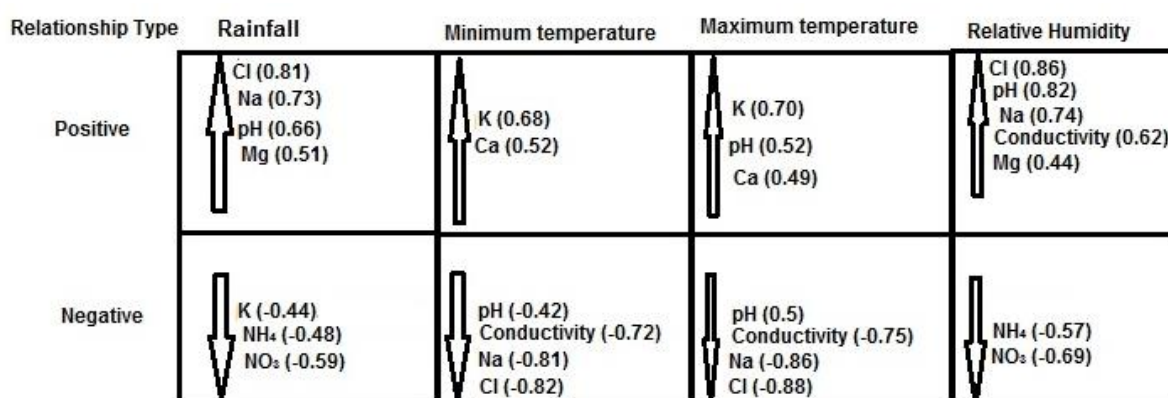


Figure 4.5. Significant correlations (Pearson) between common meteorological elements and precipitation chemistry (1993-2011) (the entire relationship is provided as appendix 4.2).

Another reason that links the major source of the precipitation chemistry in the study area is the results of the comparison of the ratio of some ions to those of the standard seawater (Reid et al, 1981; Bravo et al, 2000; Norman et al, 2001; Thimonier et al, 2008; Wang and Han, 2011). In this study, the Na^+/Cl^- and Mg^{2+}/Na^+ ratio values are close to those of seawater (Table 4.4) and therefore indicate a maritime source for these ions. The Na^+/K^+ and Na^+/Ca^{2+} ratios are, however much lower in the precipitation and are highly variable; Cl^-/SO_4^{2-} ratio in precipitation is also higher than its corresponding seawater ratio. This suggests that potassium, calcium and sulphate can still be allocated to other sources apart from the sea sprays. Sugawara (1967) attributed the sources of

potassium, calcium and sulphate to the influence of terrestrial dusts. Reid et al (1981) also noted that sulphuric acid in the atmosphere often reacts with air-borne particles of silicate minerals to release soluble cations including calcium and potassium.

Table 4.4. Comparison of the ratio values of precipitation ions (coefficient of variation in parentheses) with the corresponding values for sea water.

Ratio	Sea water	Precipitation mean (Coefficient of variation is in parenthesis)	Reference for seawater ratio
Na⁺/Cl⁻	0.86	0.87 (6)	Moller (1990); Bravo et al (2000); Norman et al (2001); Thimonier et al (2008).
Mg²⁺/Na⁺	0.23	0.22 (7)	Berner and Berner (1987).
Na⁺/K⁺	27.63	7.34 (80)	Krauskopf (1967), Reid et al (1981).
Na⁺/Ca²⁺	26.25	4.61 (51)	Krauskopf (1967), Reid et al (1981).
Cl⁻/SO₄²⁻	21.47	25.4 (63)	Krauskopf (1967), Reid et al (1981).
SO₄²⁻/Na⁺	0.25		Wang and Han (2011).
SO₄²⁻/NO₃⁻	–	1.23 (26)	Al-Khashman (2009); Wang and Han (2011).
NO₃⁻/Na⁺	0.00002	0.04 (30)	Al-Khashman (2009); Wang and Han (2011).
NH₄⁺ /NO₃⁻	–	3.25 (25)	Lang and Elliott (1991).

4.1.6.2. Relationship between precipitation chemistry and soil solution

The relationships between the precipitation and soil chemistry in this study were examined, and the results of the correlation of the precipitation with soil chemistry, and PCA suggest minimal relationship between the two source areas. In other words, the chemistry of the precipitation is not significantly related to that of the soil in the study area. The reason for the poor precipitation-soil chemistry relationship can be linked with the level of acidity in the study area, which has been shown to be minimal, since the results have not shown that the precipitation in the study area is acidic. Acidification of grassland through atmospheric deposition is known to be associated with irreversible reduction in cation exchange capacity (CEC) and the mobilization of chemical ions in toxic concentrations (Van Breeman et al, 1984; Blake et al, 1999; Blake and Goulding, 2002). The concentrations of all the investigated chemical variables in the soil solution in this study do not show that the soil is chemically

impaired. The strong relationship between the topsoil and lower soil solutions suggests mixing of the materials in the two soil profiles, and this can be interpreted to infer capability for water retention by the soil in this soil region. Another explanation for the strong relationship may be because the topsoil in the study area may have actually extended beyond 20cm soil depth. Food and Agriculture Organisation, (FAO, 1998) defined the topsoil's lower limit as 30cm depth, or at a root growth inhibiting layer (whichever is shallower). The cross-sections of the dominant soils in the North Wyke Farm Platform, NWFP (Halstow, Hallsworth, Denbigh and Fladbury, refer to Figure 3.6) also showed that lower limits of the topsoil are not the same for the entire region (White, 2008).

4.1.7 Conclusions

The main hypothesis of this chapter is that the precipitation chemistry is significantly related to the soil chemistry in the study area. The study has shown that temporal variability exists in the precipitation chemistry but did not show that either the soil or the precipitation was chemically impaired. Temporal variations in the precipitation chemistry were attributed to climatic effects and anthropogenic sources as informed by the trends and results of the comparison to the seawater ion ratio. The study accepts the hypothesis that precipitation chemistry is related to the soil chemistry in the study area because the constituents of the soil reflected the relatively slightly acidic nature of the precipitation. Strong relationships that existed in the investigated chemical variables (except Cl^- and PO_4^{3-}) between the top (0-10cm soil depth) and lower (below 10cm depth) soil layers may suggest significant mixing of the topsoil and subsoil waters. The finding of this study may have significant implication on the hydrological flowpaths of the various chemical variables.

The next aim investigates the chemical variability of the soil in the fields of the NWFP, and relates this to the existing and previous land use and land management, such that the inference that will be made from the concentration-discharge relationship in Aim 3 can be well interpreted.

4.2. Aim 2: Quantification of the spatial variability of the soil physiochemical properties

4.2.1. Introduction

Distinguishing characteristics of the fields in the present study area (North Wyke Farm Platform) include previous land management, farm size, soil series and terrain. Shepherd et al (2014) showed that the agricultural fields that were previously used for dairy farming generally contained higher concentrations of total nitrogen and carbon, and their discussion focussed on five parameters (bulk density, pH, total nitrogen, total carbon and soil organic matter) in the entire fields in the study area. Puekert et al (2012) reported results of a detailed examination of the soils physiochemical properties of one of the 15 fields attributed the observed spatial variability in the properties to the effect of previous land use and land management (Great Field at North Wyke). The present study examines the in-field and between-field variability in the distribution of the soils' bulk density, pH, total nitrogen, total carbon, organic matter and $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ isotopes. Specific objectives are to quantify spatial variability in the distribution of the afore-mentioned physiochemical variables, and seek explanations for their variability. The measures of carbon and nitrogen stocks from the farm platform were also assessed and compared for each field. The main hypothesis is that the distributions of soil parameters are directly related to land use and farm management. The implications of the spatial variability for the investigated parameters are also discussed.

4.2.2. Characterisation and spatial variability of the soil

Descriptive analysis (mean \pm standard deviation) of the overall soil samples shows that the 0-10cm soil depth is generally slightly acidic (pH = 5.6 ± 0.3), exhibited bulk density, organic matter, nitrogen and carbon of 0.9 ± 0.1 gcm^{-3} , 10.2 ± 2.0 %, 0.5 ± 0.1 % and 4.6 ± 0.9 %, respectively. Mean (\pm standard deviation) concentrations of carbon-13 ($\delta^{13}\text{C}$) and nitrogen-15 ($^{15}\delta\text{N}$) isotopes were 28.8 ± 0.7 ‰ and 6.0 ± 0.5 ‰. C: N ratio, carbon and nitrogen stocks were 8.5 ± 0.6 ratio, 411.5 ± 85.1 kgm^{-2} and 48.3 ± 9.2 kgm^{-2} , respectively (Table for the descriptive statistics is provided as appendix 4.3). Coefficients of variation of the selected parameters were generally low (being below 20 % and below, except for the carbon stock) (Figure 4.6).

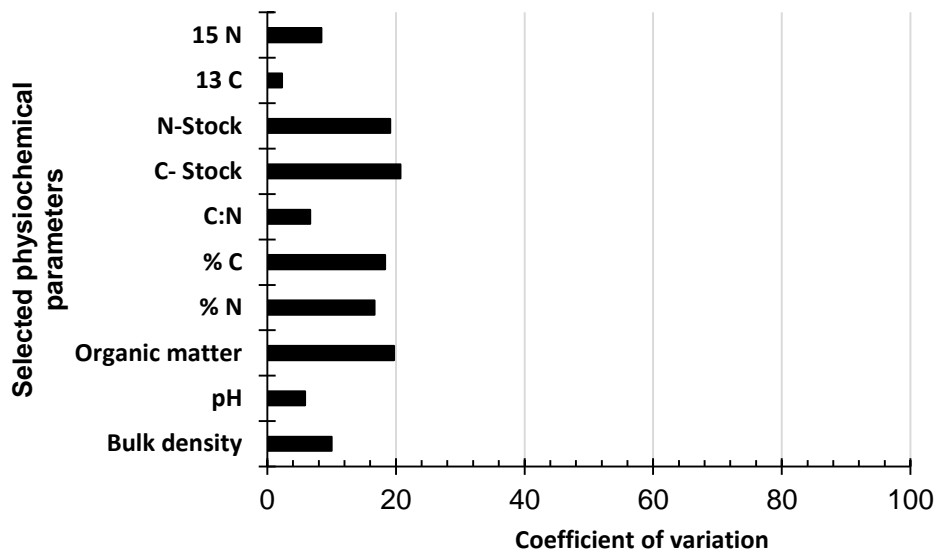


Figure 4.6. Overall coefficients of variations of selected physiochemical parameters in the North Wyke Farm Platform.

The results of the kriging interpolations (maps), corresponding error maps and semi-variograms for the investigated parameters showed that they exhibit significant spatial variability (Figure 4.7-4.12) (Note that the values are plotted in different colour scale (blue through green and yellow to red), based on the value range of each variable, and that areas in the kriging maps interpolated as ‘non-represented’ or ‘uncertain’ are areas for which estimates based on the semi-variogram model may be ambiguous). The kriging interpolation for the pH, bulk density, organic matter and other investigated parameters show their status while the error maps reflect the level of uncertainty associated with each sample points. The semi-variogram describes the lag or range at which sample values are independent of one another, and the proportion of the total variance that occurs at a distance less than the minimum sampling interval. Gini coefficient typically varies from 0 to 1; departure from 0 suggests increasing heterogeneity.

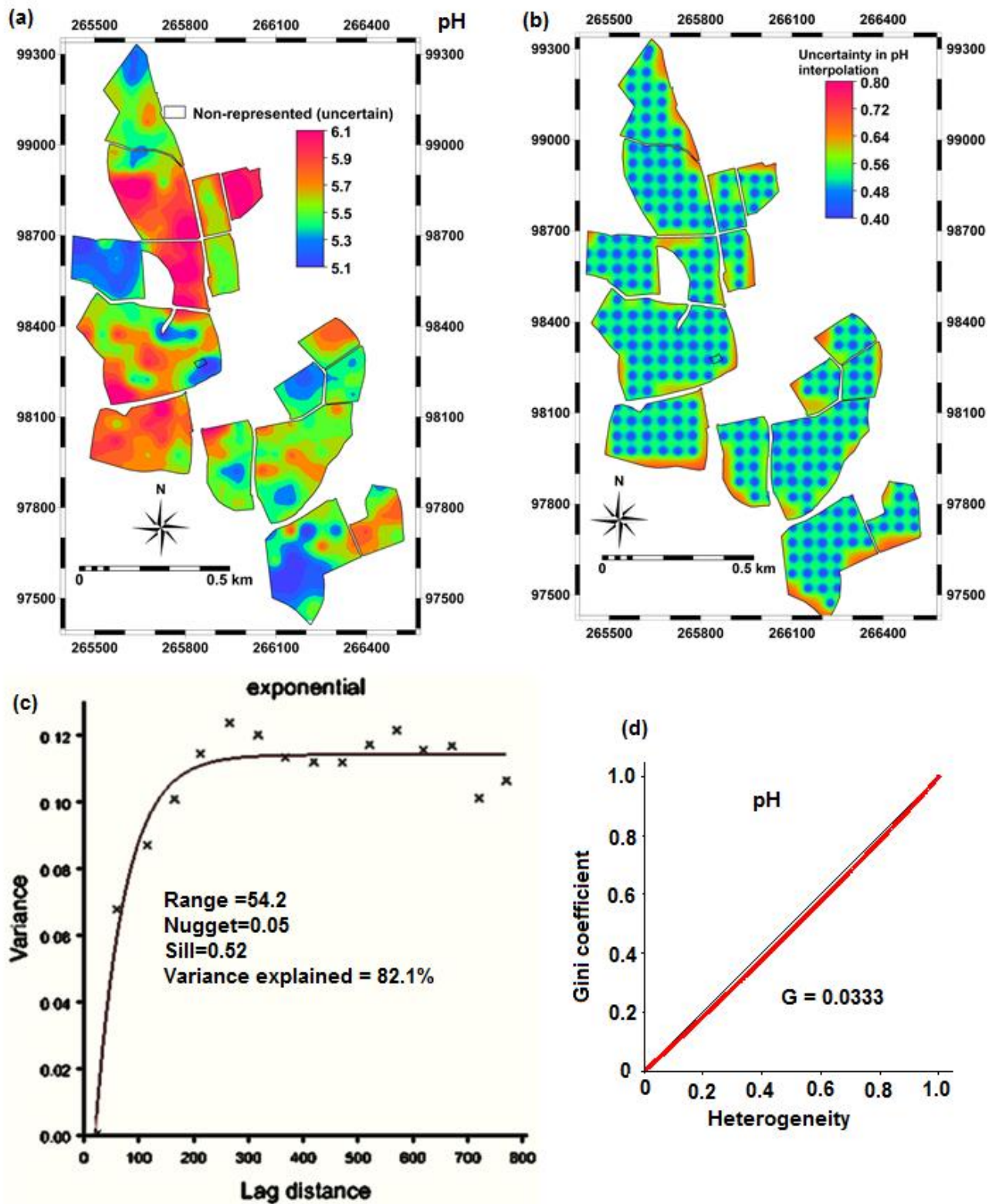


Figure 4.7: Spatial variations in the soil pH at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

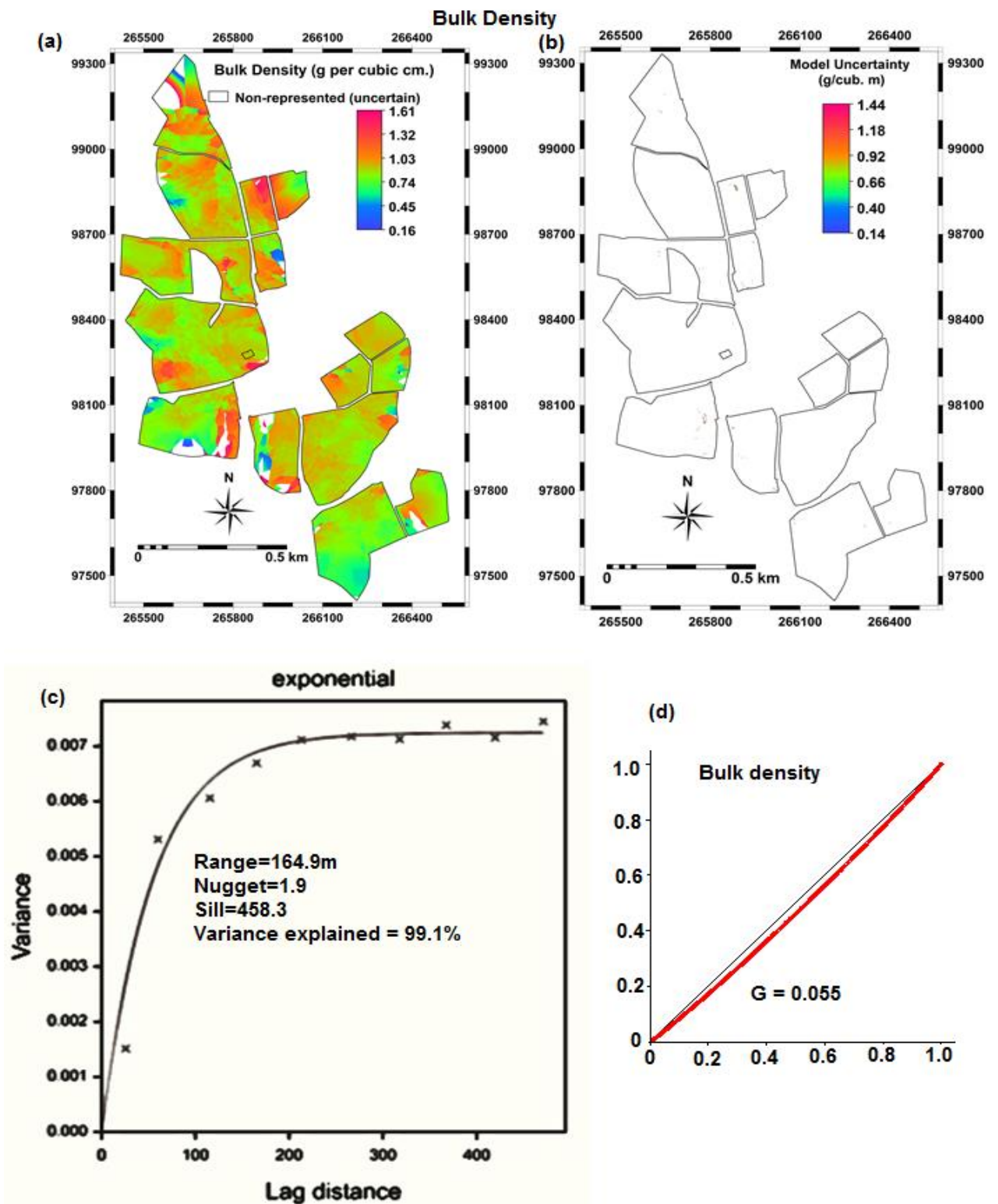


Figure 4.8: Spatial variations in the soils bulk density at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

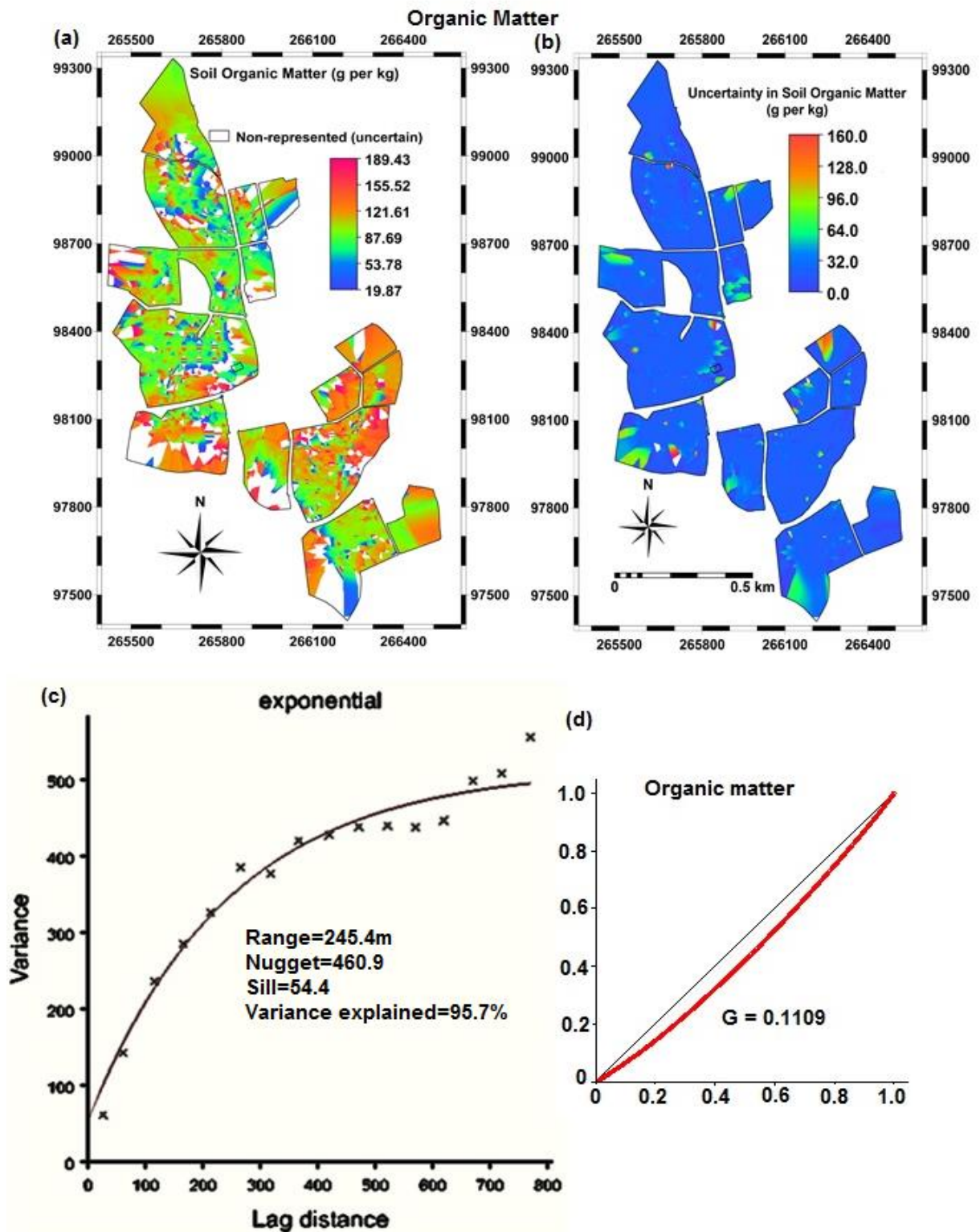


Figure 4.9: Spatial variations in the soil organic matter at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

Total carbon

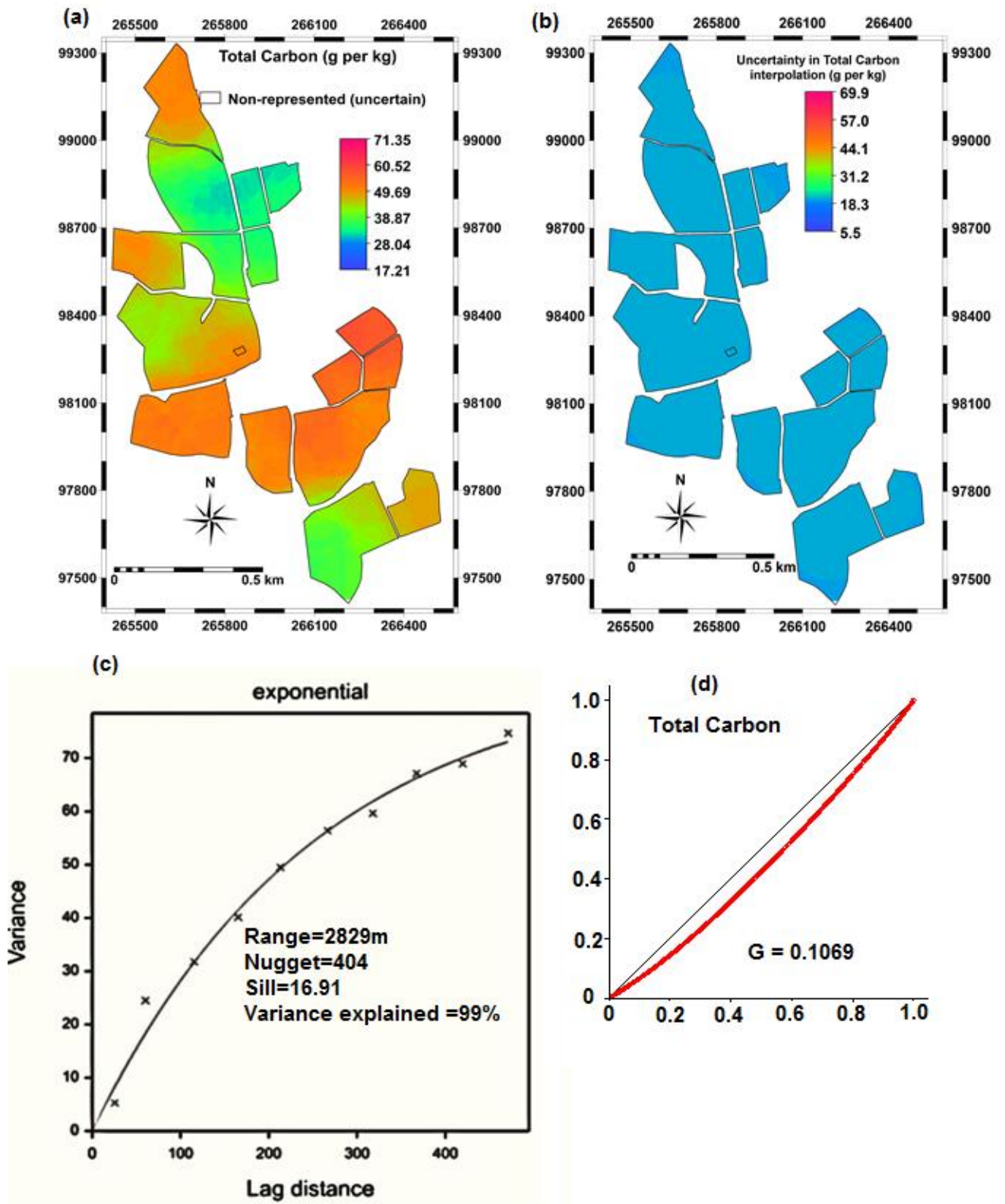


Figure 4.10: Spatial variations in total carbon at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

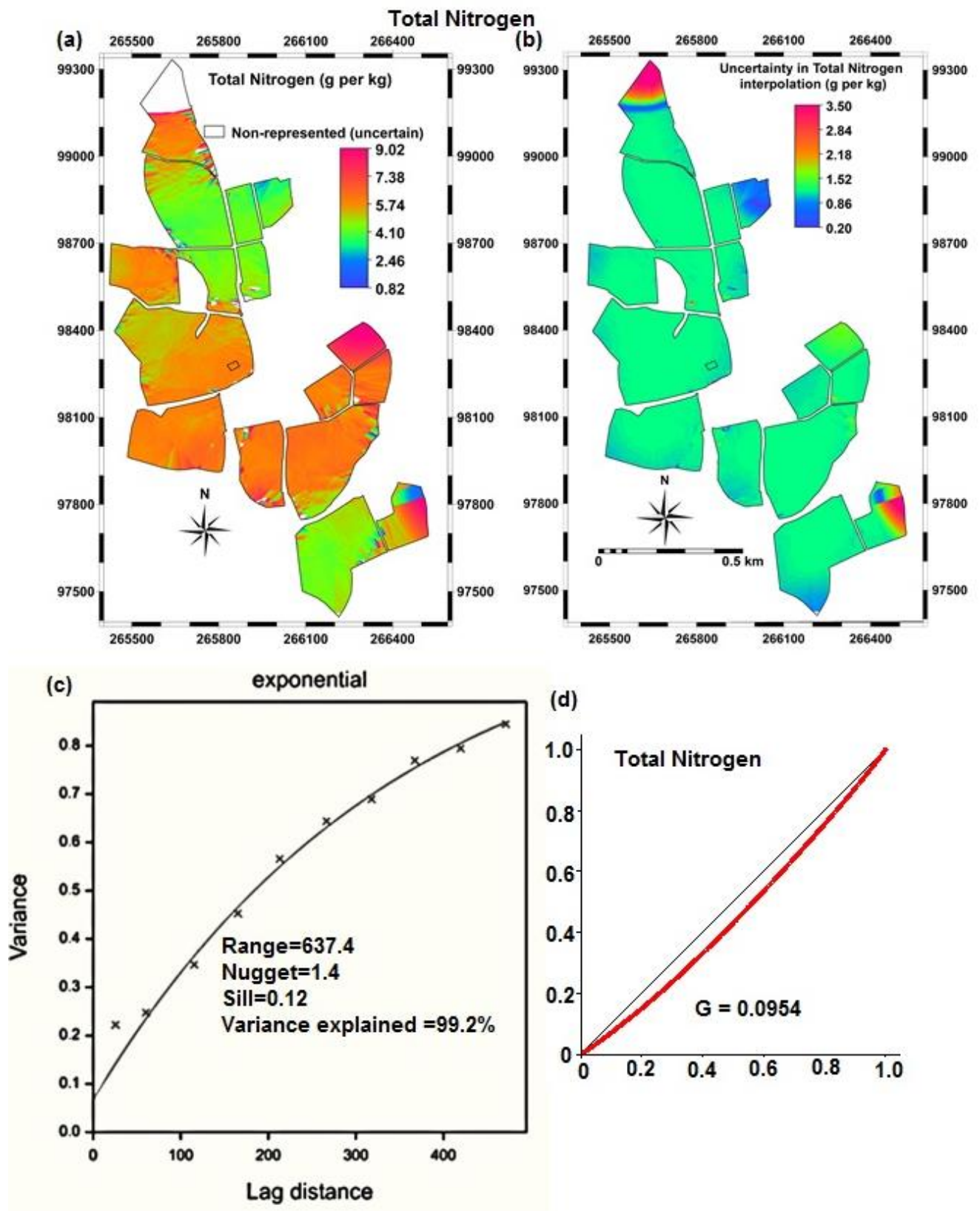


Figure 4.11: Spatial variations in the total nitrogen at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

Nitrogen-15

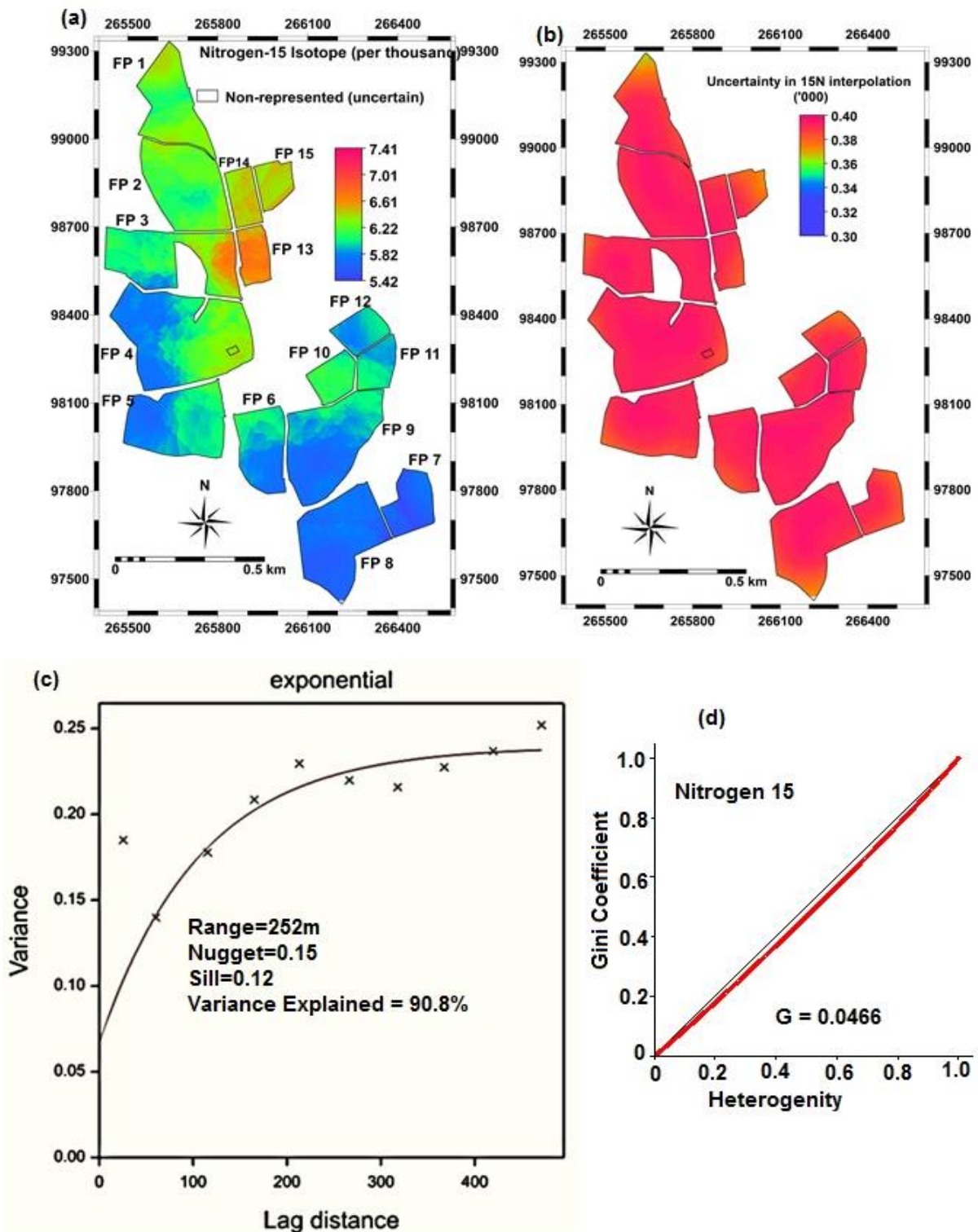


Figure 4.12: Spatial variations in nitrogen-15 isotope at the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

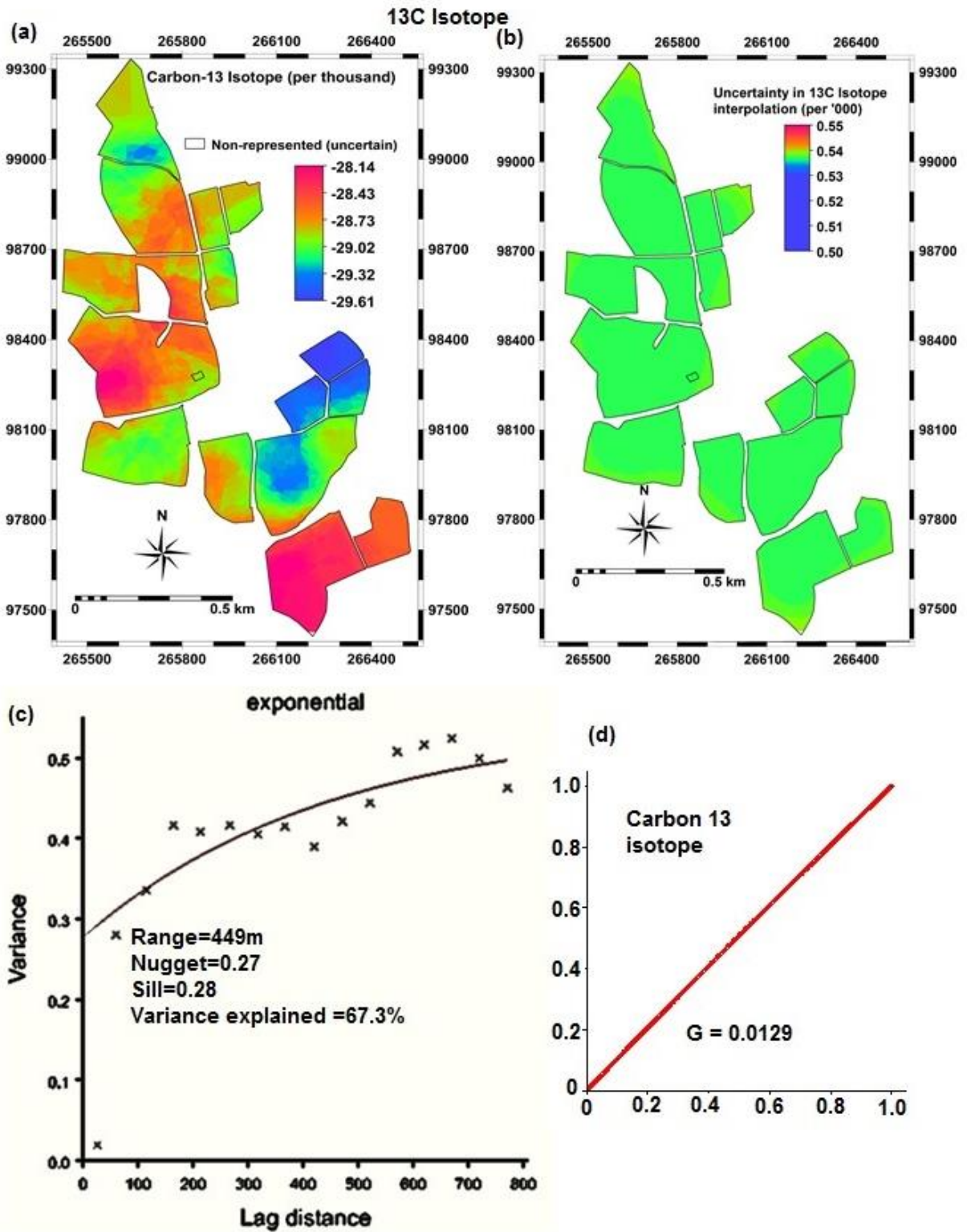


Figure 4.13: Spatial variations carbon-13 isotope concentration in the North Wyke Farm Platform; (a) 'ordinary kriging' interpolation (b) error map (c) semi-variogram with value estimates that were used to produce map (a) and Lorenz curve to ascertain the estimate (Gini coefficient, G) of the spatial variability across the entire farm platform.

Soil pH status across the fields varied from 5.1 to 6.1 units, and was generally slightly homogeneous (as suggested by the relative smoothness, low value range and the results of the Lorenz curve and Gini coefficient G (0.33)). Error map across the farm platform shows that uncertainties in the interpolation are higher at the edges than close to the sampling points of the fields (Figure 4.7a-d). Bulk density status across the farm platform exhibited variations from 0.16 to 1.61 g cm⁻³. The error map for the bulk density values shows very minimal spots with uncertainty, probably because the variance explained by the model is very high (99.1%). The Gini coefficient is 0.06, and this shows relative homogeneity across the farm platform (Figure 4.8 a-d). Figure 4.9a-d shows that organic matter varied markedly between 19.8 and 189.4 g kg⁻¹, and exhibited relatively larger heterogeneity ($G = 0.11$) than the other investigated variables. Both total nitrogen and total carbon exhibited similar range of heterogeneity ($G = 0.95$ and 0.11 , respectively) with organic matter. Total nitrogen and carbon ranged about 20-70 g kg⁻¹ and 0.82-9.02 g kg⁻¹ but the error distributions varied across the fields (Figures 4.10 d and 4.11 d). Nitrogen 15 and carbon 13 isotopes generally exhibited low ranges of mean concentrations (5.42-7.41 ‰ and -29.61- (-28.4) ‰, respectively). Field 13 (Longlands south) showed high Nitrogen 15 concentration (about 6.61-7.01‰) than most other fields in the farm platform, although the relatively higher concentrations like that occurred some less prominent spots in other fields, such as the Ware Park part of Field 3 (Poor Field) and at the Longlands South and Longland East. Ranges of difference shown in the error maps for these parameters were generally low, and both exhibited low level of heterogeneity across the fields ($G = 0.05$ and 0.04 , respectively for Nitrogen 15 and Carbon 13) (Tables 4.12-4.13).

In general, the ratio of nugget to sill ($\frac{Nugget}{sill}$) (%) of the semi-variogram were low (9.6 and 0.42 %) for soil pH and bulk density distribution across the farm platform, but was significantly higher for organic matter (845%), total carbon (239 %), total nitrogen (1167 %) $\delta^{15}C$ (125 %) and $\delta^{13}C$ (96.4 %).

4.2.3. Intra- (between) field variations

Comparative analysis of the coefficients of variation (CV) of the investigated parameters for all the fields shows that the concentrations of organic matter,

total carbon and total nitrogen exhibited relatively higher spatial variability than other parameters (Figure 4.14). Highest coefficient of variations showed occurred with the distribution of organic matter concentration in Fields 14 (Longlands North) and 4 (Burrows) (21.2 and 20.7%, respectively) while Field 6 (Golden Rove) and 10-12 (Lower Wheaty, Dairy East and Dairy North) exhibited the much lower percentage variation (less than 10%). Carbon-13 isotope, on the other hand, showed generally exhibited uniformly lower variation (< 4%) in all the fields, than all other parameters. The results of the descriptive statistics for the parameters in the fields (Appendix 4.3) showed that their (investigated parameters) values were lower than the overall means (except bulk density and nitrogen 15) at Fields 2 (Great Field) and Fields 13-15 (Longlands South, North and East). In general, spatial variability was less than 25% for all the parameters. The relationship between all the parameters showed that organic matter, total carbon and total nitrogen were highly correlated ($R^2 \geq 0.61$; $p < 0.05$) (Figure 4.15), and this may account for the similar exhibited by the three parameters (relatively higher than other parameters).

Four fields (Fields 1, 4, 8, 13-15; Pecketsford, Burrows, Higher and Middle Wyke Moor, and Longlands South, North and East, respectively) were randomly selected for intra-field variability using the 3D interpolation and vector (grid) map of the parameters (Figures 4.16a-d shows the 3D interpolation and the results of the vector maps are included as appendix (4.4 a-d). The results show that except for the elevation, where changes (lowlands and highlands) can be regionally (southern or northern) classified, other parameters exhibited undulating patterns that is more rapid in the middle of the fields in at least three of the randomly selected fields (except Pecketsford).

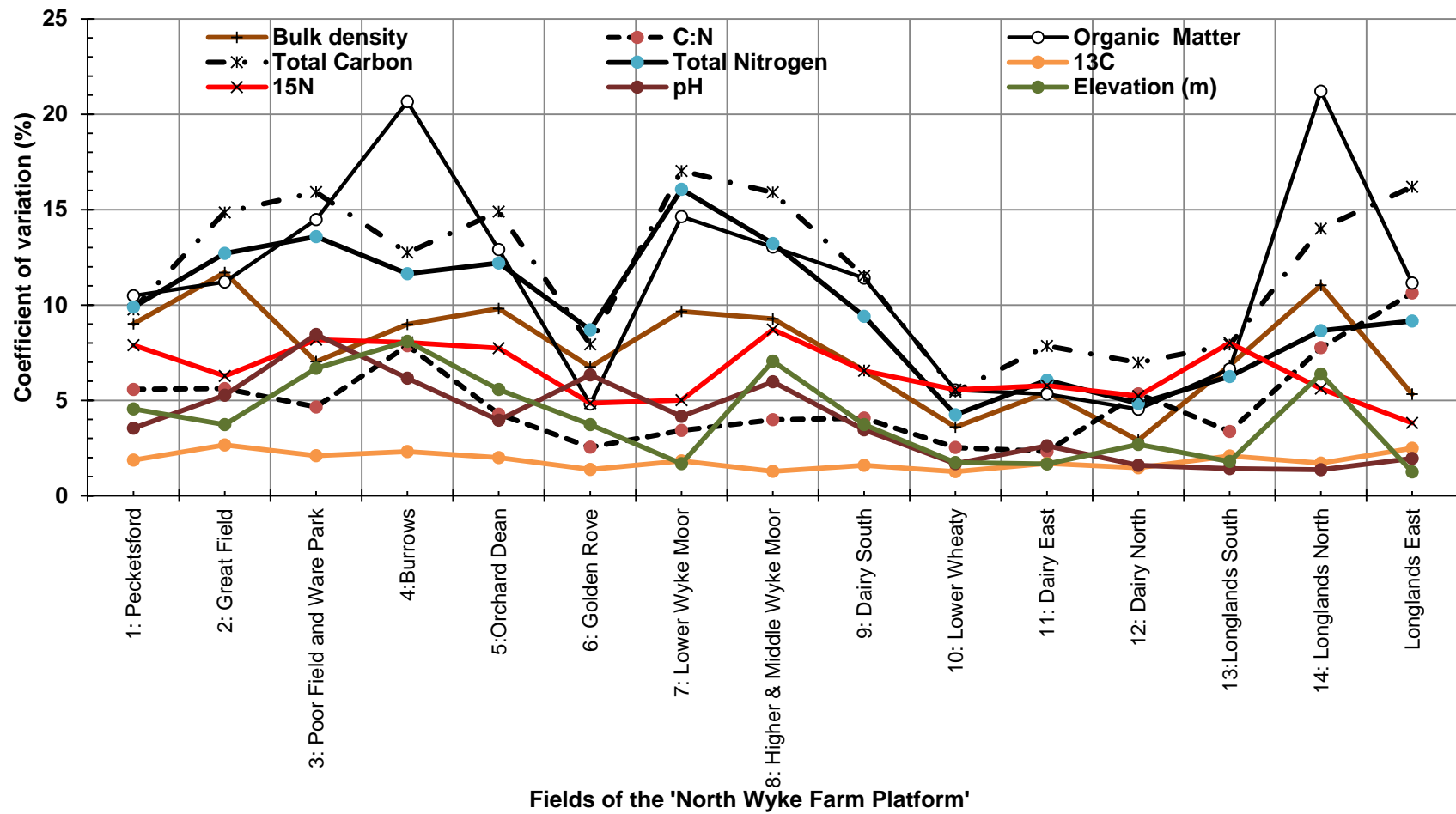


Figure 4.14. Coefficient of variation in selected soil parameters across the 15 fields of the North Wyke Farm Platform.

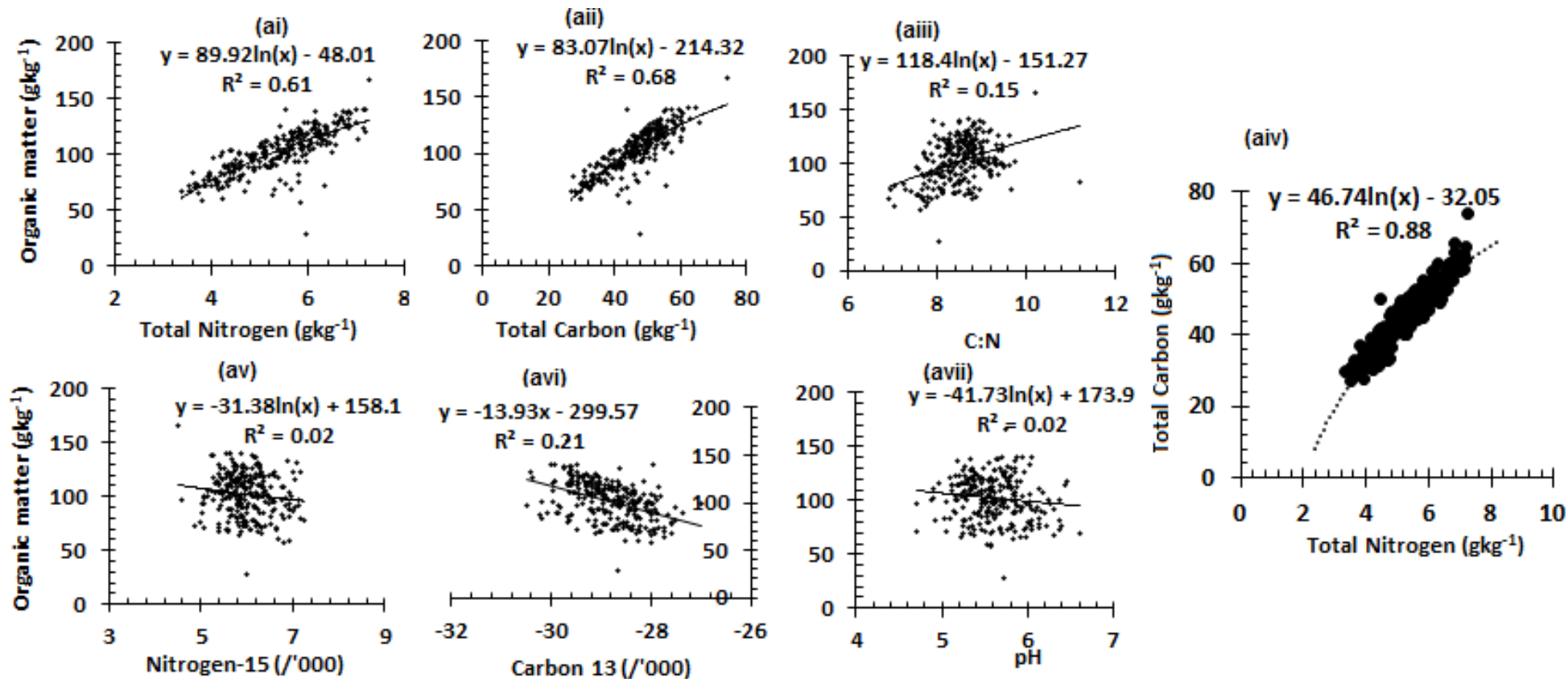


Figure 4.15: Some relationships among selected physiochemical parameters from samples of the North Wyke Farm Platform. Note that other relationships are presented as Appendix 4.3 a-c, and only the relationships between the organic matter, total carbon and total nitrogen distributions (ai, aii and aiv).

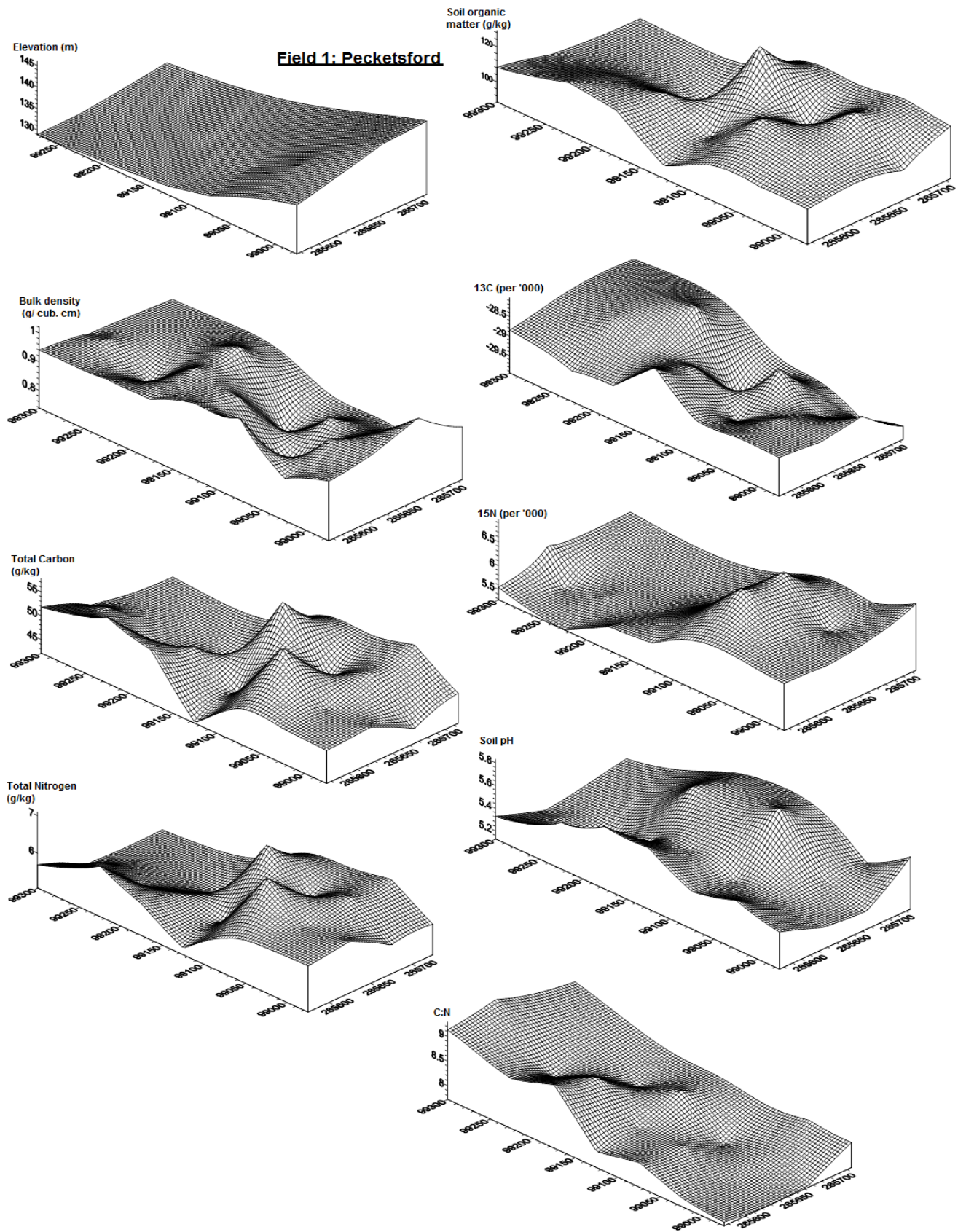


Figure 4.16 a: Patterns of spatial variability in selected physiochemical parameters across Field 1: Pecketsford. 3D (wireframe) were produced from kriging interpolations of coordinate based values in Surfer software.

