Impact of fluvial flooding on potentially toxic element mobility in floodplain soil

A thesis submitted for the degree of Doctor of Philosophy

Geography and Environmental Science

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Declaration of original authorship

I, Jessica Grace Ponting, confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

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Abstract

Global climate change is associated with significant changes to short-term weather extremes as well as long-term weather characteristics in different regions. Whilst the magnitude of climate changes are extremely uncertain, it is likely that summers will become warmer and drier, and there will be an increase in the intensity of rainfall events. These intense rainfall events will lead to an increased number of flooding events that remain for longer periods of time, and the occasional inundation of land that has rarely been flooded in the past. There is the possibility that increased flooding intensity and frequency will influence the soil properties, which in turn may affect the behaviour and mobilisation of potentially toxic elements (PTEs) in floodplain soils. It likely that many floodplains downstream of urban catchments, particularly those catchments with a history of industrial development, may harbour a legacy of contaminants that have been deposited with floodplain sediments.

To investigate the impact of fluvial flooding on PTE mobility in floodplain soils, I used the Loddon Meadow floodplain site; situated adjacent to the River Loddon in the Southeast of England, as a model floodplain, typical of a lowland floodplain downstream of an urban catchment. Preliminary work characterised the floodplain topography using geospatial techniques and compared elevation with the spatial distribution of soil PTEs concentrations. The topography of the floodplain was found to influence the deposition of some PTEs (e.g. Cr, Cu, Ni and Zn), providing strong evidence that the source of these PTEs to this floodplain site originated from point source or diffuse pollution upstream in the urban catchment. The novel combination of geospatial mapping of elevation and geochemical analyses could be adopted as a method for determining the source of PTEs to other study sites.

Analysing soil pore water chemistry provides the more useful measurement of the mobile fraction of PTEs, rather than the total concentration bound to the solid fraction. There are a number of methods for extracting pore water from soil samples; we compared an example of an *in-situ* method (Rhizon^{TM} sampler) with an example of an *ex-situ* method (centrifugation). There were no significant differences found in the pore water chemistry, despite the centrifugation exerting a pressure on the soil sample orders of magnitude higher than the Rhizon^{TM} sampler. We found, however, that in terms of useability through a range of soil moistures and consistency of sample volume extracted, the centrifuge was the preferred method for this particular study. We highlight examples where the opposite conclusion might be reached.

Laboratory mesocosm studies have reported increased PTE mobilisation with artificial flooding events. However, it can be difficult to extrapolate these finding due to the controlled conditions of the laboratory set-up (e.g. room temperatures are often higher than found in the field). We found that there was a need for on-site experiments that consider the effects of flooding using real-time field observations. We therefore took a field-based approach; extracting soil pore waters, by centrifugation, from the Loddon Meadow floodplain pre-flood, during a flood and post-flood. We found that the flooding event did not influence the mobility of all of the PTEs in the same way. However, we found concentrations of Cd, Cu and Cr significantly decreased post-flood compared to pre-flood. The dominant process identified to explain this decrease was precipitation with sulphides, which occurred during the flood and subsequently resulted in the significant decrease in concentrations post-flood. A slight increase in pH may have aided adsorption processes onto organic matter and clay minerals. We also found a decrease in dissolved organic matter in solution and this would have reduced the capability of the pore water to complex PTEs in solution. It is possible that the decreased concentrations found were a result of dilution, due to the increased water volume from the river and ground water. When analysed, the river and ground water had considerably lower concentrations of PTEs than the soil pore waters.

The impact of a flooding event on PTEs mobility is the combination of multiple processes. So, while we observed some processes increasing the concentrations of PTEs; for example, the reductive dissolution of Mn oxides, predominantly in the lower elevation areas of the floodplain. The overall net effect of the flooding event was a decrease in PTE concentrations, because processes like sulphide precipitation were dominant. There were no significant increases in PTEs mobility due to the flooding event and as such, no evidence to support the idea that floodplains become a source of PTEs. This is contrary to the evidence from laboratory studies, that found there is mobilisation of PTEs due to flooding. This study highlights the importance of understanding the dominant processes that drive the mobility of individual PTEs on specific floodplains, so that site-specific predictions can be made on the impact of future flooding on the mobilisation of legacy contaminants. Further field-based monitoring; collecting data pre-flood, during the flood and post-flood, from varying soil types and composition (e.g. clay, sand, silt, peat and loam) is required to support future modelling exercises. This would improve our capability to predict the impact of increased intensity and duration of flooding on soil porewater chemistry and PTE mobility.