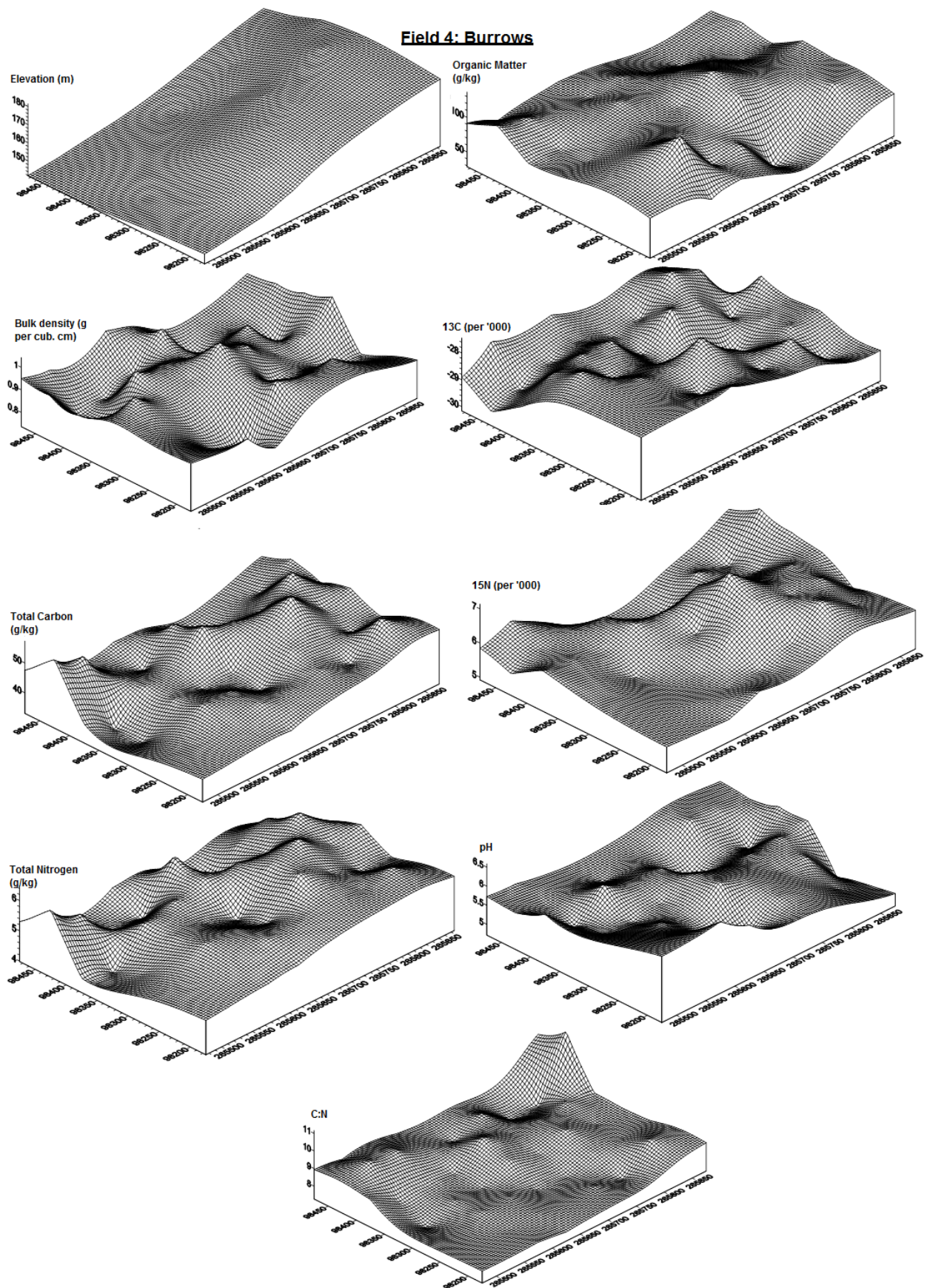


Figure 4.16 b: Patterns of spatial variability in selected physiochemical parameters across Field 4: Burrows. 3D (wireframe) were produced from kriging interpolations of coordinate based values in Surfer software.

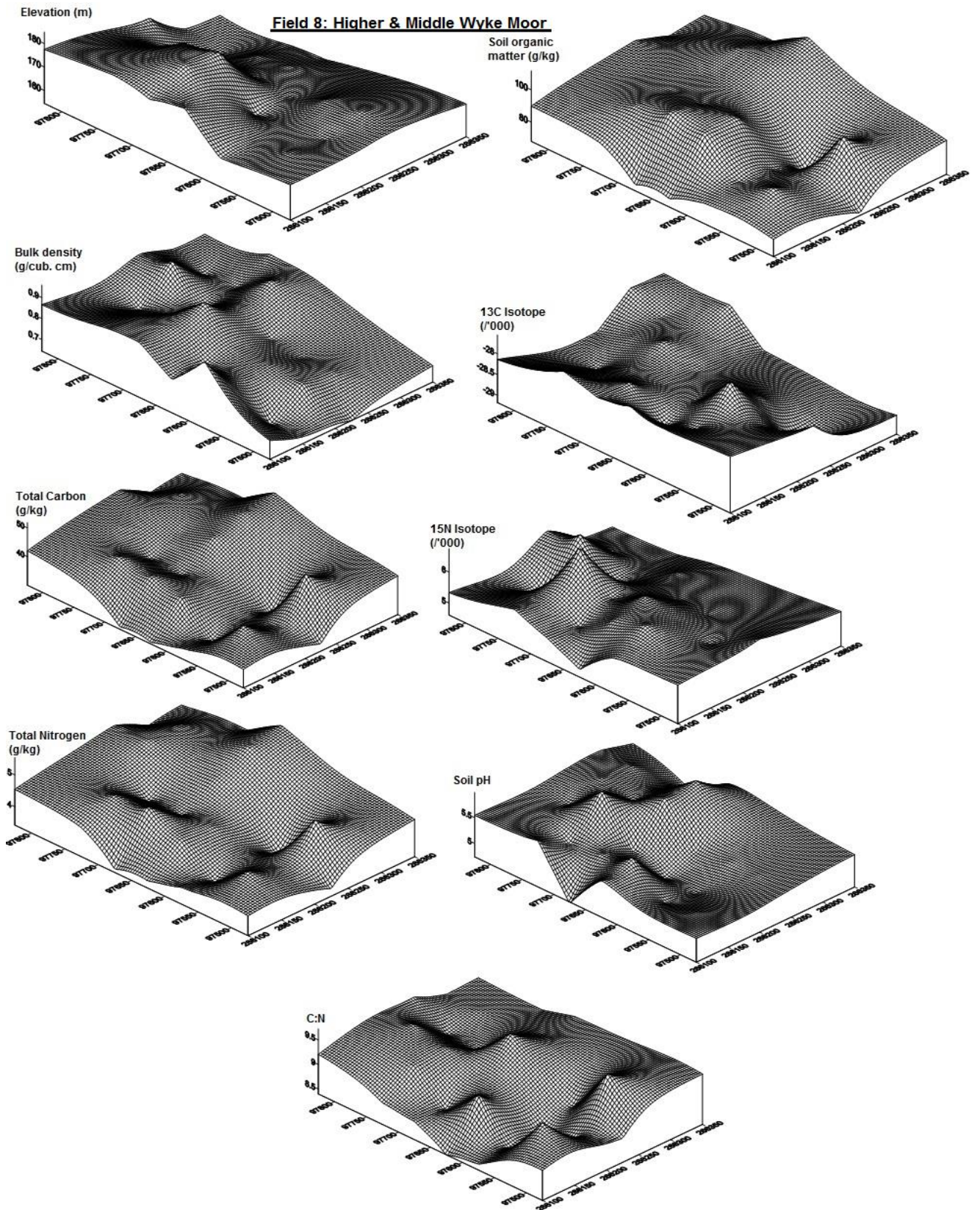


Figure 4.16 c: Patterns of spatial variability in selected physiochemical parameters across Field 8: Higher and Middle Wyke Moor. 3D (wireframe) were produced from kriging interpolations of coordinate based values in Surfer software.

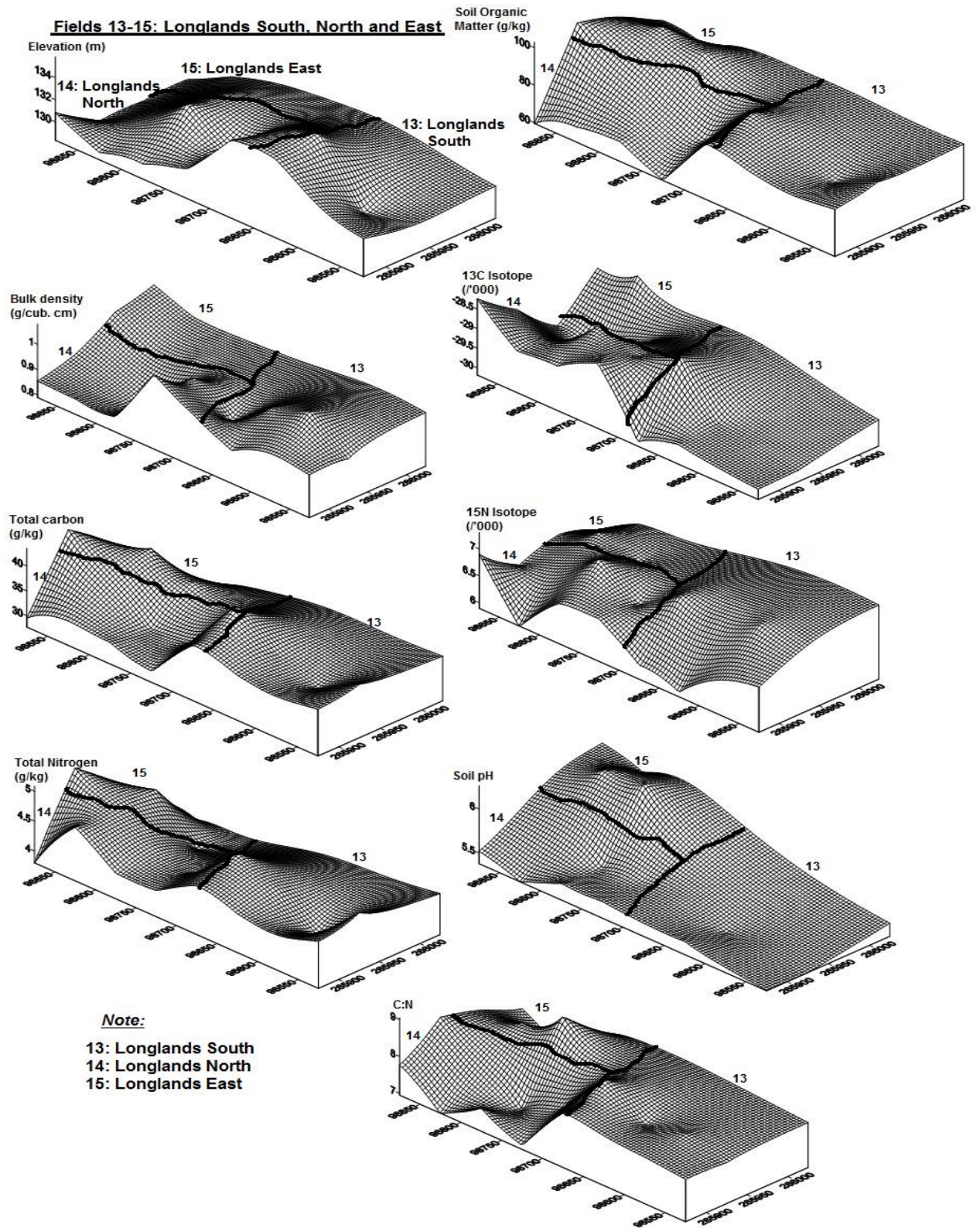


Figure 4.16 d: Patterns of spatial variability in selected physiochemical parameters across Field 13-15: Longlands South, Longlands North and Longlands East, respectively. 3D (wireframe) were produced from kriging interpolations of coordinate based values in Surfer software. The thick black line separates the Longlands South, North and East.

4.2.4. Carbon and Nitrogen stocks across the fields

Means (standard deviation on parenthesis) of carbon and nitrogen stocks from the fields were 41.7(5.1) t C ha⁻¹ and 4.9 (0.53) t N ha⁻¹. Both carbon and nitrogen stocks varied (minimum-maximum) as 30.7– 54.1 t C ha⁻¹ as 3.7-6.2 t N ha⁻¹, respectively, and their coefficients of variations were similar across the fields (Figure 4.17).

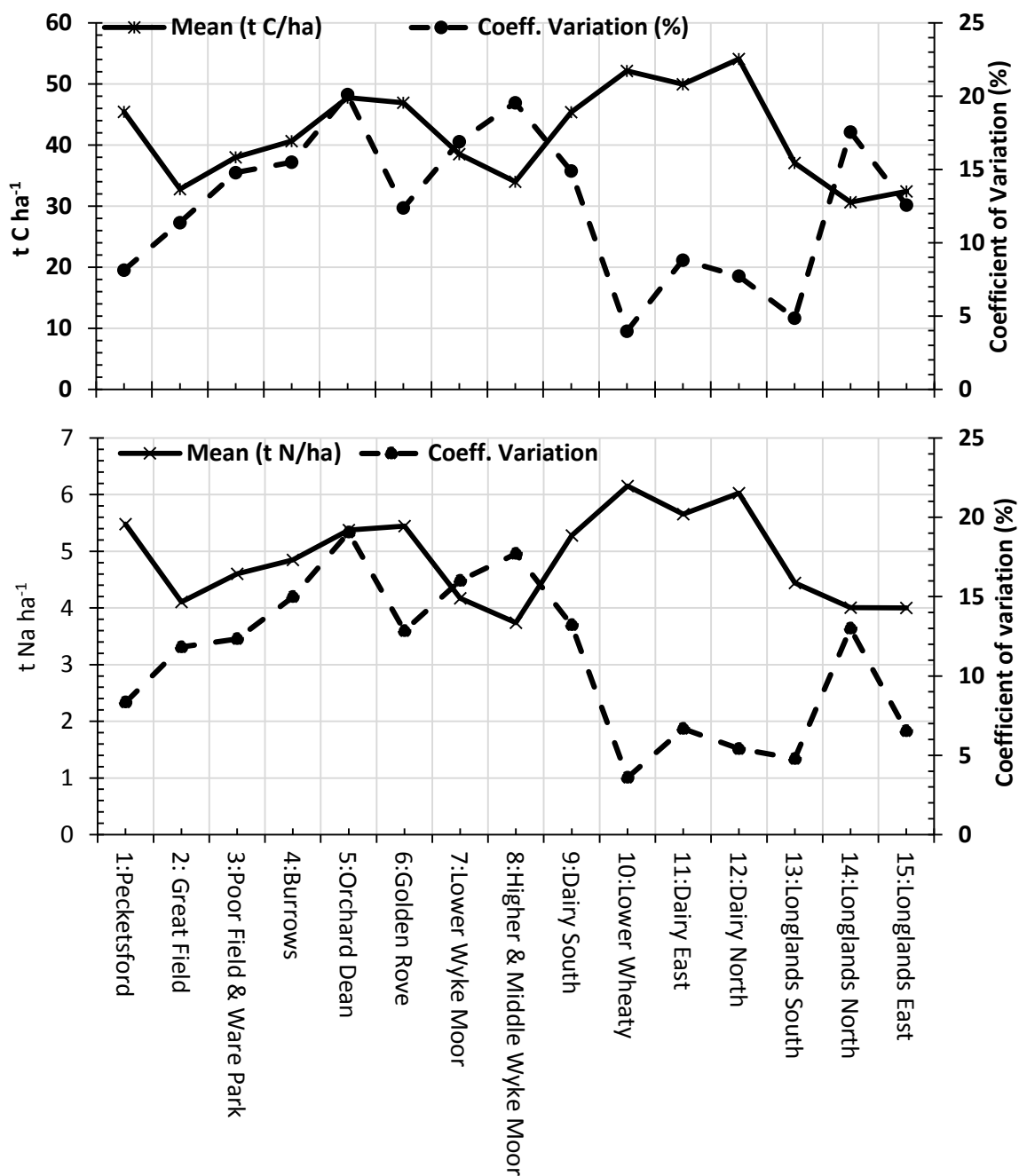


Figure 4.17: Spatial variability in Carbon and Nitrogen stocks across the North Wyke Farm Platform. Carbon or Nitrogen stock per ha (for each field) is the average of product of total carbon or nitrogen (%), bulk density (g cm⁻³) and soil depth at which sample was taken (10 cm). Note that spatial distribution of the stocks in each field is provided as appendix 4.6 a-d.

The results of stepwise regression that was analysed to establish a relationship among the investigated parameters in the entire fields show that both carbon and nitrogen stocks varied significantly with the distributions of organic matter, bulk density and elevation in decreasing order of importance (74%, 46% and 15% (eq. 4.1), and 61%, 54% and 7% (eq. 4.2) respectively).

$$Carbon_{stock} (t C ha^{-1}) = -455.29 + 0.74OM + 0.46BD + 0.15E \quad (r^2=0.74) \quad (4.1)$$

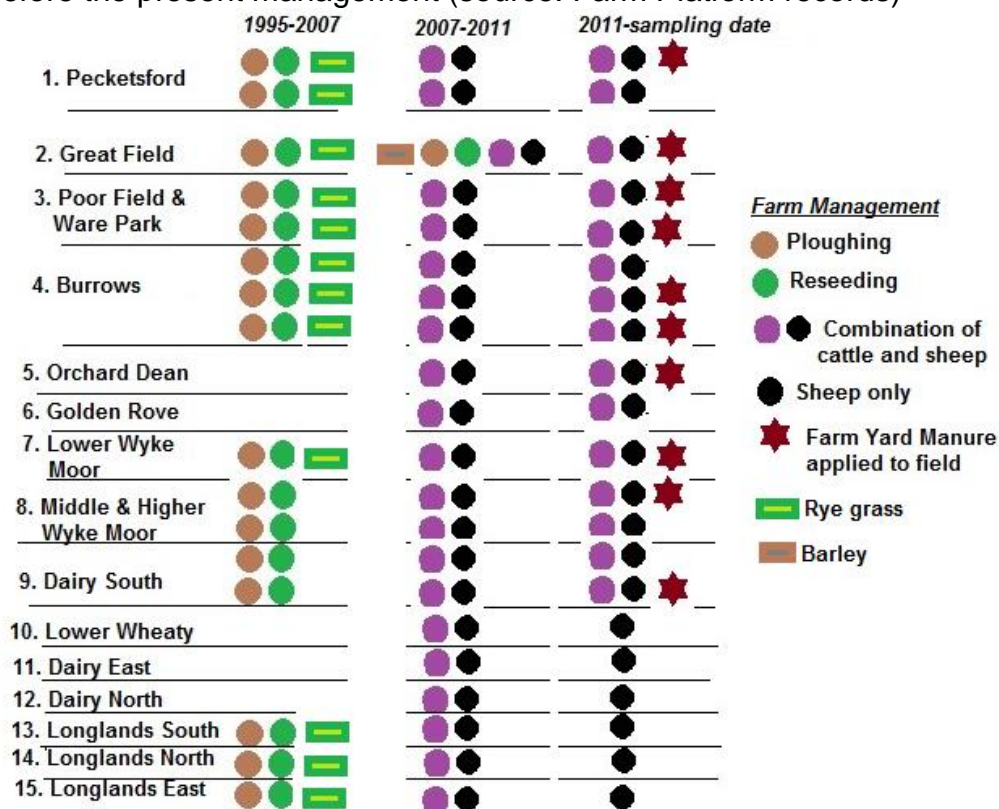
$$Nitrogen_{stock} (t N ha^{-1}) = -42.87 + 0.67OM + 0.54BD + 0.07E \quad (r^2=0.71) \quad (4.2)$$

Where: OM=organic matter (%), BD=bulk density (gcm^{-3}), E= Elevation (m).

4.2.5. Discussion

Specific objectives of this aim were to assess the inter- and intra-fields distribution of soil bulk density, pH, total nitrogen, total carbon, (including carbon and nitrogen stocks), organic matter, $\delta^{15}N$ and $\delta^{13}C$ with the intention of seeking explanations to their variability with relevance to hydrological pathways. The study area has undergone different stages and processes of land use management that are considered influential to the variability in the investigated parameters (refer to Table 3.1).

Table 3.1 (re-presented). Field management prior sampling. Fields (1, 3, 4, 8 and 9) with more than one symbolised columns were divided into 2 or more regions before the present management (source: Farm Platform records)



Although the management history of the fields shows that they (the fields) were used differently, the history is considered to be representative of normal management cycles of intensive grassland (Peukert et al, 2012). Studies have shown that different land management approaches (grazing methods-rotational, continuous and buffer, grassland burning, permanent or rotational grass cultivation, and in case of grazing; varying stock densities and nature of animals) can be proportional to their effects on the bulk density and concentrations of chemical parameters including carbon and nitrogen (Fynn et al, 2003; Vesterdal and Leifeld, 2006; Butley and Haygarth, 2007; Perie and Ouimet, 2008; Bilotta et al, 2008; Throop et al, 2012; Loveland et al, 2014; Evangelou et al, 2014; Silveira et al, 2014).

4.2.5.1. Variability in bulk density, carbon and nitrogen constituents

The soils in the study area were characterised by slightly acidic pH (5.1–6.1), low bulk density (0.6–1.6 g cm⁻³), low organic matter content (2.0–18.6 %), and low carbon and nitrogen (2.7–7.4 and 0.3–0.7 %, respectively). Carbon and nitrogen stocks, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were 30.7– 54.1 t C ha⁻¹ as 3.7-6.2 t N ha⁻¹, -30.5- -25.0 ‰ and 4.5-7.2 ‰, respectively. The ratios of nugget to sill (expressed as percentage) of the semi-variogram plots of the soil parameters suggested that pH and bulk density exhibited strong spatial dependence in their distributions across the farm platform (9.6 and 0.42 %) while the distributions of organic matter, total carbon, total nitrogen, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ exhibited weak spatial dependence.

Studies have shown that nugget to sill ratio as low as 25 % shows strong spatial dependence (Liu et al, 2013; Glendell et al, 2014) and that the spatial variability in soils exhibiting such ratio can be attributed to the effect of 'intrinsic factors' (soil formation factors, such as soil parent materials) while more than 75% nugget to sill ratio suggests weak spatial dependence that can be attributed to the effects of 'extrinsic factors' (soil management, such as variable fertilisation during growing season, cultivation or grazing practice) (Cambardella et al, 1994; Chien et al, 1997; Ruth and Lennartz, 2008). The nugget to sill ratios therefore suggest that the variations (as shown by the kriging maps and Gini coefficients) obtained in the values of most of the investigated parameters (except pH and bulk density) in the Farm Platform can be attributed to different land management practices, including fertilization and grazing) which have

been earlier noted to be within the normal intensive grassland management practices (Peukert et al, 2012).

Land management practices in the study area from 1995 till the period under study also indicated that farm yard manure (FYM) were periodically spread on the fields to improve the organic matter content in form of slurries, and faeces from grazed animals (Table 4.5). Addition of the FYM across the field (to improve their organic matter contents) can also be attributed to the variation in the concentrations of total nitrogen and carbon, especially because these three parameters (organic matter, total nitrogen and total carbon) have been shown to be significantly related ($R^2 > 60\%$; $p < 0.05$) in this study. Studies elsewhere (Chambers et al, 2001; Bot and Benites, 2005; Schimel, 1995; Conant and Paustian, 2002) indicated that the decomposition of the soil organic matter is a major supply of both carbon and nitrogen in soils, and therefore, interactively involved in ammonification, mineralisation of nitrogen, and decomposition of carbon minerals explained by the carbon and nitrogen cycles (Bot and Benites, 2005). The variability in the soil pH and bulk density in the study area has been linked to the variability in the intrinsic factors, which include also soil structure, mineralisation and elevation (Chien et al, 1997; Ruth and Lennartz, 2008). The range of bulk density in the entire farm platform indicated that fields were not severely compacted (being less than 1.6 g cm^{-3}), and the values are within the range for soils with high organic matter contents (1.0 g cm^{-3}) (Guo and Cifford, 2002; Bellamy et al, 2005). Soils have shown that bulk density primarily depends on parent material, soil aggregate, climate and soil formation processes (Wilding and Drees, 1983; Muhs, 1984; Don et al., 2007; He et al., 2010), which are intrinsic factors.

The clear lead with the nugget to sill ratio for spatial dependence results, notwithstanding, studies (Bot and Benites, 2005; Don et al., 2007) showed that while tillage and different land management can influence soil bulk density and pH, soil temperature, soil moisture and texture (intrinsic factors) can affect spatial dependence in organic matter. Lime was added to the soil in the entire farm platform to adjust the soil acidity, and this may have altered the variability of soil pH.

4.2.5.2. Inter-field variability

The results of the variations within the fields indicated that spatial variations occurred at different dimensions; being higher with organic matter, total carbon and total nitrogen at most fields than other parameters. The patterns exhibited by the selected fields (1, 4, 8, 13, 14 and 15; Pecketsford, Burrows, Middle and Higher Wyke Moor, Longlands South, North and East) suggest that concentrations of the investigated parameters (except elevation) varied more around the middle and edges of the fields rather than follow a strict pattern that can be adduced to previously segregated farms. Studies have shown that effects of grazed animals in intensively managed grassland can vary within a field and such variation can occur when grazed animals congregate in parts of field to create hotspots for above-average bulk density and organic matter (Mueggler, 1965; Wilcox and Wood, 1988; Bilotta et al, 2007; Houlbrooke et al, 2009; Zhou et al, 2010). Figure 4.18 shows examples of cases of preferential associations by grazing animals and some of their impact that can cause within field variations in the study area in the course of this study.

The variability observed in the distribution of organic matter may also explain the variability in the total carbon and total nitrogen, especially because strong relationships occurred between their concentrations. Both bulk density and elevation exhibited significant relationship with the carbon and nitrogen stocks ($R^2 \approx 0.7$), and the two soil physical parameters are therefore believed to affect the concentrations of carbon stocks in the study area. Studies (such as Jobbagy and Jackson, 2000; Janssens et al., 2005; von Lutzow and Kogel-Knabner, 2009; Schrumpf et al, 2011) indicated that soil carbon and nitrogen stocks can be affected by many factors, including changes in vegetation and plant growth, removal of biomass by harvest, mechanical soil disturbances such as plowing and nitrogen deposition. While there is yet little or no agreement on the effect of elevation on bulk density in grazed lands, grazing can influence bulk density and concentrations of soil organic matter, carbon and nitrogen (Mueggler, 1965; Post et al, 1982; Wilcox and Wood, 1988; Zhou et al, 2010).

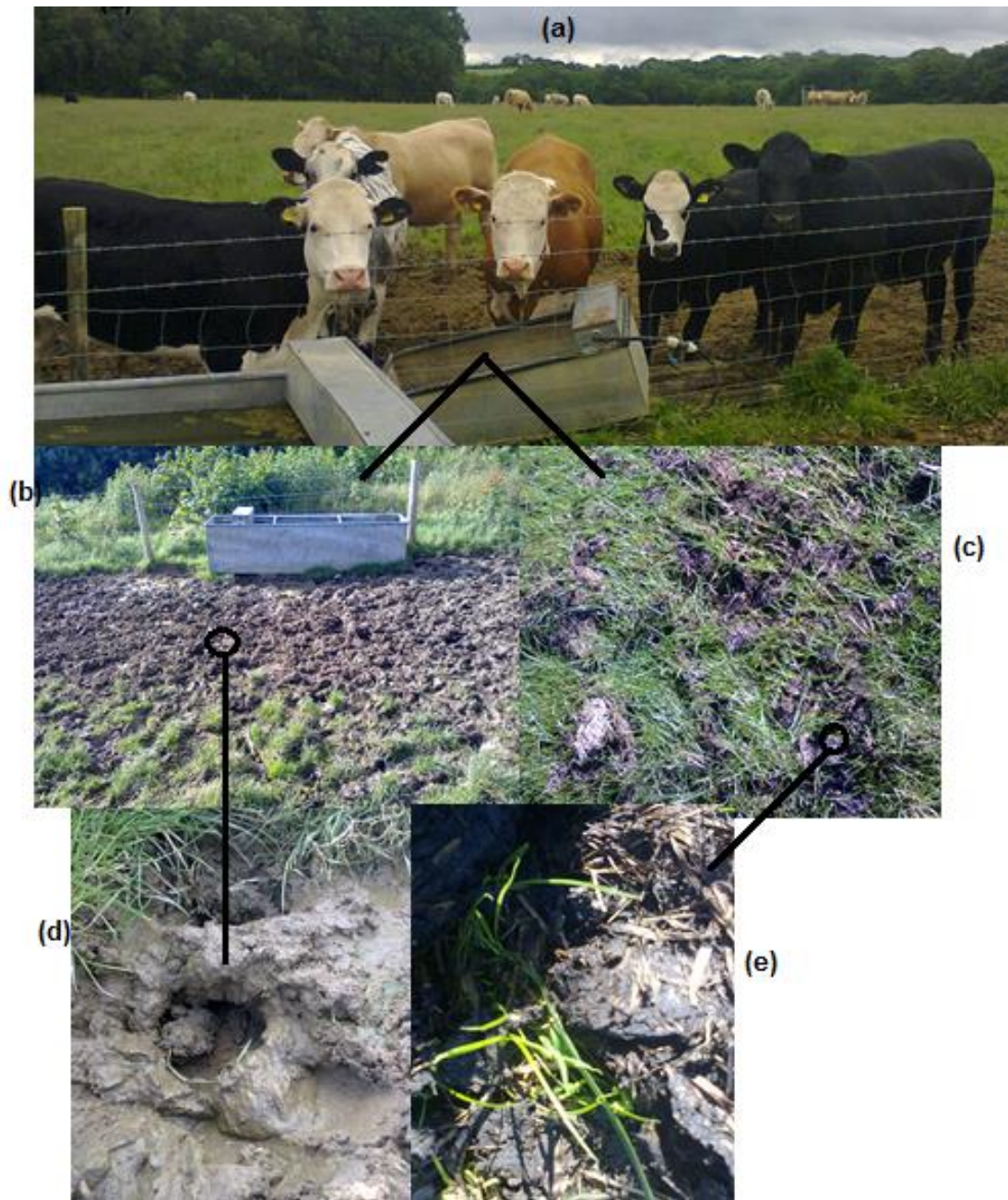


Figure 4.18a-e: Example of how congregation of grazed animals can explain the within-field variability in the concentrations of physical and chemical parameters in the study area. a. shows cattle gathering to drink water, b-c show what can be left after such congregation, d and e exemplifies a distinct effect of hoof that can alter bulk density, and the field hydrology (d), and remnant of faeces that can influence organic matter and nitrogen ions exchanges (e).

Concentrations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are usually low in soils as obtained in this study ($\delta^{13}\text{C}$ varied from -30.5 to -27 ‰ while $\delta^{15}\text{N}$ varied from 4.5 to 7.2‰ (Steele and Daniel, 1978; Schlten and Schnizer, 1998; Boutton et al, 1998; Amundson et al, 2003). Variations in the concentrations of $\delta^{13}\text{C}$ can be associated with land use change (Boutton et al, 1998), and since the variations in $\delta^{13}\text{C}$ occurred very slightly throughout the fields (less than 3% coefficient of

variation and $G = 0.01$), it indicates that the effect of land use changes across the fields in the North Wyke Farm Platform is very minimal. Concentrations of $\delta^{15}\text{N}$ on the other hand are usually used to quantify the amount of nitrogen fixation, use and release to the environment (Amundson et al, 2003). The relatively higher concentrations and variability (Coefficient of Variation $\leq 8.7\%$ and $G=0.05$) than that of $\delta^{13}\text{C}$ in this study indicated that the effect of nitrogen ions exchange (probably as organic-N compounds, ammonia and nitrate as described in the nitrogen cycle; O'Connor, 1983) can be more important than specific land use change in the study area (Steele and Daniel, 1978; Amundson et al, 2003). In addition, Chambers et al (2001) indicated that about 60% of typical fresh livestock manure is made up of nitrogen.

4.2.6. Conclusions

The study indicated that the concentrations of organic matter, total carbon, total nitrogen bulk density and pH across the investigated fields exhibited variability that can be linked with land management, further investigation will however be required to confirm this. Variability in the carbon and nitrogen stocks across the farm platform showed significant correlations with the concentrations of soil organic matter (74 and 67%, respectively) and bulk density (46 and 54%, respectively). The importance of anthropogenic sources of most of the investigated soil parameters (except elevation) therefore premised the acceptance of the main hypothesis that states that the distribution of the investigated soil parameters are related to farm management in the study area.

The main land use activities that indicated significant patterns were associated with grazing activities. Variability in the soils physiochemical parameters that are associated with grazing activities possesses significant hydrological implications (Bilotta et al, 2007). Studies have shown that the hoofs of grazed animals can affect infiltration when they by break up hard surface crusts and algae, lichen, and moss communities (Rauzi and Hanson, 1966; Thompson, 1968; Thurow et al, 1986; Abdel-Magid et al, 1987; Bilotta et al, 2007). The third and the final aim of this study is therefore to assess the hydrological behaviour of the farm platform from a case study analysis of four (1: Pecketsford, 4: Burrows, 8: Middle and Higher Wyke Moor and 15: Longland East) out of the six fields that were selected for intra-field spatial variability analysis in this Aim (Aim 2).

4.3. Aim 3: Assessment of concentration-discharge (c-q) hysteretic relationships at the farm-scale

4.3.1. Introduction

The main objectives of this Aim are to (1) examine the spatial and temporal variations in discharge and chemical effluents from selected fields in the North Wyke Farm Platform; and (2) examine the patterns of concentration-discharge (c-q) hysteretic relationships of different chemical constituents at the farm-scale. Selected chemical constituents are; water temperature, pH, dissolved oxygen (DO), conductivity, turbidity and nitrate (NO_3^-).

4.3.2. Spatial variations in discharge and chemical variables across selected fields

Hydrographs for the investigated storm events for the same period in the four fields indicated different patterns of response across the different fields and in the periods investigated (January and November). Most hydrological responses from the fields were flashy but the volumes of flow were different (Figure 4.19). More runoff was generated at Burrows (size is 11 ha) and Middle and Higher Wyke Moor (size is 6.9 ha) than the smaller (Pecketsford (4.7 ha) and Longlands East (1.5 ha)) fields. Runoff from Longlands East was lowest throughout the events (Figure 4.19).

The summary statistics of selected storm events (E.1 - E.13; Figure 4.21) show that for the same storm conditions (in terms of total rainfall and rainfall intensity), discharge parameters (mean, peak and total) and corresponding runoff chemistry varied across the selected fields (Table 4.5). Mean (standard deviation in parenthesis) values of peak discharge (Q_p) was 15.9 (16.3) $\text{m}^3 \text{s}^{-1}$ at Pecketsford, 42.8 (38.9) $\text{m}^3 \text{s}^{-1}$ at Burrows, 33.3 (24.9) $\text{m}^3 \text{s}^{-1}$ at Middle and Higher Wyke Moor, and 7.1 (6.2) at Longlands East, indicated significant variability across all of the fields. The peak discharge was also significantly different between Pecketsford, Burrows and Longlands East (Table 4.5). Mean runoff coefficient varied between 0.01 and 0.28, and does not exhibit significant spatial differences ($p > 0.05$) (Table 4.5).

Significant variations in the concentrations of nitrate and conductivity occurred at Pecketsford, Burrows and Middle and Higher Wyke Moor with Longlands East ($p < 0.05$). Dissolved oxygen and turbidity were, however, not

significantly different across the fields. Mean distribution of the investigated chemical parameters in the study area shows that runoff from the fields within the study period was generally of very low acidity (pH = 6.6), at 8.8 °C water temperature, and contains about 1778.9 μScm^{-1} , 94.1% dissolved oxygen, 1.7 mg l^{-1} of nitrate and 22.9 NTU of turbidity. The distribution of the data for all the parameters also showed that except pH and water temperature that were mostly negatively skewed, other investigated parameters were positively skewed (Table 4.5).

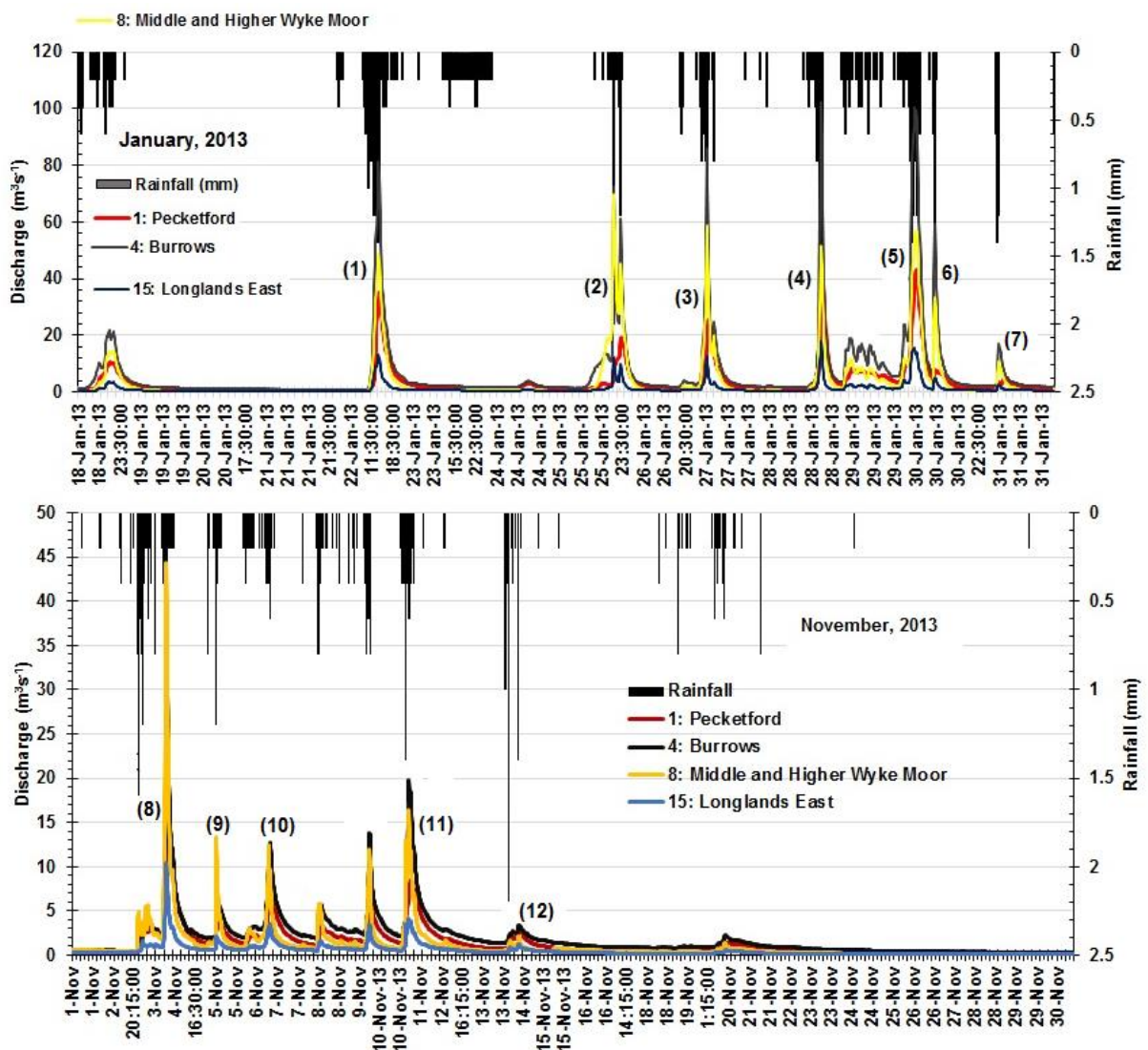


Figure 4.19: Storm hydrographs for January and November, 2013. Note that (1) January and November events are plotted on different scales good visualisation, and (2) Storm events labelled (1) – (12) are selected for event based analysis.

Table 4.5. Summary Statistics (mean \pm standard deviation) of selected events in January and November 2013 at Longlands East, North Wyke Farm Platform. Note: Mean (\pm standard deviation) values with similar superscript (^{a,b,c}) across each column are significantly different at $p \leq 0.05$.

Fields	Statistics	Peak discharge (m ³ s ⁻¹)	Mean discharge (m ³ h ⁻¹)	Total discharge (m ³ h ⁻¹)	Runoff coefficient	pH	Water Temperature (°C)	Conductivity (µScm ⁻¹)	Dissolved Oxygen (%)	Nitrate (mg l ⁻¹)	Turbidity (NTU)
Field 1 (Pecketsford)	Mean	15.9 \pm 16.3 ^a	6.4 \pm 5.8	309.7 \pm 197.5	0.1 \pm 0.05	6.5 \pm 0.3 ^a	8.8 \pm 2.9	164.7 \pm 28.4 ^a	87.3 \pm 5.1	0.4 \pm 0.2 ^a	18.5 \pm 15.5
	Min-Max	1.4-49.6	0.9-20.8	85.7-707.4	0.01-0.18	5.9-6.8	3.0-12.2	119.6-212.4	77.1-93.2	0.1-0.6	0.5-59.9
	Skewness	1.1	1.6	0.7	-0.1	-0.7	-0.6	0.06	-0.6	-0.09	1.5
Field 4 (Burrows)	Mean	42.8 \pm 38.9	12.6 \pm 11.8 ^a	615.8 \pm 438.2 ^a	0.09 \pm 0.05	6.8 \pm 0.3 ^{a,b}	8.6 \pm 2.6	175.7 \pm 27.1	95.39 \pm 2.61	0.6 \pm 0.4 ^b	16.5 \pm 11.4
	Min-Max	2.3-102.5	1.4-44.7	131.3-1520.0	0.02-0.2	6.5-7.9	4.5-11.7	124.4-237.8	90.3-100.2	0.01-1.3	4.3-37.6
	Skewness	0.4	1.7	0.8	0.36	2.0	-0.19	0.4	-0.5	0.45	0.8
Field 8 (Middle and Higher Wyke Moor)	Mean	33.3 \pm 24.9 ^b	7.9 \pm 7.1	392.3 \pm 314.5 ^b	0.3 \pm 0.7	6.6 \pm 0.09	9.2 \pm 4.6	145.1 \pm 73.7 ^b	104.2 \pm 34.4	1.3 \pm 1.2 ^c	20.44 \pm 8.3
	Min-Max	1.4-69.7	0.7-25.1	58.9-1063.5	0.02-0.28	6.4-6.7	2.9-23.1	70.2-257.6	88.8-223.1	0.2-3.8	7.7-38.1
	Skewness	-0.05	1.1	0.9	3.70	-1.1	2.1	0.4	3.7	0.70	0.6
Field 15 (Longlands East)	Mean	7.1 \pm 6.2 ^{a,b}	2.1 \pm 1.8 ^a	106.1 \pm 61.1 ^{a,b}	0.1 \pm 0.07	6.4 \pm 0.09 ^a	8.6 \pm 2.4	230.2 \pm 78.3 ^{a,b}	89.7 \pm 3.0	4.4 \pm 4.5 ^{a,b,c}	35.6 \pm 40.5
	Min-Max	0.6-17.9	0.3-6.8	33.4-231.9	0.02-0.23	6.3-6.6	4.2-11.4	114.1-339.2	85.2-94.6	0.2-10.9	1.7-165.6
	Skewness	0.5	1.6	0.62	-0.4	0.7	-0.4	0.2	0.05	0.5	2.9
Overall	Mean	24.8 \pm 27.9	7.3 \pm 8.2	355.9 \pm 335.9	0.16 \pm 0.4	6.6 \pm 0.3	8.8 \pm 3.2	178.9 \pm 64.1	94.1 \pm 18.2	1.7 \pm 2.8	22.9 \pm 23.6
	Min-Max	0.6-102.5	0.3-44.7	33.4-1520.0	0.01-0.28	5.9-7.9	2.9-23.1	70.2-339.2	77.1-223.1	0.01-10.9	0.5-165.6
	Skewness	1.3	2.3	1.6	7.2	1.8	1.4	0.6	6.6	2.4	4.3

4.3.3. Relationships between discharge and runoff chemistry

The analysis of relationships between peak discharge, runoff coefficients and the investigated chemical parameters indicated different patterns of variation (Figure 4.20). While nitrate and conductivity exhibited a significant inverse relationship with peak discharge (this means that nitrate and conductivity decreased as large discharge), pH slightly increased (between 6 and 7.5) with peak discharge. The relationship between peak discharge, runoff coefficient, turbidity, dissolved oxygen and water temperature was not significant (Figure 4.20).

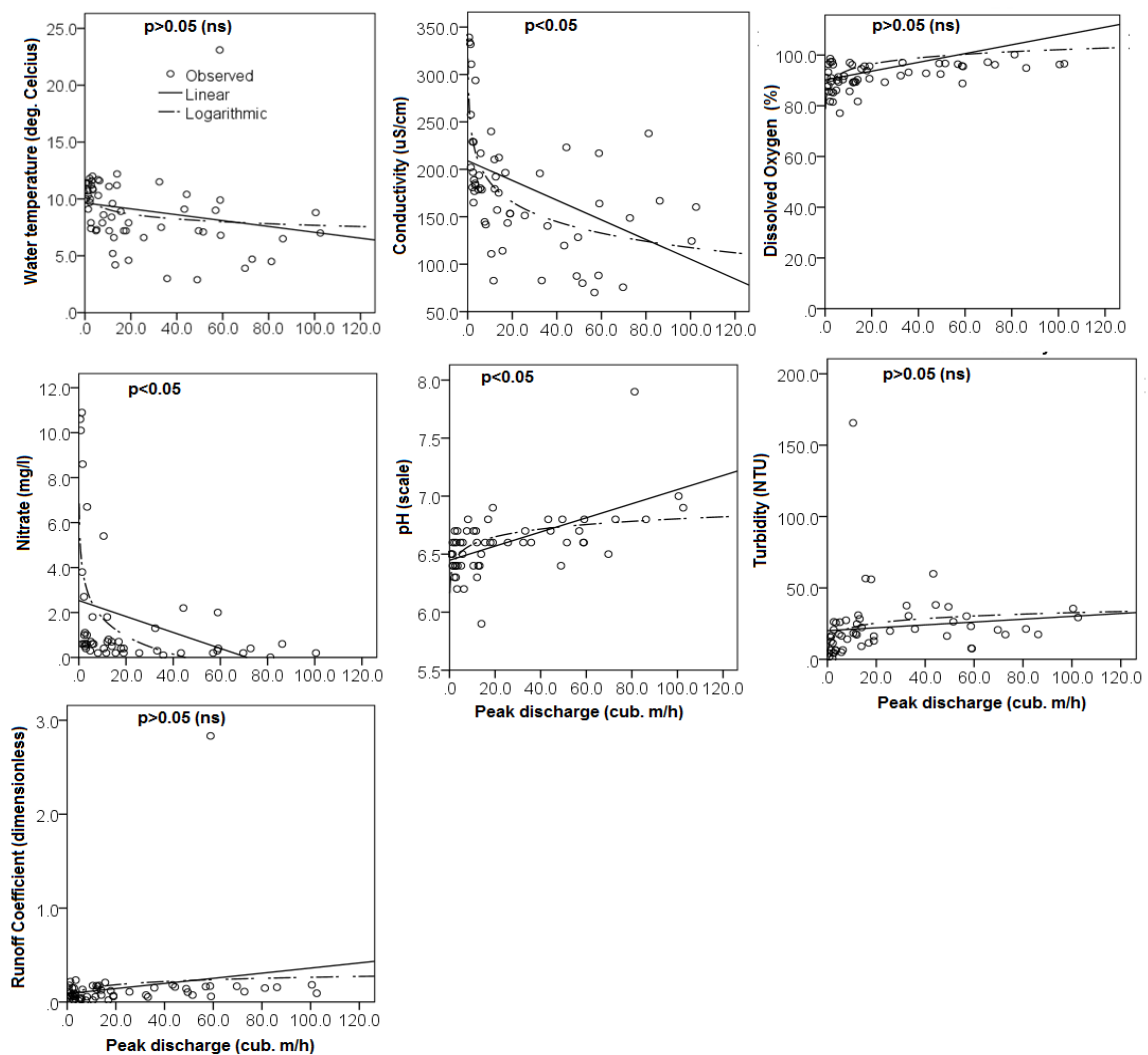


Figure 4.20. Relationship between peak discharge, runoff coefficient and the investigated chemical parameters at four selected fields (Pecketsford, Burrows, Middle and Higher Wyke Moor and Longlands East) at the North Wyke Farm Platform from January and November 2013 storm events. Data were obtained at 15 minute intervals.

4.3.4. Temporal variations in discharge and runoff chemistry

The analysis of variance tests to distinguish temporal change indicated significant differences in the mean and peak discharge values with the investigated chemical parameters in all the investigated fields between January and November 2013 (Table 4.6). More parameters (runoff temperature, pH, conductivity dissolved oxygen, nitrate and turbidity) exhibited significant differences in their concentrations between January and November at Pecketsford than observed with other fields. Turbidity and dissolved oxygen were not significantly different in January and November at Longlands East. Discharge at the Longlands East did not significantly change within the two months. Nitrate concentration varied significantly in all the fields (Table 4.6). Turbidity and dissolved oxygen level of the investigated storm event waters were consistent in both periods.

4.3.5 Concentration-discharge relationships

The event based hydrographs, chemographs and corresponding c-q plots for the 13 selected events were plotted and visually inspected for their patterns and directions. Figure 4.21a-f is the summary of the concentration-discharge patterns observed. Anticlockwise patterns dominated the pH-discharge relationship in three of the fields (except Longlands East), most of the temperature-discharge relationships exhibited the 'figure of 8' hysteresis pattern and nitrate-discharge showed a complex pattern, except at Longlands East. Dissolved oxygen-discharge relationships however varied with events (refer to Appendix 4.7).

Table 4.6. Summary (means \pm standard deviation) of the sampled events (according to month, January/November) and runoff chemistry in selected farms at the North Wyke Farm Platform. Note that the mean values with similar superscript (a,b,c) across each row are significantly different at $p \leq 0.05$.

Parameters	Pecketsford		Burrows		Middle and Higher Wyke Moor		Longlands East	
	<i>January</i>	<i>November</i>	<i>January</i>	<i>November</i>	<i>January</i>	<i>November</i>	<i>January</i>	<i>November</i>
Total rain per event (mm)	8.1 \pm 4.5 ^a	6.0 \pm 4.6 ^a	8.1 \pm 4.5 ^b	6.0 \pm 4.6 ^b	8.1 \pm 4.5 ^c	6.0 \pm 4.6 ^c	8.1 \pm 4.5 ^d	6.0 \pm 4.6 ^d
Rain intensity (mm h ⁻¹)	0.6 \pm 0.3 ^a	0.1 \pm 0.1 ^a	0.6 \pm 0.3 ^b	0.1 \pm 0.1 ^b	0.6 \pm 0.3 ^c	0.1 \pm 0.1 ^c	0.6 \pm 0.3	0.1 \pm 0.1
Peak discharge (m ³ s ⁻¹)	24.2 \pm 17.2 ^a	5.0 \pm 4.7 ^a	67.3 \pm 33.5 ^b	10.1 \pm 11.7 ^b	42.6 \pm 22.0	20.8 \pm 24.6	10.2 \pm 6.0	3.1 \pm 3.8
Mean discharge (m ³ s ⁻¹)	8.9 \pm 6.4 ^a	3.0 \pm 2.6 ^a	18.5 \pm 12.3 ^b	4.9 \pm 4.5 ^b	11.1 \pm 6.9 ^c	3.9 \pm 5.3 ^c	2.8 \pm 1.9	1.3 \pm 1.4
Runoff coefficient	0.09 \pm 0.06	0.11 \pm 0.05	0.10 \pm 0.06	0.08 \pm 0.03	0.11 \pm 0.06	0.34 \pm 0.12	0.12 \pm 0.07	0.16 \pm 0.06
Water temperature (°C)	6.8 \pm 2.0 ^a	11.5 \pm 0.7 ^a	6.7 \pm 1.5 ^b	11.2 \pm 0.6 ^b	8.6 \pm 6.2	9.8 \pm 0.5	6.8 \pm 0.1 ^c	6.5 \pm 0.1 ^c
pH	6.7 \pm 0.1 ^a	6.2 \pm 0.2 ^a	7.0 \pm 0.4 ^b	6.6 \pm 0.1 ^b	6.6 \pm 0.1	6.6 \pm 0.01	6.4 \pm 1.5	10.9 \pm 0.5
Conductivity (μ Scm ⁻¹)	144.7 \pm 17.7 ^a	191.3 \pm 13.2 ^a	169.0 \pm 34.3	184.7 \pm 9.4	84.7 \pm 12.1 ^b	225.7 \pm 16.9 ^b	171.7 \pm 35.1 ^c	308.3 \pm 37.6 ^c
Dissolved oxygen (%)	90.8 \pm 2.3 ^a	82.6 \pm 3.7 ^a	96.4 \pm 1.6	94.1 \pm 3.2	96.6 \pm 0.5	98.8 \pm 10.2	90.9 \pm 2.2	88.1 \pm 3.4
Nitrate (mg l ⁻¹)	0.2 \pm 0.1 ^a	0.6 \pm 0.01 ^a	0.4 \pm 0.2 ^b	0.8 \pm 0.3 ^b	0.3 \pm 0.1 ^c	2.4 \pm 0.8 ^c	0.6 \pm 0.3 ^d	8.7 \pm 2.2 ^d
Turbidity (NTU)	26.6 \pm 15.3 ^a	7.8 \pm 7.5 ^a	19.1 \pm 9.4	12.4 \pm 14.2	22.9 \pm 5.6	17.2 \pm 10.8	33.7 \pm 14.3	38.2 \pm 63.0

Total rain per event and rain intensity are assumed to be similar for the entire fields

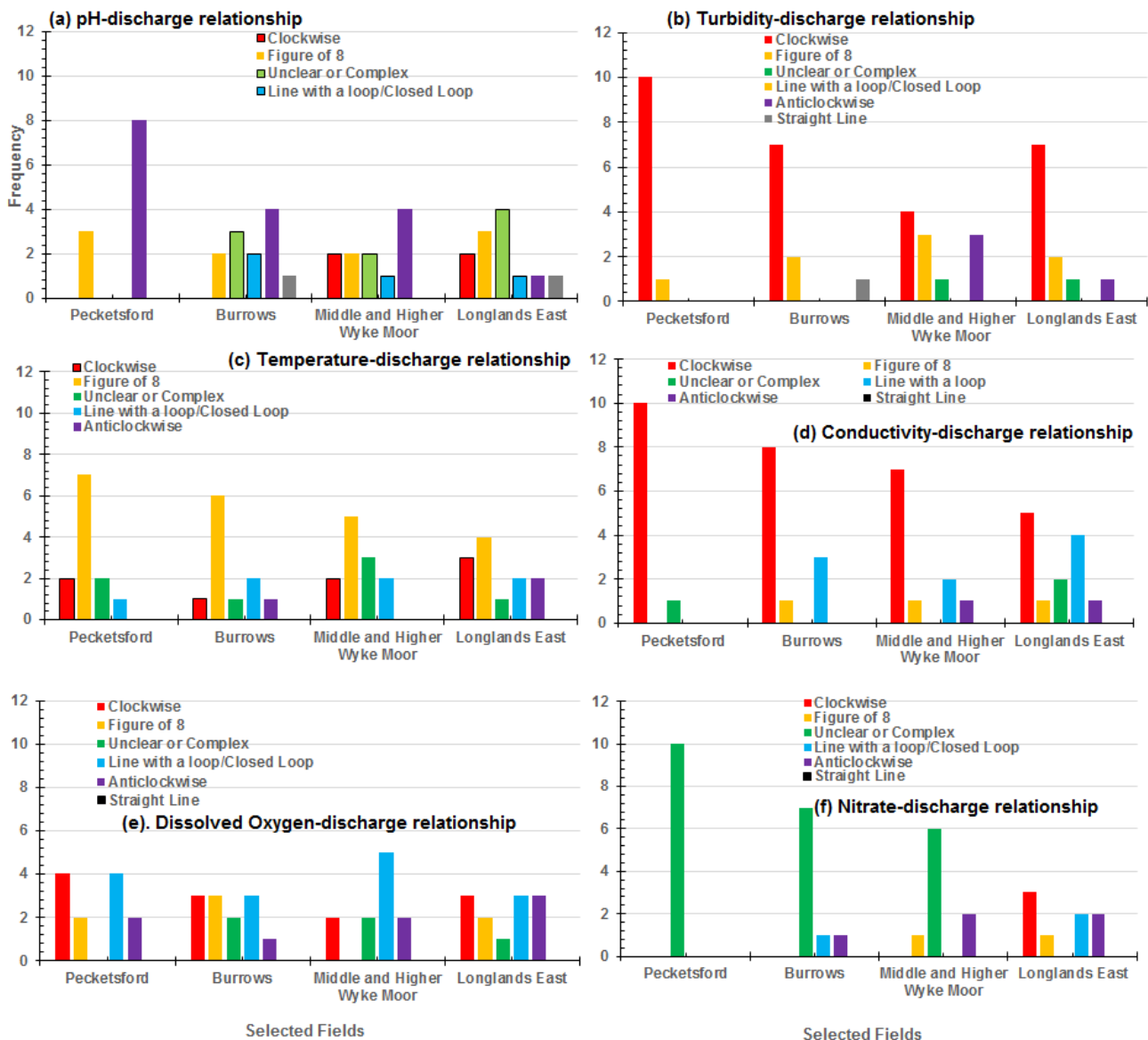


Figure 4.21 a-f: Summary of the distribution of concentration-discharge patterns at the four selected fields in the North Wyke Farm Platform. Data used were 13 storm events in January (8) and November (5 events), 2013.

4.3.5.1. pH-discharge relationship

The pH-discharge relationship across the fields exhibited anticlockwise patterns, and in many cases the relationship is complex or unclear. Corresponding chemographs of anticlockwise pH-discharge patterns indicated that anticlockwise occurs when pH rises at high discharge and peak after discharge had peaked (Figure 4.22 a). Clockwise pH-discharge relationships are produced in some fields (especially Longlands East;

Events 9, 11 (refer to Appendix 4.7 for the Table showing the pattern of c-q at each storm event, and Appendix 4.8 for details of rainfall, discharge and runoff chemistry at each event) when pH was lowest at peak discharge (Figure 4.22 b). The ‘figure of 8’ pattern occurs when pH peaked at the same time with discharge and declined early in the falling limb of the hydrograph (Figure 4.22 c). In general, pH-discharge relationships become less meaningful (sometimes forming almost a straight-line curve), when pH does not exhibit clear variation (when variations was less than 1 unit) across the event period.

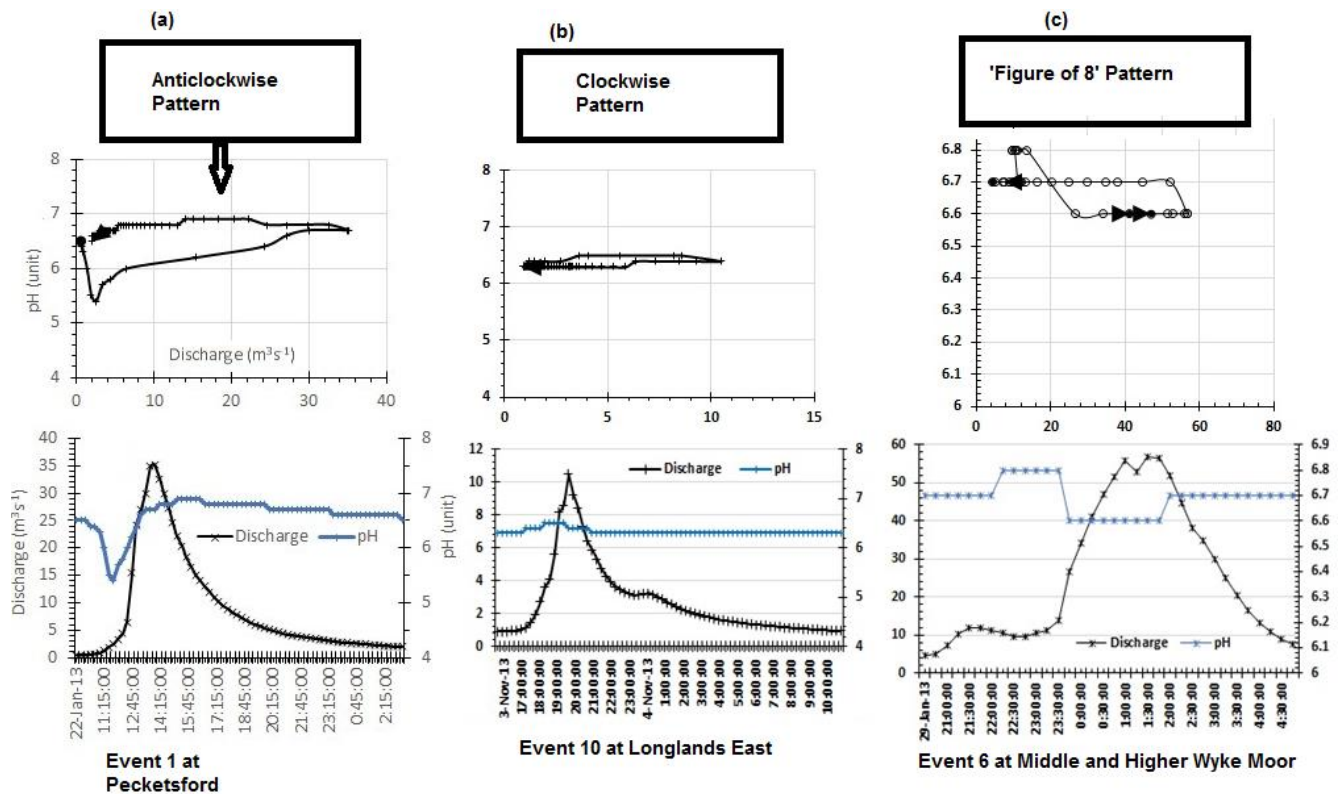


Figure 4.22 a-c. Representative pH-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.5.2. Temperature-discharge relationship

The ‘figure of 8’ pattern generally dominated the temperature-discharge relationship in all the investigated fields (Figure 4.23 b). In most cases, the ‘figure of 8’ pattern was upward facing, and the associated chemographs show that temperature was declined from the start of the event but it rises immediately after peak discharge (Figure 4.23 a). In the events where temperature rises during an event and peaked just

after peak discharge (Burrows and Pecketsford at Event 4), a downward facing ‘figure of 8’ pattern occurs (Figure 4.23 b). Temperature-discharge relationship however becomes unclear or complex when the variation is very small (such as less than 0.5°C). Temperature-discharge relationship also exhibited a clockwise pattern when temperature peaked before discharge and declined thereafter through the falling limb of the hydrograph (Figure 4.23 c).

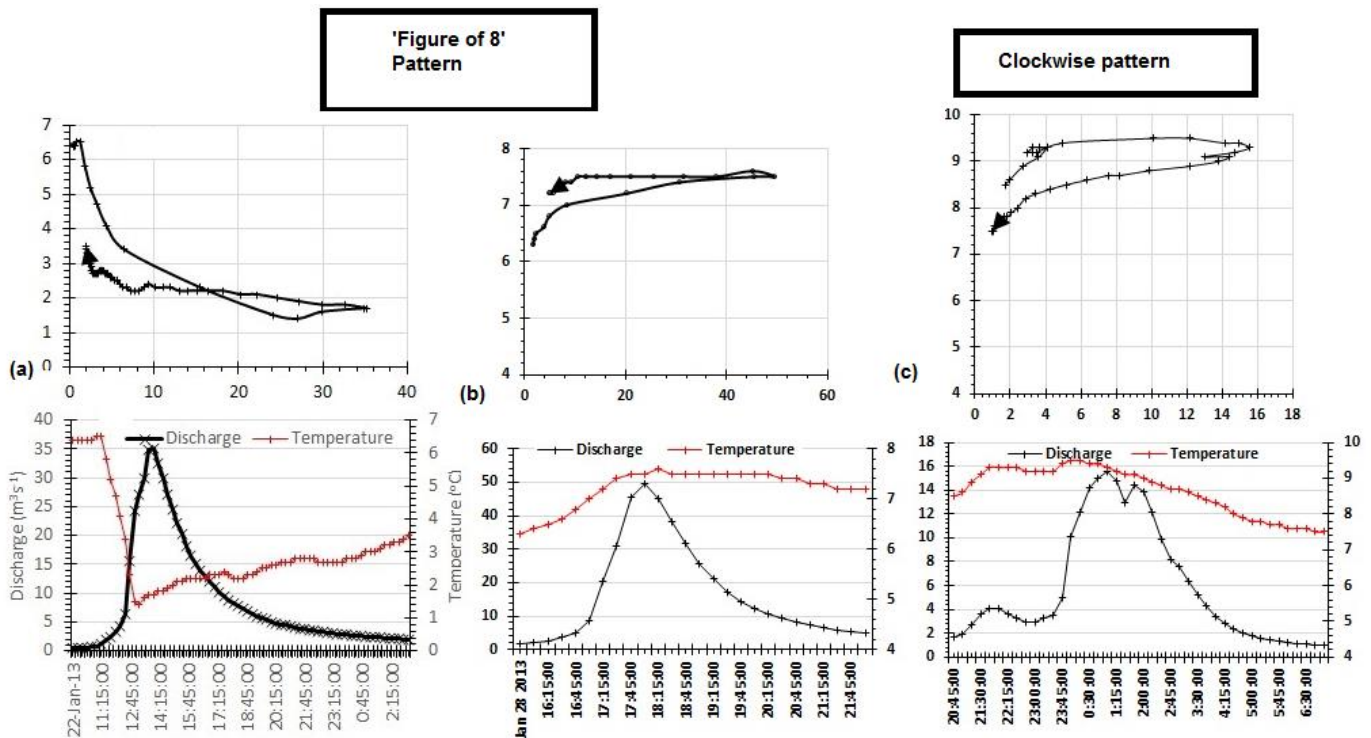


Figure 4.23 a-c. Representative temperature-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.5.3. Conductivity

Conductivity-discharge relationship exhibited upward-facing clockwise pattern at most of the studied effects for all the fields. The chemographs for the pattern indicated that conductivity was low at high discharges and rises at the falling limb of the hydrograph (Figure 4.24 a). In few cases, fluctuations in the conductivity during high runoff resulted in a ‘figure of 8’ pattern (Figure 4.24 b) while the patterns become unclear or complex under multiple-peaks events (Figure 4.24 c).

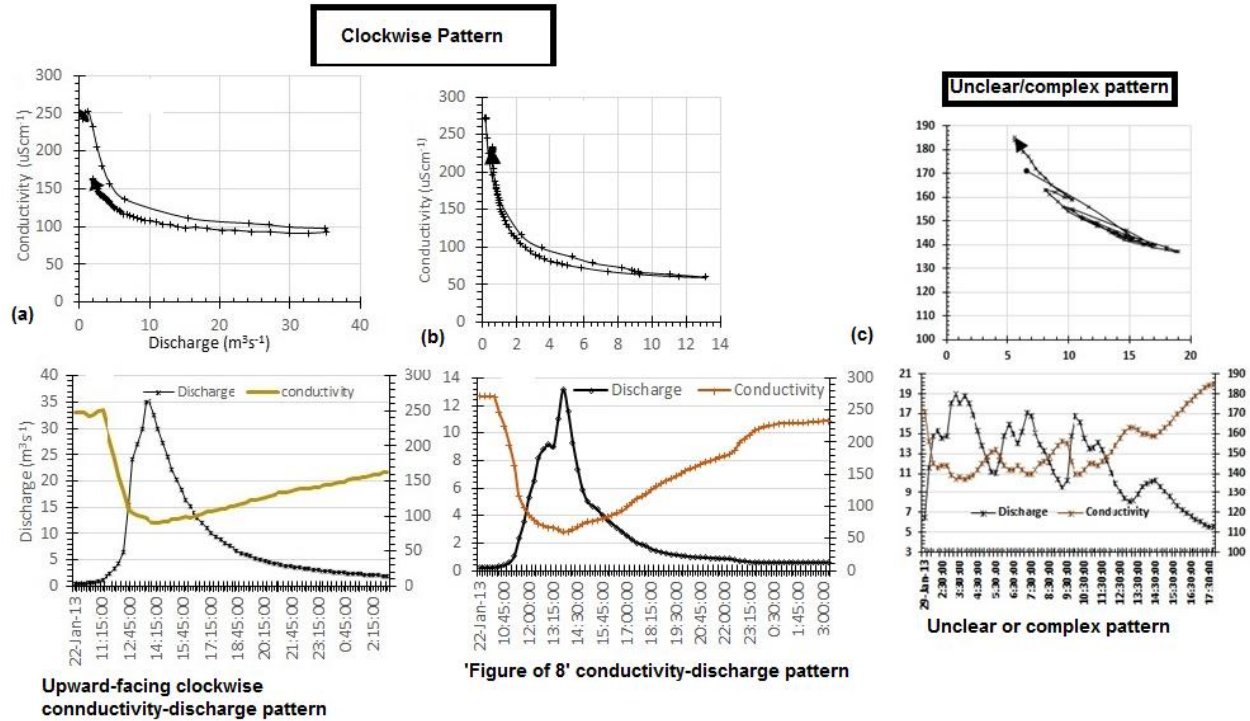


Figure 4.24 a-c. Representative conductivity-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.5.4. Turbidity-discharge relationship

The turbidity-discharge relationship exhibited patterns that are similar to those of conductivity, in terms of direction, being dominated by a clockwise direction but the slope of the turbidity-discharge relationships were generally convex; unlike the concave shaped conductivity-discharge patterns (compare Figure 4.24 and 4.25). Chemographs of conductivity-discharge relationship are also different from those of turbidity-discharge because turbidity generally peaked before the discharge to produce their clockwise directional loops (Figure 4.25 a). In some events that turbidity peaked at (or about) the same time with discharge, 'figure of 8 loop' or a more complicated form was formed (Figure 4.25 b).

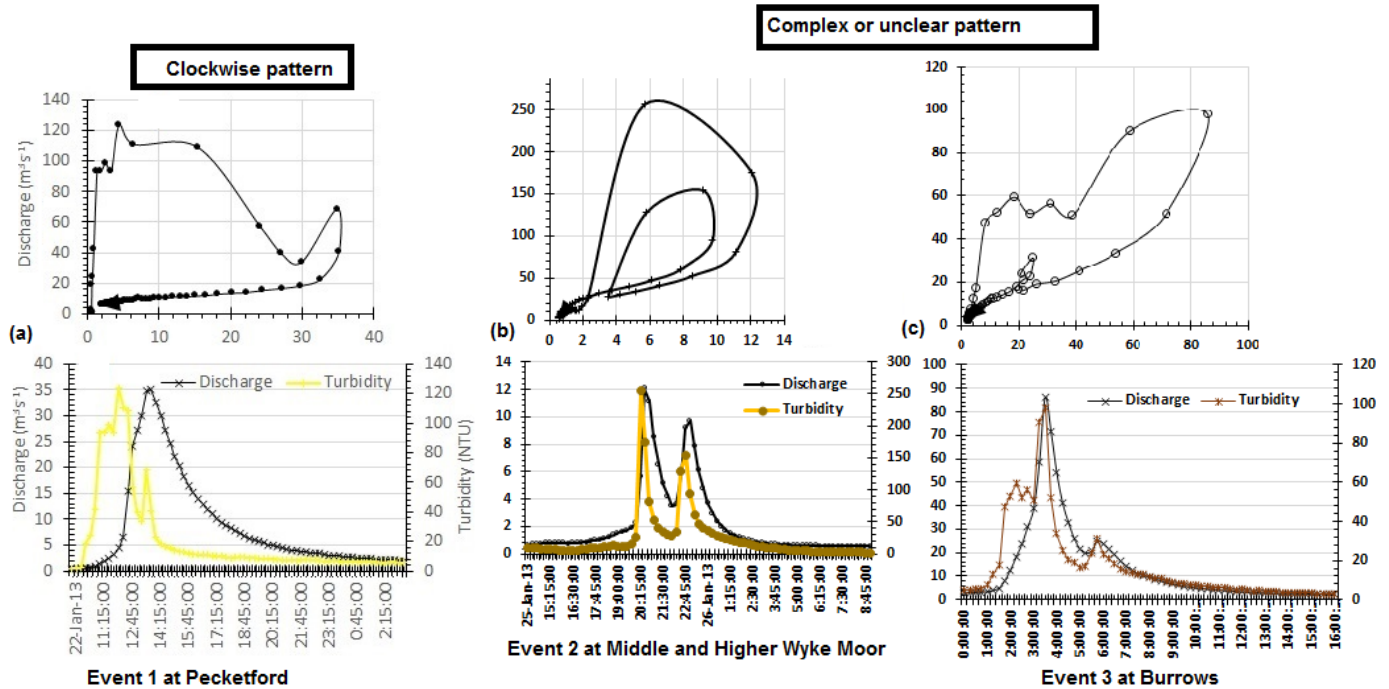


Figure 4.25 a-c. Representative turbidity-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.5.5. Dissolved oxygen-discharge relationship

Dissolved oxygen-discharge relationship generally produced concave loops that can be classified as ‘loop with a line’ because projected line merged with to form a loop at mid-way (Figure 4.26 a). In some cases of DO-q relationships, the line merged at the point of curvature, and thereby forming a ‘figure of 8’ pattern or more complex unclear patterns. Chemographs for most of the ‘loop with a line’ pattern indicate that this pattern (loop with a line) in DO-q relationship occurred because dissolved oxygen and discharged peaked at the same time during an event. In the events that DO did not peaked at the same time with discharges (such as most events in November), DO-q relationship exhibited clockwise directional loops or anticlockwise (in case of more than one peak in hydrograph (Figure 4.26 b-c). The general patterns of the plots for individual event indicated that dissolved oxygen concentration in runoff was more affected by the monthly pattern of event distribution than the other investigated chemical parameters (refer to Appendix 4.7).

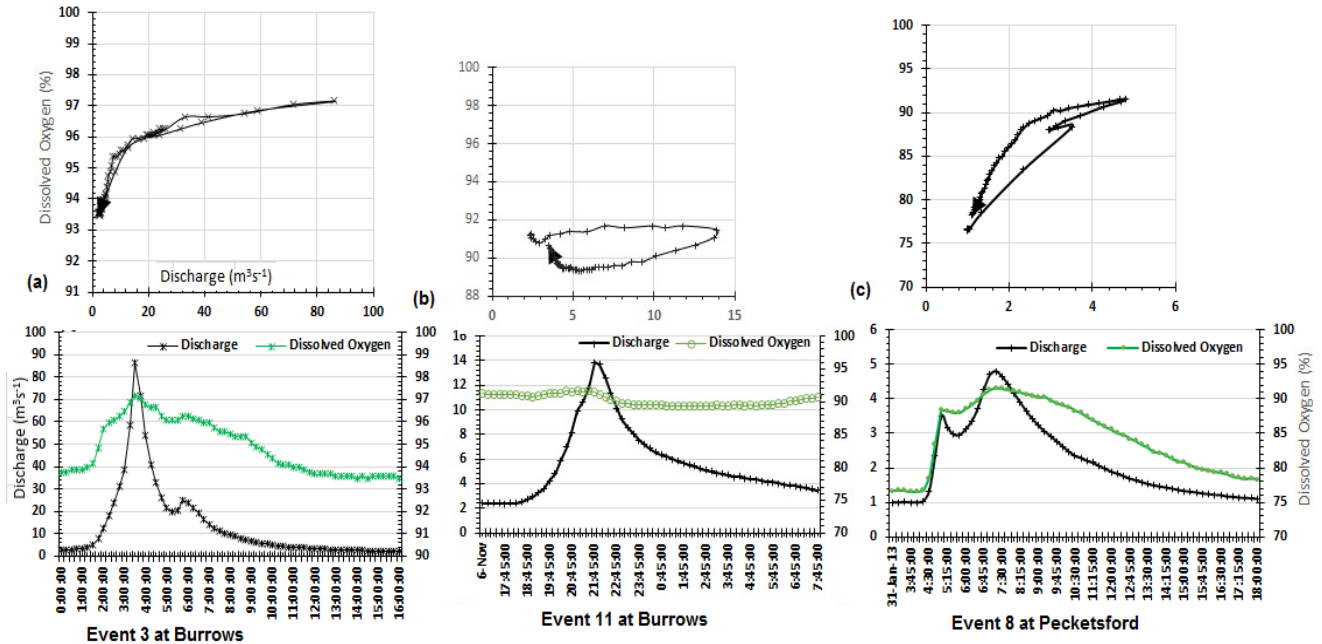


Figure 4.26 a-c. Representative dissolved oxygen-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.5.6. Nitrate-discharge relationship

Except for Longlands East, nitrate-discharge relationships exhibited haphazardly unclear shapes, and their chemographs indicated that concentrations of nitrate decline rapidly at high runoff (Figure 4.29 a). Most c-q relationships at Longlands East were clockwise patterns while those of other fields were unclear patterns. There was also anticlockwise patterns and 'line with a loop' but these were fewer. Comparison of the chemographs that produced a haphazard pattern with those that produced clockwise or anticlockwise pattern indicated that within-event fluctuations occurred more rapidly in the concentrations that produced the haphazard patterns (Figure 4.29 a-c).

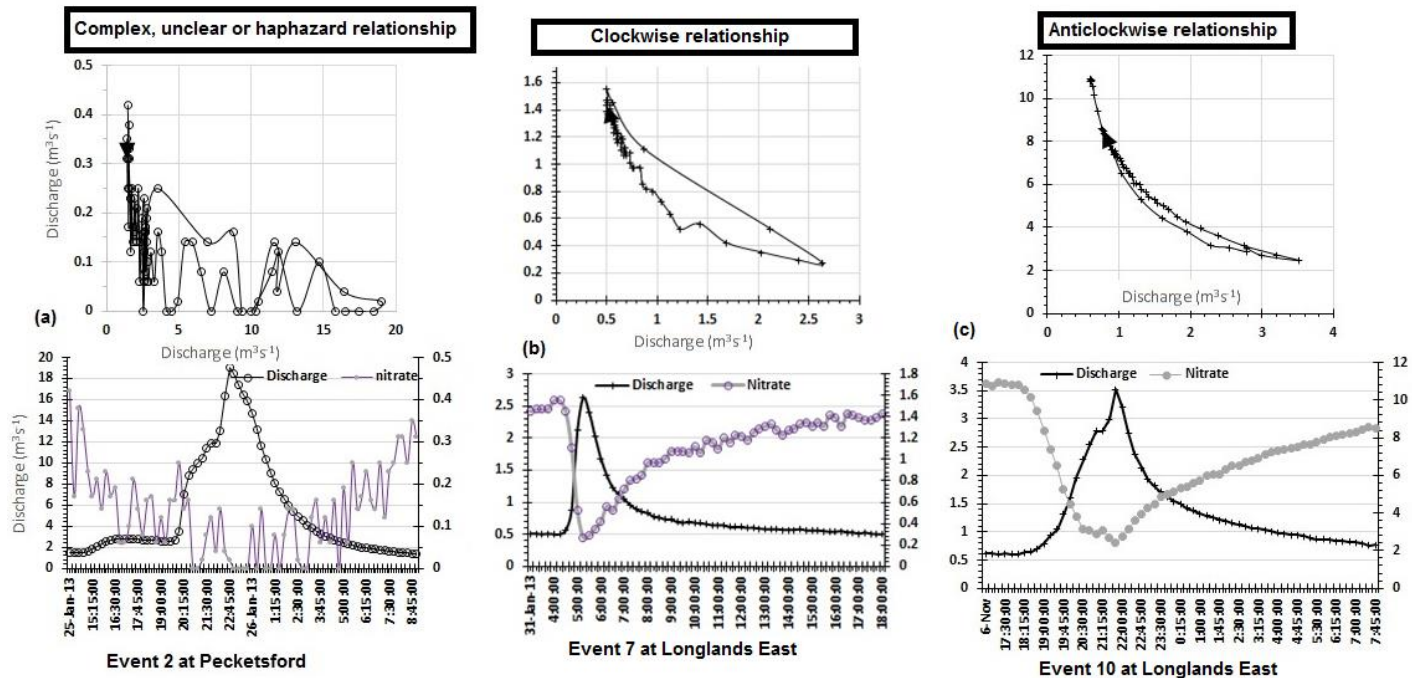


Figure 4.27 a-c. Representative nitrate-discharge relationship at selected fields in the North Wyke Farm Platform. Individual plots and their patterns are included as Appendix 4.7 and 4.8, respectively.

4.3.6. Discussion

This aim was focussed on investigating concentration-discharge relationships at the farm scale from selected fields on the North Wyke Farm Platform. Land use and terrain characteristics of selected fields have been examined in the earlier sections and the results showed that the presently investigated fields are different in terms of the area covered, dominant soil series, land use and slope. Specifically, the study investigated the runoff characteristics and concentration-discharge characteristics of the effluent's pH, temperature, conductivity, turbidity, dissolved oxygen and nitrate in 2013 (January and November).

4.3.6.1. Runoff Coefficients (RC)

The RC is defined as the portion of rainfall that becomes direct runoff during an event, and has been determined in studies in runoff generation as a diagnostic variable (Kadioglu and Sen, 2001; Merz et al, 2006; Mohmoud et al, 2014). The mean RC determined for the 13 sampled events in the four selected fields (Pecketsford, Burrows, Middle and Higher Wyke Moor and Longlands East) were within the value range for

pasture, grazed land and cultivated soils (Mohmoud et al, 2014). Runoff coefficients in the fields tended to increase with peak discharge within the period of study but this relationship was not significant. It is, however, likely that longer term evaluation of RC in the study area produces significant direct relationships with peak discharge in the area, especially as the mean values for the total sampled events indicated seasonal variations, which may become pronounced with land use. The relatively statistically non-significant differences in the values of runoff coefficient across selected fields suggest that the hydrological characteristics of selected fields may not be significantly different for the window of time used for the current investigation.

4.3.6.2. Spatial variations

The study showed that discharge and runoff chemistry exhibited significant variations across the selected fields. While variations in discharge were related to the sizes of the fields, peak, mean and total discharge values were comparatively lower at the Longlands East (the smallest field), than the three other fields studied, the concentrations of most of the investigated chemical variables were not. Larger concentrations of conductivity, nitrate and turbidity were recorded at Longlands East.

The concentration of nitrate in the runoff water was generally low, being far less than the 30 mg l⁻¹ recommended limit in surface water bodies (DEFRA, 2007). The use of electrical conductivity as a hydrological tracer and for water chemistry assessment (e.g. Nakaruma, 1971; Moore et al, 2008; Gali et al, 2012) suggested that the smaller Longlands East field contained higher concentrations of dissolved solids than the larger fields. Analysis of the land use in the North Wyke Farm Platform (Aim 2) showed that Longland East was at the time of this study being grazed with sheep (about 40 ewes and ram per period) only, and was characterized by soil pH of about 5.9-6.1 units and 0.9-1.03 g cm⁻³ soil bulk density but was not shown to be significantly different from other fields, except for its relatively smaller size (than the other selected fields for this aim). The high content of the runoff chemistry may also have resulted from previous (until 2011) land use, which had involved grazing of both cattle and sheep, cultivation of barley, rye and ploughing (refer to Table 4.5). An explanation to the relatively higher concentrations of conductivity, nitrate and turbidity is probably the lower discharge from

the field relative to the larger fields. The results of the relationship between the parameters showed that nitrate and conductivity exhibited inverse relationship with peak discharge (that is the higher the discharge, the lower the nitrate and conductivity. Peak discharge's relationship with turbidity was not significant). The results is in line with the observation of previous studies on nitrate-nitrogen (e.g. Cooper, 1993; Woltemade, 2000; DEFRA, 2007; Groffman and Marshall, 2013; Maltby, 2014), which noted that because water (runoff) progressively depletes nitrate, its concentration is often lower under larger water flow.

4.3.6.3. Concentration-discharge relationships

Concentration-discharge relationships vary with the chemical substances, field properties and source of materials from the fields (Haygarth et al, 2004; Jiang et al 2012). The selected fields (Pecketsford, Burrows, Middle and Higher Wyke Moor, and Longlands East) showed similar dominant patterns of concentration-discharge hysteresis for conductivity, turbidity, water temperature and nitrate but the patterns exhibited by pH-discharge and dissolved oxygen-relationship were different.

4.3.6.3.1 Nitrate

Nitrate-discharge relationship generally showed nitrate concentration to be lower during high discharges (than during low discharges), resulting into complex hysteresis pattern or anticlockwise directional pattern (depending on the complexity of within-storm variation in nitrate concentrations. Peak discharge exhibited inverse relationship with nitrate concentration across selected, suggesting that nitrate was not being flushed out of the fields during high discharges. The inverse relationship between high discharge and nitrate concentration, and the anticlockwise directional pattern in this study suggest that nitrate was more supplied through subsurface pathways than through surface pathways (Evans and Davies, 1998; Jiang et al, 2012). The patterns also suggest that nitrate concentration in the study area may not be well linked with the atmospheric input but with diffuse input from land use (House and Warwick, 1998). The Department for Environment, Food and Rural Affairs (DEFRA, 2007) noted that agriculture accounts for about 61% of the nitrate-nitrogen in the surface water in England and Wales (DEFRA,

2007), which is presumably why the wider area of the Taw catchment is designated as a Nitrate Vulnerable zone (NVZ).

4.3.6.3.2. pH and Conductivity

The pH and electrical conductivity values also varied significantly with peak discharge, but differently (pH tends to increase with high discharge while conductivity conversely decreases at increasing peak discharge). The dominant hysteresis pattern exhibited by electrical conductivity at all the investigated fields was clockwise, and the chemographs showed that conductivity was low at high discharges and high at low discharges. Electrical conductivity has been used in many studies, either as surrogate to provide information about the total dissolved solids or as tracer for hydrological investigations because of its high correlation with dissolved salts (Nakaruma, 1971; Moore et al 2008; Pellerin et al, 2008; Gali et al, 2012). Conductivity generally exhibited its lowest concentration at peak discharge to form concave-shaped (or negative; Evans and Davies, 1998) clockwise hysteresis pattern that is associated with a dominant pre-event source of input of dissolved solids. Variations in pH values with discharge on the other hand, suggest that while anticlockwise patterns dominated the pH-discharge relationship at Pecketsford, the clockwise and 'figure of 8' patterns were also important at Burrows, Middle and Higher Wyke Moor and Longlands East. The interpretation of this finding is that variations in the runoff pH are influenced by both event and pre-event chemical concentrations in the fields. pH values in the fields have been largely controlled by addition of lime on the field prior to the study, and this may have significantly informed the results of the study (please refer to Chapter 3 and Table 4.5 for discussion about the management of the fields).

4.3.6.3.3. Water temperature

Water temperature generally displayed a non-significant inverse relationship with peak discharges, suggesting that water temperature reduces throughout a storm event. The event-based temperature-discharge also shows that temperature generally decline from the beginning of a storm event in all the fields. Studies have shown that except for significant climatic, anthropogenic or hydrological interference (Webb and Nobilis, 1994; Webb et al, 2003), which was not recorded at any time of this study, water temperature

will often vary with precipitation or seasonal change (Shanley and Peters, 1988), and this accounted for the significant difference in the runoff temperature at most fields (except at the Middle and Higher Wyke Moor) between the January and November events. The dominant 'figure of 8' water temperature-discharge pattern suggests the influence of both the pre-event and event water on variation of runoff temperature. Water temperature-discharge relationships in the study exhibited different proportions of clockwise and anticlockwise direction that can be attributed to the previous level of dryness of the soil before and event, with dry antecedent conditions favouring clockwise and wet antecedent conditions favouring anti-clockwise hysteresis (Hornberger et al, 2004; Abell et al, 2013).

4.3.6.3.4. Turbidity and dissolved oxygen

Turbidity-discharge relationships in this study mostly exhibited convex-shaped clockwise direction pattern, which showed turbidity peaked prior to discharge peak. In a few cases, turbidity peaked at the same time with discharge to produce complex patterns which also follow a clockwise direction. A clockwise direction turbidity-discharge relationship indicates the dominance of pre-event source of materials that were flushed with runoff during a storm event (Qutram et al, 2013; Abell et al, 2013). The logarithmic relationship between turbidity and peak discharge was also not significant, and with the clockwise pattern suggest the pre-event pathway. Studies have suggested that turbidity can inform researchers about sediment availability, in intensively managed grasslands by one or more of the following processes; (a) trampling, poaching and pugging and general disturbance of soil by grazed animals, (b) readily mobile colloids that have resulted from slurry or manure application and general animal faeces, and (c) detachment of colloids due dissolution of cementing agents and enzymatic hydrolysis of organic materials that were once bound (Bilotta et al, 2007; Bilotta et al, 2008).

Dissolved oxygen-discharge (DO-q) relationships reveal a generally different pattern between most events in January and others in November. While most events in January showed DO to peak at same time with discharge to produce a complicated pattern of a 'loop (both clockwise and anticlockwise) and a line', most events in

November produced clockwise patterns. William (1989) referred to similar 'loop and a line' concentration-discharge pattern as 'single-valued line plus loop' and associated the concentration-discharge to the event condition in which concentration does not synchronise with discharge in the middle of the hydrograph, although it varied directly with discharge at the beginning or at the end of the event. The logarithmic relationship between discharge and dissolved oxygen showed that they exhibit a non-significant relationship. Another explanation for the line pattern is the small range of the data, and its small variations during storm events.

4.3.6.4. Insights into the hydrological processes from the analysis of c-q relationship

Conductivity-discharge and turbidity discharge relationships observed in this study exhibited clockwise patterns during most of the investigated rainfall-runoff events at all the selected fields. Clockwise hysteresis patterns have been interpreted to indicate flushing of materials from the ground and vegetation surfaces at the start of a rainfall event (Holden, 2005), lateral flushing of readily available excess solute and suspended solids in the near surface horizons (Bishop et al, 2004). Clockwise hysteresis also occurs when chemicals interact with the surface and near-surface in the course of transmitting feedback flushing typical of quick lateral transport of leached nutrients via saturation excess flow (Hornberger et al, 2004; Weiler and McDonnell, 2006). The dominance of complex or irregular nitrogen-discharge patterns at the larger three of the selected fields (Pecketsford (Field 1), Burrows (Field 4), Middle and Higher Wyke Moor (Field 8)) indicate 'spatial variability of the nutrient along the flow channel' (Murphy et al, 2012) in these fields. At the Longlands East (Field 15), which is a smaller field, the study indicated clockwise hysteresis pattern, and this is interpreted to suggest that nitrate was flushed via saturation excess flow into the flow channel (Hornberger et al, 2004; Weiler and McDonnell, 2006). The significantly higher concentration of nitrate at the Longlands East during the November events ($p < 0.05$) indicated recent application of manure before the event. Previous study of nitrate in North Wyke fields and elsewhere indicated concentrations of nitrate in runoff can be affected by wetting and drying of soil (Blackwell et al, 2012) and the rate of application of N fertiliser and farmyard manure

due to farm management (Scholefield and Stone, 1995; Jarvis, 1999; Brown et al, 2001). Studies (Scholefield and Stone, 1995; Dixon et al, 2010) have also noted that a large fraction of nitrate may be locked up in the upper soil profile (O-horizon) in well fine-textured soil, waiting to be flushed out during a storm event. Variations in the nitrate-discharge relationship may also be explained by the effect of microbial biomass concentrations (due to fertiliser and farm manure treatment) following soil drying and rewetting (Blackwell et al, 2012). Dissolved oxygen-discharge relationships of 'line and loop' in January and mostly clockwise pattern in November indicated variability in solute concentrations at the source area within the fields. The 'figure-of-8' hysteresis pattern exhibited by water temperature-discharge relationship indicated that temperature responds to both surface and subsurface conditions.

The clockwise patterns exhibited by most of the c-q relationships (conductivity, turbidity, nitrate and water temperature) suggest that the materials that contributed to the runoff concentration were close to the gauge station (having travelled a short distance) (Klein, 1984) and that the runoff was dominated by event water (Davies and Evans, 1998). The anticlockwise patterns which dominated the pH-discharge relationship at three (Pecketsford, Burrows and Middle and Higher Wyke Moor) indicated that some chemicals also travel far from the gauging station (Klein, 1984) and that the runoff was dominated by pre-event water (Evans and Davies, 1998). The figure-of-8' and the unclear (haphazard) loop of some of the parameters during some of the storm events suggest that the pre-event and event water sometimes mix before reaching the gauge station. The implication of this is that the saturation-excess overland flow is an important mechanism in the study area. Saturation-excess overland flow occurs as excess water runs off after the soil is saturated, and it includes translatory flow (when previously stored water is released) and return flow (refer to Section 2.2.1.2). Runoff mechanism that can be explained by clockwise hysteresis patterns are often fast macropore or surface flow (Holden, 2005; Bishop, 2004). Granger et al (2010b) showed from a study of the hydrological response of clay soils at North Wyke from $\delta^2\text{H}$, indicated indicated that Hortonian overland flow may be occurring in the study area.

4.3.7. Conclusions

The concentrations of nitrate, conductivity and turbidity in the investigated fields have been identified with pre-event flow by examining chemographs and concentration-discharge relationships. Farm management procedures (including grazing, application of manure, slurry and lime) and farm management history are identified as potential causes of the spatial variability of the concentrations of the chemical parameters in the selected fields. Spatial variations in the fields' responses to rainfall (in terms of discharge and discharge peak) were linked with the different sizes of the investigated fields (larger volume of discharge was recorded in large farms than the smaller fields). The study found that the pre-event contribution dominated the variations in turbidity, nitrate and conductivity while variations in temperature, pH and dissolved oxygen varied with the influence of event contributions. The investigated parameters also showed evidence of temporal differences (variations occurred in their concentrations, and at least nitrogen showed varying concentration-discharge patterns in January and November). Indications from the results of the c-q relationships suggest that saturation-excess and Hortonian overland flow are prominent flow paths in the study area.

Chapter 5

5. Synopsis of findings, Conclusions and Recommendations

5.1. Synopsis of findings

This research was conducted based on three possible foci for farm scale hydrology; precipitation, soil and land use. Movement of water from precipitation through a catchment to other parts of the environment has received a great deal of research attention in recent years, because pollutants can be transferred with water from their source areas to vulnerable areas, with significant environmental consequences (Shen et al, 2014; Sundström et al, 2014; Xia et al, 2014). The farm scale approach focussed in this study therefore exemplifies an important environment whose misuse is of significant threat to the immediate and larger society. The research focussed on intensively managed grasslands, which have been globally recognised as key to increase food production, and as potentially vulnerable areas to pollution and degradation (Tscharrntke et al, 2005; Eriksson and Cousins, 2014). The aims of the research were to investigate the (1) temporal variability in precipitation and soil chemistry, (2) spatial variability of soil properties, and (3) concentration-discharge hysteretic relationships at the farm-scale. The intensively managed fields of the North Wyke Farm Platform in Devon, United Kingdom were used as study area. The fields of the North Wyke Farm Platform have been cultivated under different land management (before 2011) until the present experimentally planned tri-focused land management (grassland, planned reseeding and intensive leguminous uses).

5.1.1. Temporal variability in precipitation and soil chemistry

Comparison of the precipitation and soil chemistry at the study area indicated that the soil water in the fields was not significantly related to the precipitation as at the time of investigation. Low correlation between precipitation and soil chemistry suggests that the fields were not contaminated as the precipitation chemistry was also within the minimum limit of environmental guidelines (Chapman, 1996). Sources of major precipitation ions (such as chloride, sodium and phosphate) were traceable to anthropogenic sources, especially sea-salts, and they exhibited significant level of variations with the temporal variations in rainfall and temperature as have also been

noted in many studies (e.g. Buishand et al, 1988; Whitlow et al, 1992; Xiao et al, 2014). Soil water chemistry at 0-10 cm and below 10cm soil depth, which exhibited significant relationship ($p < 0.05$) for all the investigated parameters (except chloride and phosphate) indicated that land use is an important factor in the soil chemistry (by consequence runoff chemistry) in the study area.

5.1.2. Spatial variability of soil properties

Spatial variability in the distributions of bulk density, pH, carbon, nitrogen, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and organic matter was investigated from data obtained from the 15 fields in the study area. Small within-field and between spatial variability occurred in the distribution of bulk density, carbon and nitrogen, and the variability was found to be related to the effect of trampling of the soil, organic deposition by the grazing animals and previous treatment of the farms to improve the organic matter and pH levels. Animal related activities that often account for variability in soil physiochemical properties include soil pugging (plastic deformation associated with deep hoof imprints of grazed animals when the animals' load exceeds the bearing capacity of the soil), poaching (elastic deformation of soils associated with animals trampling on very wet soil) and soil compaction, when the soil bearing capacity of these impact is exceeded (Bilotta et al, 2007). Spatial variability in the investigated parameters across the fields were generally less than 25%, and this does not suggest poor land management of the area.

5.1.3. Concentration-discharge hysteretic relationships at the farm-scale

Hysteretic plots of five parameters (pH, temperature, conductivity, dissolved oxygen, turbidity and nitrate) at 13 events (8 in January and 5 in November, 2013) were investigated in four fields (Pecketsford, Burrows, Middle and Higher Wyke Moor, and Longlands East). The fields were different in terms of their sizes (4.7, 11.0, 6.9 and 1.7 ha, respectively), slope (0-12 %, 0-25 %, 2-8 % and 2-6 %, respectively) and dominant soil series but have been partly or wholly ploughed, reseeded and grazed between 1995 and 2005. The sampled fields (except the Middle and Higher Wyke Moor) were also cultivated with barley within the period. Runoff coefficient varied between 0.1 and 0.3, and there was no significant spatial difference across the fields. Nitrate and conductivity values were much higher in the runoff at the Longlands East, and this can be traced to

the concentrations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, which were found to be equally higher at the Longlands East than the three (Pecketsford, Burrows, and Middle and Higher Wyke Moor) other investigated fields under refer Aim 2. Except that the rate and volume of discharge at the Longlands East was relatively low (mean peak at the period of study was $7.1 \text{ m}^3 \text{ s}^{-1}$ compared to $15.9 - 42.8 \text{ m}^3 \text{ s}^{-1}$ in the other fields), contrasting features of the Longlands East compared with the other fields are its smaller size (1.5 ha, compared to 4.7-11.0 ha), and its relatively higher (1.0 g cm^{-3}) bulk density. McDowell et al (2014) noted that chemical parameters such as nitrate are often emitted from small areas of a field (called critical source area) that emits in huge concentration in commensuration with surface flow pathways, as well as input and land use. Both conductivity and nitrogen concentrations were low at high discharges during most of the events studied. The results of hysteresis however showed that nitrate-discharge relationship was mostly clockwise at the Longlands East while it complex (or unclear) at the other three fields. The conclusion in Aim 3 that both the chemographs and hysteresis pattern indicated dominance of pre-event contributions of turbidity, nitrate and conductivity, suggested that flushing of the previously accumulated sources of these materials in the fields is a likely explanation for the occurrence. The relatively higher mean bulk density at Longlands East also indicates a lower porosity than the soils in other fields, which may affect transfer of chemical materials in soils. Review of the farm records also showed that the fields have been sprayed with farm yard manure as part of the management procedure for soil quality enhancement. The c-q relationships indicated that the Hortonian and saturation-excess overland flows are the prominent flow mechanisms in the study area,

5.2. Conclusions

The study evaluated precipitation-soil water chemistry relationship, soil variability and concentration-discharge relationship at the farm-scale based on datasets from the North Wyke Farm Platform between 2011 and 2013. The three main hypothesis were that (1) precipitation and soil water chemistry are significantly related (2) significant relationships exists between the distribution of soil physiochemical characteristics and the managements of the fields, and that (3) hydrological behaviour of fields underlain by

certain dominant soils in the study area are different from that of other fields. The study rejected the first and third hypothesis, and concluded that relatively higher concentrations of nitrate and conductivity in the runoff at the Longlands East was related to the relatively higher carbon and nitrogen isotopes and bulk density at same field. The study therefore associated variability in the runoff chemistry with land use and soil compaction. The study also noted that sodium and chloride ions were dominant in the precipitation chemistry, and therefore suggests their further investigation as conservative tracers in the soil and runoff chemistry. It also showed that the study area was dominated by surface runoff.

5.3. Limitations of the study and recommendations for further research

As an international PhD student from Nigeria, the pressure of time limit and limited financial availability were main distractions during the course of this study. Other significant source of distraction was waiting for data to be generated and certified by the Farm Platform and Rothamsted Research before use. The challenge of not able to do a separate field work other than what was planned by the Farm Platform as a result of my financial and technical limitations were also important sources of limitations in the course of this research.

Based on the results of this study, a few other studies are recommended, and they include:

- (1) Conducting a laboratory investigation of the concentration-discharge hysteresis such that parameters (concentration, slope, rainfall volume, soil and vegetation) can be varied. The natural environment is such a complex ecosystem that changes over a short period may not be easily identified, but the laboratory environment can be varied and the effects promptly visualised and noted; and
- (2) investigating the soil water chemistry at different slope, soil series and vegetation from make-up monitoring stations in addition to the existing to the station of the Environment Change Network (ECN) at Burrows (Field 4) because soil water chemistry can vary with change in slope and vegetation (Parton et al, 1987; Sariyildiz et al, 2005; Xu et al, 2014). Variations in soil water chemistry across

varying slopes can provide answers to the changing concentration-discharge relationships in some fields.

APPENDICES

Appendix 3.1. Ion balance estimates of the mean precipitation chemistry at North Wyke (1993–2011).