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Chapter 1

1.0. General Introduction

1.1. Climate change & environmental pollution

Global climate change is influenced by human-induced changes in atmospheric composition, which is now thought to be large enough to exceed the natural bounds of variation and capable of greatly impacting human and ecological systems (Karl and Trenberth, 2003; Landis et al., 2013). The Climate Change synthesis report (IPCC, 2014) states that human influence on the climate is causing increased mean temperatures, resulting in an increase in the likelihood of heat waves, the number of areas affected by droughts, wildfires, and the thawing of permafrost or earlier spring snowmelt (Blöschl et al., 2017; Rohr et al., 2013). In conjunction, there will be an increase in the frequency and intensity of heavy precipitation events and the occurrence of extreme storms, such as cyclones and hurricanes, rising sea level and increased ocean pH and salinity (Rohr et al., 2013; Wenning et al., 2010). Changes in climate that lead to drought or floods and rising sea levels may also cause displacement of many people, causing more pressure on the land available (Foley et al., 2005). Human actions such as burning coal, oil, and gas for energy, conversion of natural ecosystems to managed landscapes, and climate mitigation (e.g. biofuels) will exacerbate the impacts of climate change, leading to a combined influence on the fate and distribution of chemical contaminants (Foley et al., 2005; Karl and Trenberth, 2003; Rohr et al., 2013; Stahl et al., 2013). Increased urbanisation has led to soil sealing through the creation of impermeable surfaces. So, as environmental change increases storm intensity, a greater volume of water inundates these areas, leading to greater surface runoff and a reduction in the capacity of the catchment to buffer the flood risk (Pathirana et al., 2014).

1.1.1. The influence of climate change on pollutant behaviour

Climate change and human actions will influence the exposure of many species to pollutants contaminating the air, water and food (Balbus et al., 2013). Climate change has the potential to affect: (i) the release of contaminants from soils, (ii) the transport to water courses, (iii) the biogeochemical processes within water courses and, (iv) contaminant concentrations via changes in river flows that dilute or concentrate contaminants, and (v) the ability for organisms to tolerate or detoxify contaminants. Thus, climate change affects the sources, pathways and receptors of environmental contaminants (González-Alcaraz and van Gestel, 2015; Landis et al., 2013; Moe et al., 2013; Stahl et al., 2013). Increasing temperatures can result in fires that provide a source of pollutants to the atmosphere; such as iron (Fe) and mercury (Hg) that are sequestered in the vegetation and released through volatilisation and transport of particulates (Stahl et al., 2013). Increased temperatures can also increase the metabolic rates of many organisms, thereby increasing the potential for bioaccumulation and biomagnification of some contaminants to receptors; this is known as climate induced sensitivity, where changes in climate alters the ability of an organism to tolerate toxic environments (Hooper et al., 2013). Increasing sea levels may impact the source of pollutants, by release from the land due to chloride (Cl^-), sodium (Na^+), and sulphate (SO_4^{-2}) cations competing with pollutants for sorption sites on sediments or soils, thereby releasing them into the environment. Increasing intensity of hydrological cycles, results in flooding and this influences processes involved in the mobilisation of pollutants, therefore potentially affecting the source and pathway through altered patterns of soil erosion and sedimentation (Arnell et al., 2015). Redox sensitive PTEs (e.g. arsenic (As), copper (Cu) and chromium (Cr)) can be present in the environment in different oxidation states, that differ in their level of toxicity (Rinklebe et al., 2016; Rutkowska & Szulc, 2014). When flooding occurs, soils undergo changes (e.g. fluctuating redox conditions) which may alter the speciation or oxidation state of some PTEs. Speciation of PTEs is an important factor to consider as this will largely determine their mobility and bioavailability (Hooda, 2010). For example, while trivalent Cr (III) is a naturally occurring form of the element, under oxidising conditions it is oxidised to a more mobile and toxic form as hexavalent Cr (V) (Dhal et al., 2013; Ding et al., 2016; Landrot et al., 2012; Trebien et al., 2011; Wuana et al., 2011). The mobilisation of bioavailable pollutants will impact receptor organisms, like earthworms and springtails; it has been found that metals like Hg significantly reduce the ability of earthworm survival below -6 °C and reduce the cold shock tolerance of springtails. This phenomenon is known as toxicant-induced climate sensitivity, where exposure to contaminants alters an organism's ability to tolerate climate stress (Bindesbol, Anne-Mette, 2008). The joint effect of climatic and toxicant stress on organisms will impact survival and reproduction, thereby influencing species richness and food-web structure (Moe et al., 2013).