Ion	Jan.-Dec.		Dec-February		March-June		June-Sept.		Oct-Nov.	
	mg ^l ⁻¹	meq ^l ⁻¹	mg ^l ⁻¹	meq ^l ⁻¹	mg ^l ⁻¹	meq ^l ⁻¹	mg ^l ⁻¹	meq ^l ⁻¹	mg ^l ⁻¹	meq ^l ⁻¹
Ca ²⁺	0.613	0.031	0.346	0.017	0.915	0.046	0.527	0.026	0.856	0.043
Mg ²⁺	0.338	0.028	0.390	0.032	0.345	0.028	0.300	0.025	0.318	0.026
K ⁺	0.634	0.016	0.306	0.078	0.256	0.007	0.901	0.023	0.964	0.025
Na ⁺	2.944	0.128	3.680	0.16	2.751	0.12	2.415	0.105	2.856	0.124
NH ₄ ⁺	0.317	0.018	0.297	0.017	0.637	0.035	0.281	0.016	0.161	0.009
SO ₄ ²⁻	0.327	0.007	0.330	0.007	0.47	0.01	0.384	0.008	0.148	0.003
PO ₄	0.018	0.0002	0.019	0.001	0.012	0.0001	0.026	0.0003	0.012	0.0001
Cl ⁻	5.207	0.147	6.324	0.178	4.578	0.129	4.188	0.12	5.604	0.158
NO ₃ ⁻	0.329	0.005	0.340	0.006	0.514	0.008	0.299	0.005	0.222	0.004
CO ₃ ²⁻	2.251	0.075	1.093	0.036	2.853	0.095	2.236	0.075	3.281	0.109
Calculated TDS	13.00		13.14		13.35		11.63		14.425	
Sum of cations		0.222		0.235		0.237		0.199		0.227
Sum of anions		0.234		0.227		0.242		0.206		0.274
Cation–Anion ratio		1.04		1.04		1.03		1.07		1
Difference		0.012		0.008		0.005		0.007		0.047
% difference		2.56		1.62		1.05		1.66		9.40

Appendix 3.2: Some field activities during soil data preparation for Aim 2.



(a). 2012 Soil Sampling Team, North Wyke Farm Platform
Source: Griffiths, 2012: Farm records.
L-R: Noacco V, Ramezani K, Tuomenien E and Eludoyin A (this author)



(b). Peukert S and Eludoyin A.
PS was not on field when the farm technical manager took (a). I assisted in her nested sampling but the results are not used for my study.



(c) Eludoyin A and Noacco, V after a day sampling in the rain. Toumenien is in background. Ramezani was somewhere on the field (tired) not covered.



(d). Eludoyin A, holding the GPS after finished fixing the points for sampling on a sampling day



(e). Eludoyin A, doing soil sampling



(f) In the laboratory to keep the samples after a windy sampling day



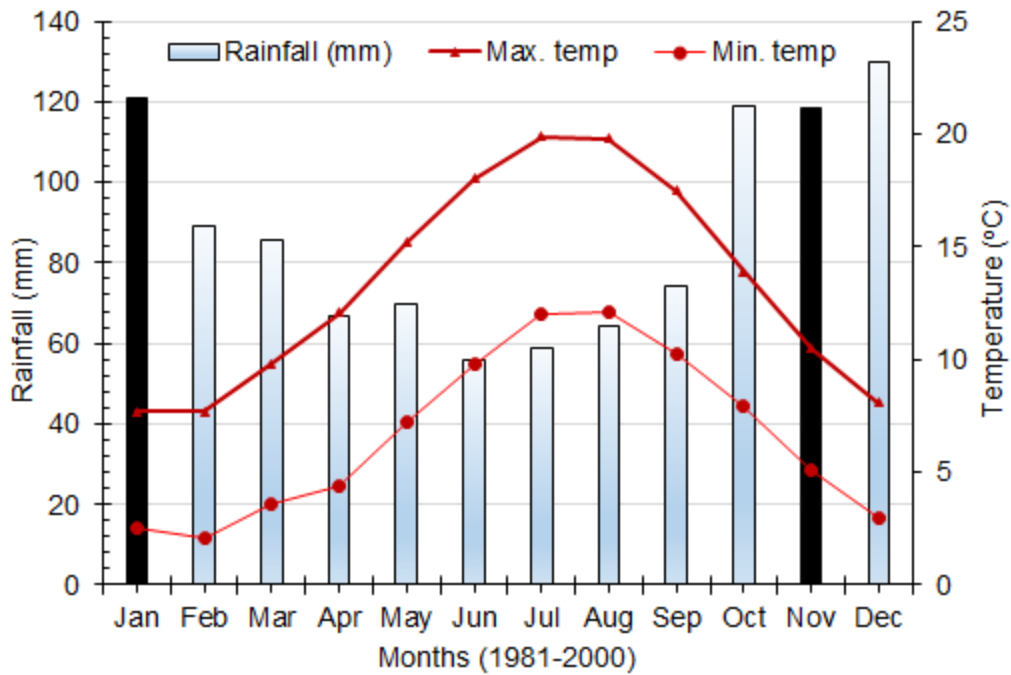
(g). Working in the laboratory with others to prepare soil samples for analysis



(i) One of the field vehicles for sampling collection. Drivers was either Peukert S or Tuomenien E (when PS was not around)

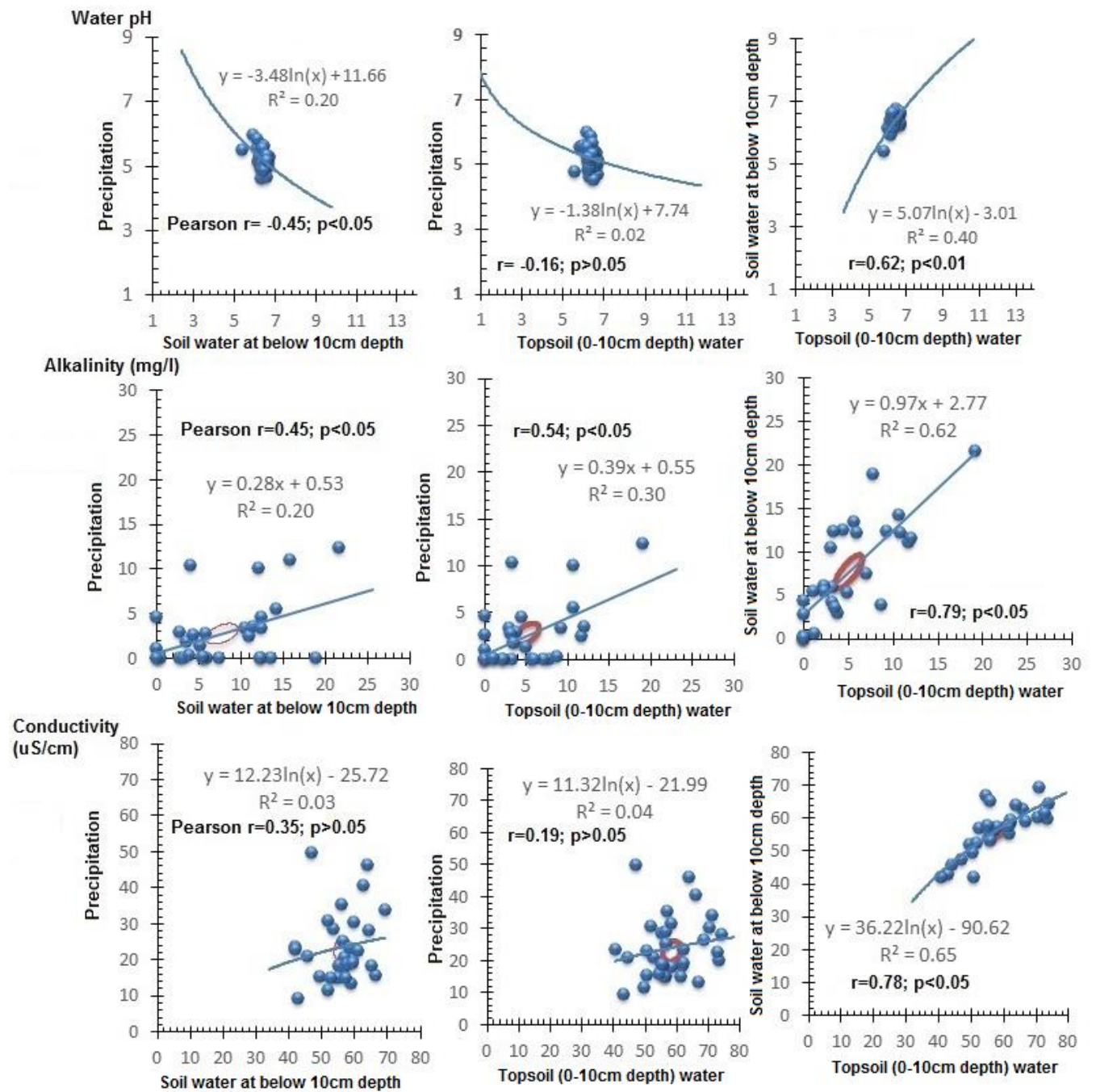


(j). The usual field companions; pegs, sampling cores, plot samplers, spade and soil samples.

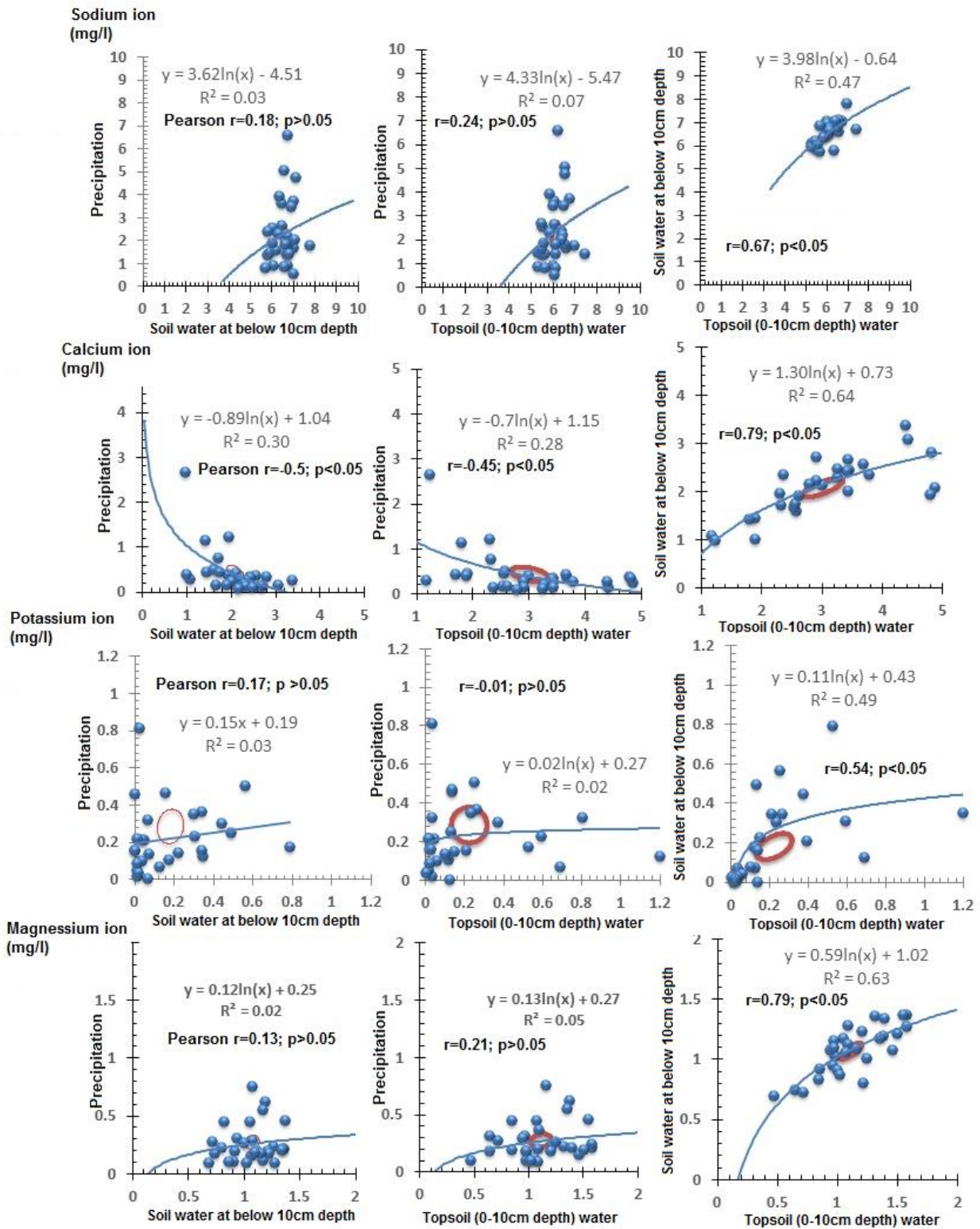


Appendix 3.3. Monthly averages of rainfall and temperature in 1981-2000 for the North Wyke, Devon, United Kingdom. Rainfall bar in black colour indicate the month for which concentration-discharge was investigated. The months are representative of winter (January) and autumn (November) in the study area. Data were obtained from the Met Office website (<http://www.metoffice.gov.uk/public/weather/climate/gcj0z3b55>).

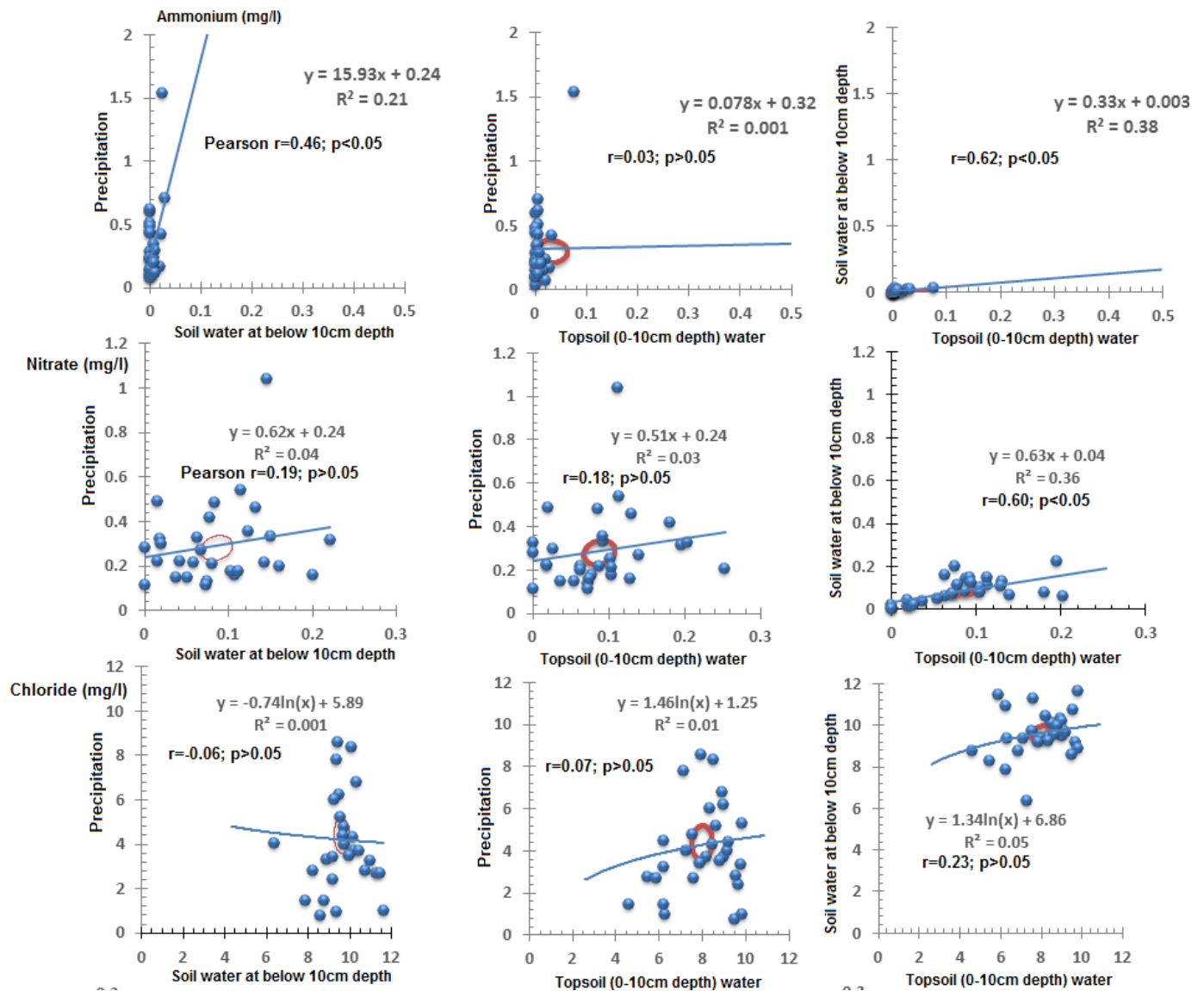
Appendix 4.1. Relationship between precipitation and soil water chemistry at North Wyke.



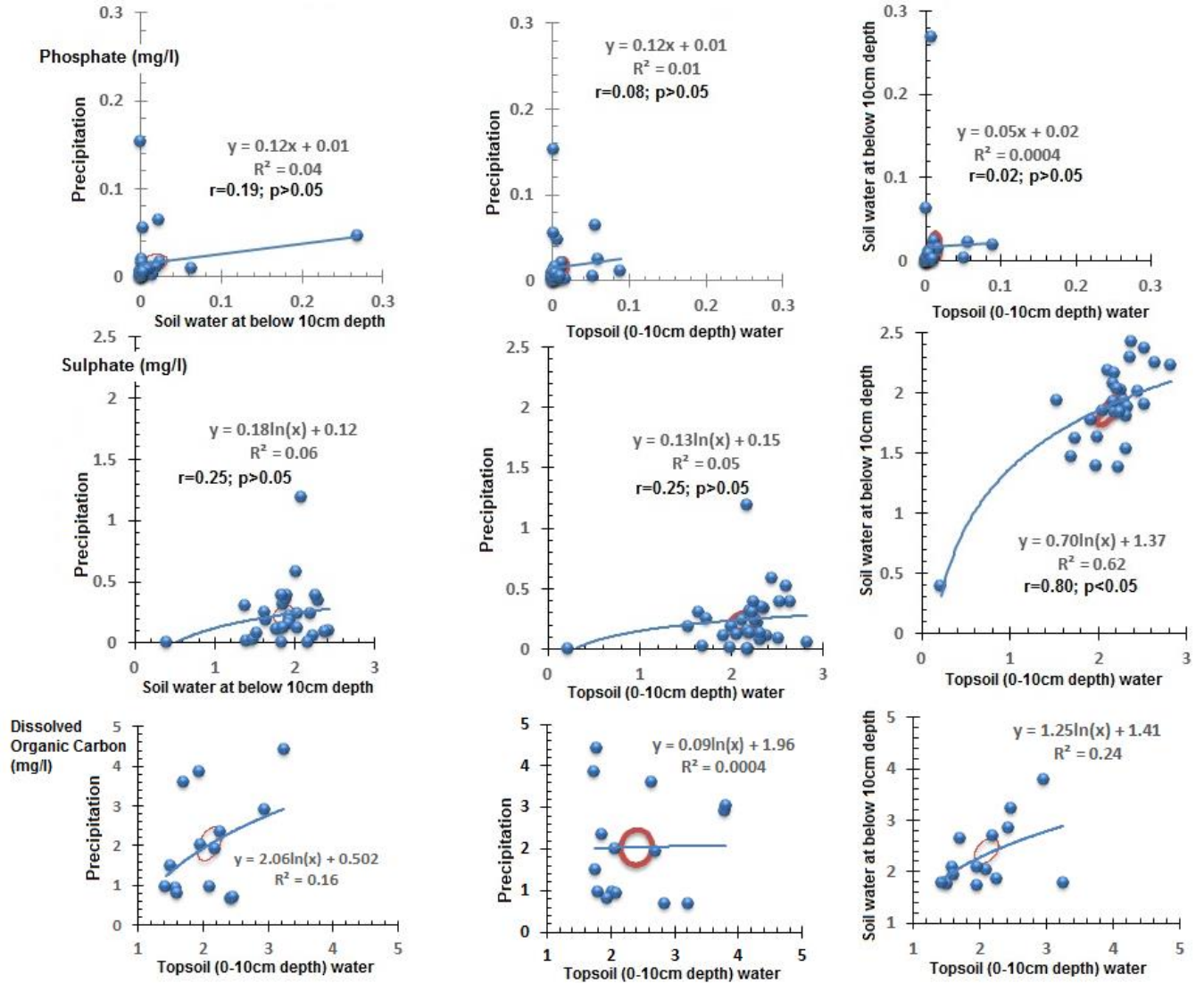
Appendix 4.1 (continues). Relationship between precipitation and soil water chemistry at North Wyke.



Appendix 4.1 (continues). Relationship between precipitation and soil water chemistry at North Wyke.



Appendix 4.1 (continues). Relationship between precipitation and soil water chemistry at North Wyke.



Appendix 4.2. Correlations between common meteorological elements and investigated precipitation chemistry.

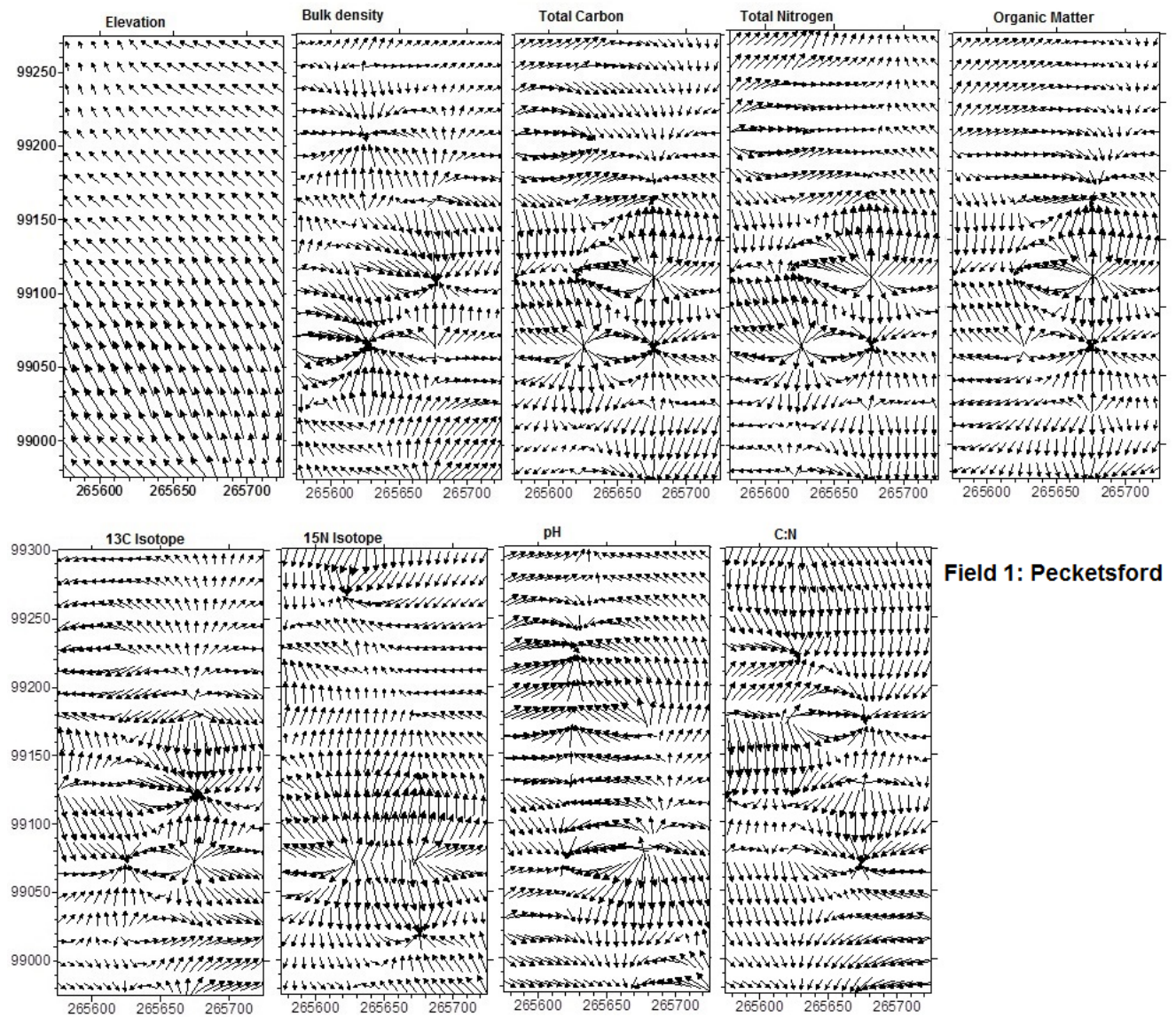
	Rainfall	Minimum Temperature	Maximum Temperature	Wind speed	Relative Humidity
pH	0.66*	-0.42	-0.52*	0.47	0.82**
Alkalinity	0.11	0.28	0.25	-0.34	-0.08
Conductivity	0.73**	-0.72**	-0.75**	0.52*	0.62*
Ca²⁺	-0.09	0.52*	0.49	-0.64*	-0.25
K⁺	-0.44	0.68*	0.70*	-0.66*	-0.63*
Mg²⁺	0.51*	-0.53*	-0.55*	0.37	0.44
Na⁺	0.73**	-0.81**	-0.86**	0.71**	0.74**
NH₄⁺	-0.48	-0.03	0.11	-0.22	-0.57*
Cl⁻	0.81**	-0.82**	-0.88**	0.77**	0.86**
NO₃⁻	-0.59*	0.22	0.36	-0.43	-0.69*
SO₄²⁻	-0.38	0.34	0.38	-0.49	-0.27
PO₄³⁻	-0.36	0.30	0.33	-0.36	-0.38
DOC	-0.86**	0.82**	0.88**	-0.79**	-0.87**

** Correlation coefficient is significant at $p < 0.01$.

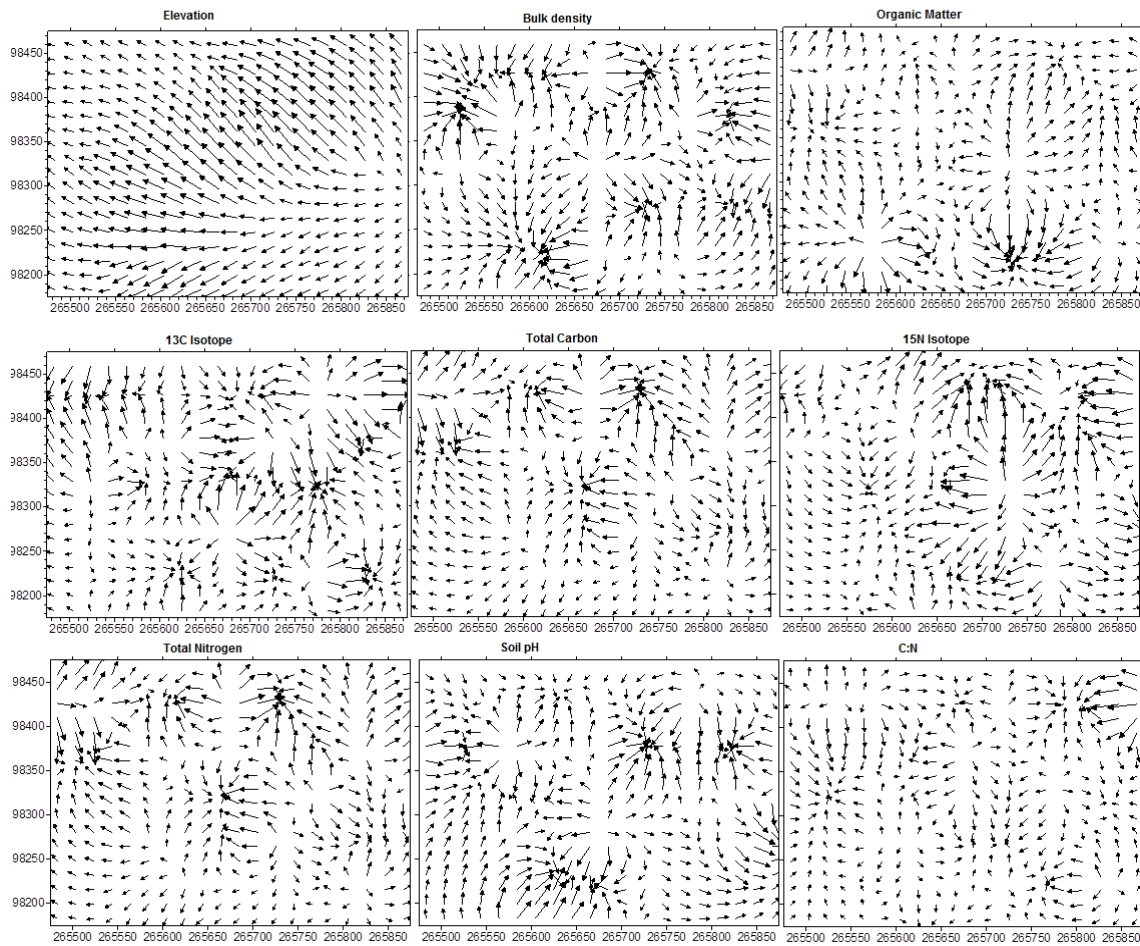
* Correlation coefficient is significant at $p \leq 0.05$.

Appendix 4.3. Descriptive statistics (mean, minimum-maximum values are in parenthesis) of the investigated soil parameters at the North Wyke Farm Platform.

Field Id	Elevation (metres)	Total Nitrogen (gkg ⁻¹)	Total Carbon (gkg ⁻¹)	C:N	Carbon isotope (‰)	Bulk Density (gcm ⁻³)	Nitrogen isotope (‰)	pH	SOM (gkg ⁻¹)	C Stock (t C ha ⁻¹)	N Stock (t N ha ⁻¹)
1	136.5 (129.1-148.4)	6.0 (5.1-7.4)	49.7 (42.0-59.4)	8.3 (7.7-9.3)	-28.9 (-30- -28)	0.9 (0.7-1.0)	6.1 (5.2-7)	5.5 (5.1-5.8)	111.5 (88.1-139.7)	45.5 (38.6-53.2)	5.5 (4.6-6.2)
2	146.4 (137.5-155.9)	4.3 (3.5-5.6)	34.3 (26.9-45)	8.0 (7-8.8)	-28.9 (-30.5- -27.6)	1.0 (0.7-1.1)	6 (5.3-6.6)	5.9 (5.3-6.4)	77.3 (65.4-96.8)	32.8 (22.2-39.7)	4.2 (2.6-4.9)
3	166.4 (133.9-147.5)	6.8 (4.3-5.4)	57.1 (32.5-44.8)	8.9 (7.6-8.2)	-27 (-29.7- -28.7)	1.0 (0.7-0.9)	6.3 (5.2-7.1)	5.6 (5.3-6.4)	138.7 (81-109.5)	38 (28.1-49.2)	4.6 (3.6-5.8)
4	161.2 (139.4-181.5)	5.4 (4.0-6.5)	45.4 (32.9-57.5)	8.4 (7.2-11.2)	-28.6 (-30.2- -27.4)	0.9 (0.7-1.0)	5.9 (5-7.2)	5.6 (4.7-6.6)	88.7 (28.0-139.6)	40.7 (24.7-52.7)	4.9 (3.0-5.9)
5	158.7 (145.5-175.9)	5.8 (4.3-7.3)	51.7 (36-74.1)	8.9 (8.2-10.2)	-29 (-29.9- -27.9)	0.9 (0.8-1.1)	5.9 (4.4-7.1)	5.8 (5.3-6.5)	120.8 (89.8-166.3)	47.8 (27.8-70.3)	5.4 (3.3-7.9)
6	172.3 (163.2-182.6)	5.8 (4.8-6.4)	49.7 (42.9-54.8)	8.6 (8.3-9)	-28.7 (-29.3- -28.0)	0.9 (0.8-1.1)	5.9 (5.4-6.5)	5.6 (5.1-6.4)	109 (99.3-118.1)	46.9 (35.5-54.8)	5.5 (4.0-6.4)
7	173.7 (169.8-177.5)	5.2 (3.8-6.3)	48.3 (33.2-59.9)	9.2 (8.6-9.7)	-28.7 (-29.5- -28.0)	0.8 (0.7-0.9)	5.6 (5.1-5.9)	5.6 (5.2-5.9)	97.6 (71.3-114.3)	38.5 (29.3-49.2)	4.2 (3.0-5.2)
8	166.6 (134.5-185)	4.5 (3.4-5.6)	40.9 (29.5-52)	9.1 (8.4-9.7)	-28.2 (-29.2- -27.5)	0.8 (0.6-1)	5.6 (4.6-6.8)	5.4 (4.7-6.1)	93.1 (66.9-112.1)	34 (20.9-45.7)	3.7 (2.4-4.9)
9	168.3 (158-182)	5.9 (5.1-7.2)	51 (40.1-62.3)	8.6 (7.7-9.1)	-29.1 (-29.7- -27.9)	0.9 (0.8-1)	5.9 (5.3-6.9)	5.6 (5.3-6)	118.0 (89.1-140.8)	45.4 (34.0-60.1)	5.3 (4.4-6.7)
10	164.4 (159.9-167.7)	6.8 (6.4-7.2)	57.5 (53.0-60.9)	8.5 (8.3-8.9)	-29.6 (-30- -29.1)	0.9 (0.9-1)	5.9 (5.3-6.3)	5.3 (5.2-5.5)	118.2 (108.4-128.6)	52.2 (49.1-54.9)	6.2 (5.8-6.5)
11	173.6 (170.6-178.1)	6.3 (5.8-6.9)	55.1 (50.3-63.1)	8.8 (8.6-9.2)	-29.4 (-30.4- -28.8)	0.9 (0.9-1)	6.1 (5.6-6.6)	5.4 (5.3-5.6)	119.9 (110.2-131.5)	50.0 (43.9-58.5)	5.7 (5.1-6.3)
12	159.2 (153.5-164.8)	6.6 (6.1-6.9)	58.8 (53.5-65.9)	9.0 (8.5-9.6)	-29.6 (-30.4- -29.2)	0.9 (0.9-0.9)	5.8 (5.4-6.3)	5.8 (5.7-5.9)	124.6 (117.4-129.8)	54.1 (50.1-62.2)	6 (5.7-6.5)
13	133.9 (130.6-135.9)	4.6 (4.1-4.9)	38.1 (34-43.1)	8.4 (8.1-8.9)	-29.5 (-30.1- -28.3)	1.0 (0.9-1.1)	6.8 (5.9-7.2)	5.5 (5.4-5.6)	87.6 (78.8-96.4)	37.1 (33.9-38.7)	4.4 (4.1-4.7)
14	132.7 (128.3-153.4)	4.4 (3.8-5.1)	33.5 (29.5-43.6)	7.6 (6.9-8.6)	-28.9 (-29.8- -28.2)	0.9 (0.8-1.1)	6.6 (5.9-7.2)	5.5 (5.3-5.6)	75.7 (59.5-103)	30.7 (24.4-39.1)	4.0 (3.3-4.6)
15	130.6 (128.6-132.6)	4.2 (3.9-4.7)	33.8 (27.7-39.8)	8.1 (7.1-9.1)	-29.3 (-30.2- -28.6)	1.0 (0.9-1.0)	6.7 (6.4-7)	6.2 (6-6.3)	90.5 (80-101)	32.4 (26.9-36.5)	4.0 (3.8-4.3)
Total	155 (128.3-185)	5.4 (3.4-7.3)	46.6 (26.9-74)	8.6 (6.9-11.2)	-29.0 (-30.5- -27)	0.9 (0.6-1.1)	6.1 (4.5-7.2)	5.6 (4.7-6.6)	102.9 (28-166.3)	41.8 (20.9-70.3)	4.6 (2.4-7.9)

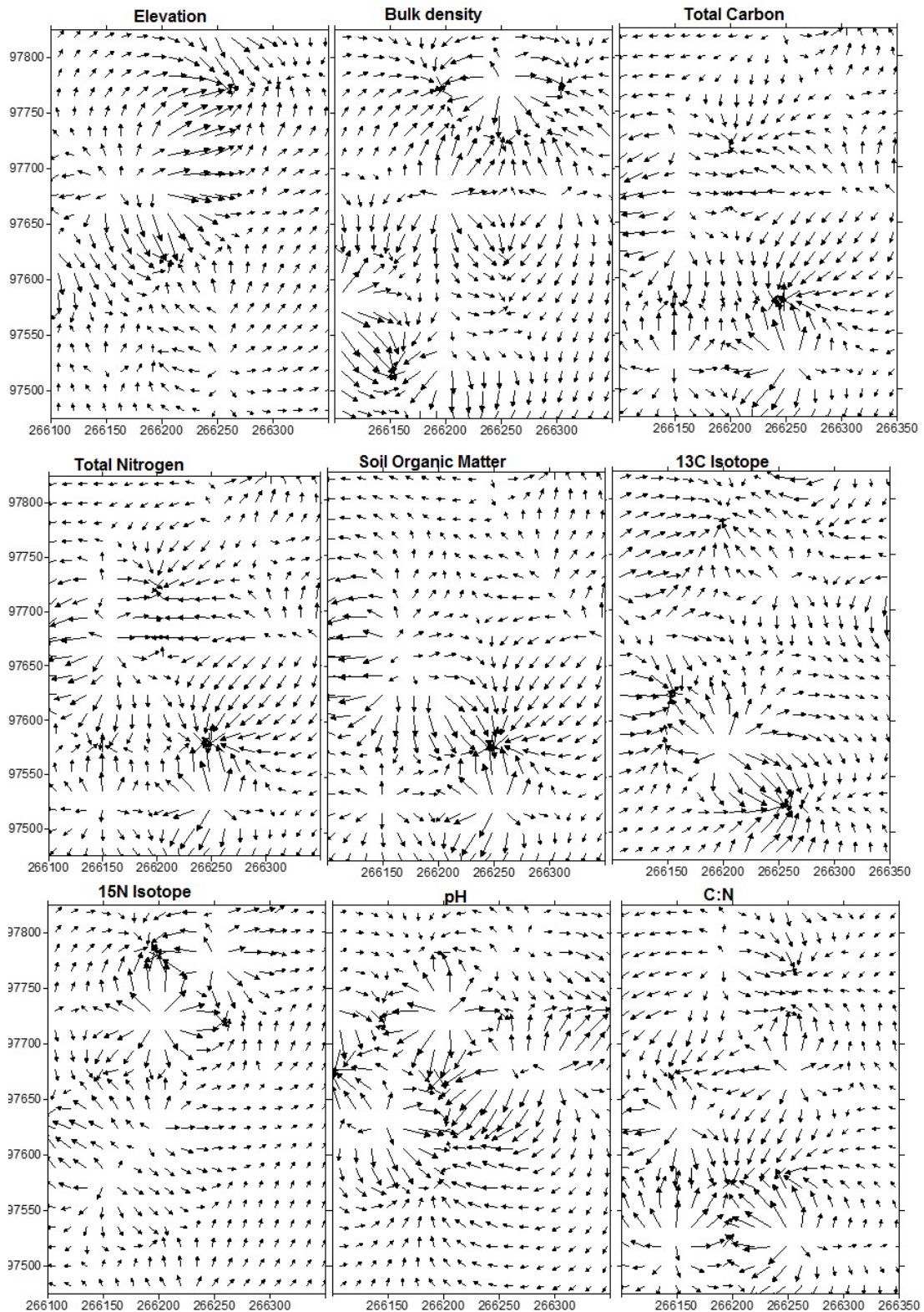


Appendix 4.4a: Vector ('1-grid') map information showing the spatial variability in the magnitude of concentration of selected physiochemical parameters in Field 1 (Pecketsford). A vector (line) is drawn at each grid of interpolation. Magnitude is indicated by arrow length and the arrows point in the direction of lower magnitude from the region of higher magnitude (concentration).



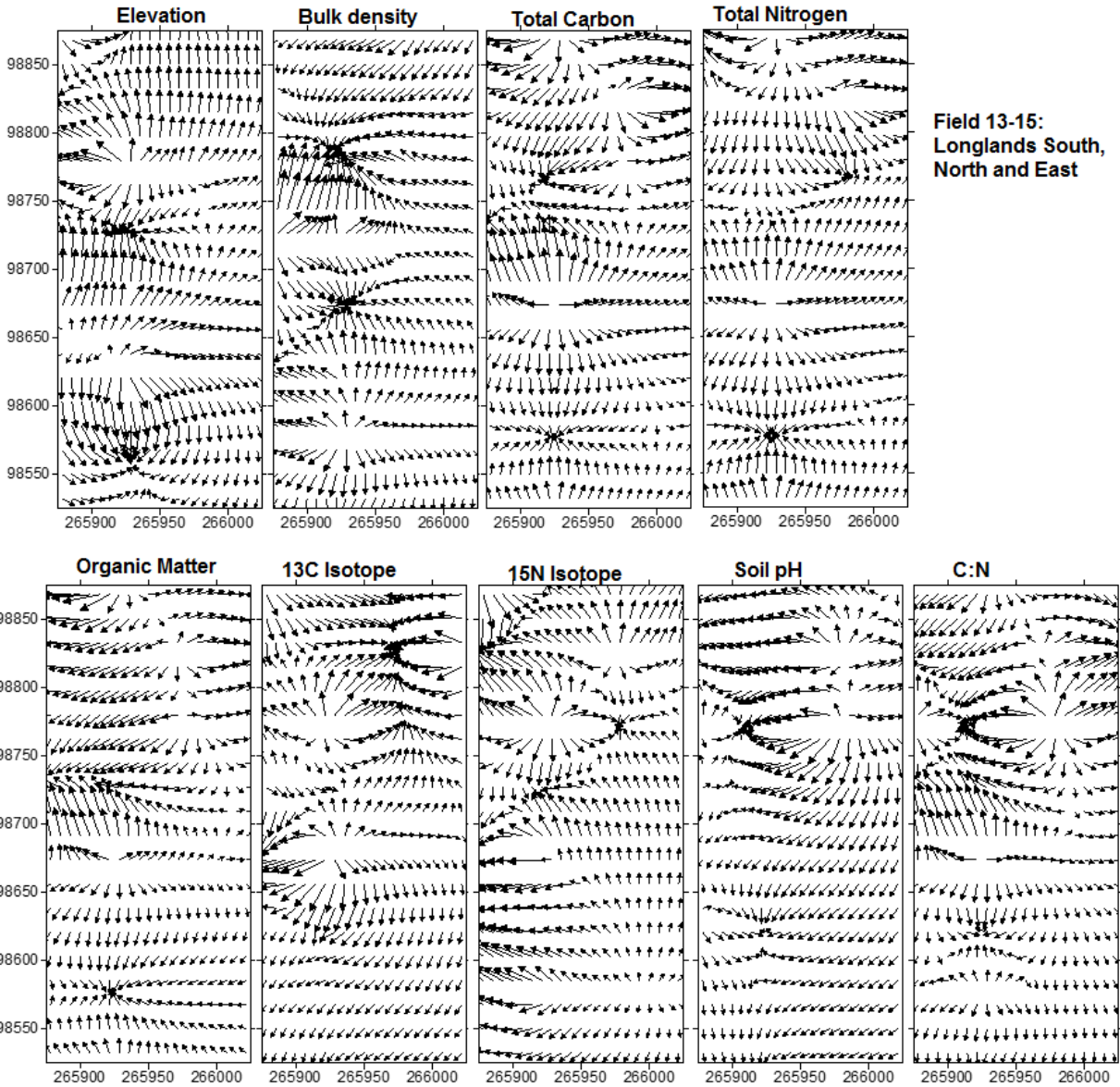
Field 4: Burrows

Appendix 4.4b: Vector ('1-grid') map information showing the spatial variability in the magnitude of concentration of selected physiochemical parameters in Field 4 (Burrows). A vector (line) is drawn at each grid of interpolation. Magnitude is indicated by arrow length and the arrows point in the direction of lower magnitude from the region of higher magnitude (concentration).

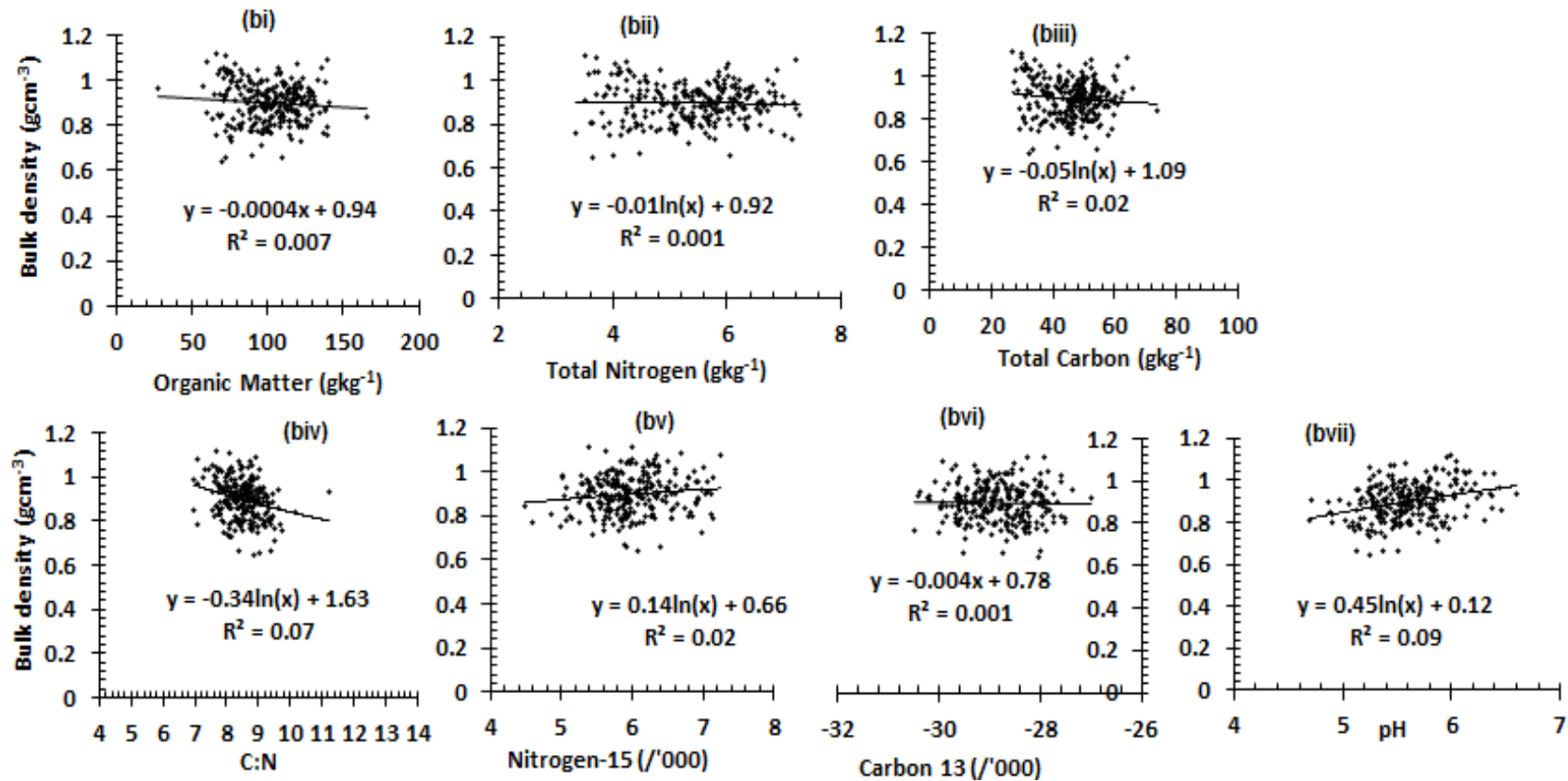


Field 8: Higher & Middle Wyke Moor

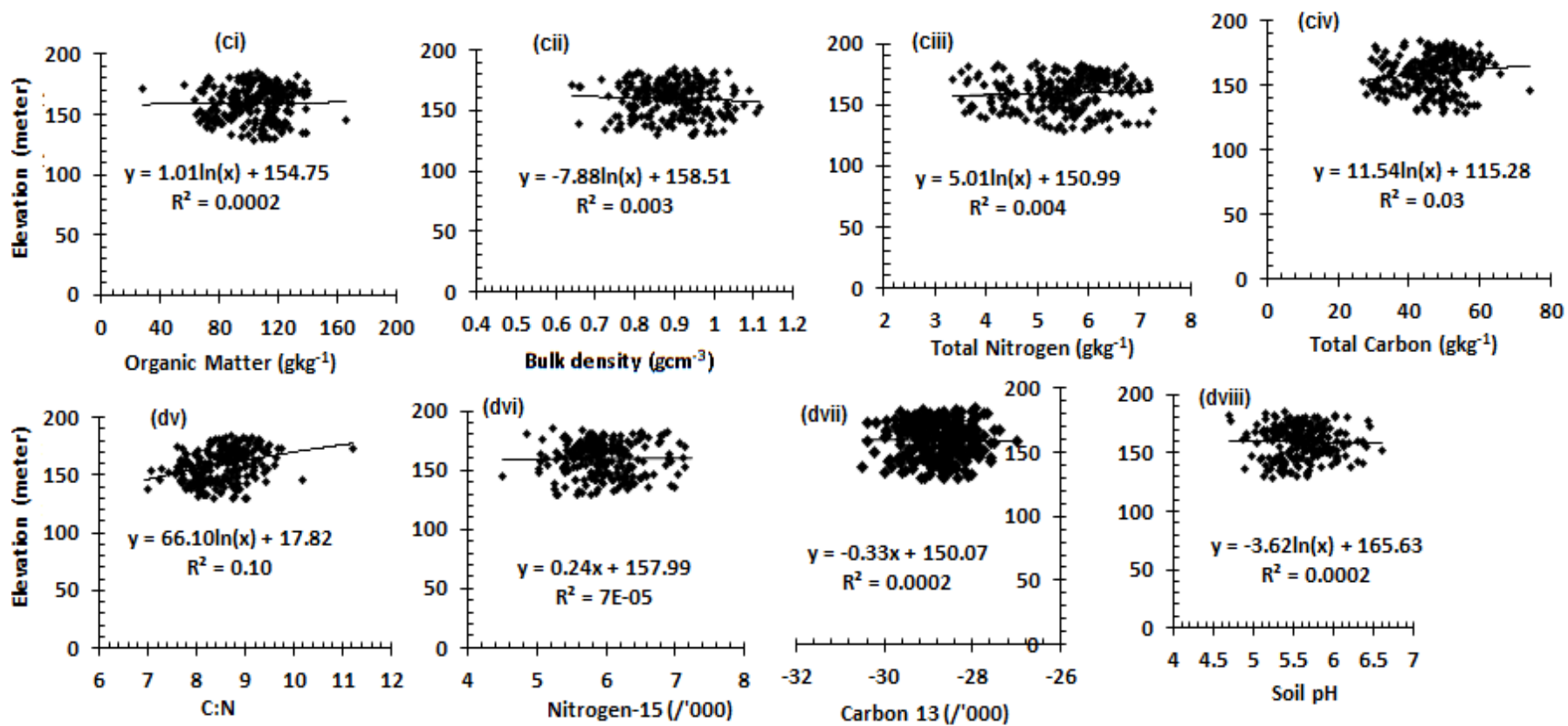
Appendix 4.4c: Vector ('1-grid') map information showing the spatial variability in the magnitude of concentration of selected physiochemical parameters in Field 8 (Higher and Middle Wyke Moor). A vector (line) is drawn at each grid of interpolation. Magnitude is indicated by arrow length and the arrows point in the direction of lower magnitude from the region of higher magnitude (concentration).