1.1.2 Climate change impacts in the UK

The UK Climate Projections (UKCP18) use information from the Intergovernmental Panel on Climate Change (IPCC) and incorporate these with projections from the Hadley Centre global circulation models. These have given rise to estimates that UK winter rainfall will increase (average change -2% to +35%) and summer rainfall will decrease (average change -47% to +2%) (Lowe et al., 2018). The average daily rainfall in the UK, over the winter, has shown an upward trend since the 1960's (Bell et al., 2012; Lowe et al., 2018; Maraun et al., 2008; Osborn and Hulme, 2002). Projected trends in climate change in the 21st Century are similar to UKCP09, with a general move towards warm, wet winters and hot, dry summers; although natural variations mean that some cold, dry winters and cold, wet summers will still occur (Lowe et al., 2018). The implications of projected increases in rainfall depends upon: the individual characteristics of both the rainfall itself and the capacity of the receiving catchment, with regards to storage and drainage (Arnell et al., 2015; Bell et al., 2012). Thus, while there is some uncertainty regarding the effect that future climate change will have on river levels (Prudhomme and Davies, 2009), a warming climate already seems to have led to an intensification of the hydrological cycle, with an expected increase in the magnitude and timing of river floods (Blöschl et al., 2017). In the last twenty years, flooding events have occurred with increasingly frequent intervals across the UK (Wilby et al., 2008). It has been argued that short-duration extreme rainfall events will intensify more than the daily average rainfall (Chan et al., 2014). Surface water run-off depends on the intensity as well as the frequency of rainfall. Therefore, future increases in the intensity of precipitation events may result in more frequent flooding events in the UK (Maraun et al., 2008).

1.2. Approach of the thesis

1.2.1. Aim and Objectives

The aim of this research was to determine the mechanisms influencing the mobility of potentially toxic elements (PTEs) in floodplain soil pre-flood, during a flood and post-flood. A field-based sampling regime was adopted as this provides more realistic measurements than laboratory mesocosm experiments. My aim was achieved by the following objectives:

- Selecting and characterising a floodplain site (i.e. quantifying topography and total soil concentrations of PTEs).
- Identifying the most appropriate method of measuring PTE mobility in the floodplain soils.
- Extracting soil pore water samples (representing the mobile fraction) from across the floodplain pre-flood, during a flood and post-flood.
- Analysing soil pore waters to assess changes in PTEs concentrations across the floodplain (spatially) and over time (temporally).
- Explaining the mechanisms responsible for changes in pore water PTEs concentrations.

1.2.2. Key research questions

Does flooding mobilise PTEs in floodplain soils?

What are the key mechanisms influencing the mobility of PTEs in floodplain soils?

1.2.3. Thesis hypothesis

Flooding events increase the mobility of PTEs as a result of release from the solid phase (floodplain soil) into the liquid phase (soil pore water). The magnitude of the change in pore water concentration is dependent on soil properties and flooding duration which, together, determines the key mechanisms driving mobilisation (i.e. adsorption/desorption, complexation, precipitation and reductive dissolution of oxides).

1.2.4. Thesis structure

Chapter 2; The impact of extreme rainfall on the mobility of potentially toxic elements in floodplain soil – A review

This chapter is a published paper in *Science of the Total Environment*. It presents a global perspective of climate change; how this will affect weather systems and flooding, and the subsequent effects on PTE mobility in floodplain soils. A key output from this work is the conceptual model, depicting the key processes influencing the mobility of PTEs after a soil becomes flooded. Knowledge gaps identified (e.g. the need for field-based studies) led to the experimental design in Chapter 5.

Chapter 3; Influence of floodplain topography on soil potentially toxic element concentrations

This chapter is formatted as a paper to be submitted to *Environmental Science: Processes & Impacts.* It presents a geospatial characterisation of the Loddon Meadow floodplain site, that is also used in Chapters 4 and 5. The paper clearly identifies the correlation between floodplain elevation and pseudo-total concentration of key PTEs found in the floodplain soil; identifying pollution from upstream in the catchment as the source of PTEs at the study site.