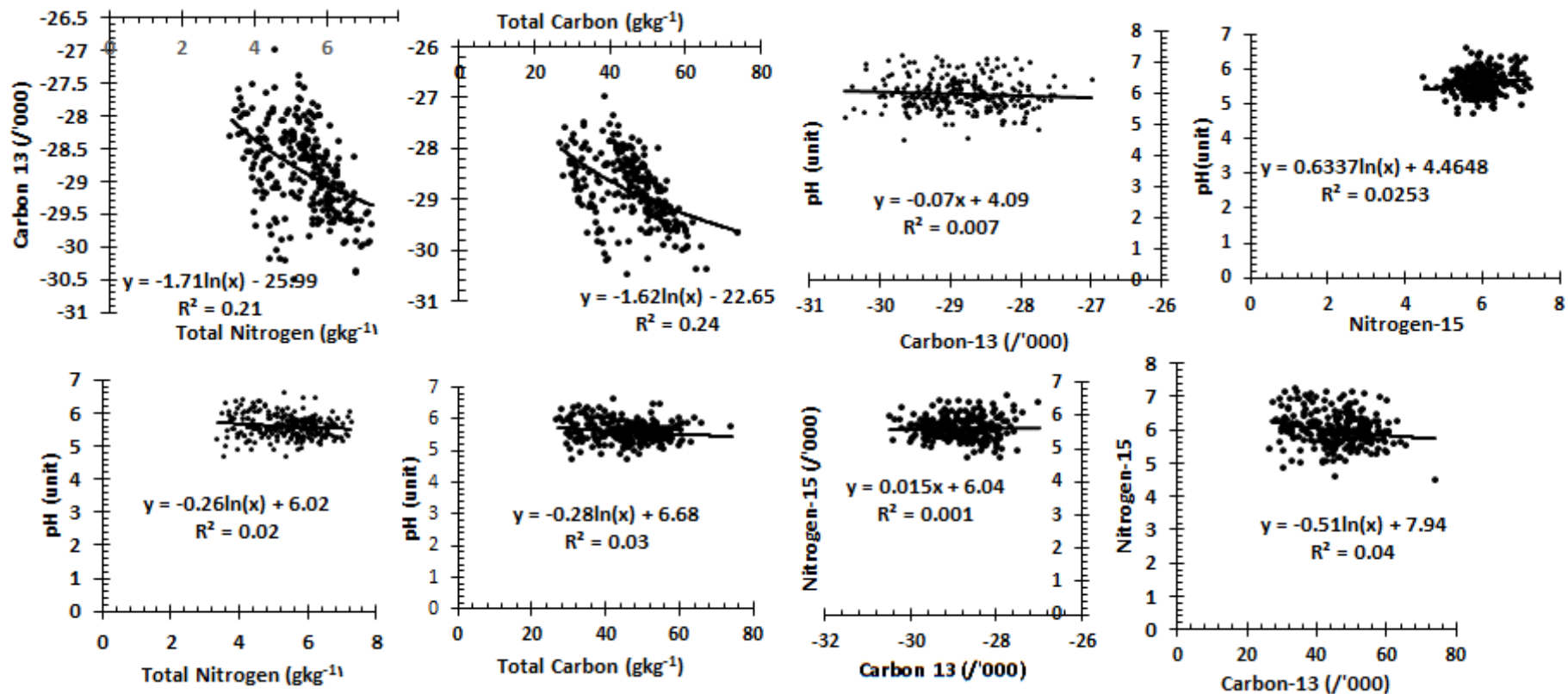
Appendix 4.4d: Vector ('1-grid') map information showing the spatial variability in the magnitude of concentration of selected physiochemical parameters in Field 13-15 (Longlands South, North and East). A vector (line) is drawn at each grid of interpolation. Magnitude is indicated by arrow length and the arrows point in the direction of lower magnitude from the region of higher magnitude (concentration).



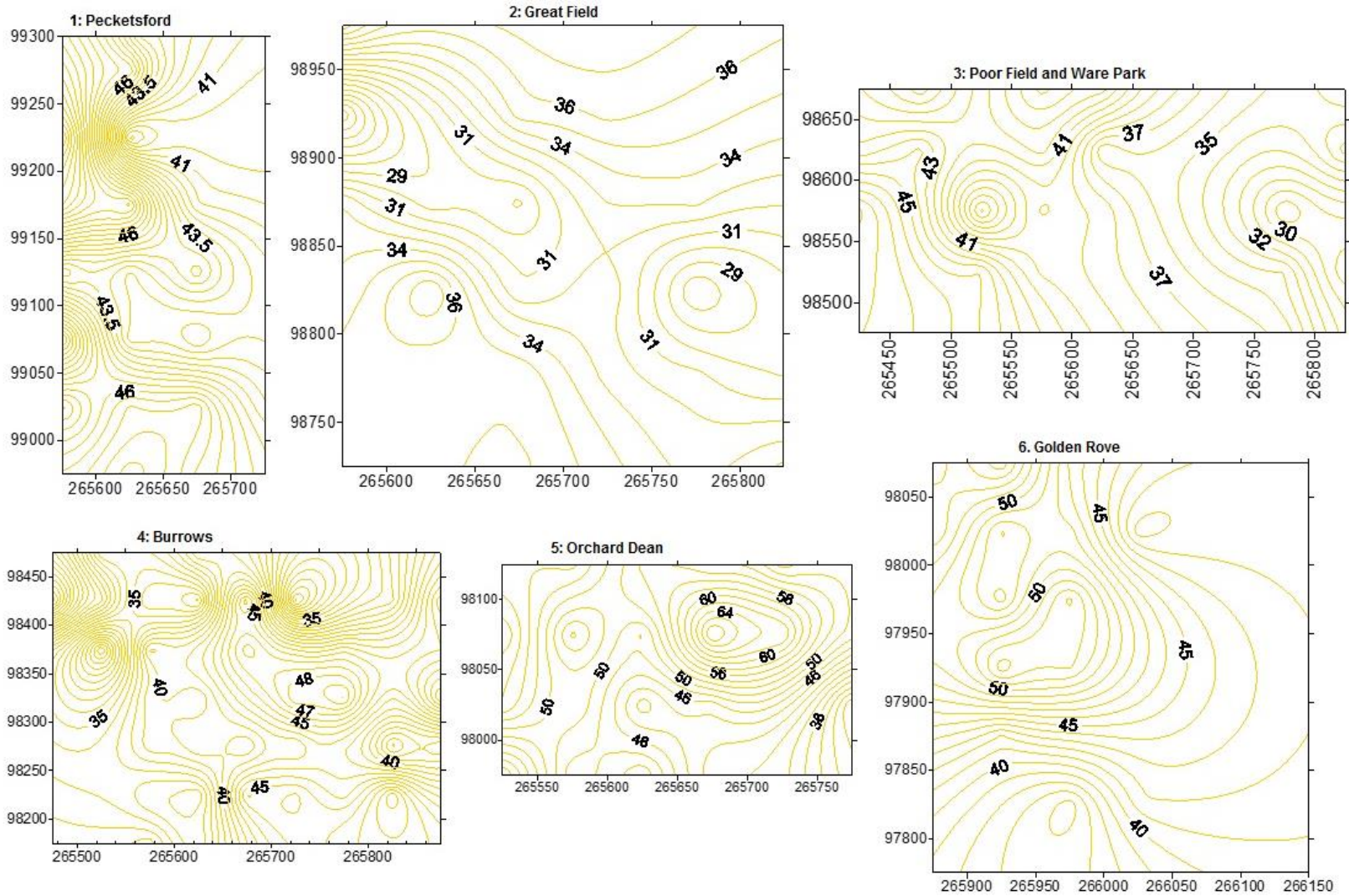
Appendix 4.5a: Relationships among selected physiochemical variables in the North Wyke Farm Platform's soils.



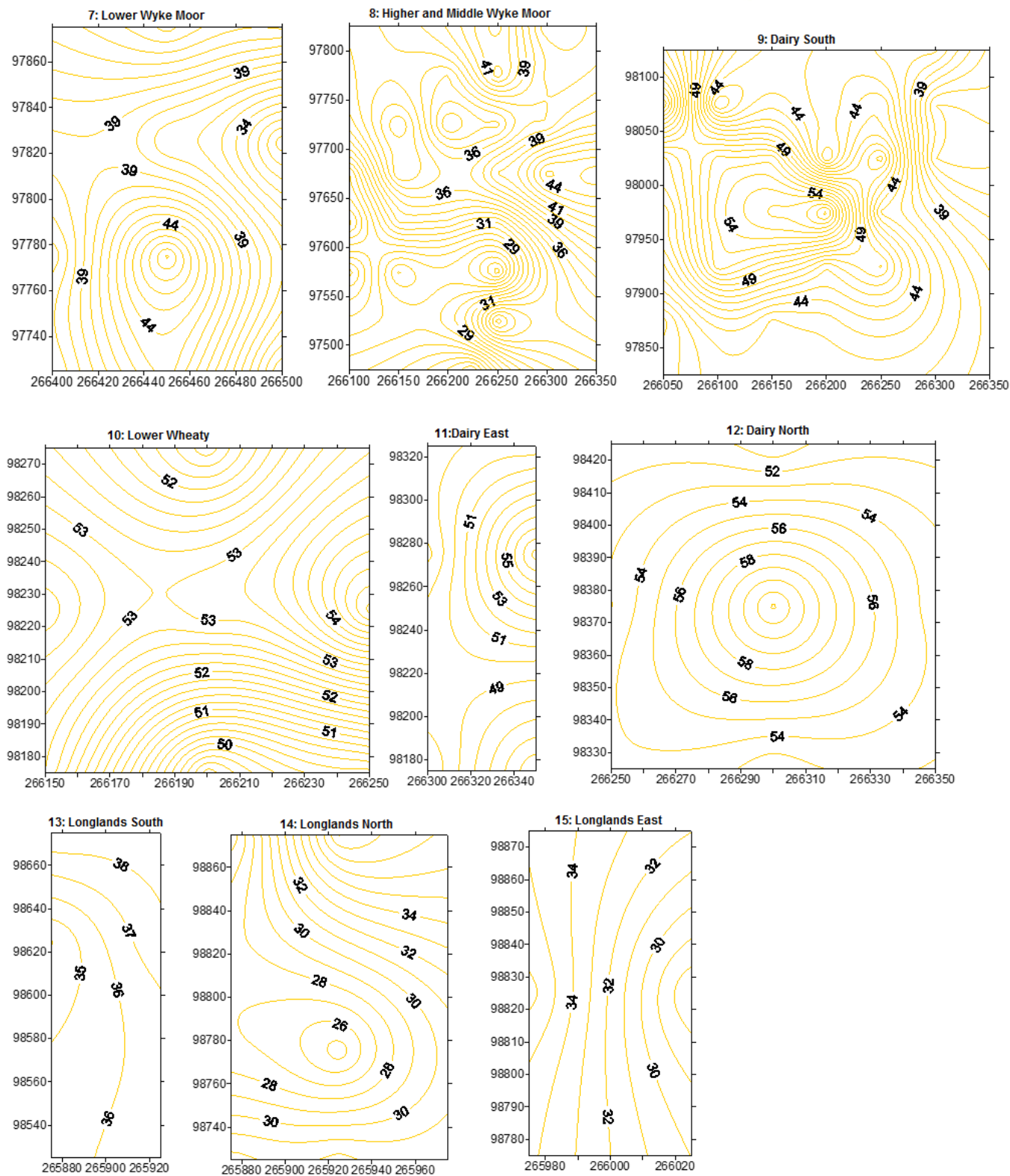
Appendix 4.5b: Relationships among selected physiochemical variables in the North Wyke Farm Platform's soils.



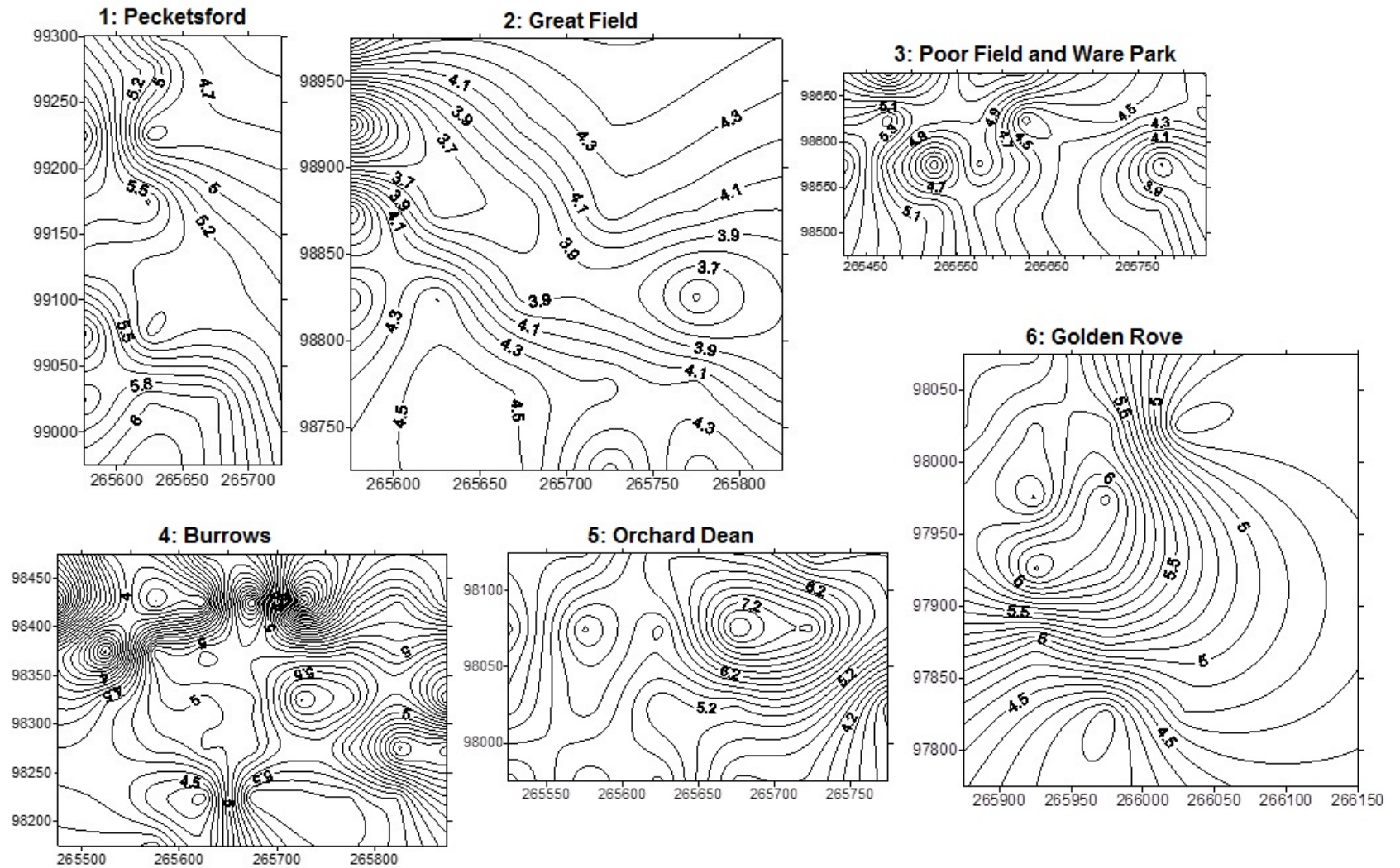
Appendix 4.5c: Relationships among selected physiochemical variables in the North Wyke Farm Platform's soils.



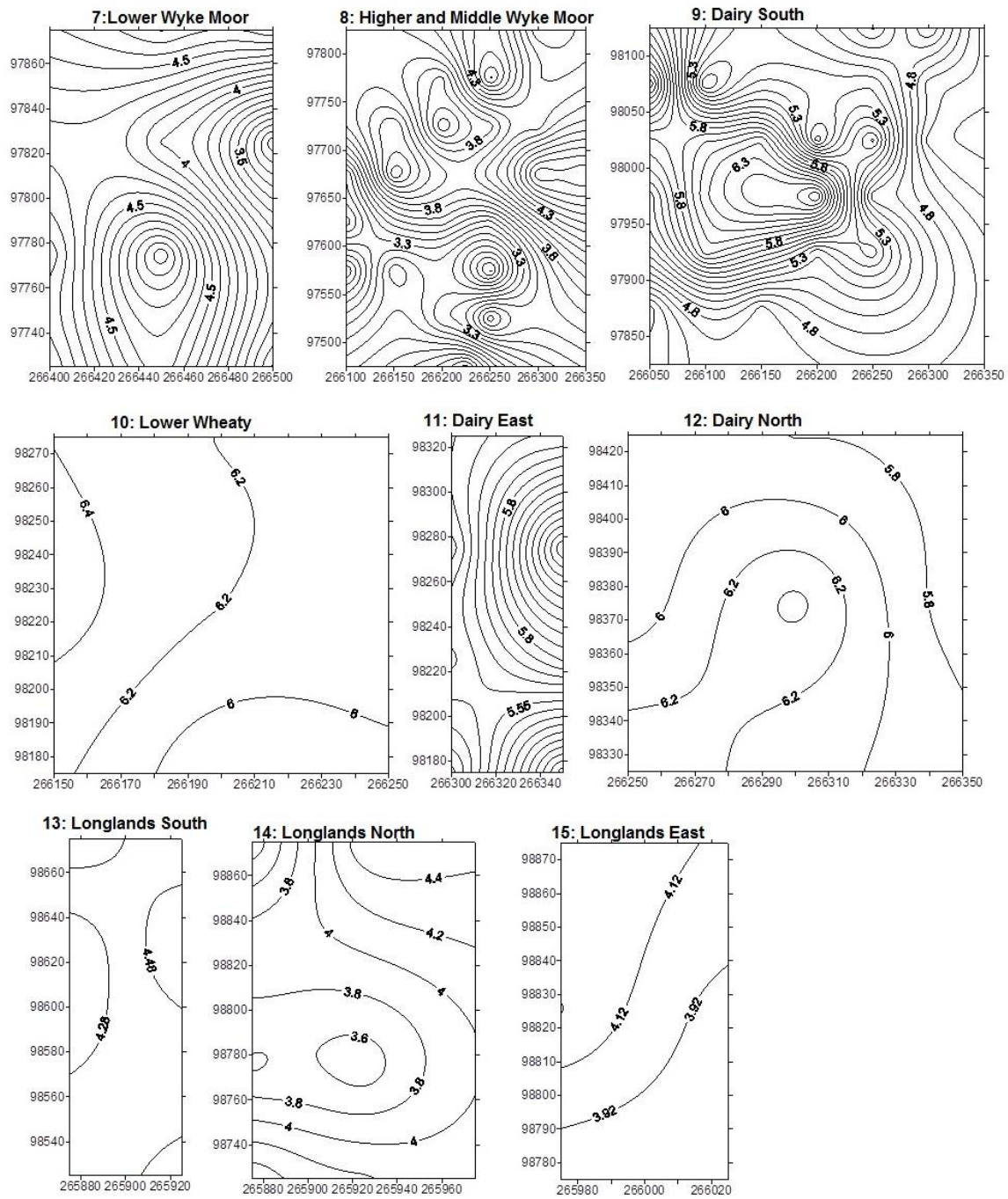
Appendix 4.6a: Spatial variations of Carbon Stocks (in t C ha⁻¹) across the fields of the North Wyke Farm Platform.



Appendix 4.6b: Spatial variations of Carbon Stocks (in $t\ C\ ha^{-1}$) across the fields of the North Wyke Farm Platform.



Appendix 4.6c: Spatial variations of Nitrogen Stocks (in $t\ N\ ha^{-1}$) across the fields of the North Wyke Farm Platform.



Appendix 4.6d: Spatial variations of Nitrogen Stocks (in $t N ha^{-1}$) across the fields of the North Wyke Farm Platform.

Appendix 4.7. Event-based c-q relationships across the selected fields.

Event	Temperature			Conductivity			Dissolved Oxygen				Turbidity				pH				Nitrate					
	4	8	15	1	4	8	15	1	4	8	15	1	4	8	15	1	4	8	15	1	4	8	15	
	Field 1																							
Event 1	F8	-	F8	C	C	-	C	F8	LP	-	LP	LP	C	-	A	C	A	-	A	LP	-	-	-	-
Event 2	SL	A	SL	A	C	C	A	LP	LP	U	LP	A	C	F8	F8	F8	A	U	A	U	U	U	U	U
Event 3	F8	F8	F8	F8	C	U	U	C	F8	U	LP	LP	C	C	F8	C	A	U	A	U	U	U	U	C
Event 4	F8	F8	F8	A	C	C	C	C	LP	U	LP	LP	C	C	C	C	A	A	A	U				
Event 5	C	C	C	C	C	C	C	C	F8	LP	A	A	F8	F8	F8	F8	A	F8	F8	F8	U	U	U	C
Event 6	U	SL	C	C	U	U	U	LP	A	LP	A	A	-	-	-	-	A	A	A	A	U	LP	U	LP
Event 7	F8	F8	C	F8	C	C	C	-	A	U	A	C	C	C	C	C	C	U	LP	LP	U	A	U	C
Event 8	F8	C	F8	F8	C	F8	C	C	-	C	C	F8	C	C	A	SL	A	A	A	C	U		A	LP
Event 9	F8	A	F8	F8	-	C	C	A	C	C	A	C	C	C	C	C	C	A	LP	A	U	U	A	A
Event 10	F8	F8	U	A	C	C	C	LP	C	C	C	C	C	C	A	C	F8	LP	C	C	U	U	F8	A
Event 11	U	F8	U	U	C	C	-	U	C	F8	U	U	C	-	U	U	F8	F8	U	U	U	U	U	U
Event 12	C	F8	U	C	C	C	F8	LP	C	F8	U	F8	C	C	C	C	U	U	F8	U	U	U	-	F8

Legend

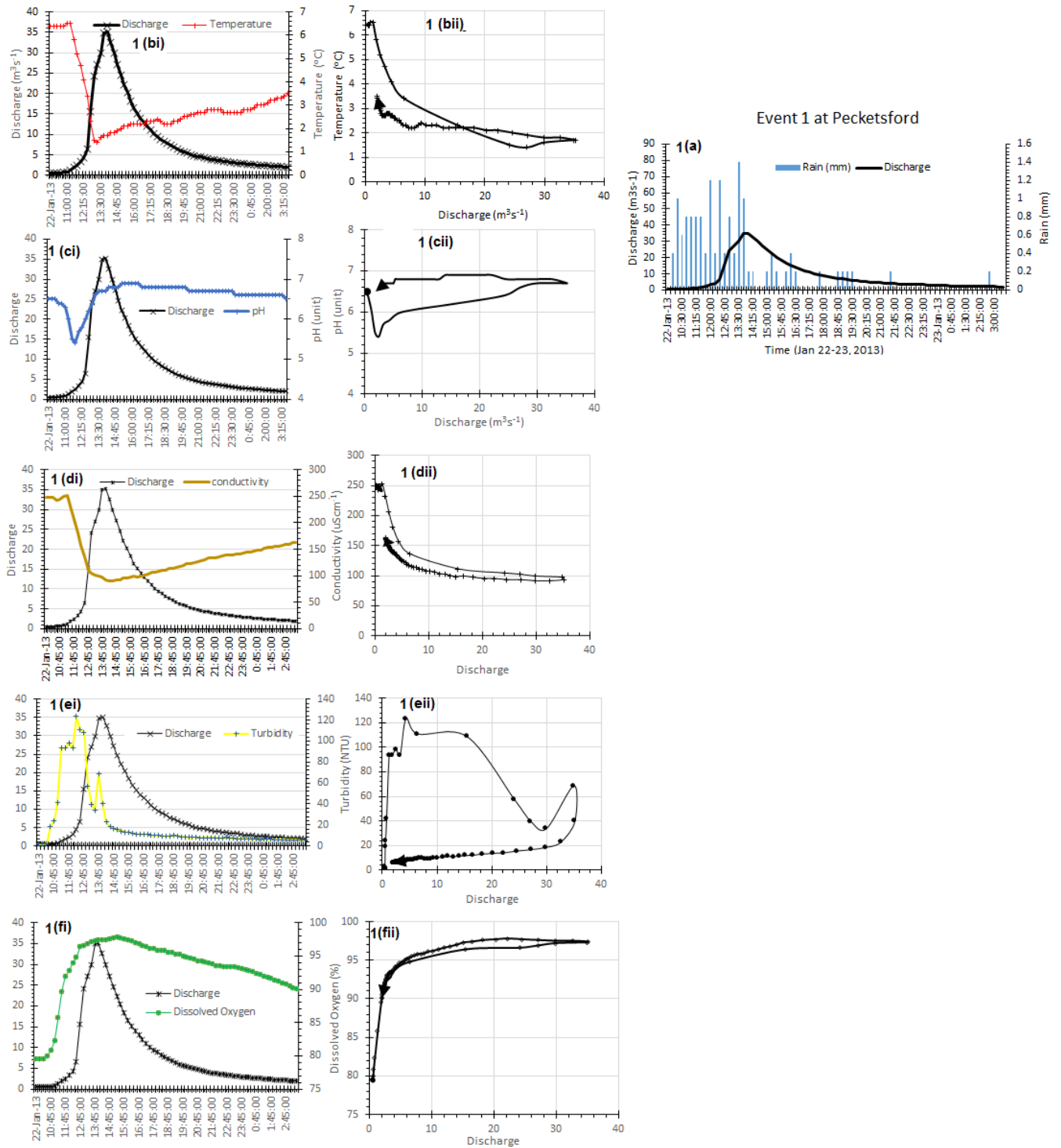
c-q shape and Interpretation

- F8: Figure of 8
- C: Clockwise
- A: Anticlockwise
- U: Unclear, irregular or complex loop
- LP: Line with loop
- SL: Single line

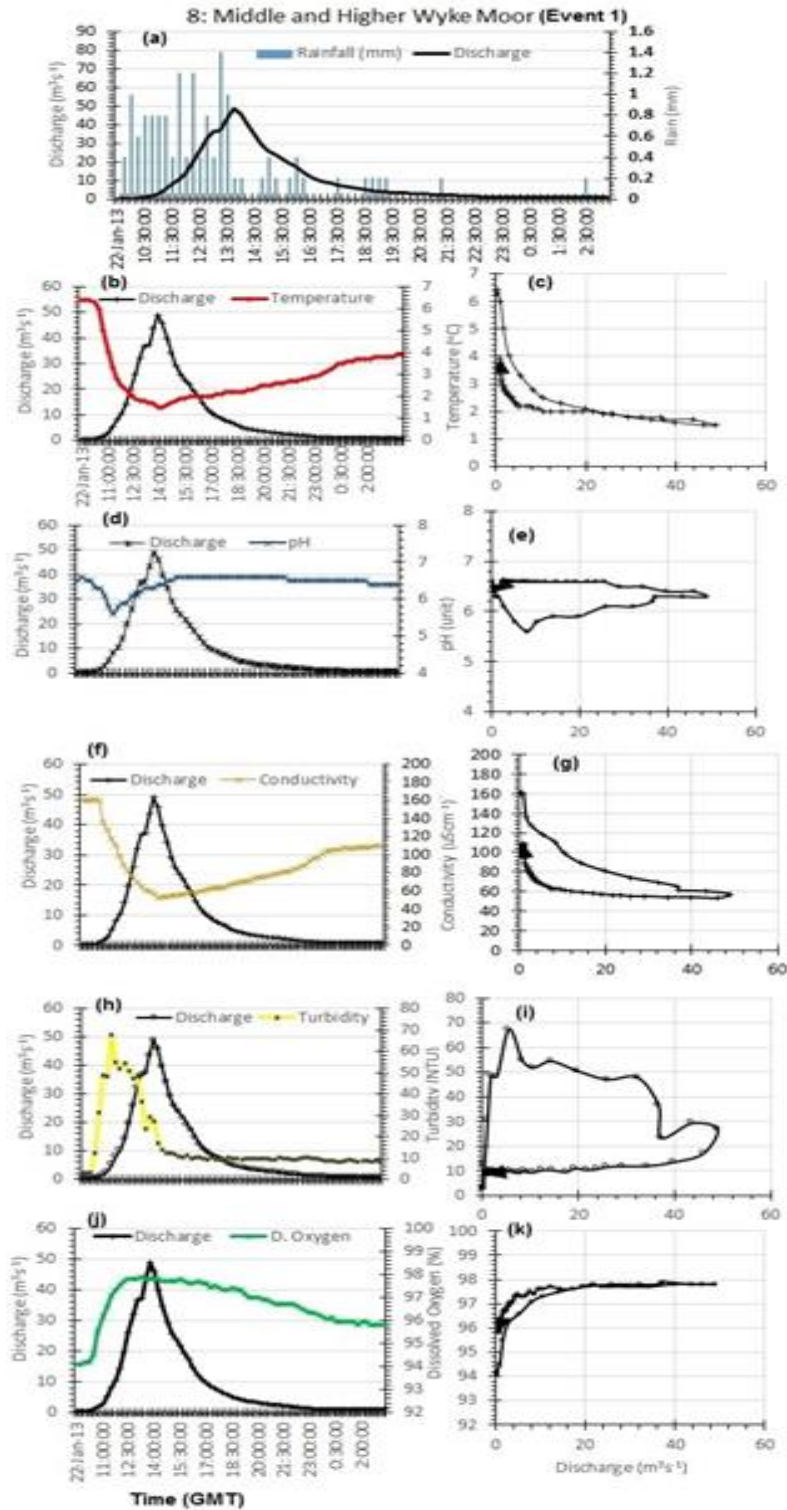
Field Number and Name

- Field 1: Pecketsford
- Field 4: Burrows
- Field 8: Middle and Higher Wyke Moor
- Field 15: Longlands East

Appendix 4.7. Hydrographs, chemographs and hysteresis plots investigated in the thesis.

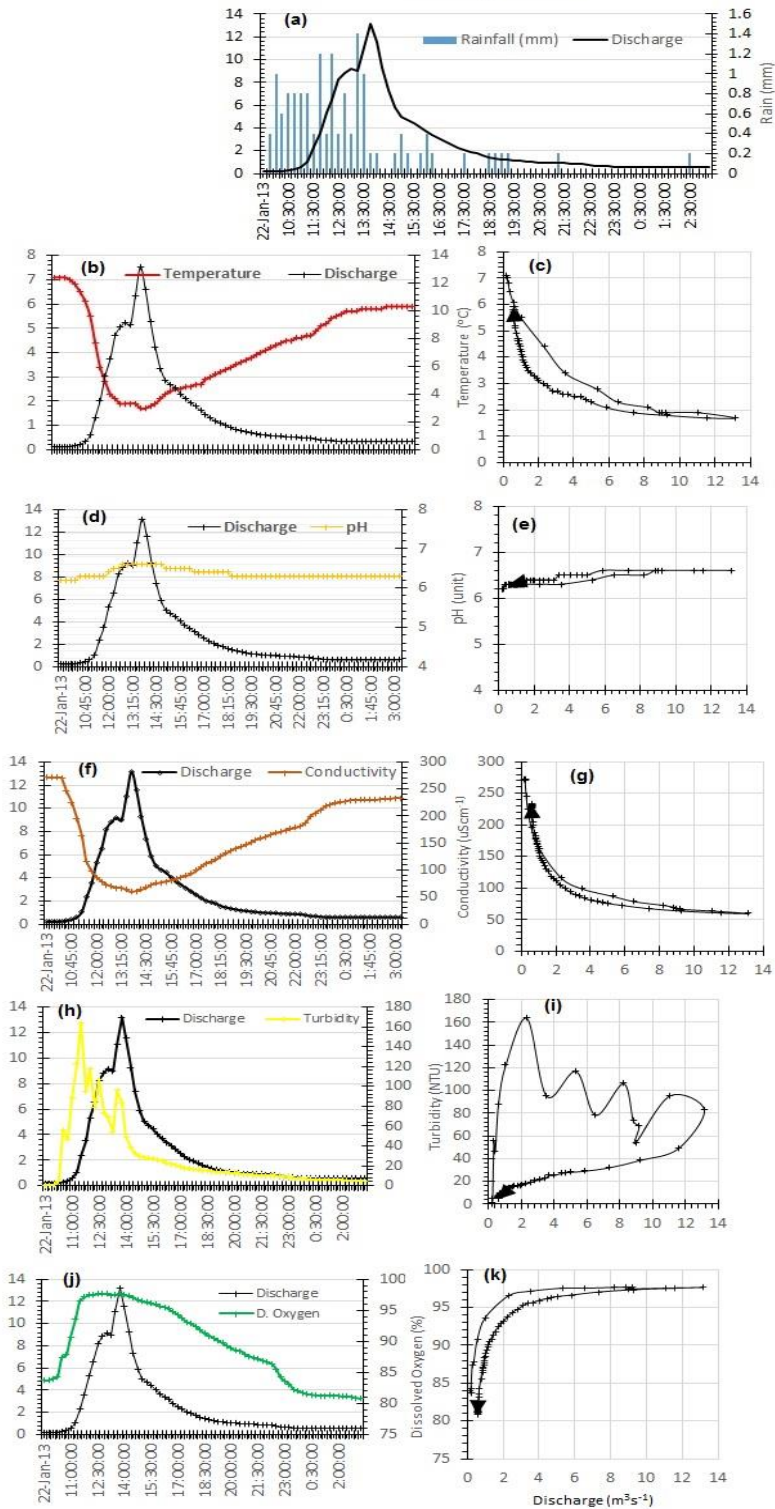


EVENT 1: PECKETSFORD.

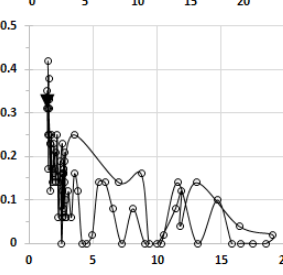
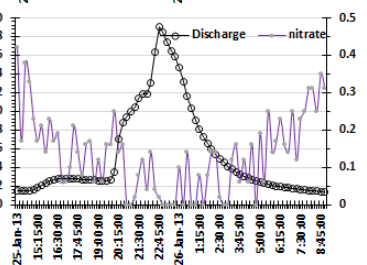
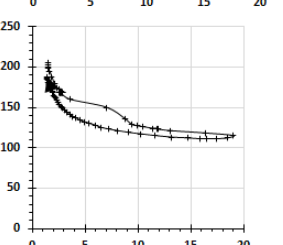
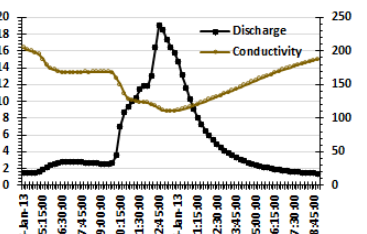
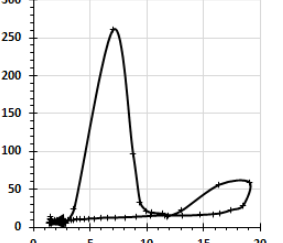
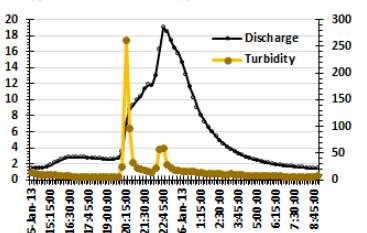
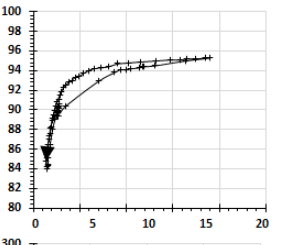
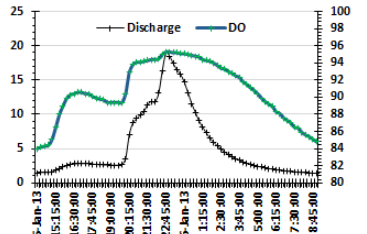
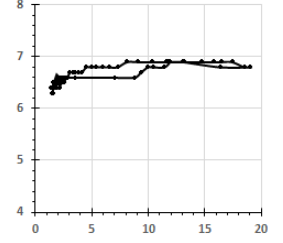
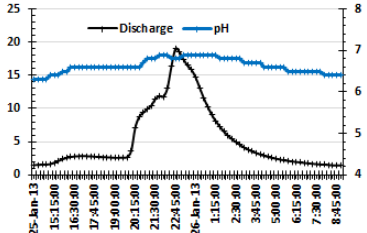
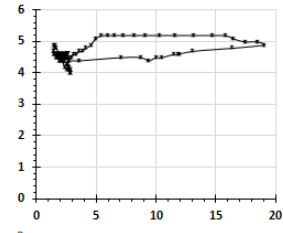
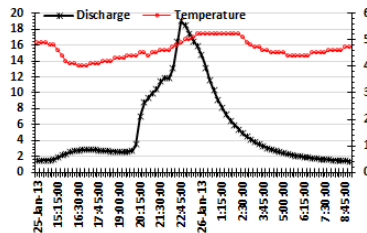
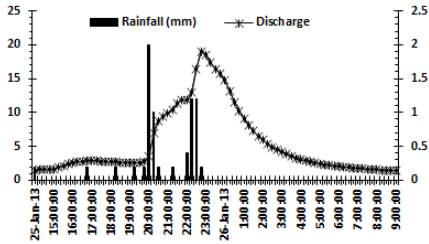


EVENT 1: MIDDLE AND HIGHER WYKE MOOR.

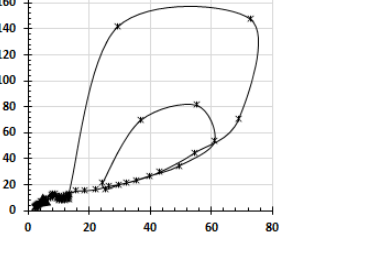
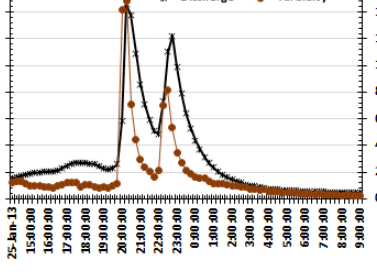
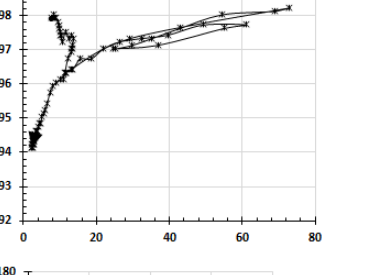
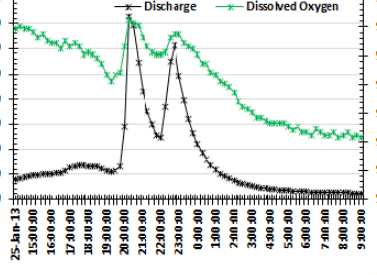
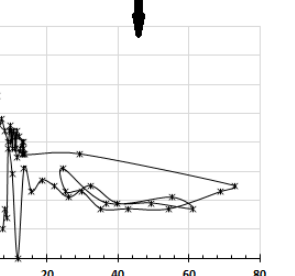
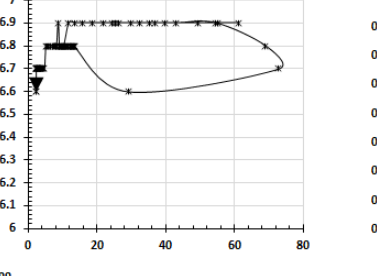
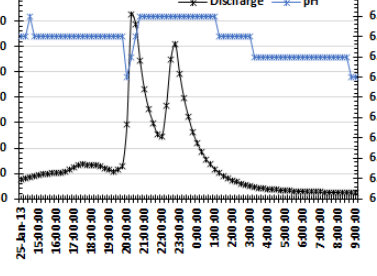
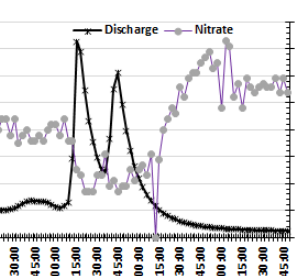
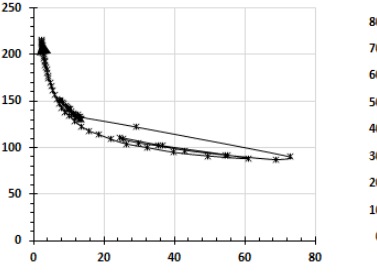
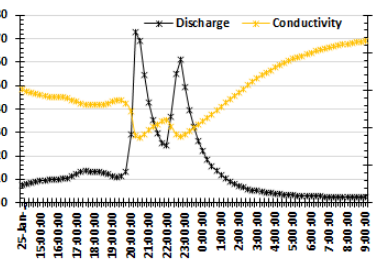
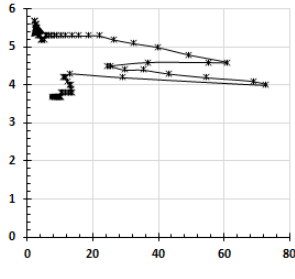
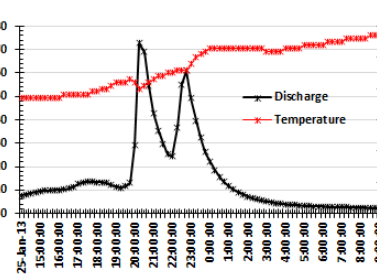
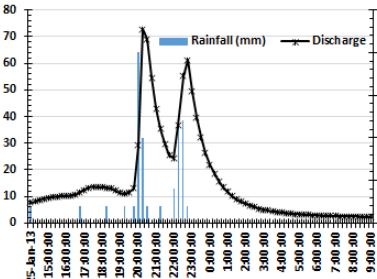
15: Longlands East



EVENT 1: LONGLANDS EAST.

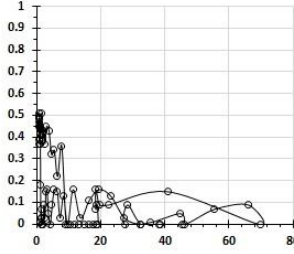
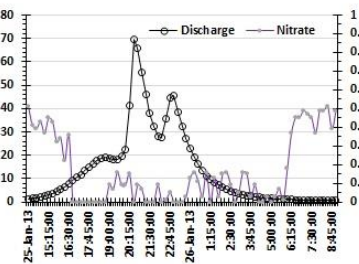
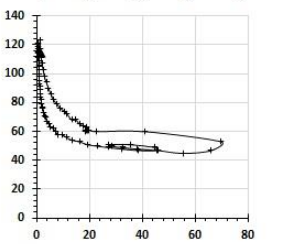
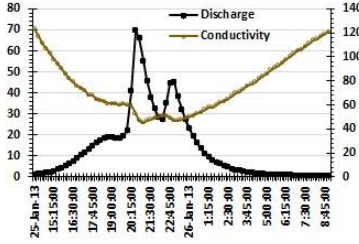
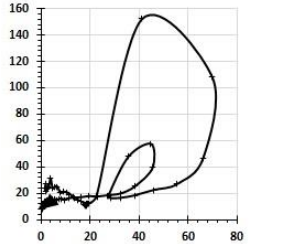
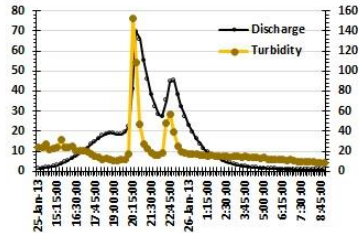
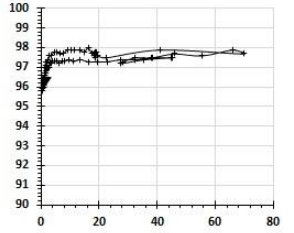
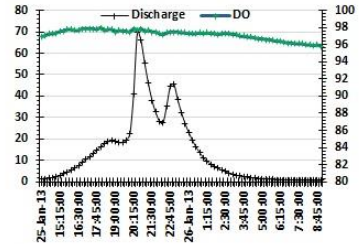
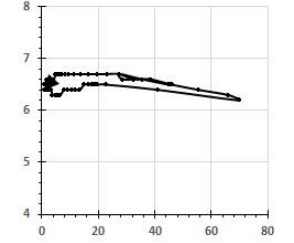
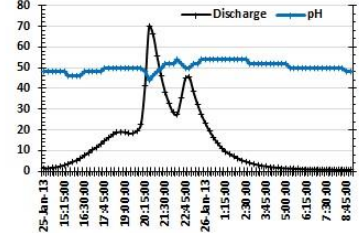
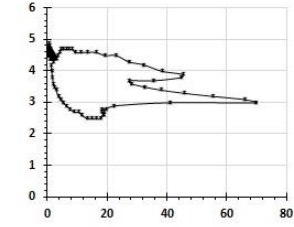
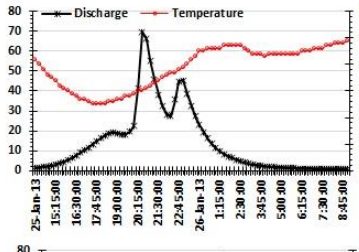
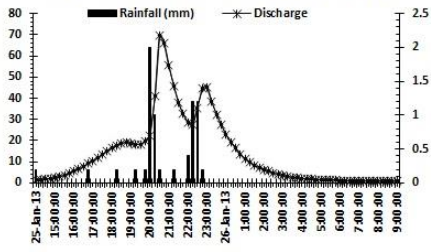


EVENT 2: PECKETSFORD.



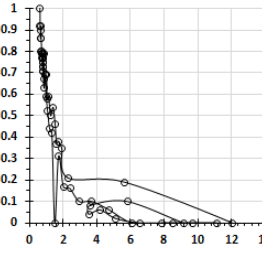
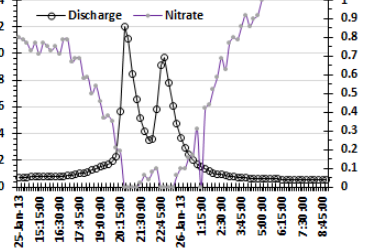
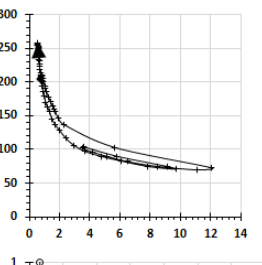
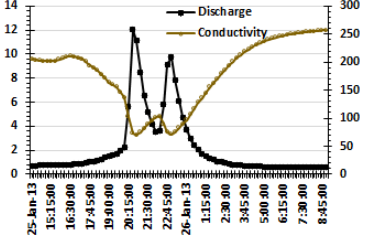
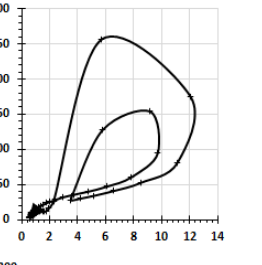
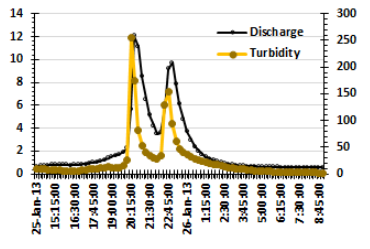
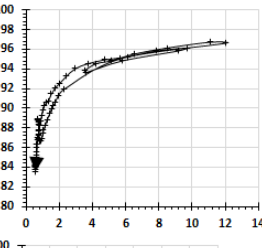
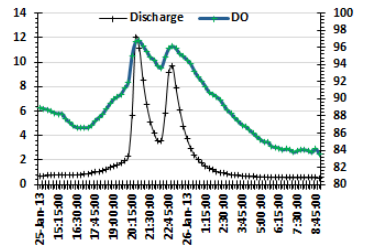
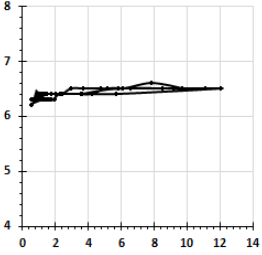
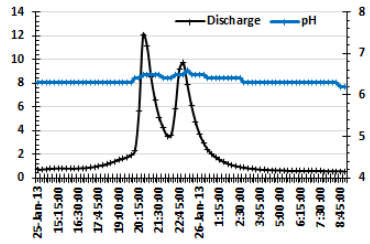
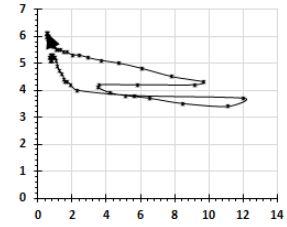
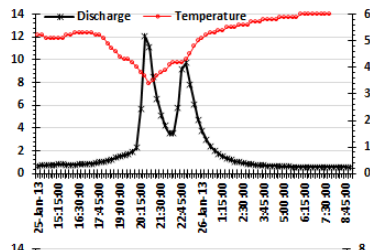
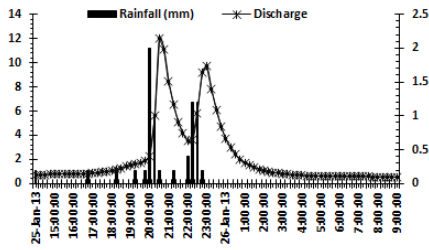
EVENT 2: BURROWS.

8: Middle and Higher Wyke Moor (Event 2)



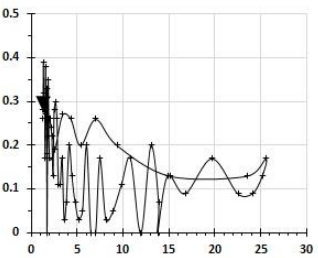
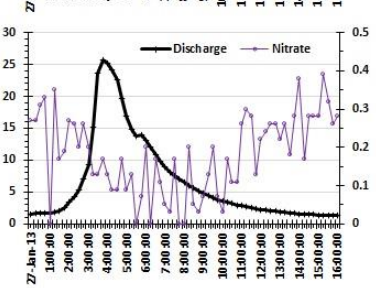
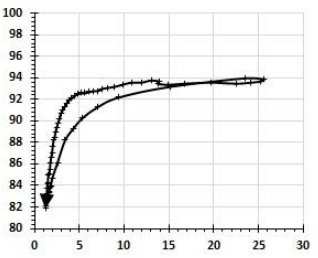
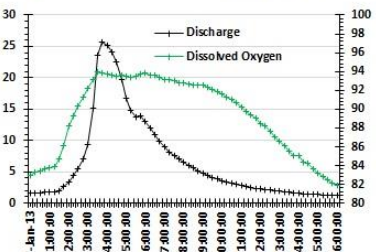
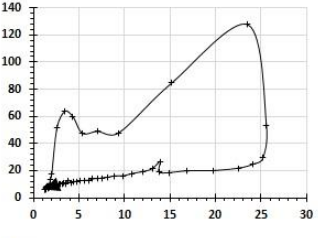
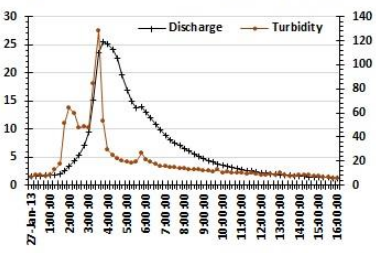
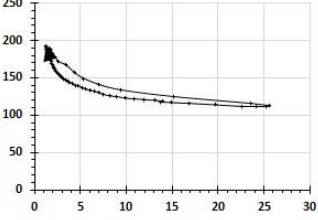
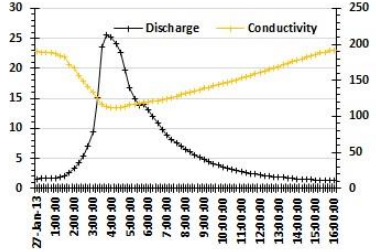
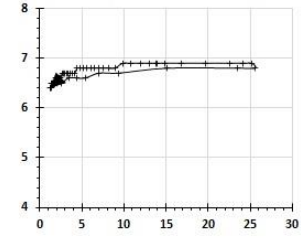
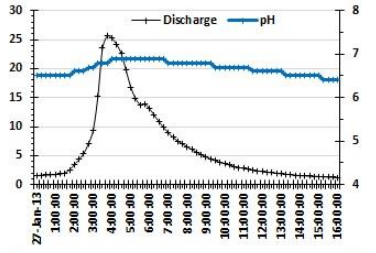
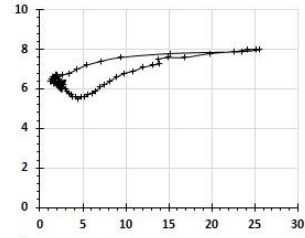
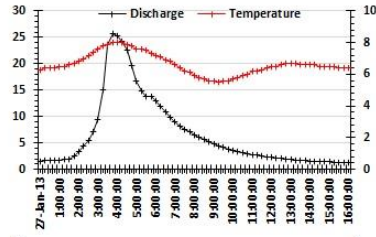
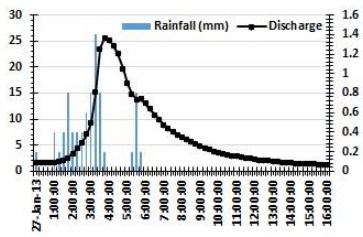
EVENT 2: MIDDLE AND HIGHER WYKE MOOR.

Longlands East (Event 2)

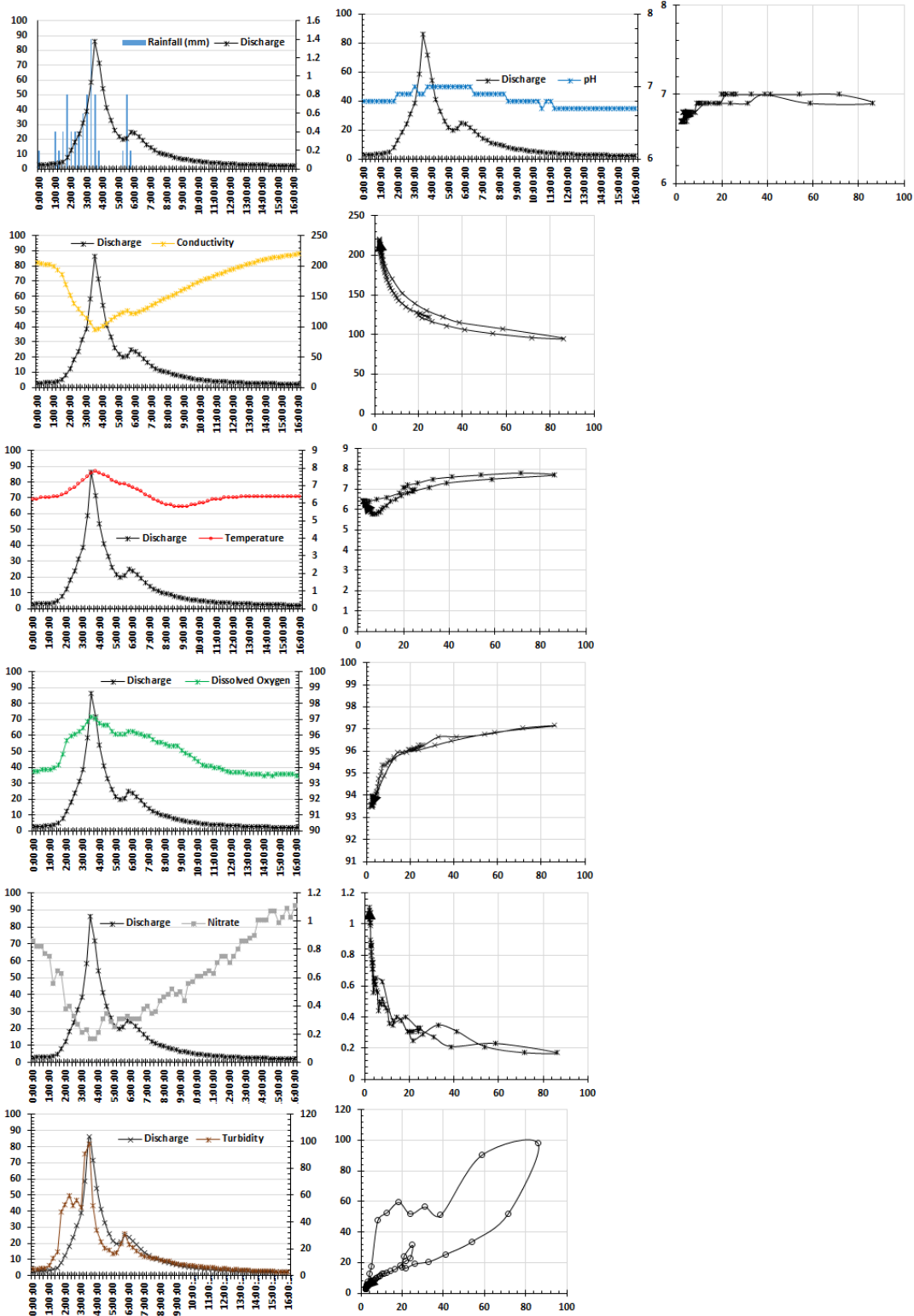


EVENT 2: LONGLANDS EAST.

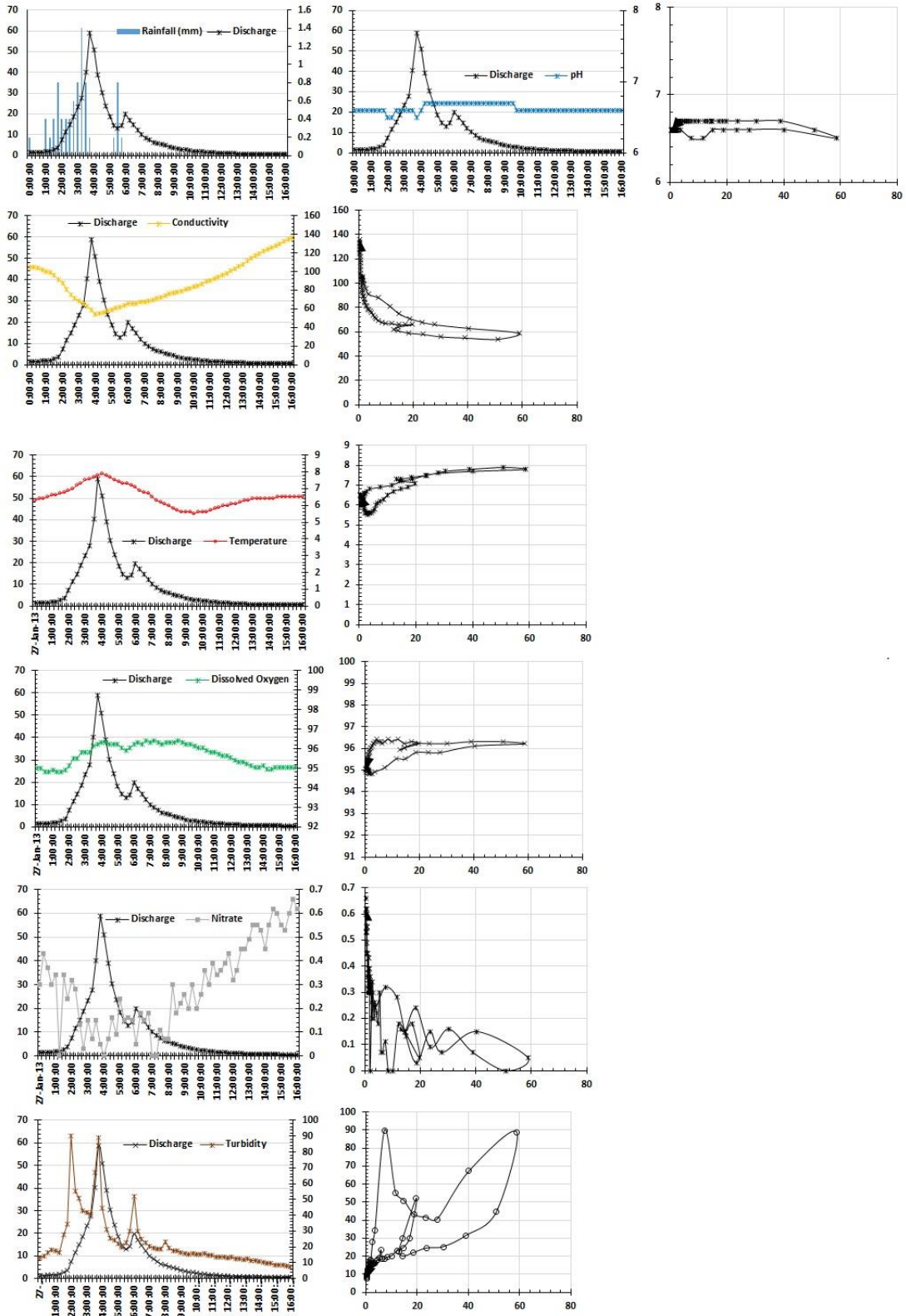
1: Pecketsford (Event 3)



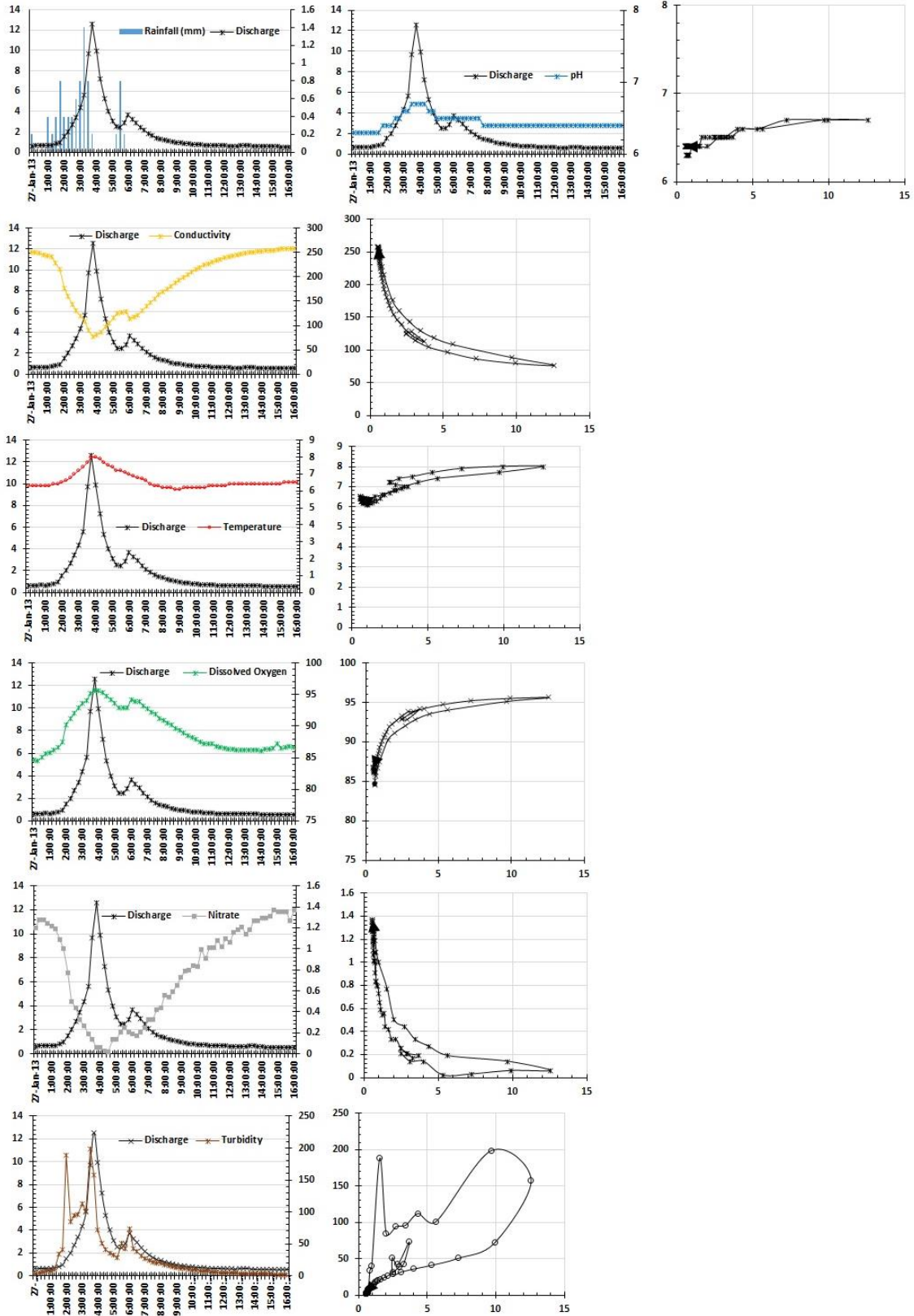
EVENT 3: PECKETSFORD.



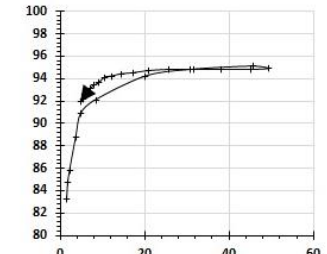
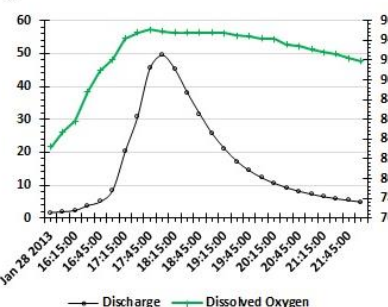
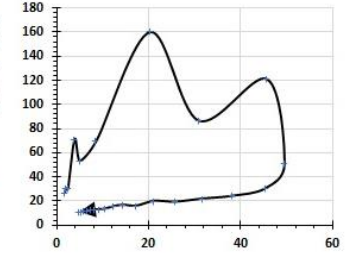
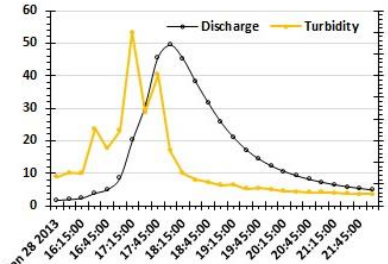
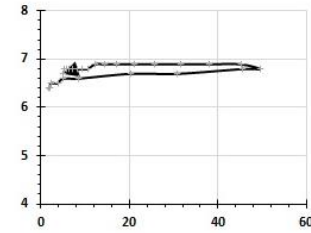
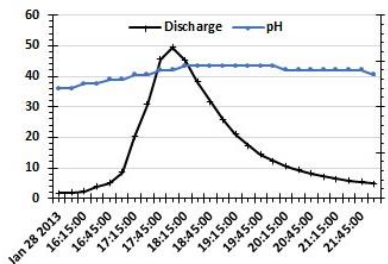
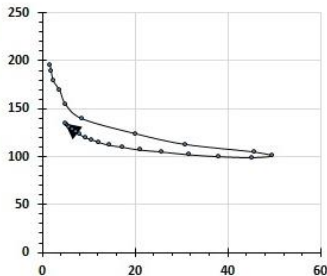
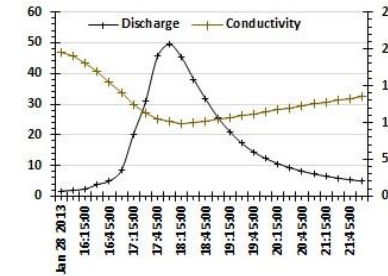
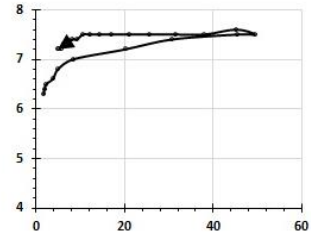
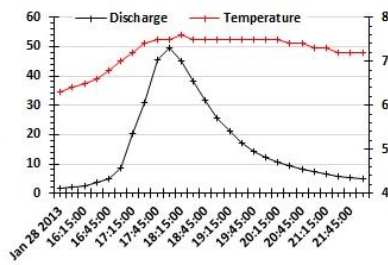
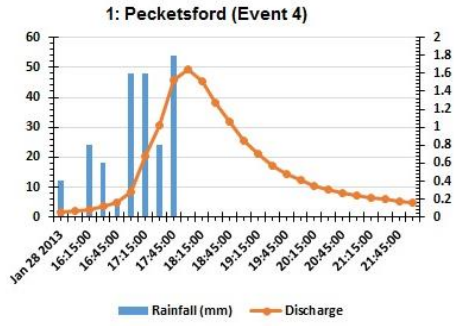
EVENT 3: BURROWS.



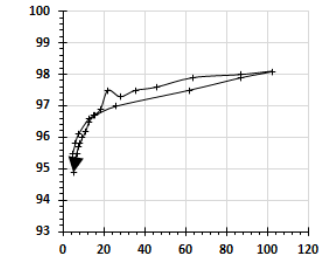
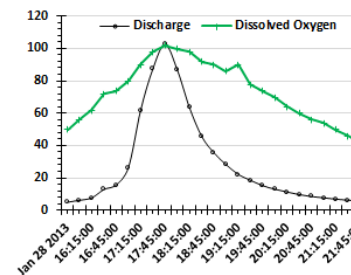
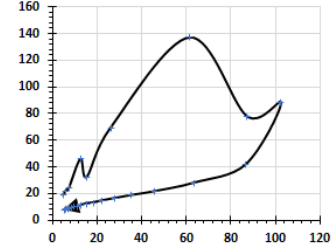
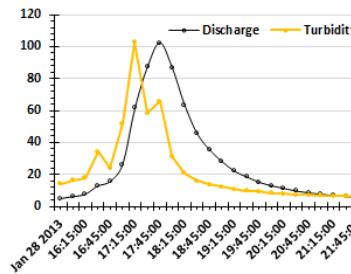
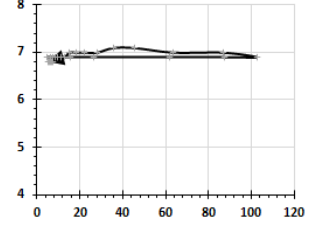
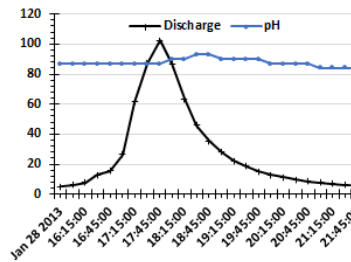
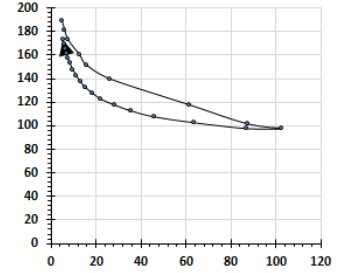
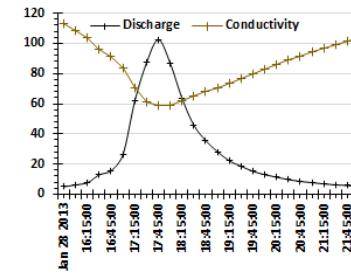
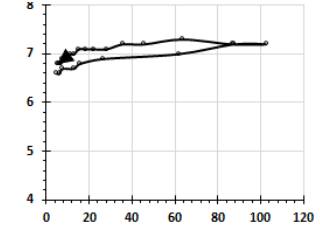
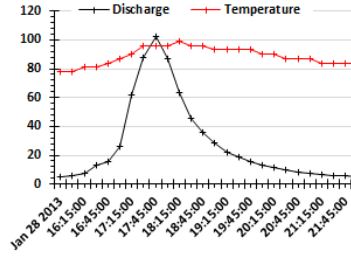
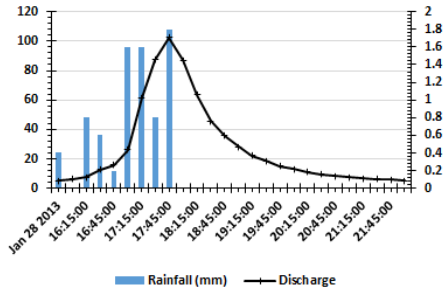
EVENT 3: MIDDLE AND HIGHER WYKE MOOR.



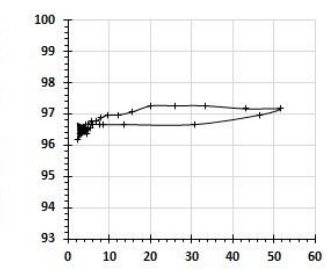
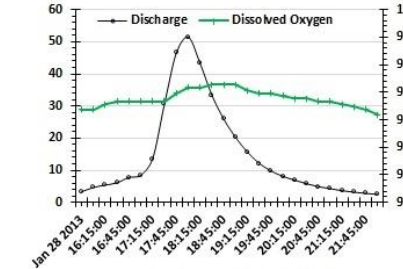
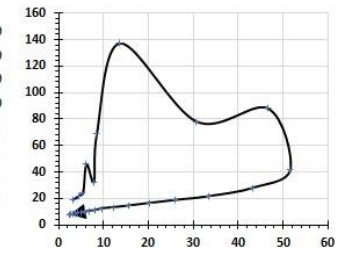
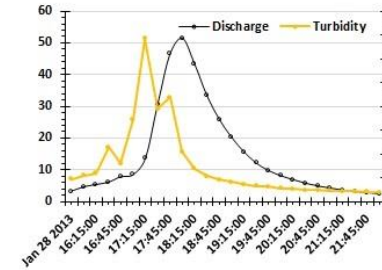
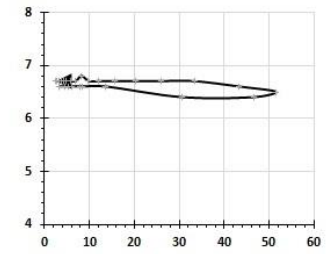
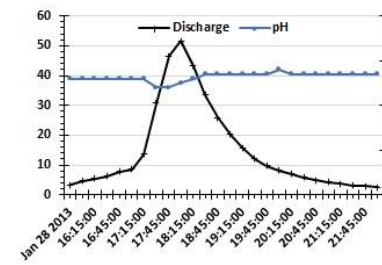
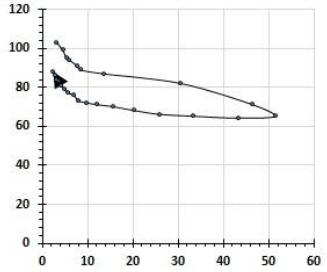
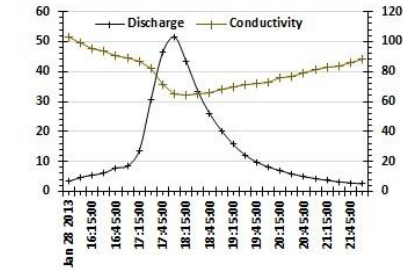
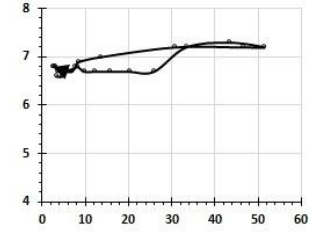
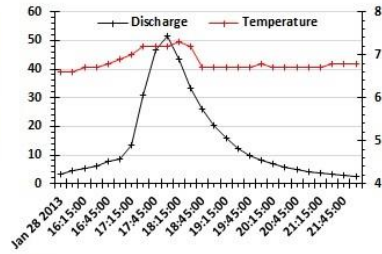
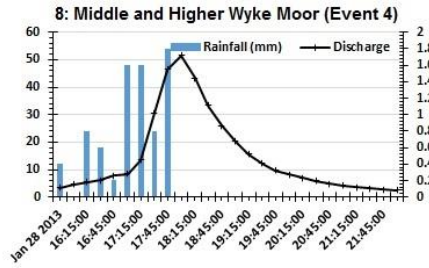
EVENT 3: LONGLANDS EAST.



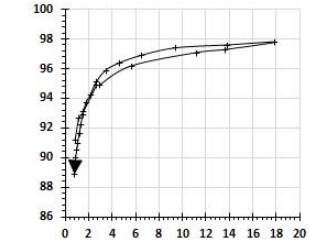
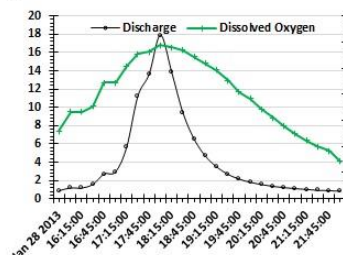
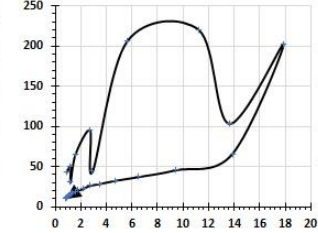
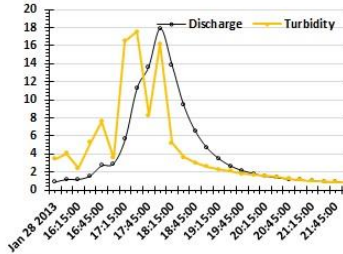
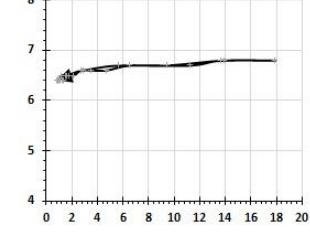
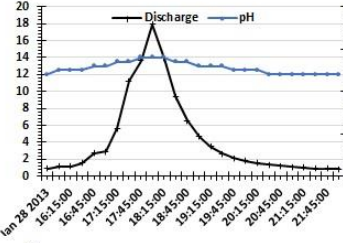
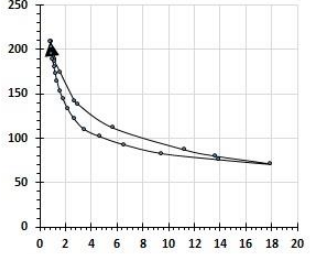
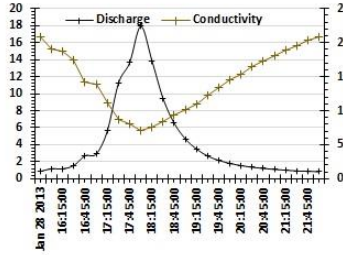
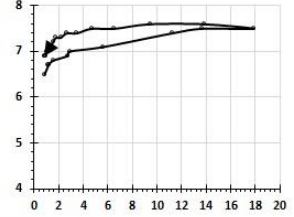
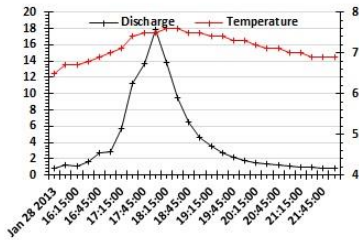
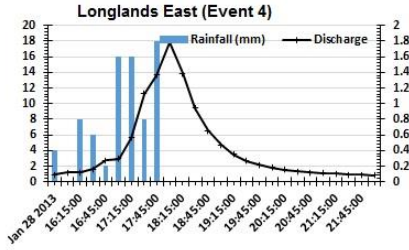
EVENT 4: PECKETSFORD.



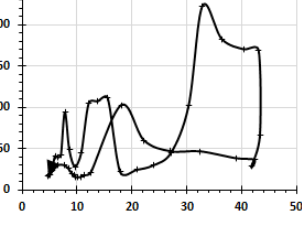
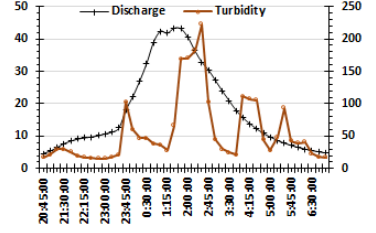
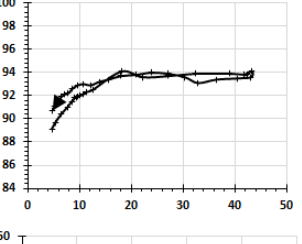
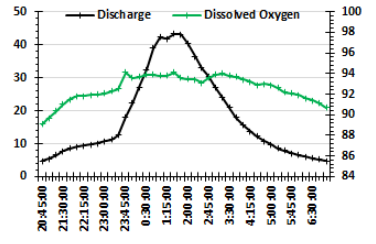
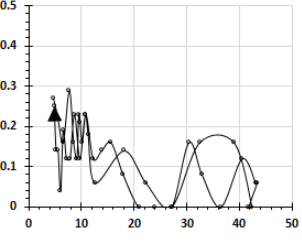
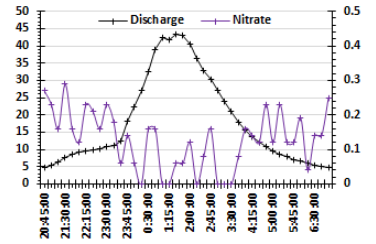
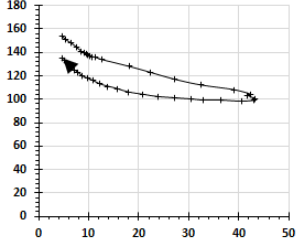
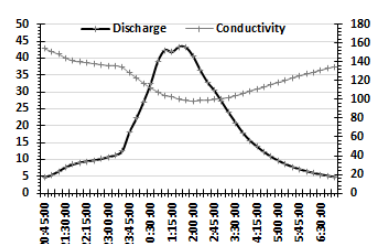
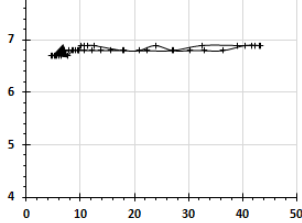
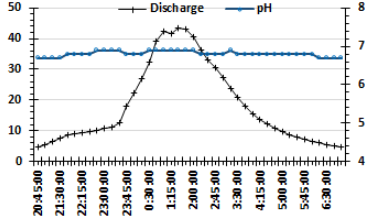
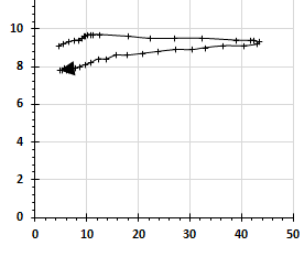
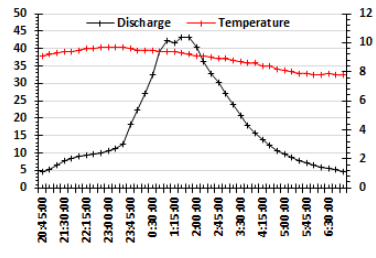
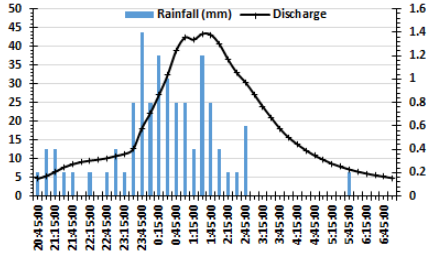
EVENT 4: BURROWS.



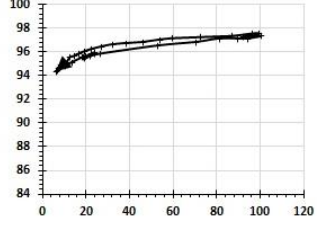
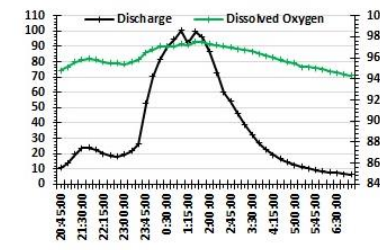
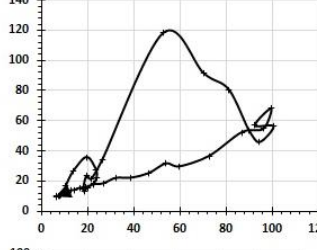
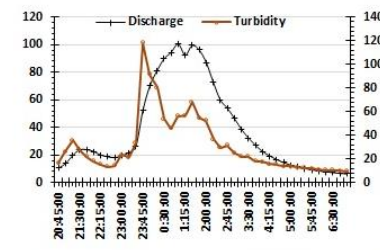
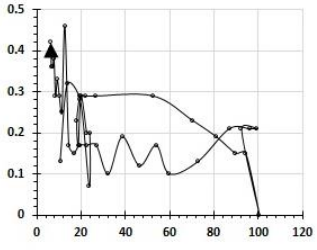
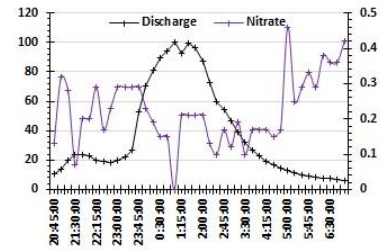
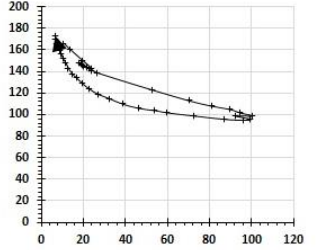
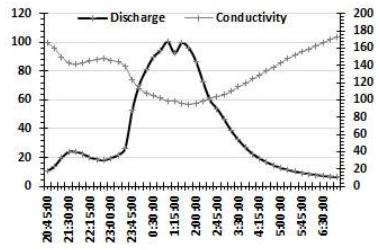
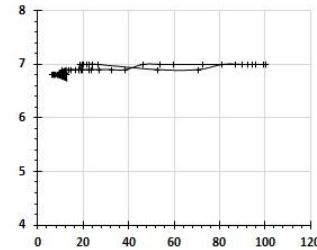
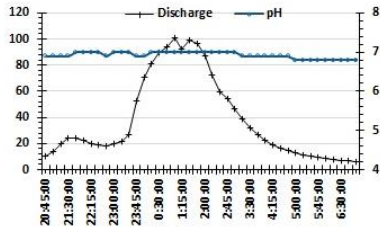
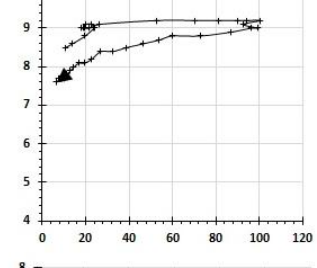
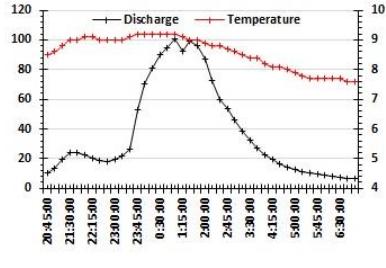
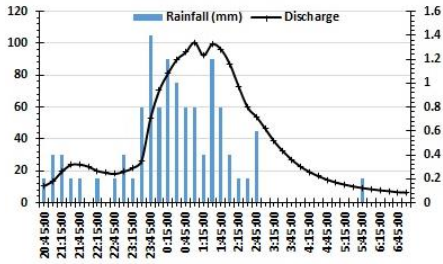
EVENT 4: MIDDLE AND HIGHER WYKE MOOR.



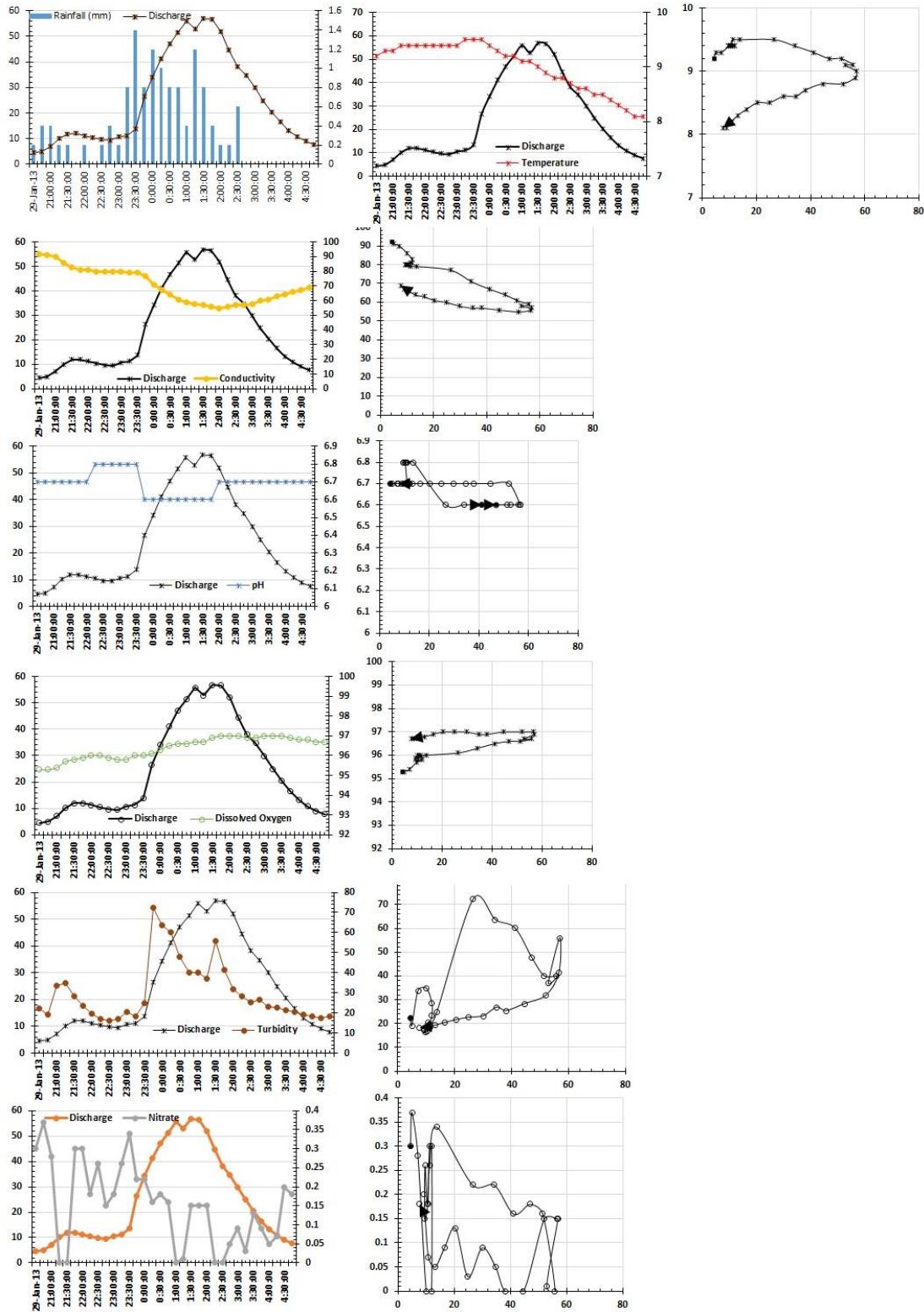
EVENT 4: LONGLANDS EAST.



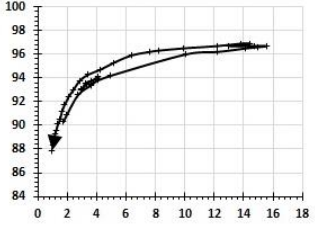
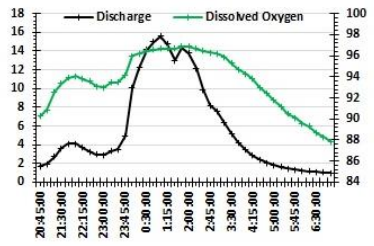
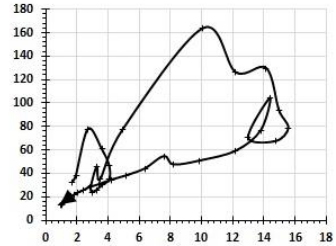
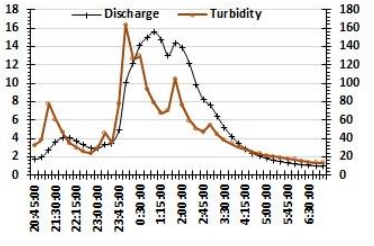
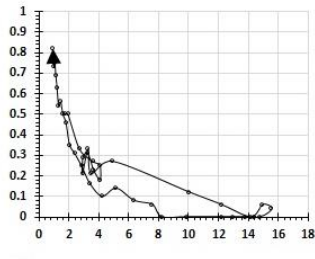
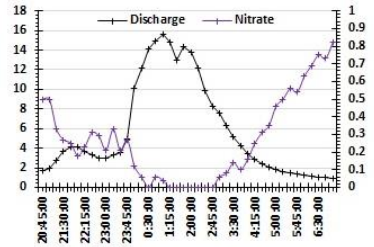
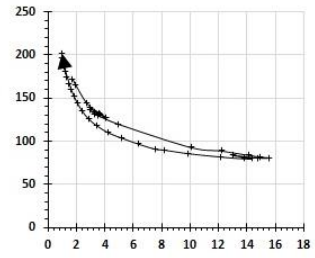
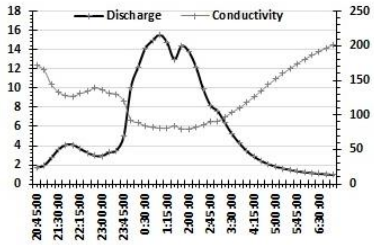
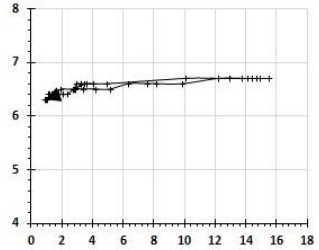
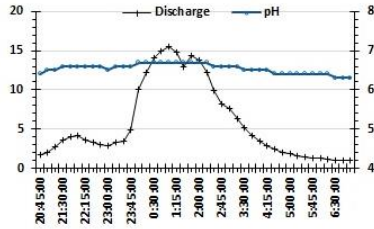
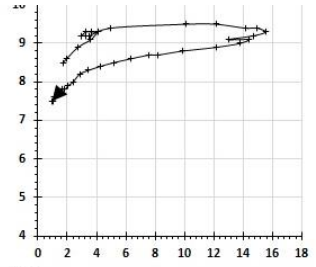
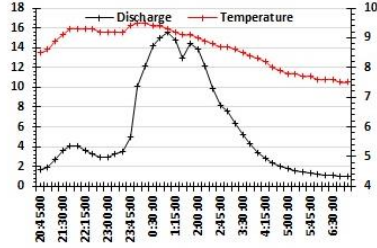
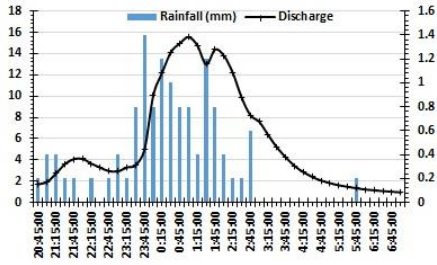
EVENT 5: PECKETSFORD.



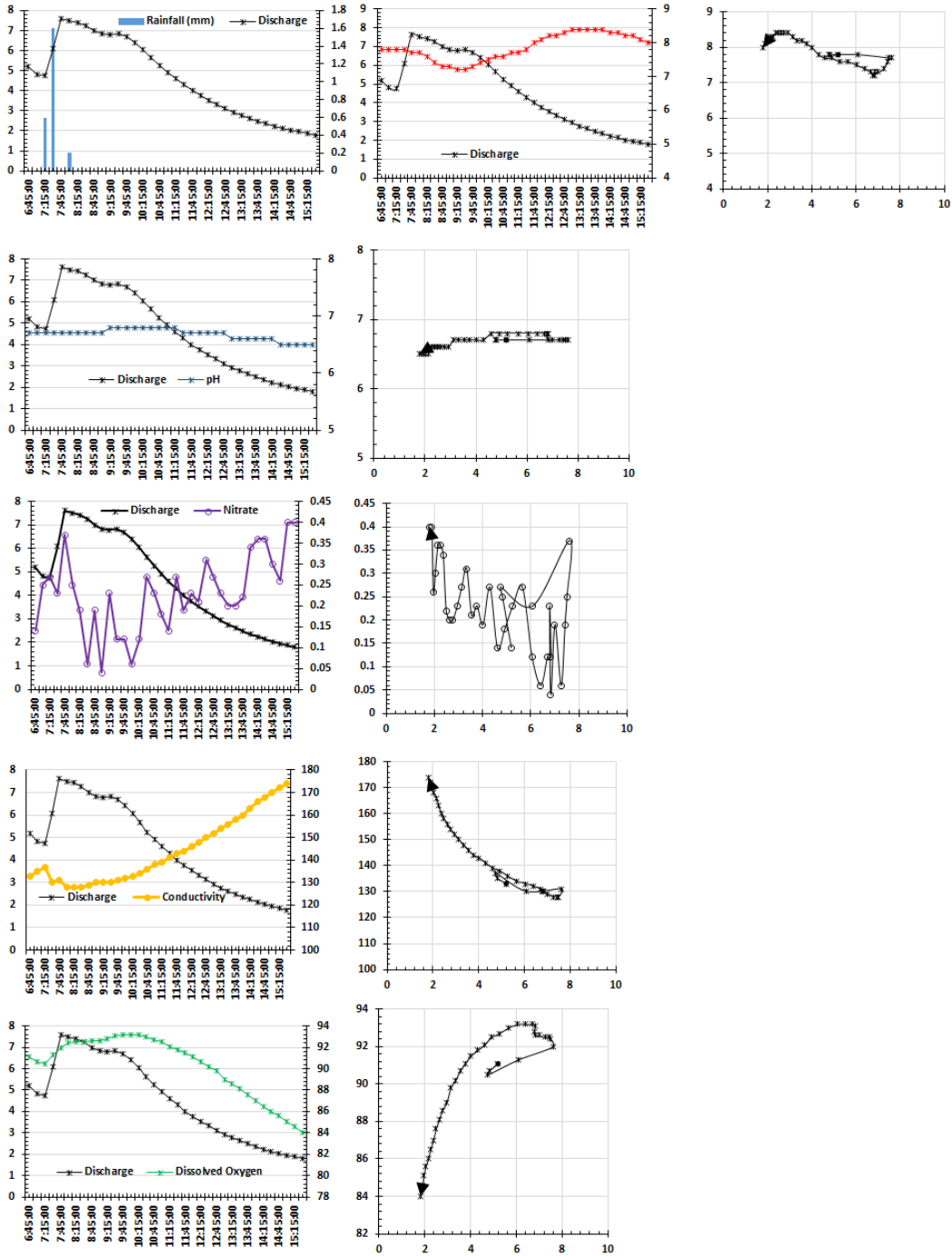
EVENT 5: BURROWS.



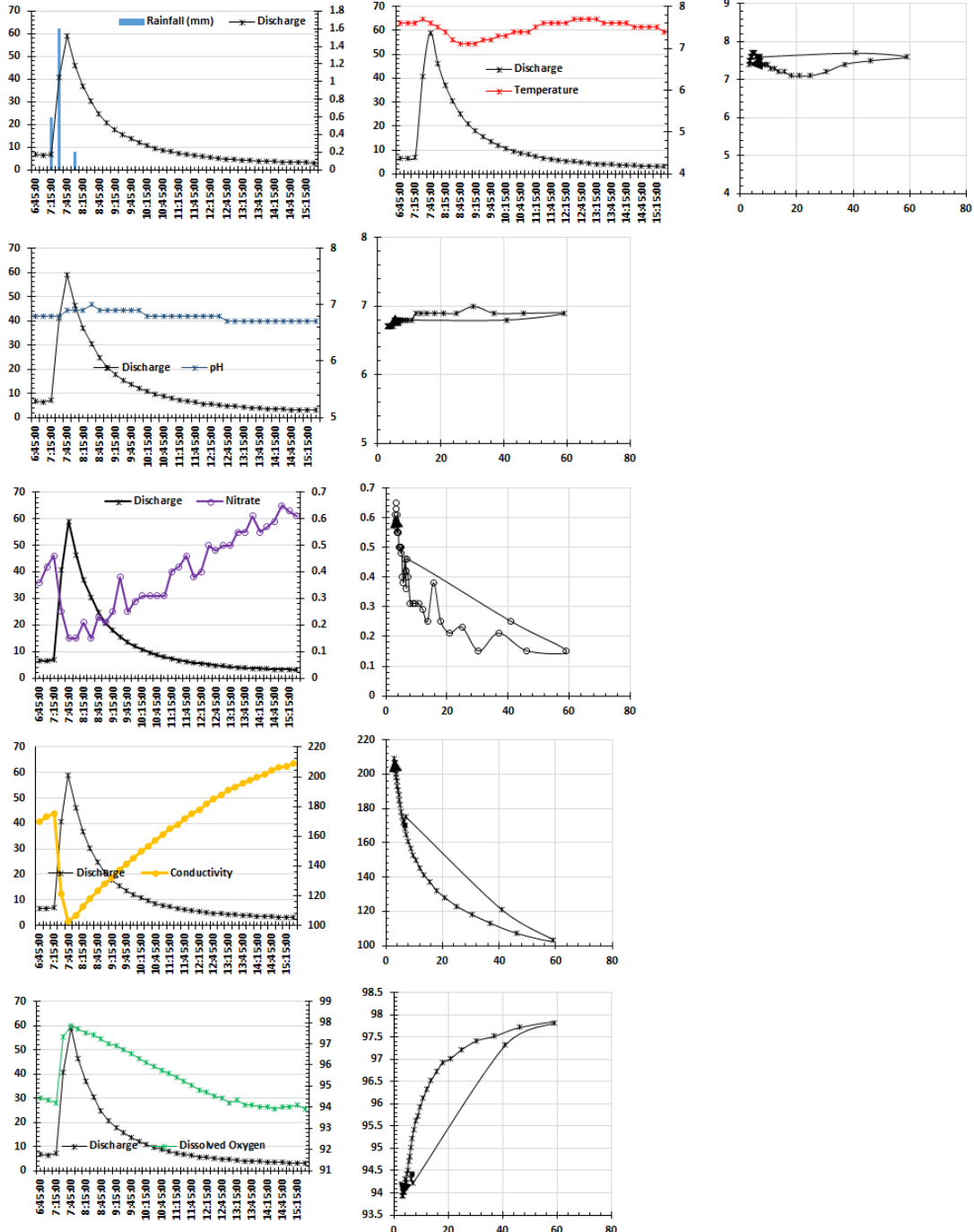
EVENT 5: MIDDLE AND HIGHER WYKE MOOR.



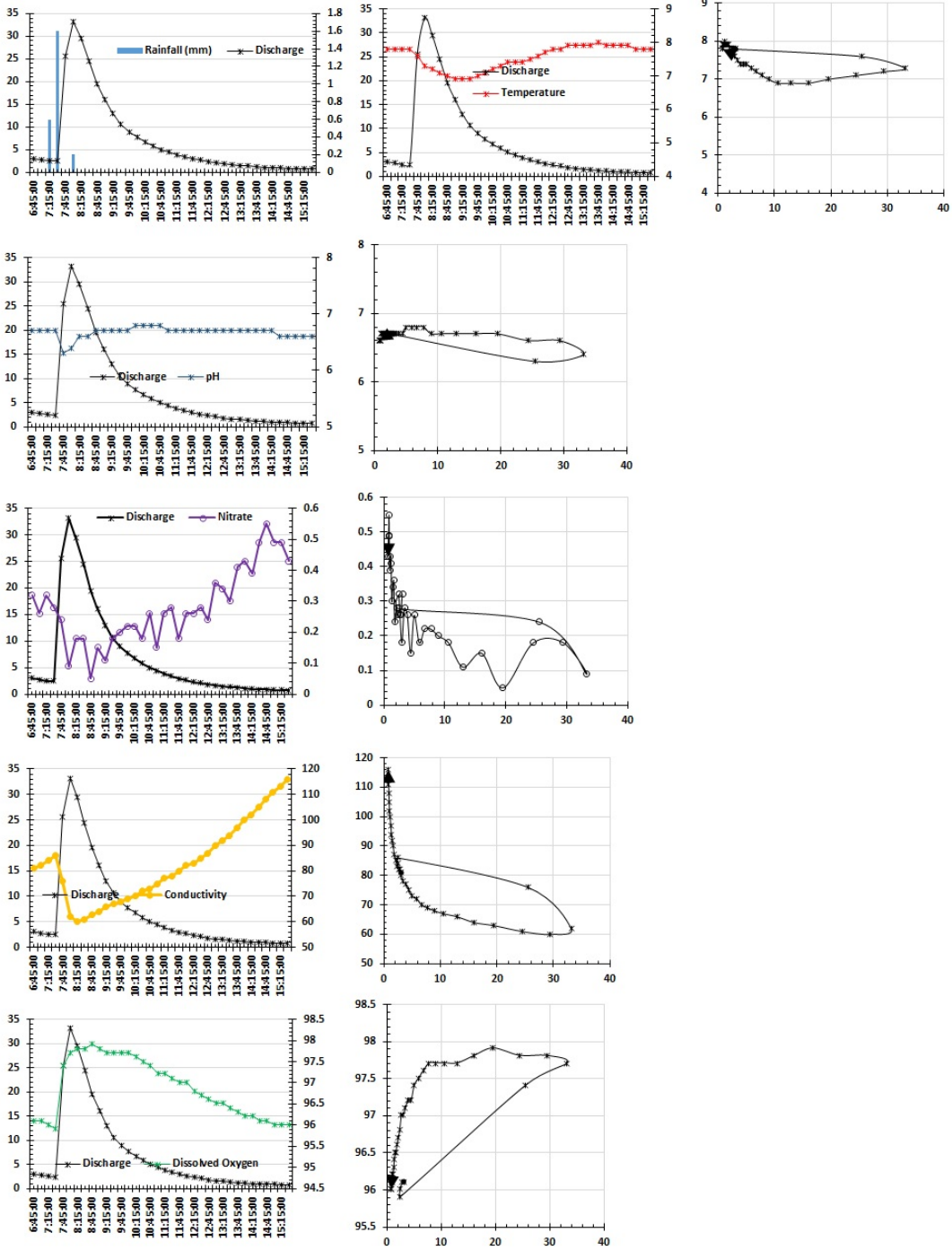
EVENT 5: LONGLANDS EAST.