Chapter 4; Analysis of cation and anion mobility in floodplain soils: A comparison of in-situ and ex-situ soil pore water extraction methods

This chapter is formatted as a methods paper to be submitted to *Soil Systems Special Issue "Assessment and Remediation of Soils Contaminated by Potentially Toxic Elements (PTE)"*. It presents a comparison of pore water extraction methods; investigating the practical and scientific differences (strengths and weaknesses) between different methodological approaches. The results of this work were used to justify the pore water extraction method used in Chapter 5.

Chapter 5; Field observations to establish the impact of fluvial flooding on potentially toxic element (PTE) mobility in floodplain soils

This chapter is formatted as a paper to be submitted to *Science of the Total Environment*. It presents the results of field-based sampling in the winter of 2018-2019; collecting and analysing soil pore waters, from across the floodplain pre-flood, during a flood and post-flood. Multivariate statistical analysis was used to elucidate which of the key processes identified in the literature review dictate the mobility of a range of different PTEs.

Chapter 6; General discussion

This chapter provides an overview for the PhD research in the context of where the current understanding was in the research area. It pulls together the main findings from the PhD thesis and discusses research needs that are required to advance our understanding further. Global climate change and environmental pollution are two important topics of research; this PhD has demonstrated that field-based observations are required to better understand the dominant processes that drive PTE mobility in floodplain soils, so that site-specific predictions can be made on the environmental fate of legacy contaminants.

Chapter 7; Activities

This chapter showcases relevant work and activities completed throughout the PhD period. This includes: co-supervising BSc and MSc research projects, research presentations, and collaborations. The collaborations have resulted in co-authored published papers (references provided, but not included as thesis chapters) with other researchers at the University of Reading (Kelly *et al.* 2020) and University of York (Kiss *et al*. 2021). The specific contributions that I made to the two published papers are also detailed for clarity.

Kelly, T.J., Hamilton, E., Watts, M.J., **Ponting, J**. and Sizmur, T., 2020. The effect of flooding and drainage duration on the release of trace elements from floodplain soils. *Environmental Toxicology and Chemistry*, 39(11), pp.2124-2135. DOI 10.1002/etc.4830 https://setac.onlinelibrary.wiley.com/doi/full/10.1002/etc.4830

Kiss, T.B., Chen, X., **Ponting, J**., Sizmur, T. and Hodson, M.E., 2021. Dual stresses of flooding and agricultural land use reduce earthworm populations more than the individual stressors. *Science of The Total Environment*, 754, p.142102. DOI 10.1016/j.scitotenv.2020.142102 https://www.sciencedirect.com/science/article/pii/S004896972035631X?dgcid=author

Appendices

The appendices are included at the end of the thesis and comprise supporting information (tables and figures) for Chapters 2, 3, 4 and 5.

Chapter 2

This chapter is a paper published in the journal *Science of the Total Environment*

Ponting, J., Kelly, T.J., Verhoef, A., Watts, M.J., Sizmur, T., 2021. The impact of increased flooding occurrence on the mobility of potentially toxic elements in floodplain soil – A review. Sci. Total Environ. 754, 142040. https://doi.org/10.1016/j.scitotenv.2020.142040

2.0. Abstract

The frequency and duration of flooding events are increasing due to land-use changes increasing run-off of precipitation, and climate change causing more intense rainfall events. Floodplain soils situated downstream of urban or industrial catchments, which were traditionally considered a sink of potentially toxic elements (PTEs) arriving from the river reach, may now become a source of legacy pollution to the surrounding environment if PTEs are mobilised by unprecedented flooding events.

When a soil floods, the mobility of PTEs can increase or decrease due to the net effect of five key processes; (i) the soil redox potential decreases which can directly alter the speciation, and hence mobility, of redox sensitive PTEs (e.g. Cr, As), (ii) increasing pH increases chelation of metal cations (e.g. Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}), (iii) dissolved organic matter (DOM) increases, which chelates and mobilises PTEs, (iv) Fe and Mn hydroxides undergo reductive dissolution, releasing adsorbed and co-precipitated PTEs, and (v) sulphate is reduced and PTEs are immobilised due to precipitation of metal sulphides. These factors may be independent mechanisms, but they interact with one another to affect the mobility of PTEs, meaning the effect of flooding on PTE mobility is not easy to predict. Many of the processes involved in mobilising PTEs are microbially mediated, temperature dependent and the kinetics are poorly understood.

Soil mineralogy and texture are properties that change spatially and will affect how the mobility of PTEs in a specific soil may be impacted by flooding. As a result, knowledge based on one river catchment may not be particularly useful for predicting the impacts of flooding at another site. This review provides a critical discussion of the mechanisms controlling the mobility of PTEs in floodplain soils. It summarises current understanding, identifies limitations to existing knowledge, and highlights requirements for further research.

Key words; floodplain soil, flooding, climate change, potentially toxic elements, contamination, mobility

2.1. Introduction

Flooding is a major event that currently affects an estimated 20 to 300 million people per year, and accounts for around 40% of natural disasters occurring worldwide, threatening both social security and sustainable development (Euripidou and Murray, 2004; Hirabayashi and Kanae, 2009). Alterations to land use and land cover are having widespread implications for catchment characteristics; with soil sealing and impermeable surfaces increasing surface run-off, as well as a reduction of natural buffering environments such as forests and wetlands, meaning there is less capacity to accommodate flood waters in the same river reach (Dadson et al., 2017; Kundzewicz et al., 2014). There is growing evidence, from climate models, that short-term extreme weather events (e.g. high-frequency rainstorms, heat waves and wind storms) are likely to become increasingly frequent in many parts of the world, threatening the long-term functioning of the terrestrial system (Harvey et al., 2019; Kharin et al., 2007; Madsen et al., 2014; Pendergrass, 2018; Stagl et al., 2014). It is likely that populations will experience warmer and drier summers, and an increase in the intensity of heavy rainfall, contributing to more frequent pluvial, fluvial, groundwater or coastal flooding, and resulting in the occasional inundation of land that has rarely been flooded in the past (Barber et al., 2017; Kundzewicz et al., 2014; Schaller et al., 2016). The likelihood of flooding is also determined by antecedent soil moisture conditions. The proportion of soil pore space that is filled with water at any given time is largely dependent on local hydrological processes and stores including; infiltration, surface and sub-surface runoff (when rainfall intensity exceeds infiltration capacity), redistribution and drainage to/from groundwater, evaporation, and transpiration (Stagl et al., 2014).

Soil contamination is among the most serious threats to soil resources globally (Nriagu et al., 2007; Srivastava et al., 2017; Tóth et al., 2016b). Since many commercial, industrial, residential and agricultural developments have historically been situated adjacent to rivers; they contribute to the contamination of river sediments, and these sediments are often deposited onto the floodplain soils downstream by overbanking river water during a flooding event (Arnell et al., 2015; Nshimiyimana et al., 2014; Zhao et al., 1999). Here we use the term PTEs, also referred to in the literature as ‘trace elements’ or ‘heavy metals’, to encompass all metals, metalloids, non-metals and other inorganic elements in the soil–plant–animal system, of which their mobility and potential toxicity to that system and/or humans is largely dependent upon their concentration, bioavailability and chemical form (Hooda, 2010; Rodgers et al., 2015). The term "mobility” is a concept that has been frequently used to estimate the risk of contamination from the soil to the surrounding environment by PTEs (Domergue and Vedy, 1992). Here we define mobile PTEs as those elements that are dissolved in soil pore water or associated with colloids and thus capable of leaching from the soil profile, or being taken up into plants or soil organisms. The mobility and subsequent fate of PTEs in periodically (occasionally) flooded soils (such as floodplain soils) are imperfectly understood. The legacy of historic contamination and continuing increases in emissions from urban activities pose a serious environmental threat globally (de Souza Machado et al., 2016; Srivastava et al., 2017). Human actions to mitigate and adapt to the impacts of climate change may influence the fate of contaminants, with climate change itself also potentially affecting the toxicity of the contaminants within the environment (Stahl et al., 2013).

The aim of this literature review is to provide an understanding of the factors involved in the mobility of PTEs in soil by pulling together interdisciplinary knowledge in this area. The review will first consider in more detail the expected changes to global rainfall patterns, the implications of these changes for flooding, and the role that floodplains play during inundation, as well as the changes they undergo. The review will then showcase how PTEs have entered the floodplain soil and how flooding influences soil biogeochemical processes which, in turn, influence PTEs mobility, using examples from the literature. Finally, this knowledge is used to identify gaps that will help to make recommendations for future research into the effects of flooding on the mobility and fate of PTEs.