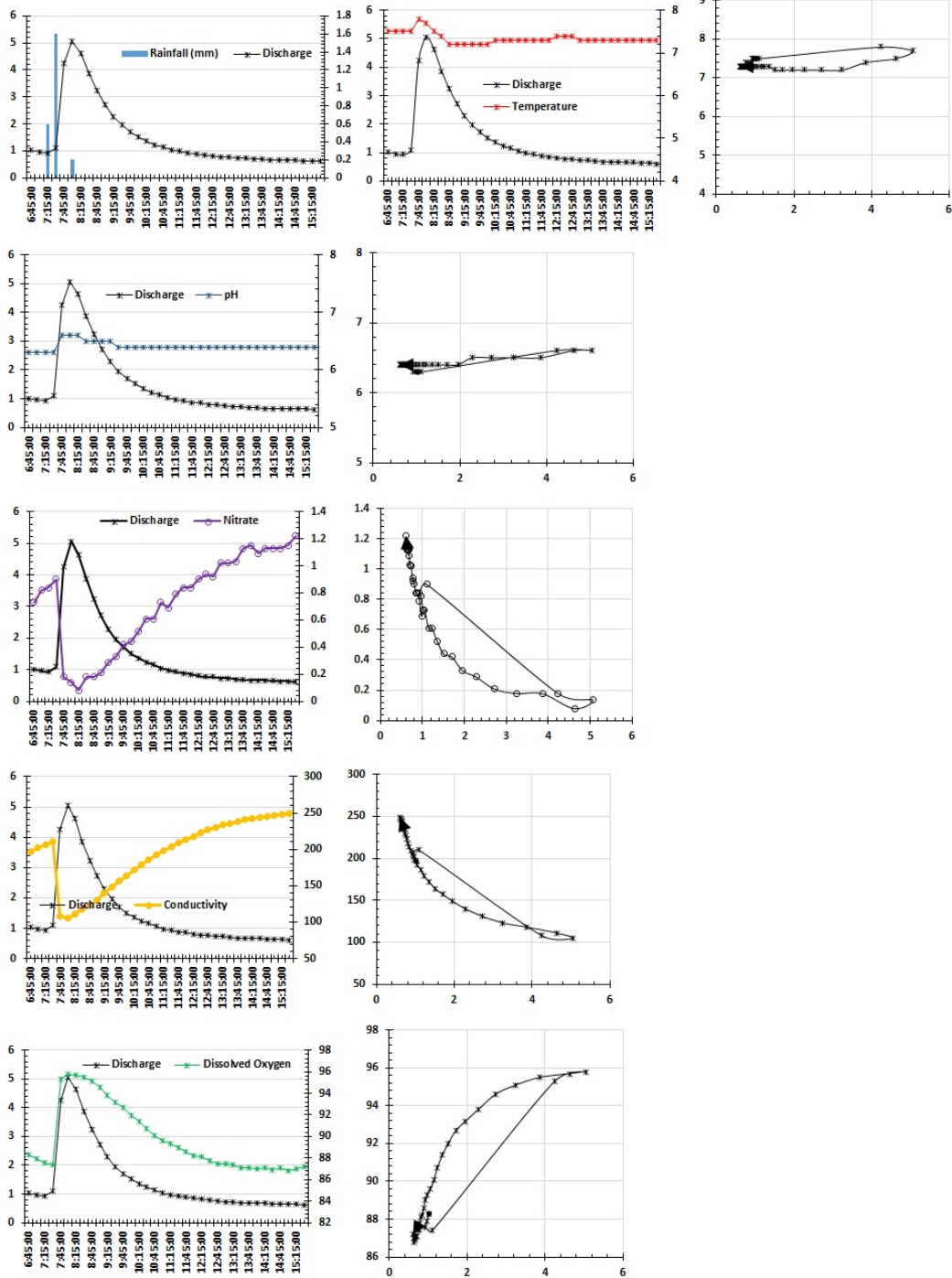
EVENT 6: PECKETSFORD.



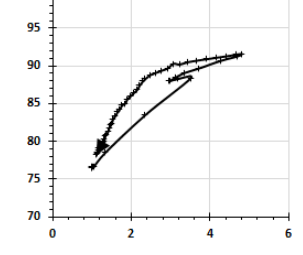
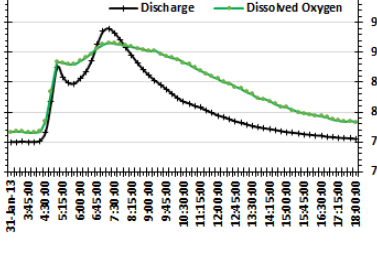
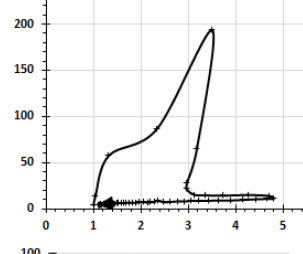
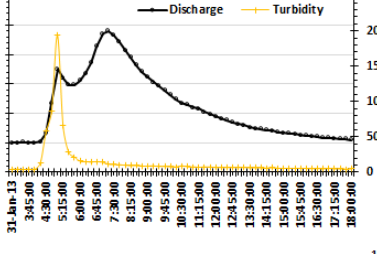
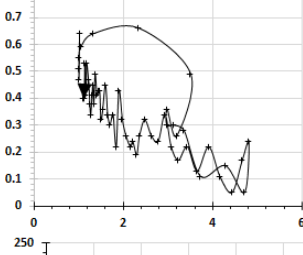
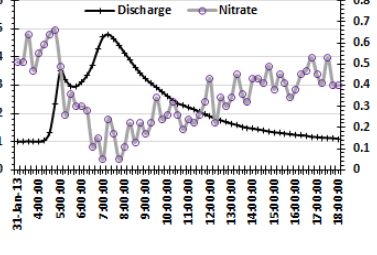
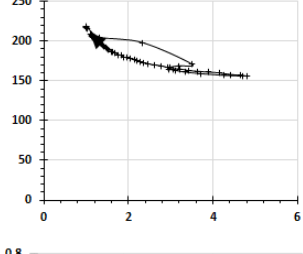
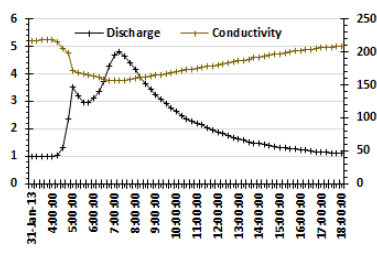
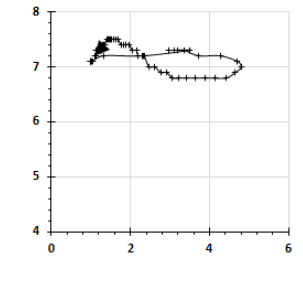
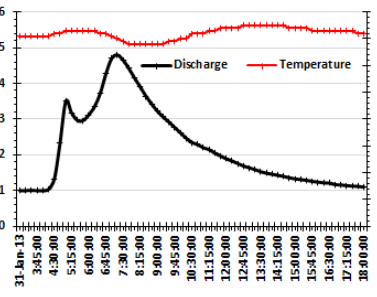
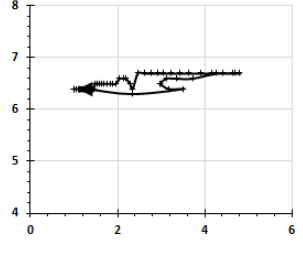
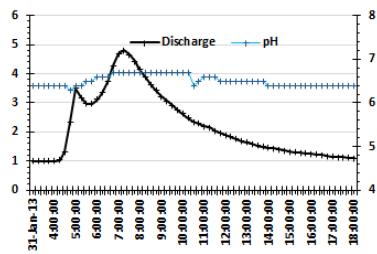
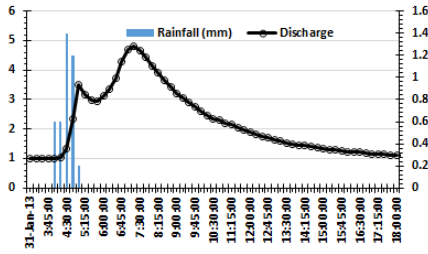
EVENT 6: BURROWS.



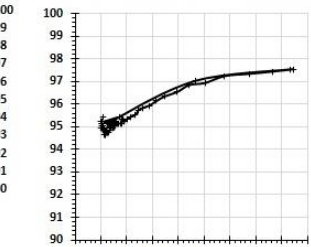
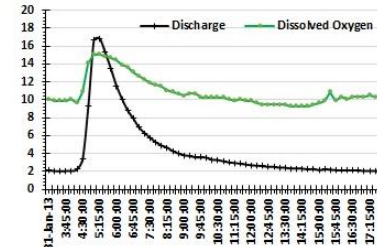
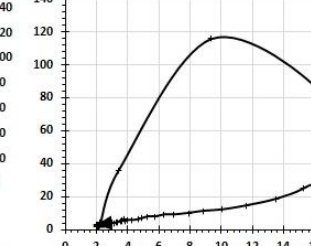
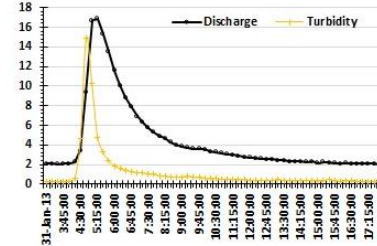
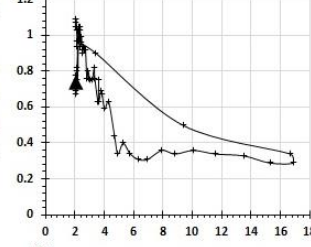
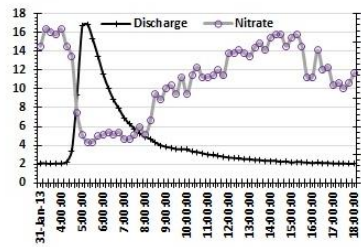
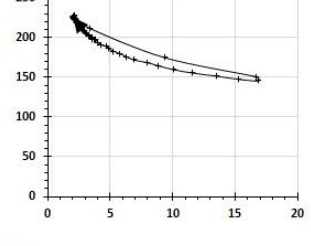
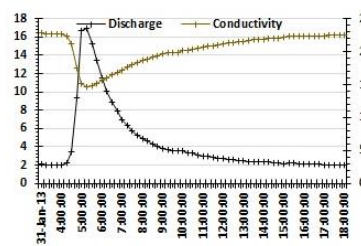
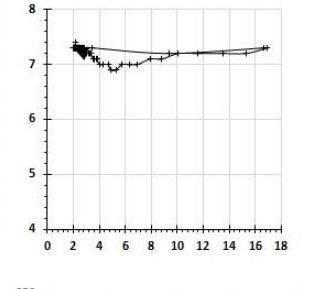
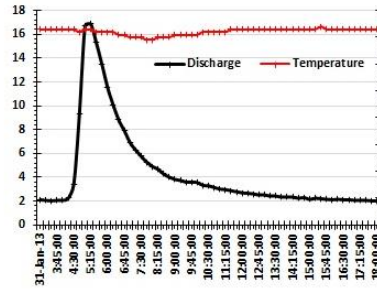
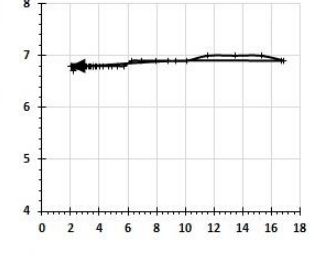
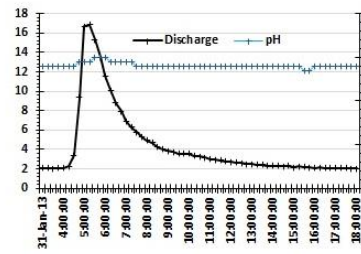
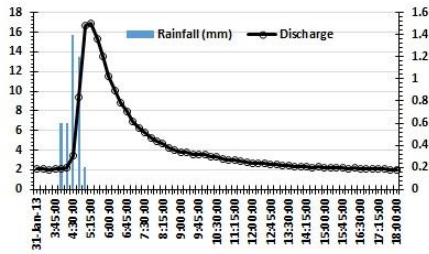
EVENT 6: MIDDLE AND HIGHER NORTH WYKE.



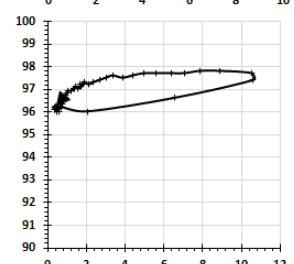
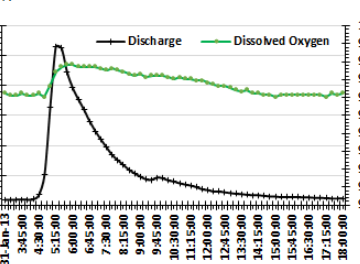
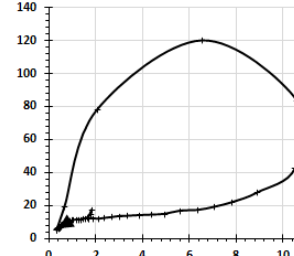
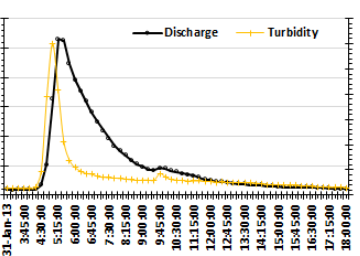
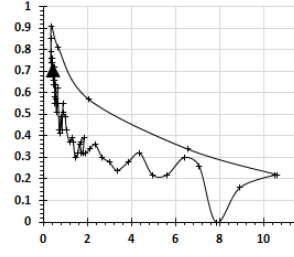
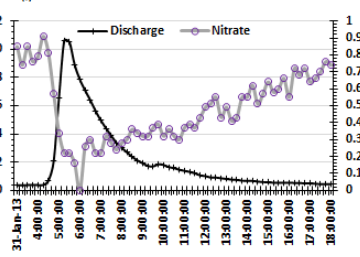
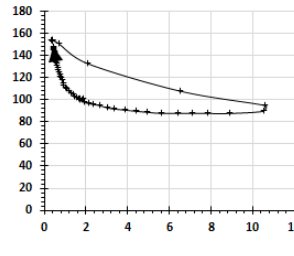
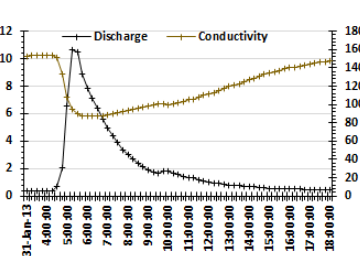
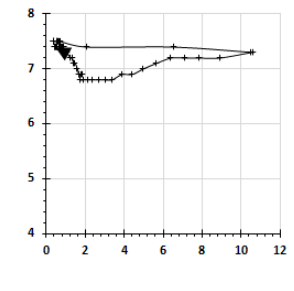
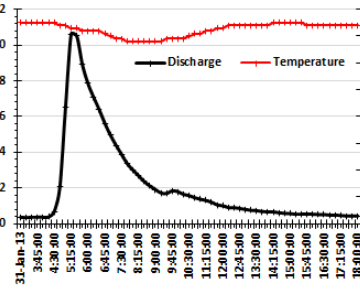
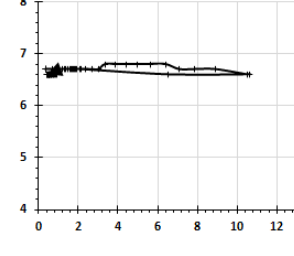
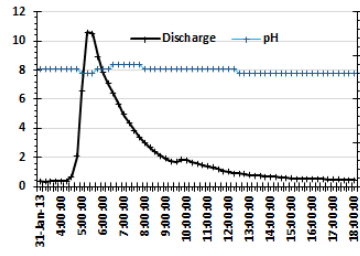
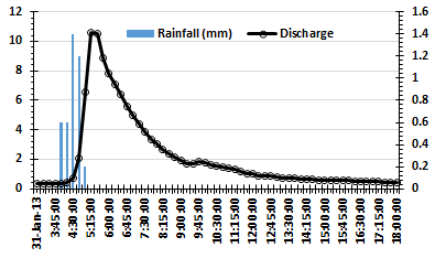
EVENT 6: LONGLANDS EAST.



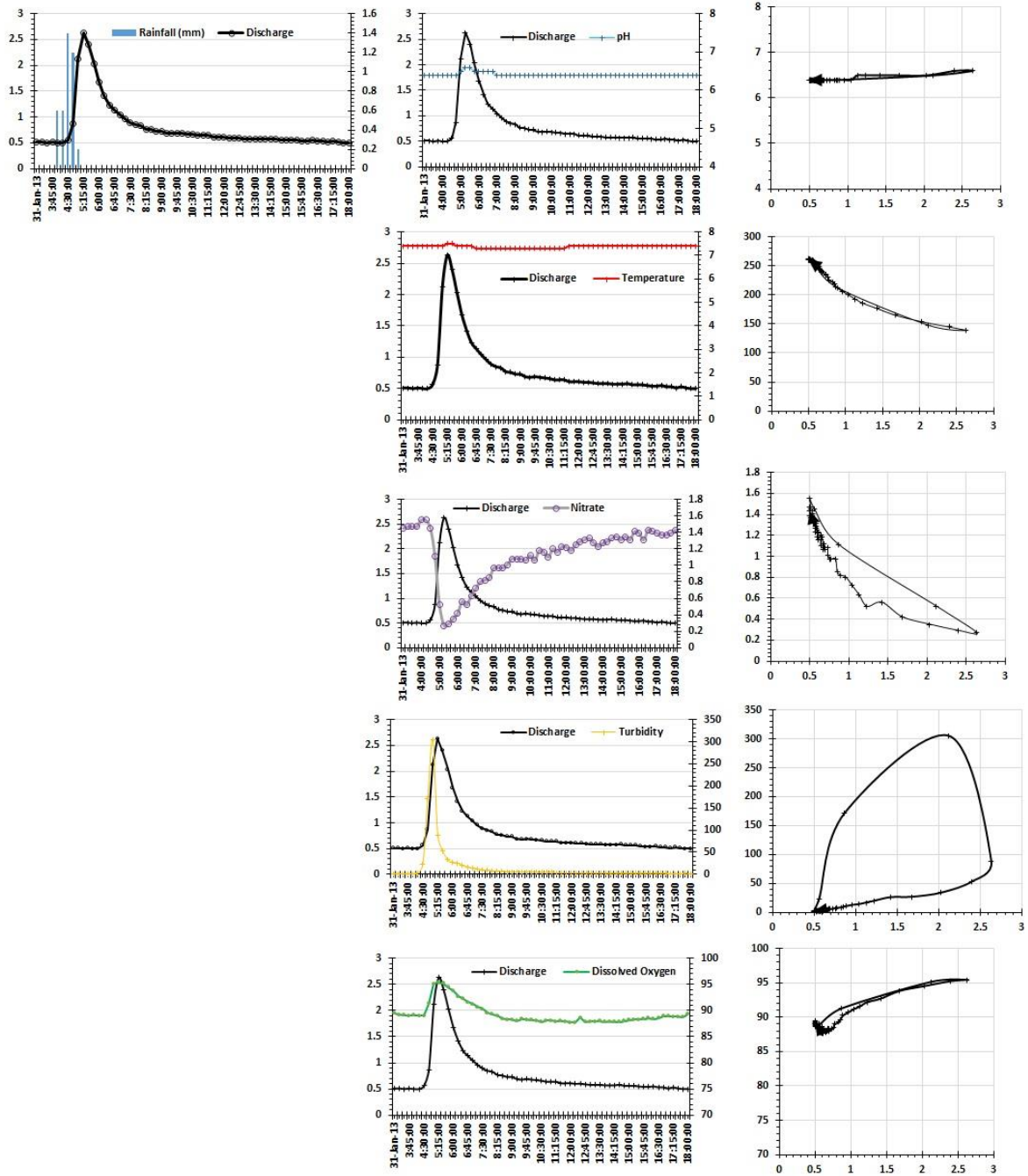
EVENT 7: PECKETSFORD.



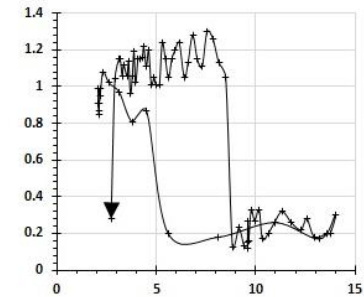
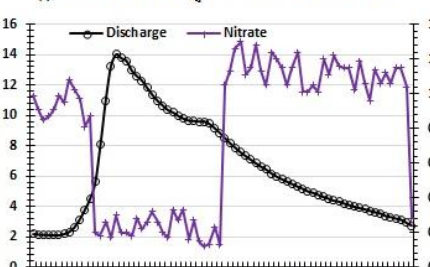
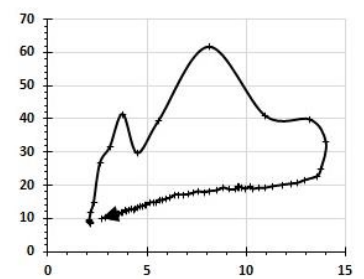
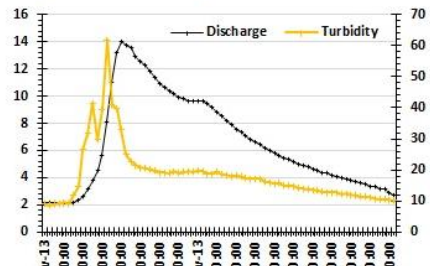
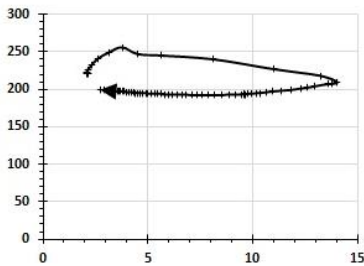
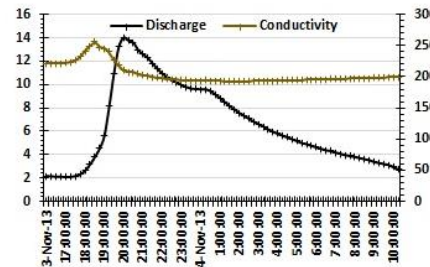
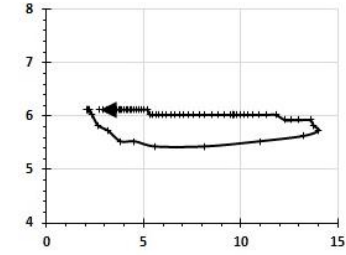
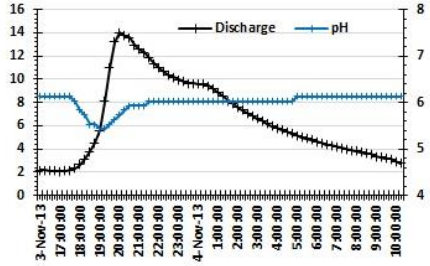
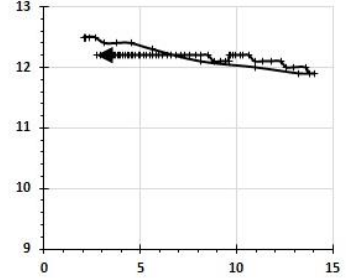
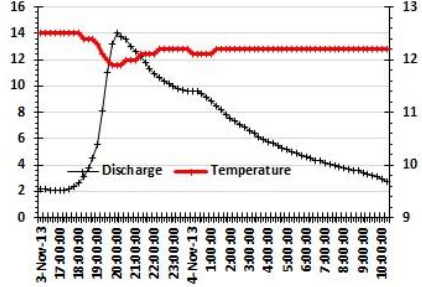
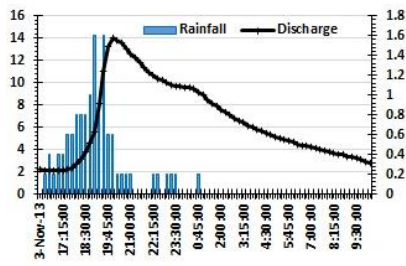
EVENT 7: BURROWS.



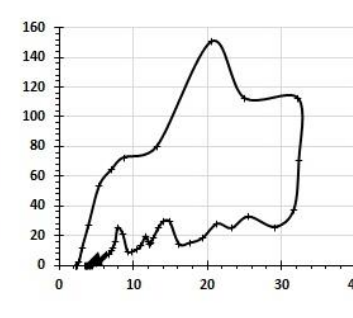
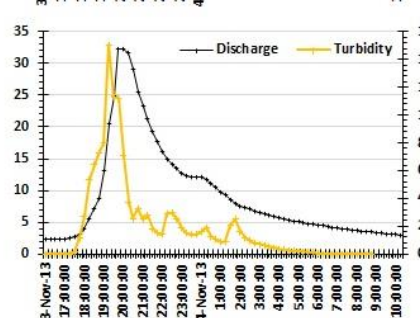
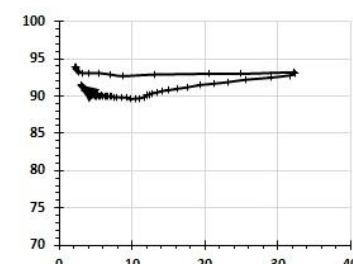
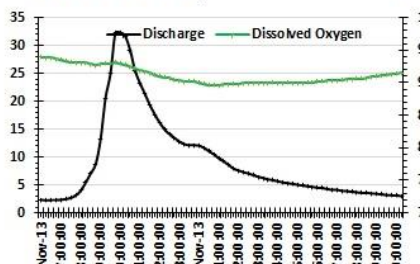
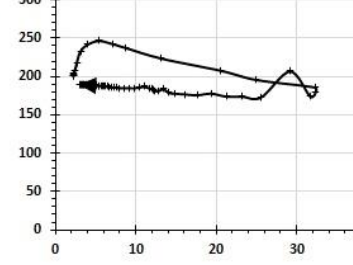
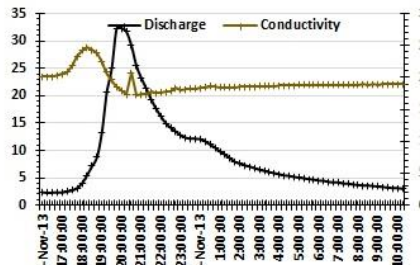
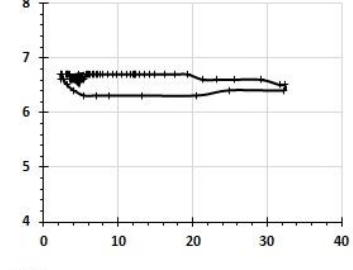
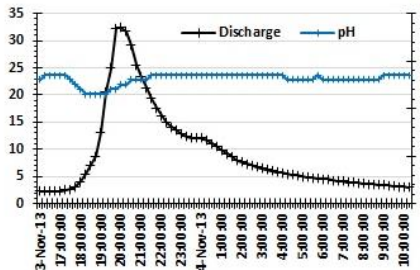
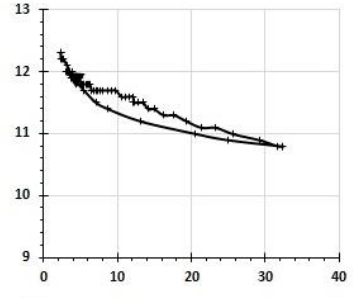
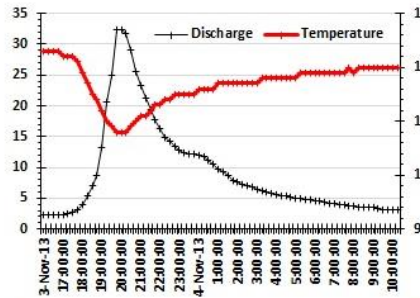
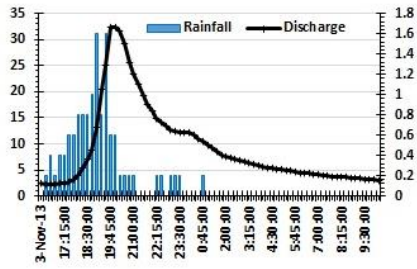
EVENT 7: MIDDLE AND HIGHER WYKE MOOR.



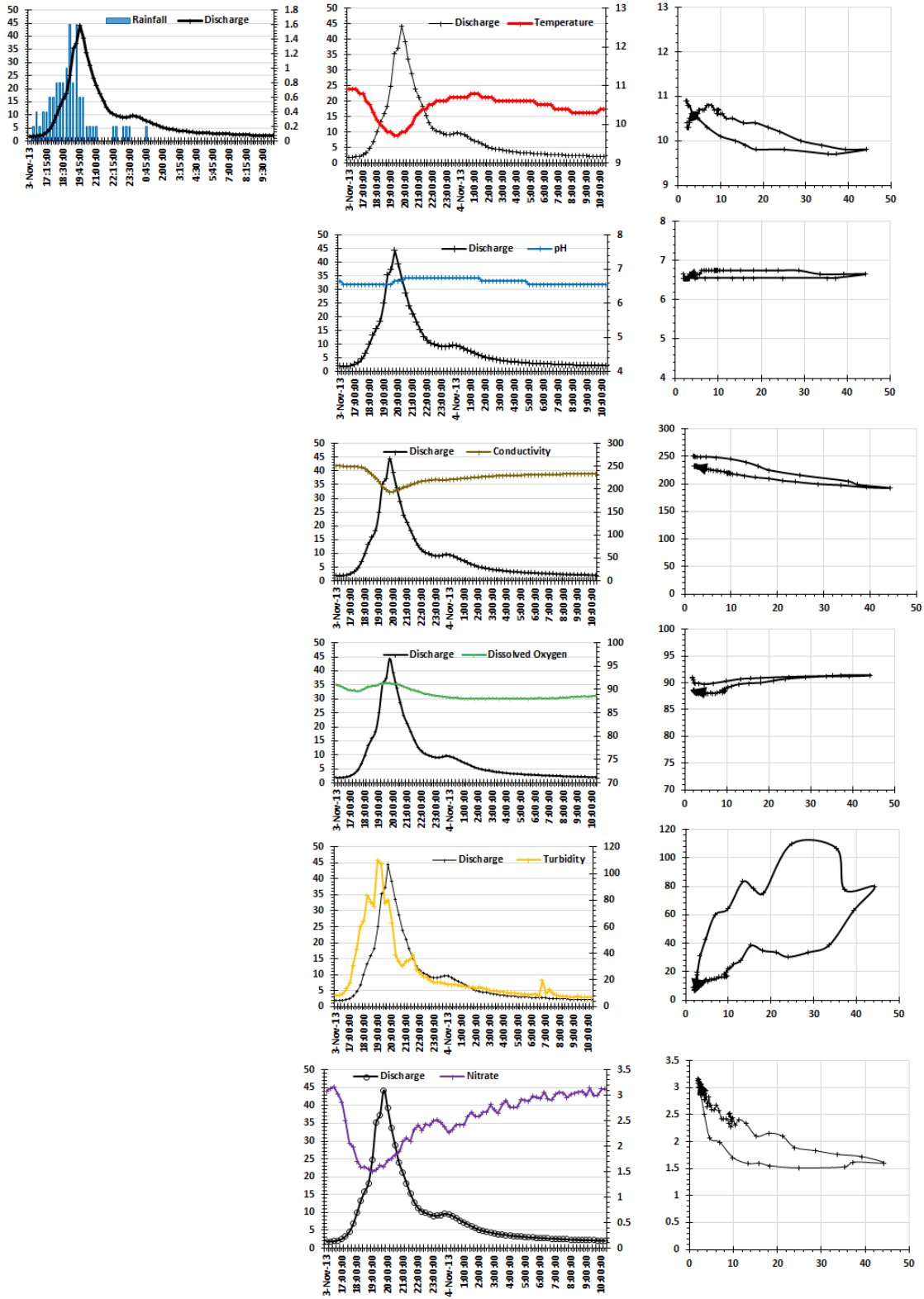
EVENT 7: LONGLANDS EAST.



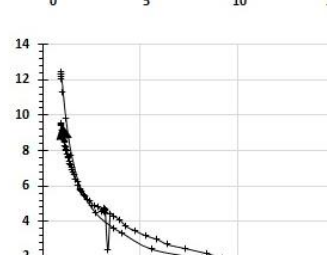
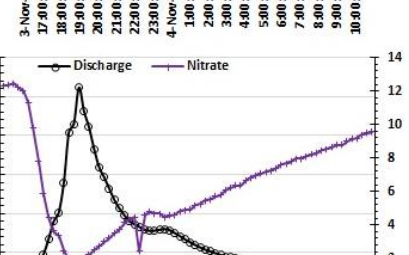
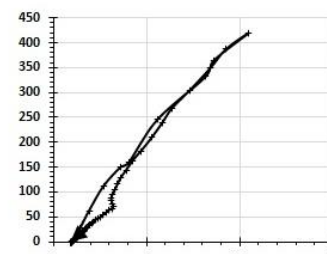
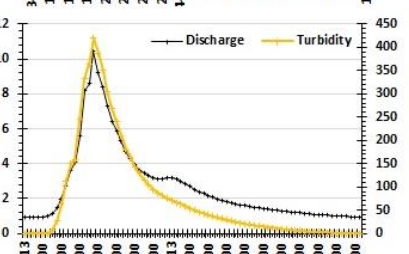
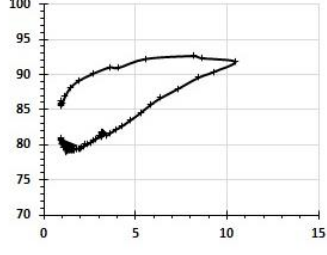
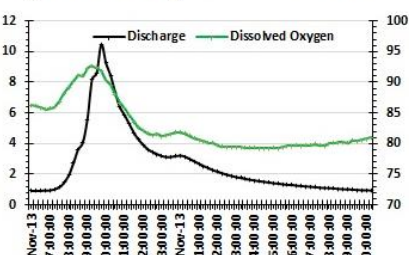
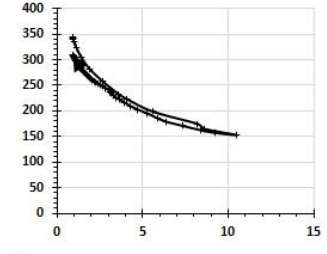
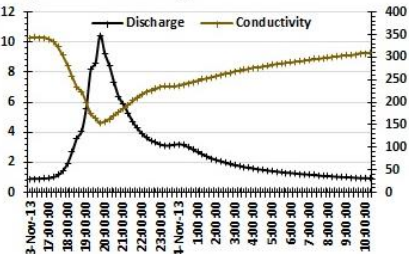
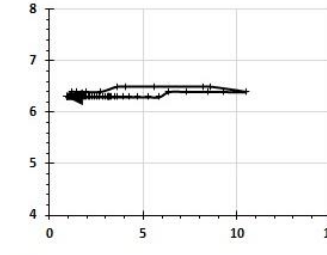
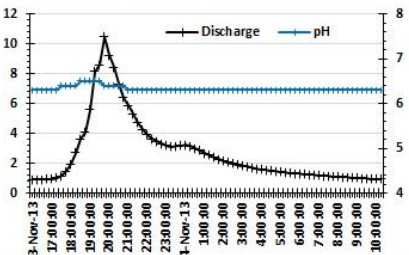
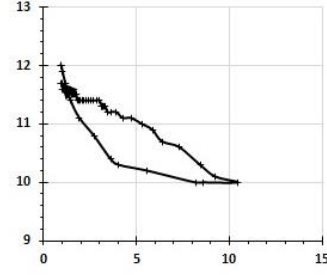
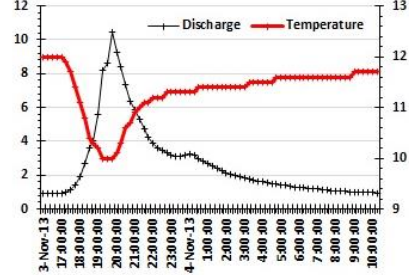
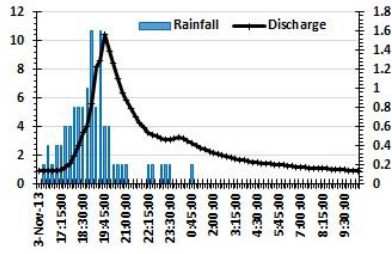
EVENT 8: PECKETSFORD.



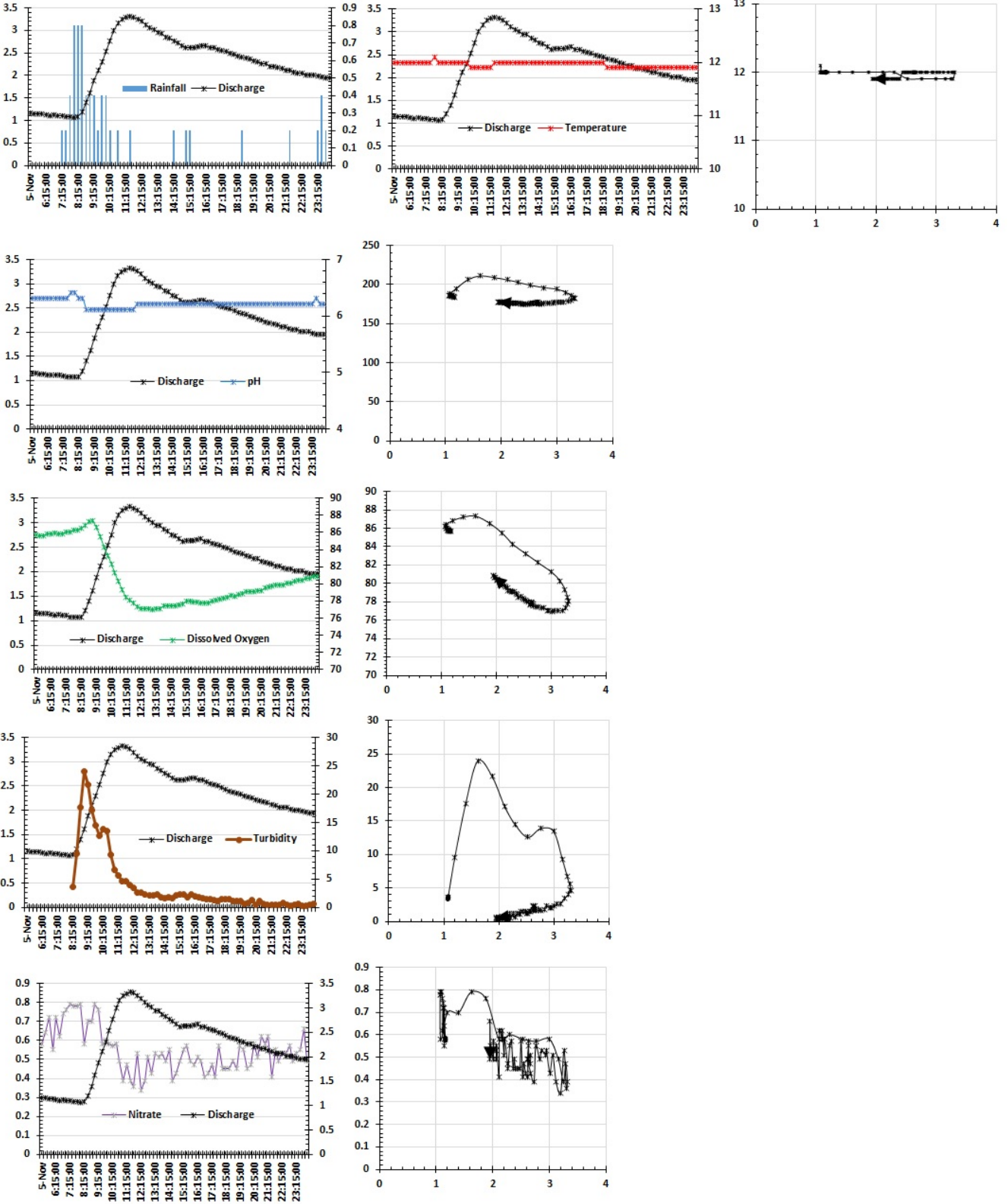
EVENT 8: BURROWS.



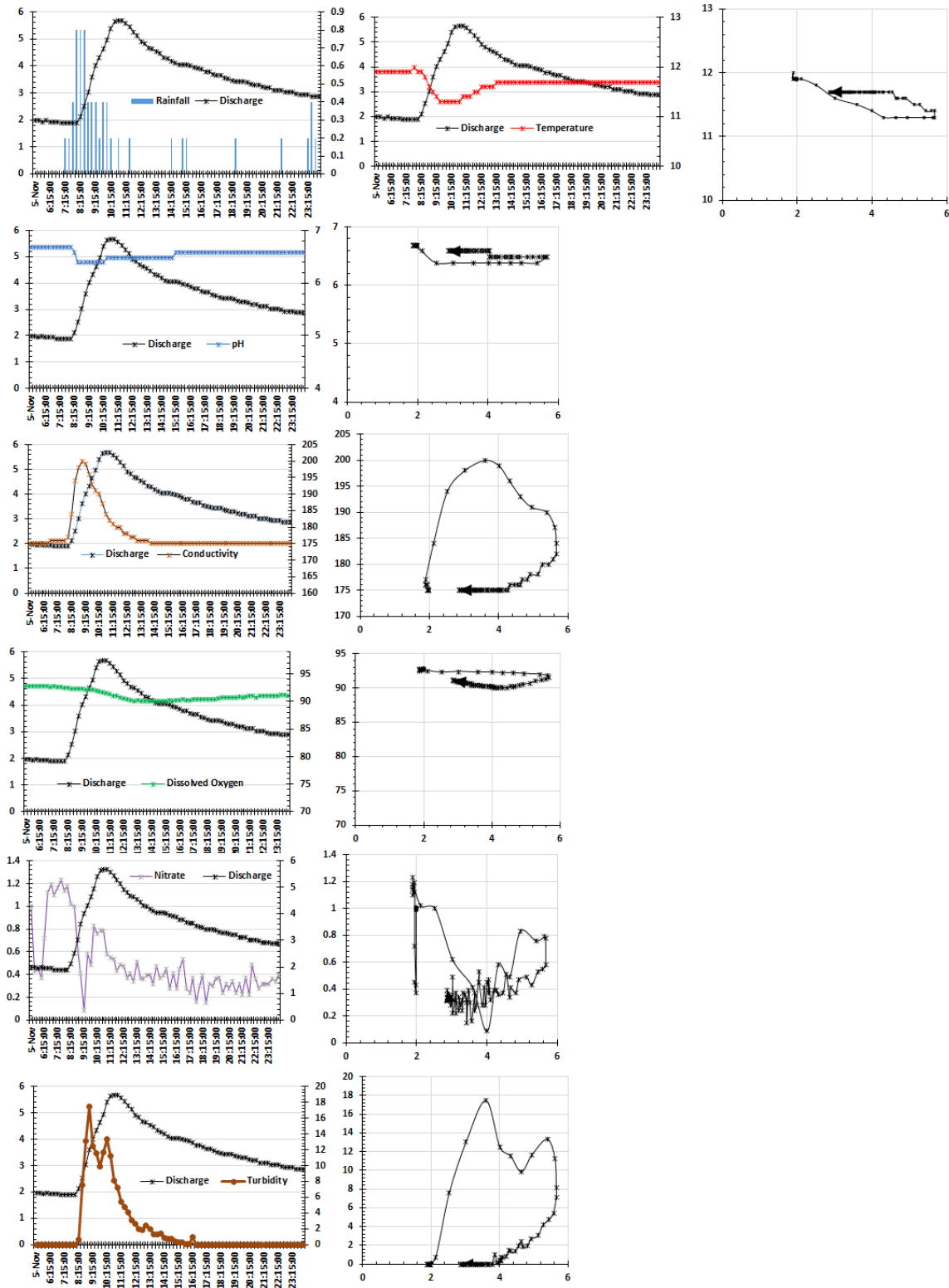
EVENT 8: MIDDLE AND HIGHER WYKE MOOR.



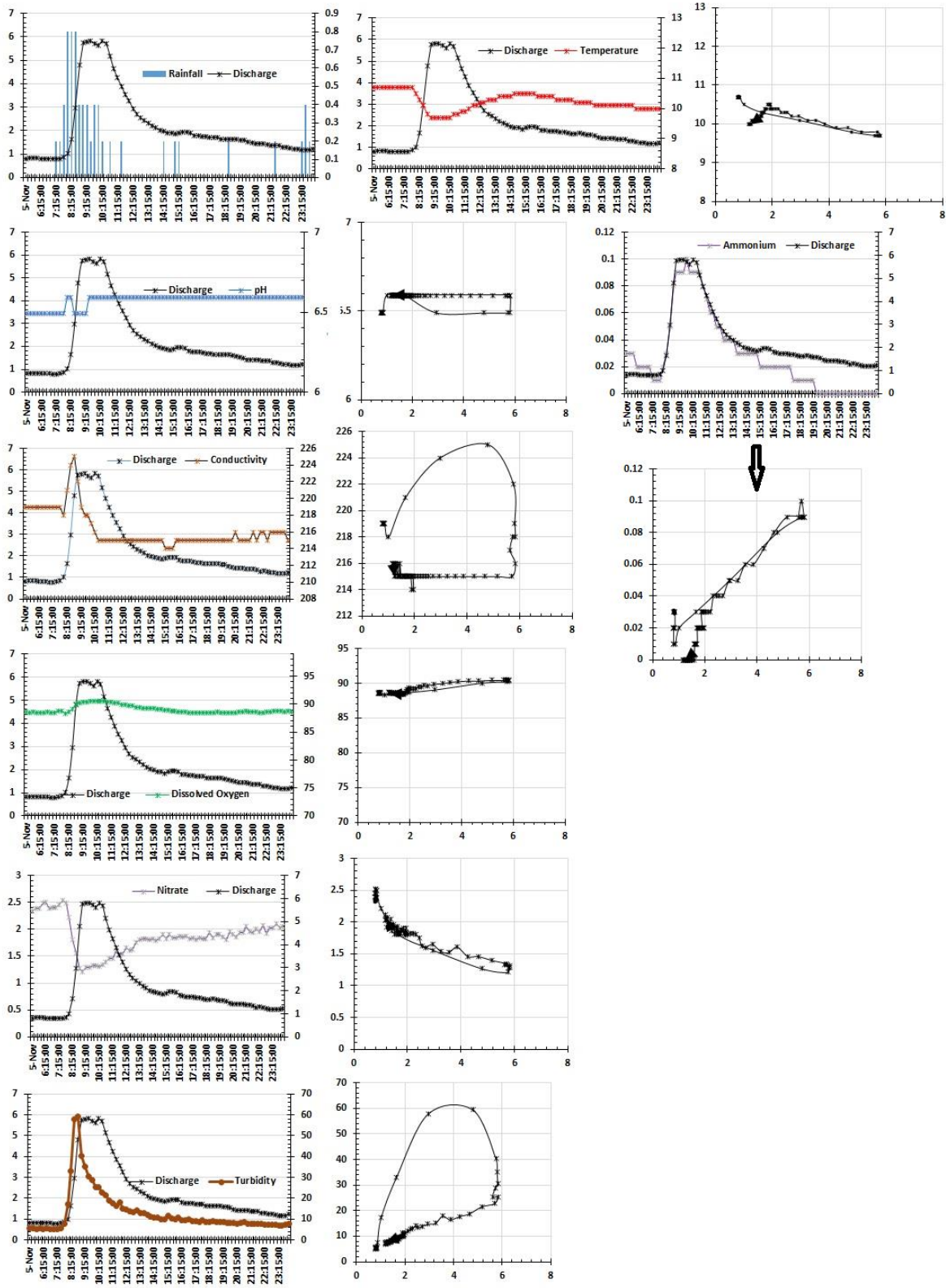
EVENT 8: LONGLANDS EAST.



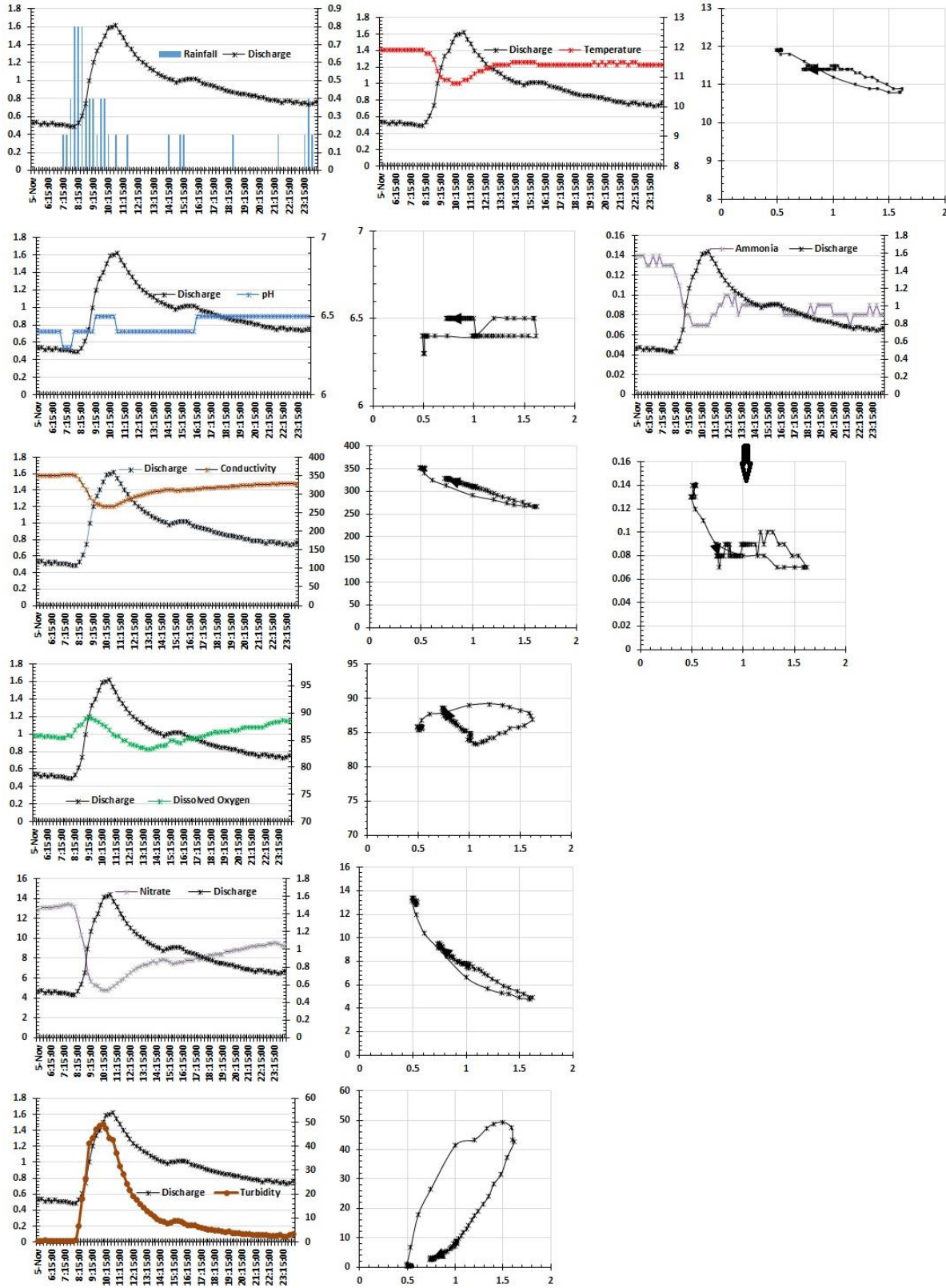
EVENT 9: PECKETSFORD.



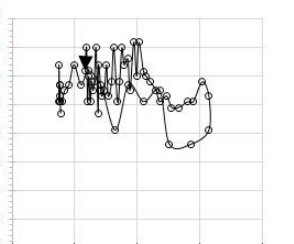
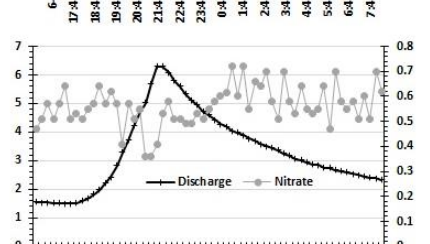
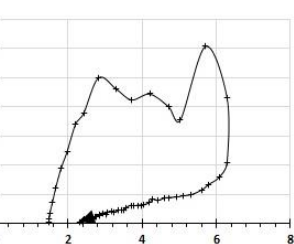
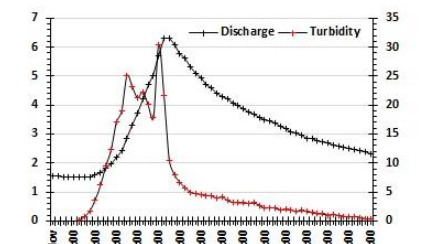
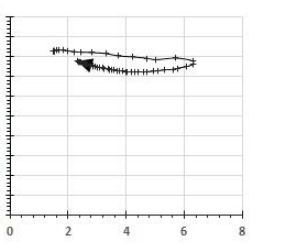
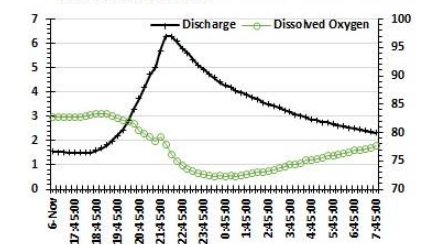
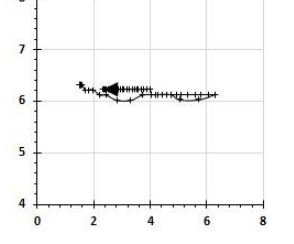
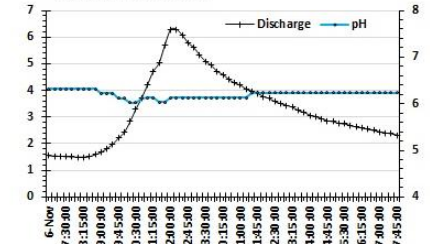
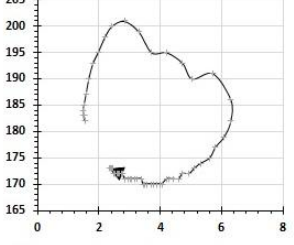
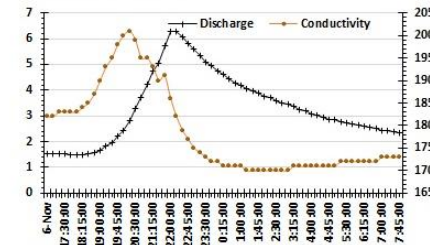
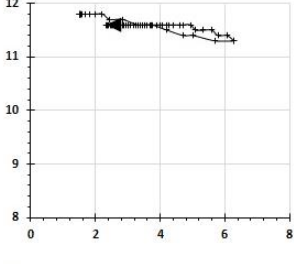
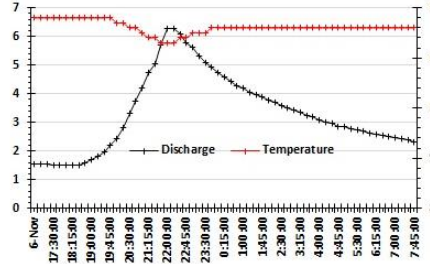
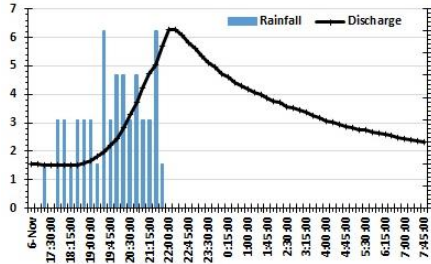
EVENT 9: BURROWS.



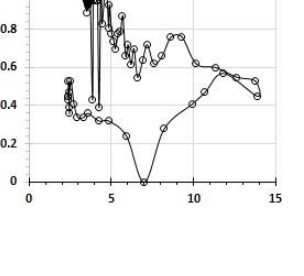
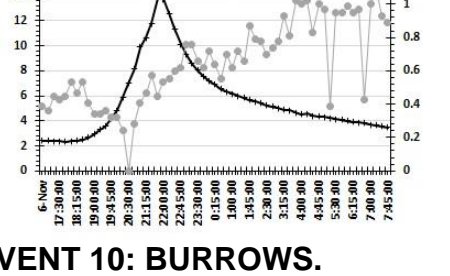
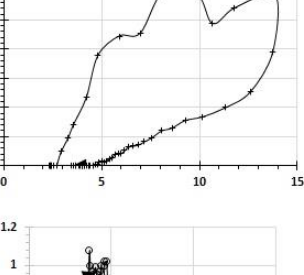
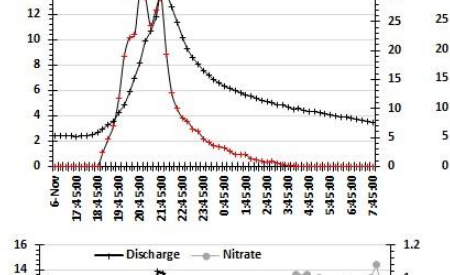
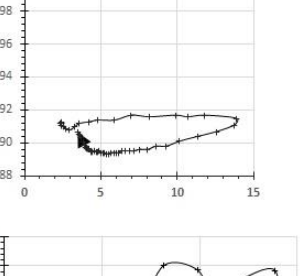
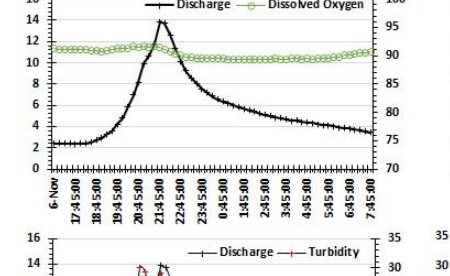
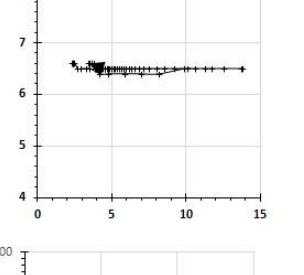
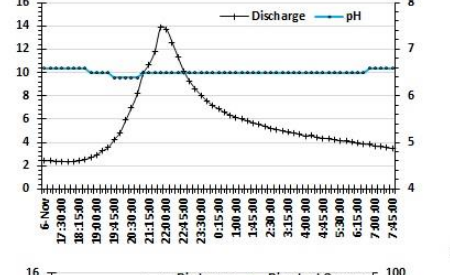
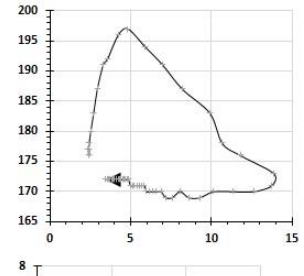
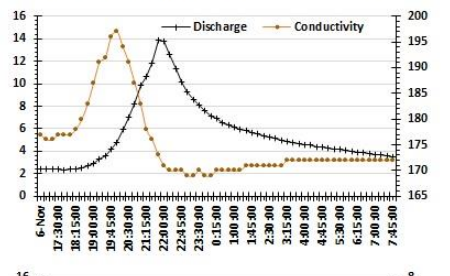
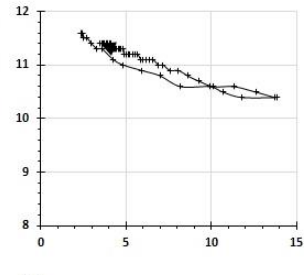
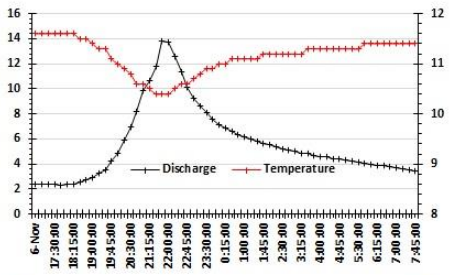
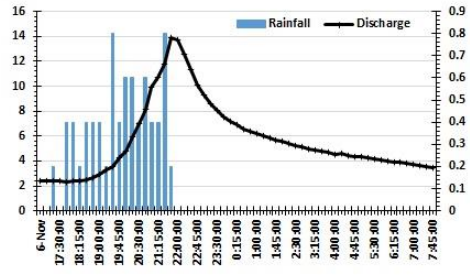
EVENT 9: MIDDLE AND HIGHER WYKE MOOR.



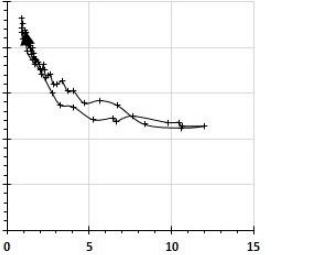
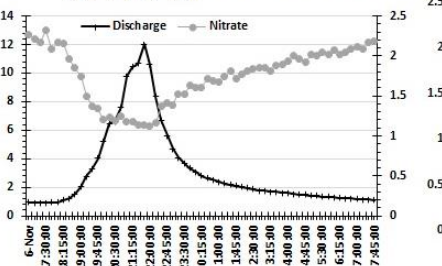
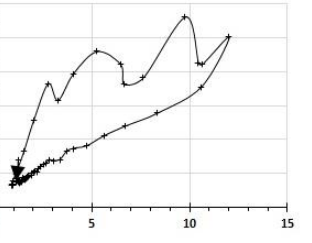
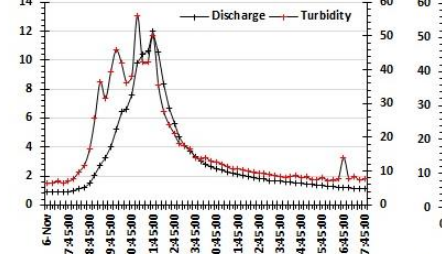
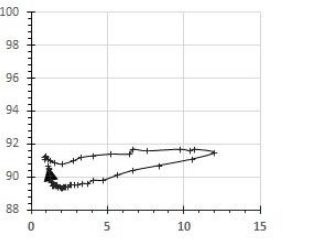
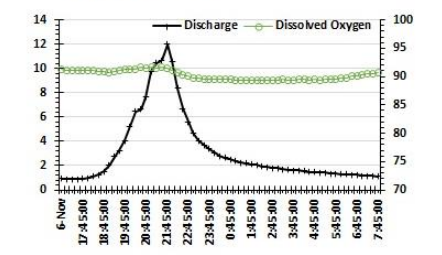
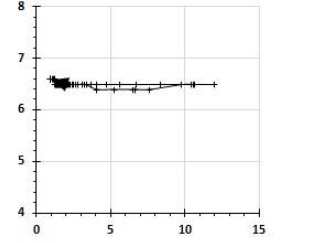
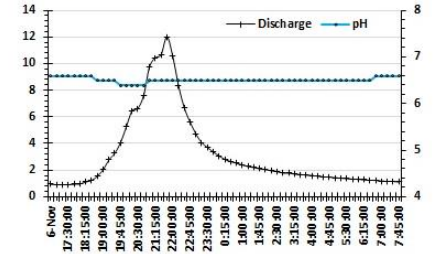
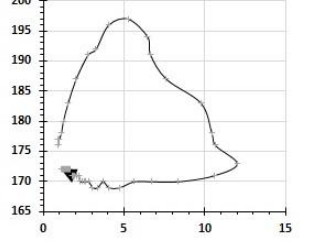
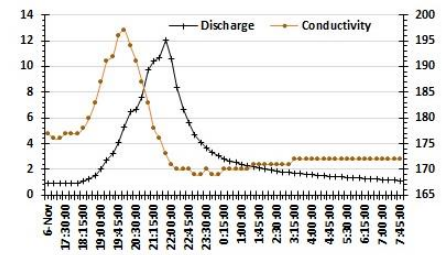
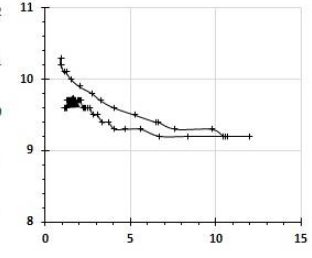
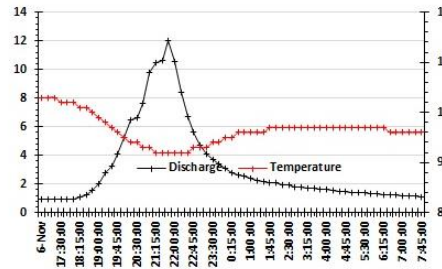
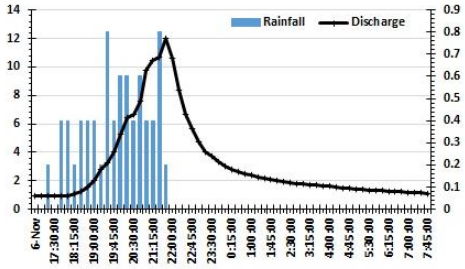
EVENT 9: LONGLANDS EAST.



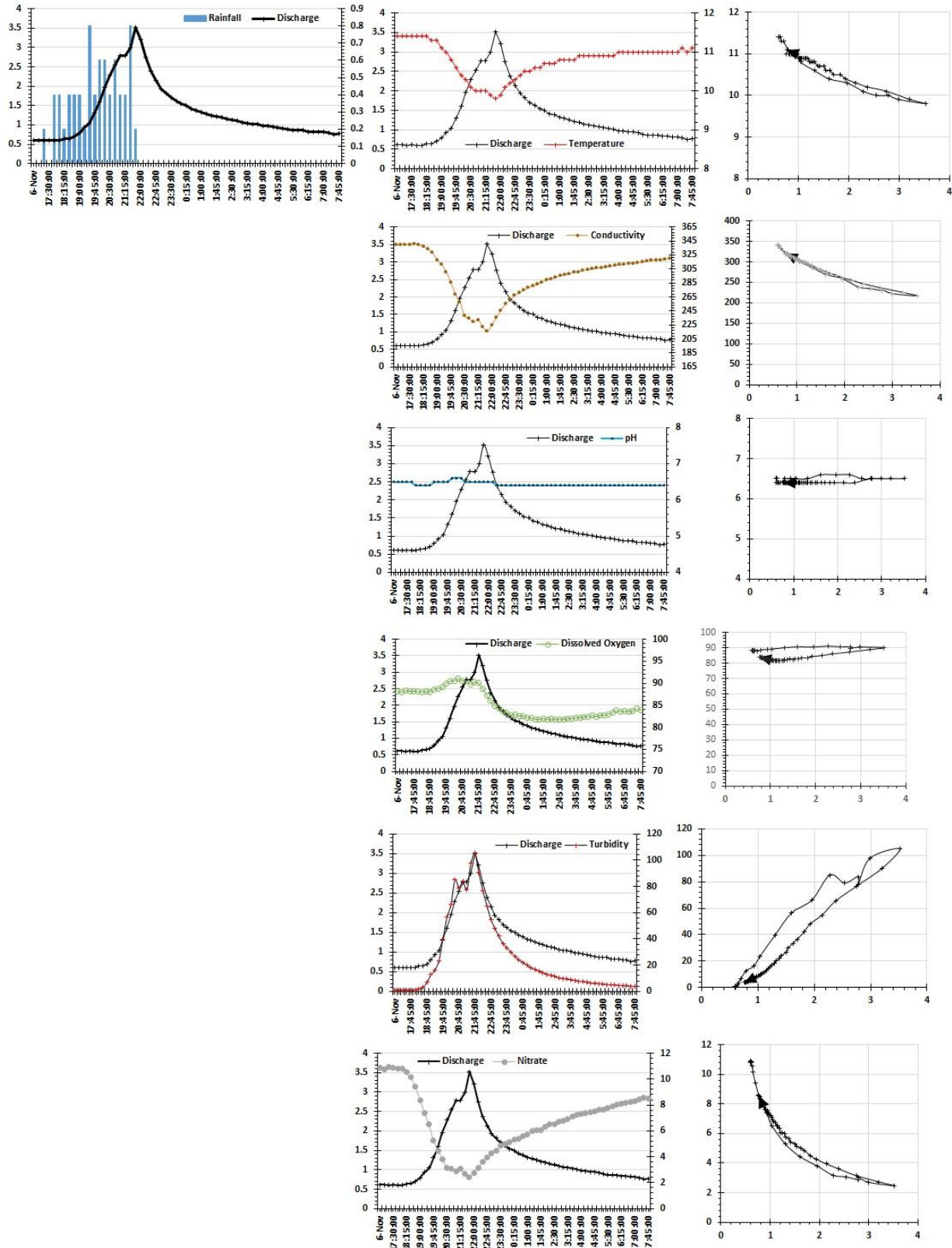
EVENT 10: PECKETSFORD.



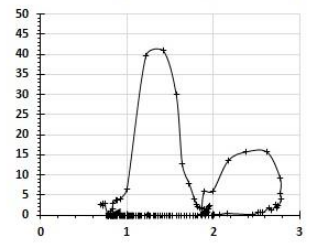
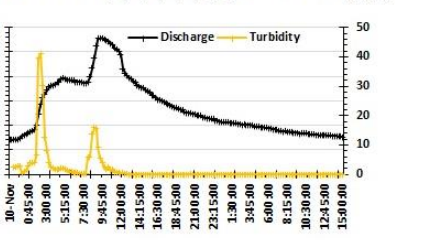
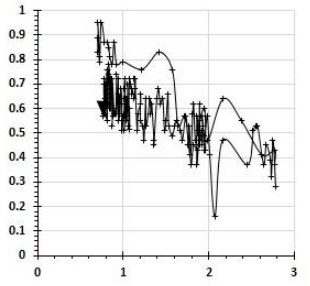
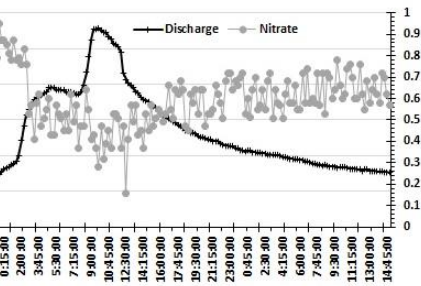
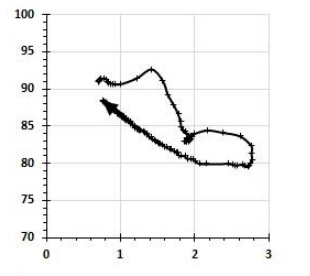
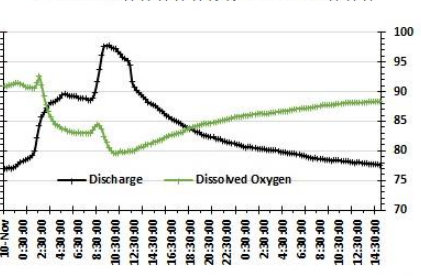
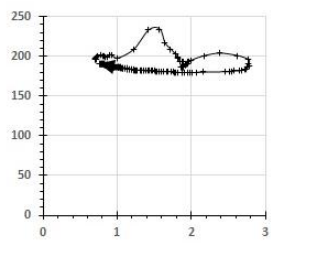
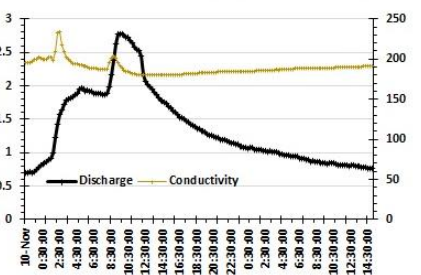
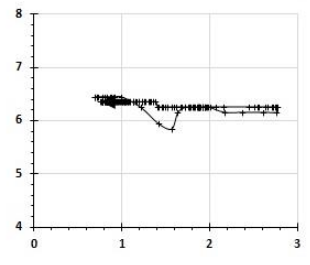
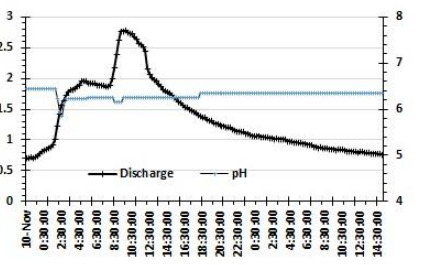
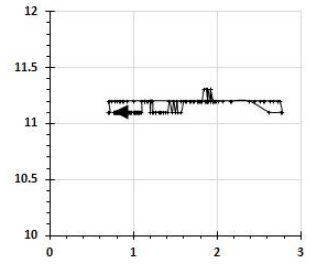
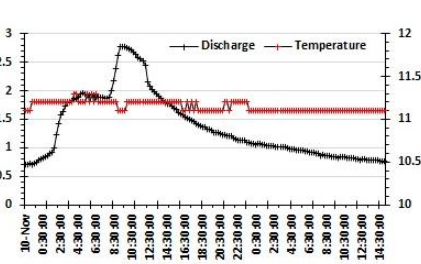
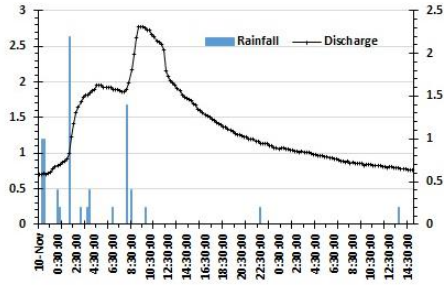
EVENT 10: BURROWS.



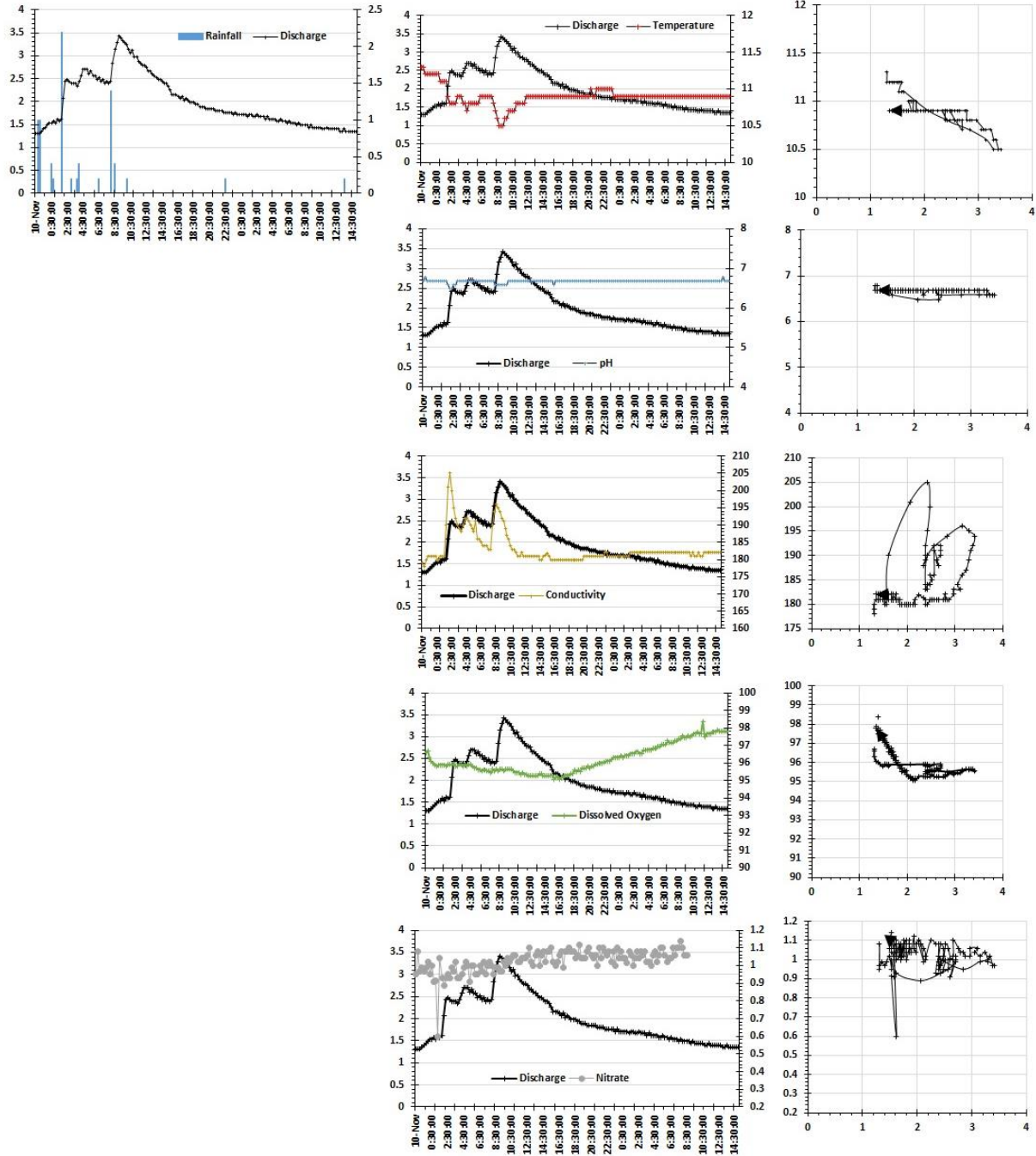
EVENT 10: MIDDLE AND HIGHER WYKE MOOR.



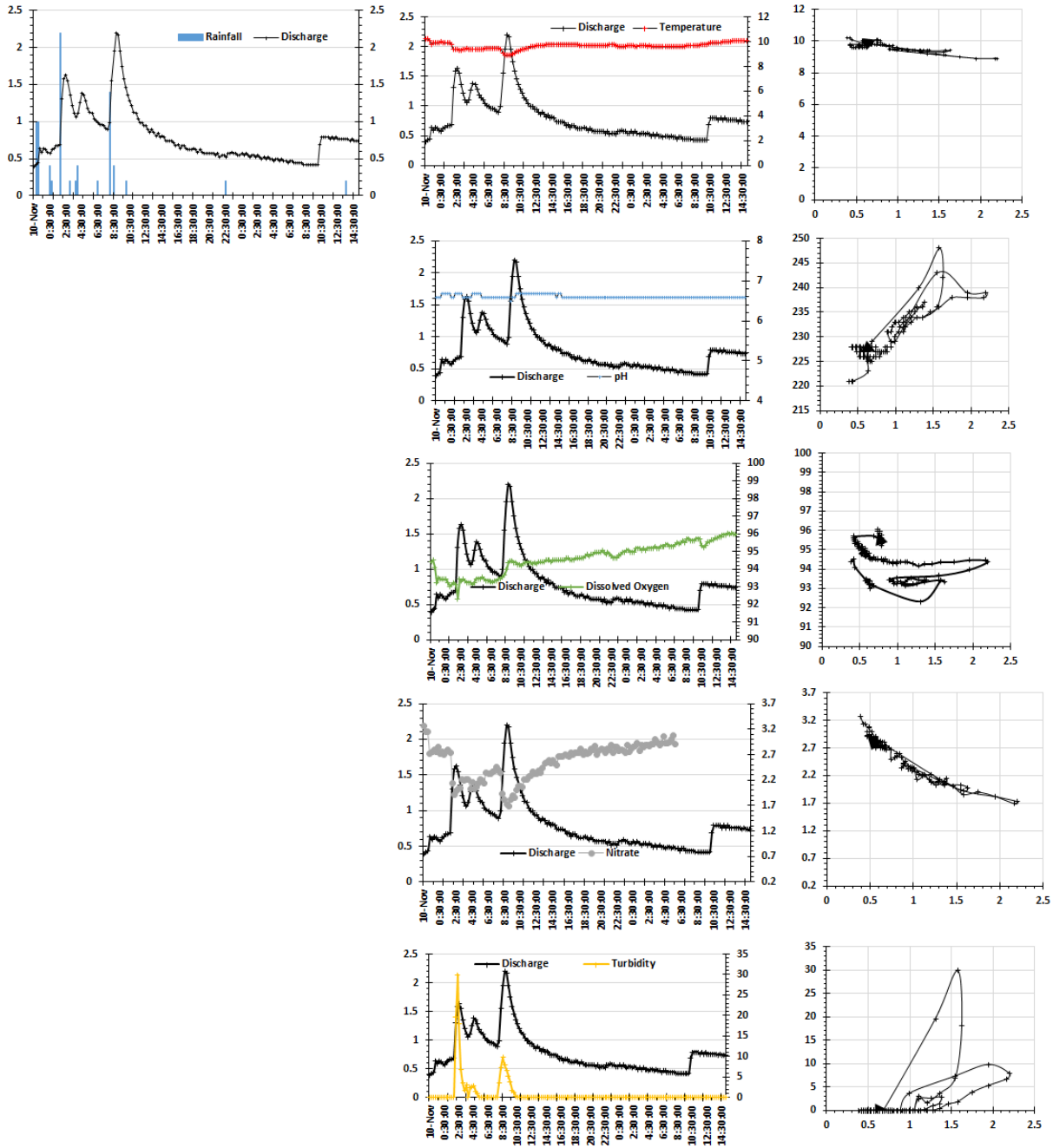
EVENT 10: LONGLANDS EAST.



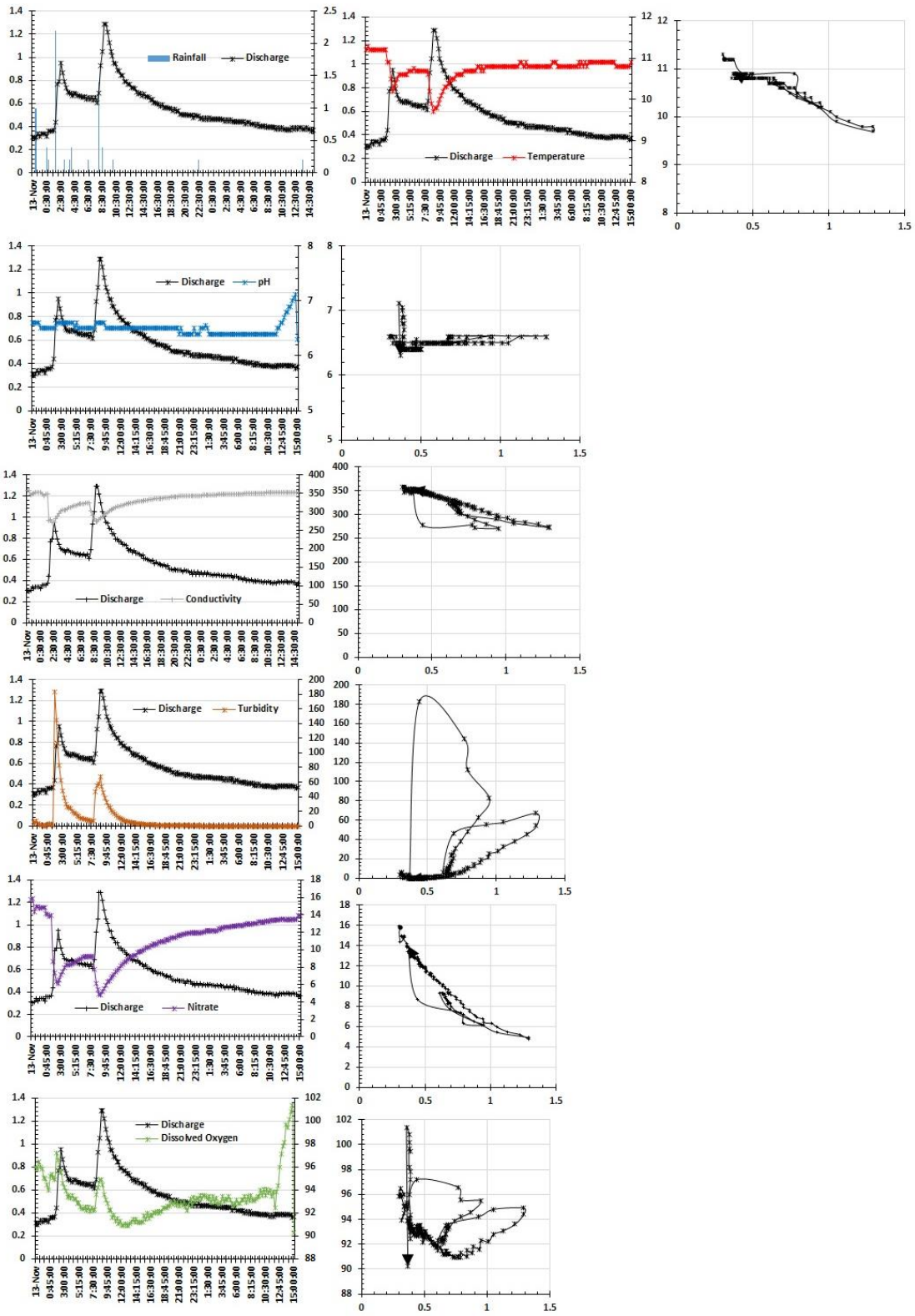
EVENT 11: PECKETSFORD.



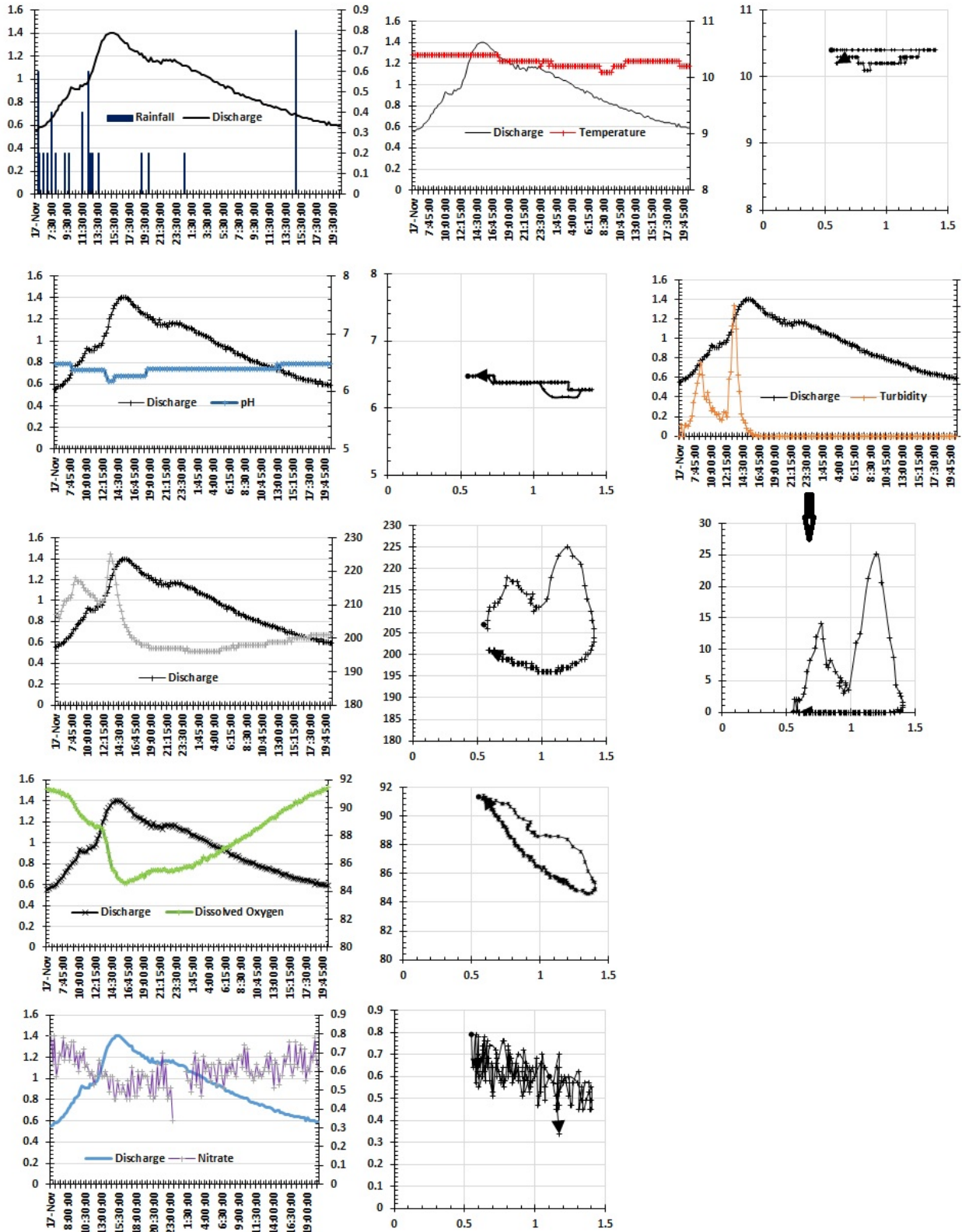
EVENT 11: BURROWS.



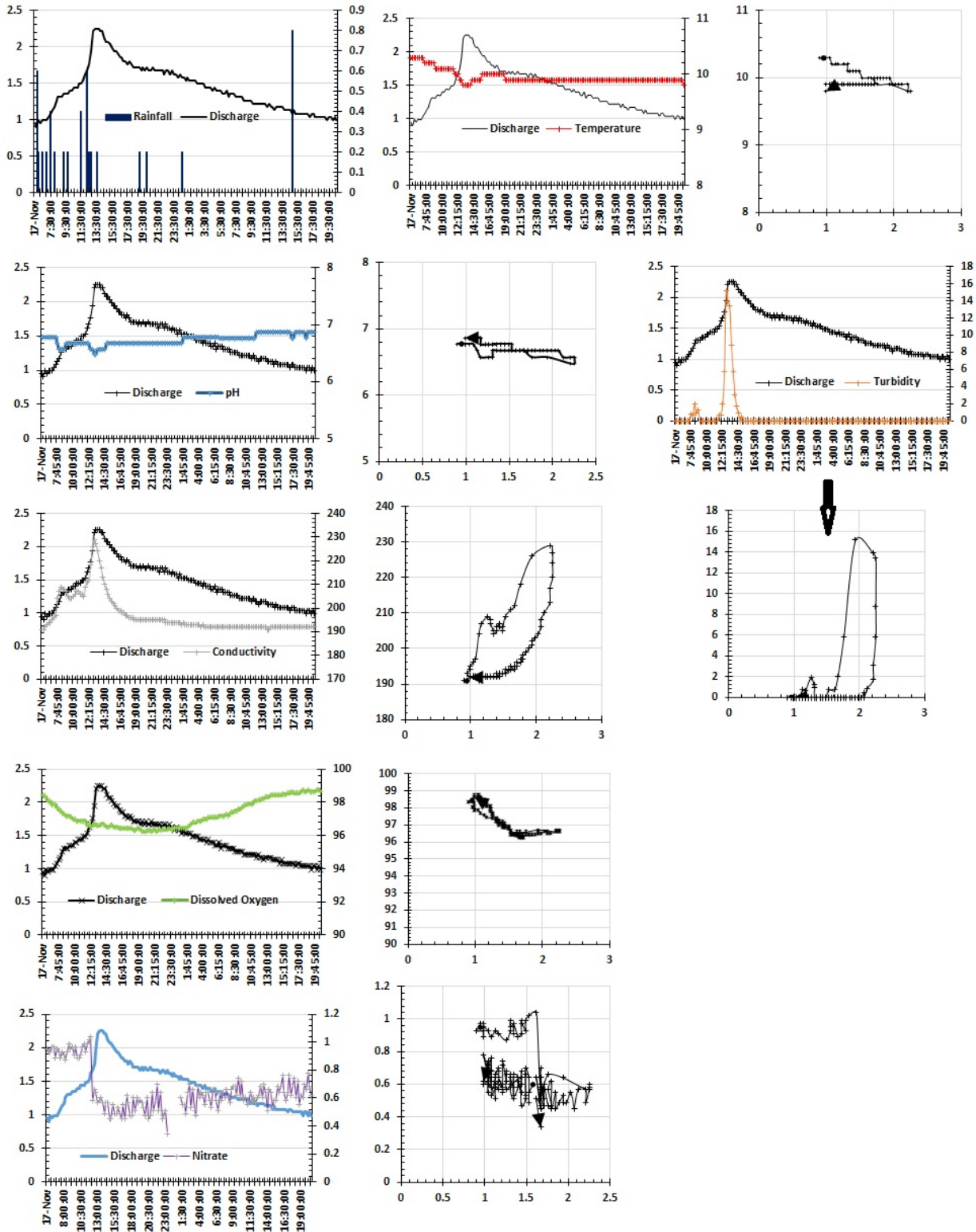
EVENT 11: MIDDLE AND HIGHER WYKE MOOR.



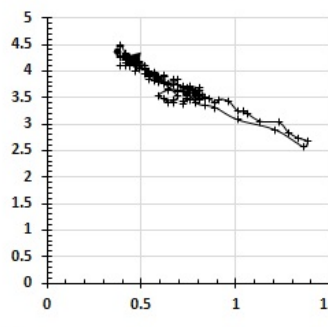
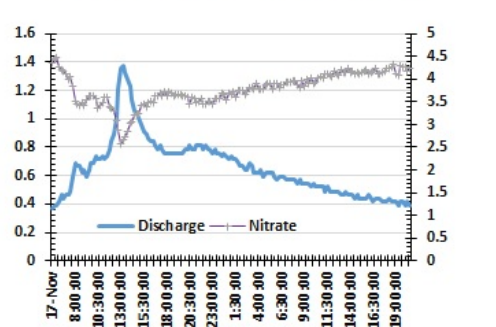
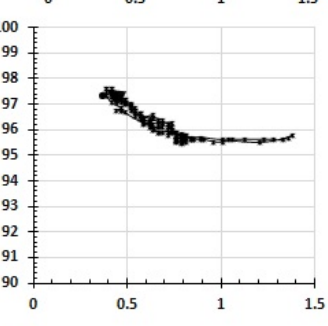
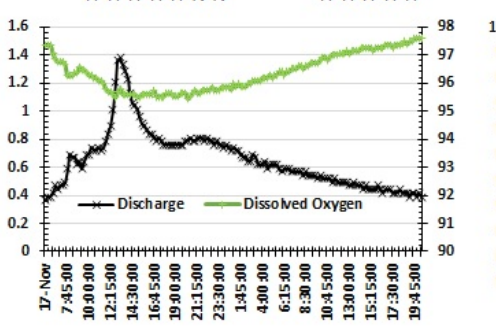
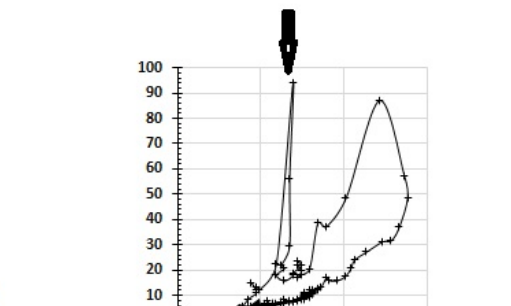
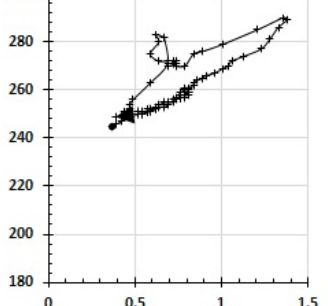
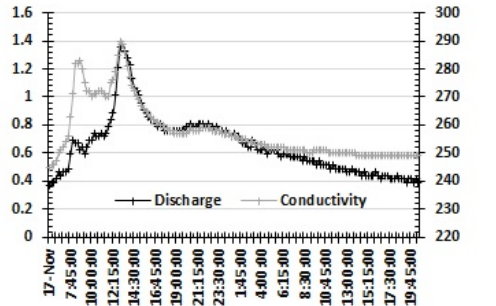
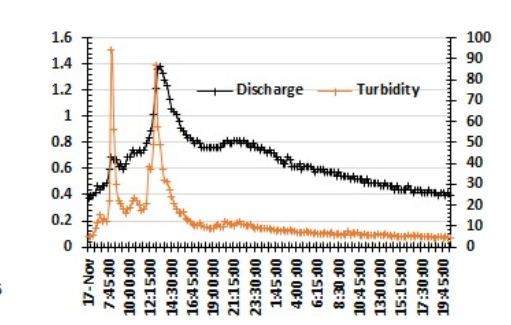
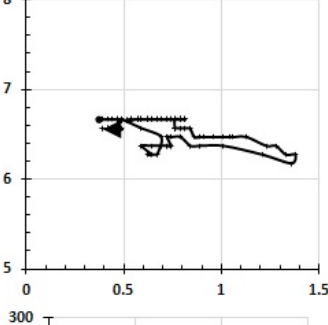
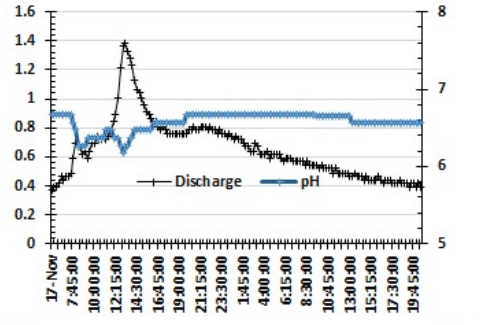
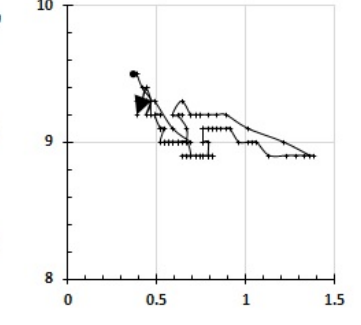
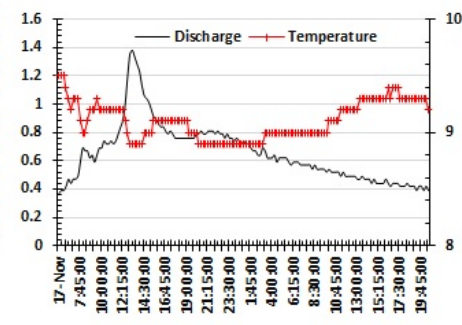
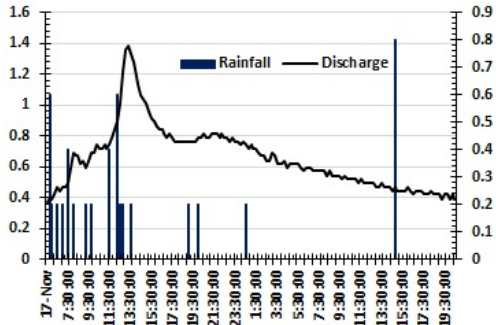
EVENT 11: LONGLANDS EAST.



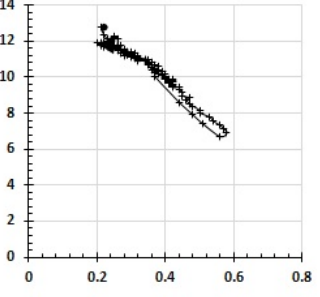
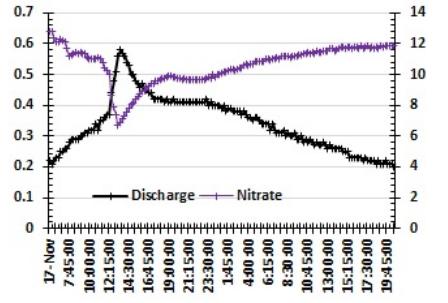
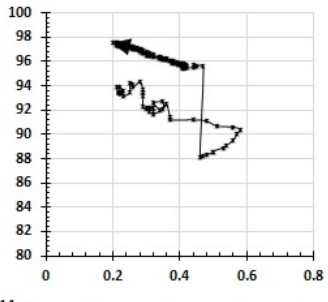
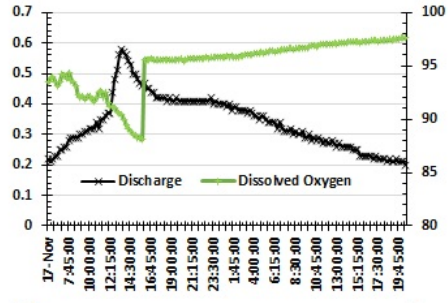
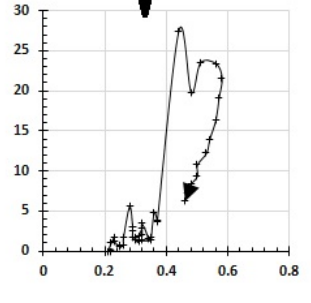
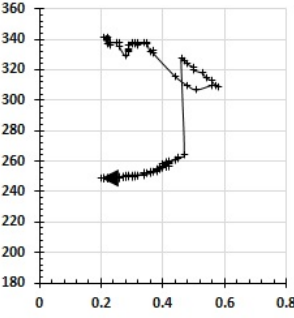
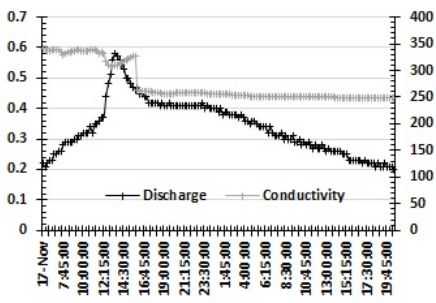
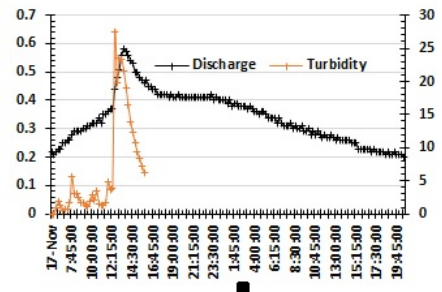
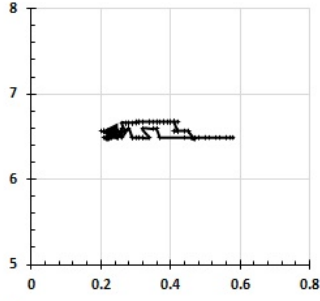
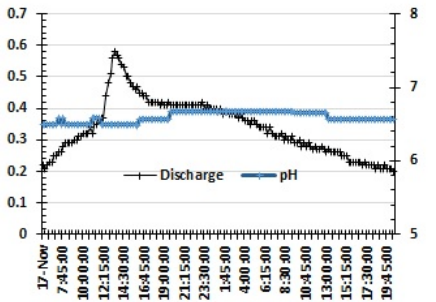
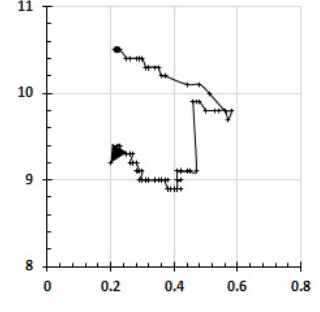
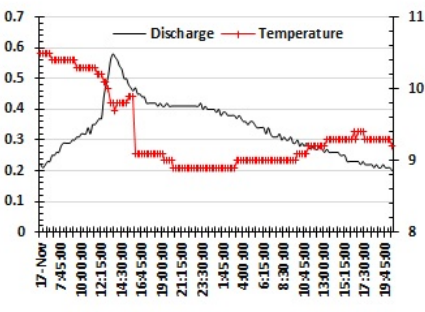
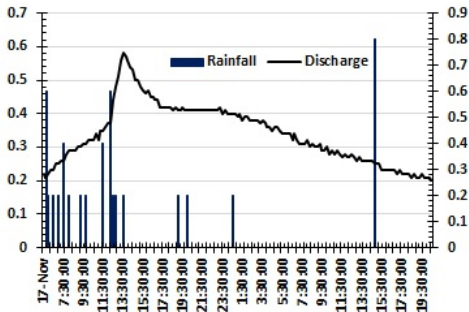
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EVENT 12: BURROWS.



EVENT 12: MIDDLE AND HIGHER WYKE MOOR.



EVENT 12: LONGLANDS EAST.

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