2.1.1. Expected changes to global rainfall patterns and implications for flooding

Anthropogenic (human) activities including intensified land use; urbanisation, forestry, cultivation, and fossil energy use have increased atmospheric greenhouse gas concentrations which are driving changes in climate and leading to increases in rainfall intensity and surface run-off that are associated with increased flood risk (Bronstert, 2003; Chang and Franczyk, 2008; Kharin et al., 2007; Kundzewicz et al., 2014; Wheater and Evans, 2009). Mean global temperatures have risen by 1.1 °C since the end of the 19th century; the “Paris Climate Agreement” seeks to contain global mean temperatures well below 2°C and, ambitiously, below 1.5°C (Alfieri et al., 2017; Bronstert, 2003; Huddart et al., 2020; Mullan et al., 2019). The Intergovernmental Panel on Climate Change (IPCC) has predicted that under the A1B (medium) emissions scenario, temperatures will increase between 1.1 and 6.4 °C by the year 2100, leading to an increase in atmospheric water holding capacity and therefore variations to seasonal rainfall (Arnell et al., 2015; Bell et al., 2012; Chan et al., 2014; Clemente et al., 2008; González-Alcaraz and van Gestel, 2015; Jenkins et al., 2009). It has been argued that we will experience an intensification of short-duration heavy rainfall events rather than a uniform increase in the daily average rainfall (Chan et al., 2014; Hirabayashi et al., 2008; Kharin et al., 2007; Kundzewicz et al., 2014).

An IPCC Special Report (SREX) on climate extremes (IPCC, 2012) assessed it is *likely* there have been statistically significant increases in the number of heavy precipitation events in more regions than significant decreases, with strong regional and sub-regional variation. The observed changes to precipitation extremes have been found to be far less spatially coherent or statistically significant compared with changes found in temperature extremes (Kundzewicz et al., 2014). Projected scenarios with 4°C warming showed more than 70% of the global population will face increased flood risk (Alfieri et al., 2017). Increases in flood frequency are expected in; Europe, America, Southeast Asia, eastern Africa, and Peninsular India. Populations in regions such as Bangladesh, Mumbai and Thailand are potentially at higher risk from flooding due to predicted increases in rainfall, coupled with changes in land use (e.g. irrigation schemes and construction of dams), and increasing population size requiring rapid expansion of urban areas (Hirabayashi et al., 2013; Kundzewicz et al., 2014; Tockner et al., 2010). However, climate projections tend to have relatively low levels of model confidence, particularly for the prediction of fluvial floods because there is still relatively limited evidence and the causes of regional changes to flood occurrence are complex (Hirabayashi et al., 2013).

Flooding tends to be heterogeneous as it is affected not only by variability of the climatological and hydrological systems but also by land-use and the effect is has on the storage capacity of the receiving catchment (storage and drainage basin conditions). Changes to the characteristics of precipitation (the frequency, intensity and timing of rainfall) will have decisive implications for flood risk (Bronstert, 2003; Hirabayashi and Kanae, 2009; Kundzewicz et al., 2014). However, pre-existing high river levels and groundwater levels, as well as saturated soils are equally important to establish the capacity of the receiving catchment to cope with further rainfall (Maggioni and Massari, 2018; Wilby et al., 2008). The extent of flooding in a particular catchment will depend largely on the topography (variation in elevation), along with vegetation type, proportion of land used for cultivation and the extent of urbanised areas positioned upstream (Arnell et al., 2015; Bell et al., 2012; Bronstert, 2003; Chang and Franczyk, 2008; Kundzewicz et al., 2014; Qiao et al., 2019). Urbanisation is a global issue; with more than half the world's population now living in cities, the process of urbanisation is leading to greater human occupation of floodplains, often with inadequate drainage planning (Kundzewicz et al., 2014; Pathirana et al., 2014).

The probability of flooding occurring in a particular region is often related to regional processes like El Niño Southern Oscillation (ENSO) cycle and the North Atlantic Oscillation (NAO) that, in turn, cause global impacts. The intensity (frequency and amplitude) of both ENSO and NAO are influenced by other modes of variability, for example; Pacific Decadal Oscillation (PDO) and Interdecadal Pacific Oscillation (IPO) which cause opposite atmospheric and sea surface temperatures and can therefore determine the magnitude of floods (Grimm and Tedeschi, 2009; Johnson et al., 2020). ENSO is a rapid warming of the sea surface temperature (by 1–5 °C) of the equatorial Pacific over the duration of a few weeks, resulting in extreme rainfall and increased cyclone activity in some regions, and risk of drought and forest fires in others (Berz et al., 2001; Grimm and Tedeschi, 2009; Karl and Trenberth, 2003; Kundzewicz et al., 2014; Tedeschi and Collins, 2016). Periods of extreme rainfall and subsequent flooding have been found to correlate with ENSO events in North and South America as well as in Africa (Berz et al., 2001; Brönnimann, 2007; Kundzewicz et al., 2014). NAO is an atmospheric pattern that affects the severity of winter temperatures and precipitation over Europe and eastern North America (Karl and Trenberth, 2003). Intense rainfall is a common cause of river basin flooding; however, in high latitude regions it is changes in temperatures altering the timing of seasonal snowmelt and causing glacier retreat that commonly causes flooding, for example in north-eastern Europe, Central and South America, and in polar regions such as the Russian Arctic (Blöschl et al., 2017; Hirabayashi et al., 2008; Kharin et al., 2007; Kundzewicz et al., 2014; Stagl et al., 2014). Rising global sea-level (11-16cm in the 20th century and a further 0.5m predicted this century) will certainly increase risk of flooding caused by tidal processes, with current estimates that 630 million people live on land below projected annual flood levels for 2100 (Kulp and Strauss, 2019). While there is uncertainty regarding the effect that future climate change will have on river levels (Prudhomme and Davies, 2009), changes made to land-use, and land cover, for example by urbanisation, will drive changes in the local climate (at the kilometre scale) influencing the hydrometeorological regime and resulting in more flooding (Foley et al., 2005; Hirabayashi and Kanae, 2009). Pathirana et al. (2014), using a 3D atmospheric model coupled with a land surface model (WRF-ARW) in southern India, found that in three out of four simulated cases there was a significant increase in local extreme rainfall when urbanisation in the area increased. This work was conducted in southern India, however the model could be applied and validated to other regions to establish whether this correlation is found globally.

2.1.2. The role of floodplains during floods

Floodplains are by definition dynamic environments subjected to fluctuations between flooding and drying (Vijver et al., 2007). They are distinctive landscape features, often on low-lying ground, and characterised by a high spatio-temporal heterogeneity (Schulz-Zunkel et al., 2015; Stuart and Lapworth, 2011; Tockner et al., 2010; Tockner and Stanford, 2002). Periodic overbank inundation from the adjacent watercourse, overland flow, subsurface flow, and changes to the groundwater levels result in a constantly changing water balance and degree of floodplain saturation (Stuart and Lapworth, 2011; Tockner and Stanford, 2002). Floodplain topography and variations in elevation are usually slight but have an important effect on the degree of soil saturation across the floodplain, depending on the overall water balance from surface and sub-surface run-off (Arnell et al., 2015; Kundzewicz et al., 2014; Qiao et al., 2019).

There are various sources and pathways of water that can lead to the inundation of a floodplain, including lateral overflow of rivers or lakes, rising groundwater, upland sources, and direct precipitation. Several different factors and water sources normally contribute to a flooding event, thus making flooding a complex phenomenon to study (Junk et al., 1989; Tockner and Stanford, 2002). Fluvial flooding tends to occur when excessive rain falls over an extended period of time, leading to a river exceeding its capacity, or because of heavy snow that subsequently melts and, via surface run-off, rapidly fills the river channels when infiltration is low because of frozen soils below the snow layer (Blöschl et al., 2017).

River flow regimes are affected by the increased rainfall and this also has the potential to affect erosion and generate additional sediment loads and particulate organic matter (POM) for deposition within river channels, lakes and estuaries (Arnell et al., 2015; Le Gall et al., 2018; Rinklebe and Du Laing, 2011). Intense rainfall over a short timescale (usually less than six hours i.e. "flash floods") can also cause rivers to overbank leading to an intense, high velocity torrent of water that moves through river beds, disturbing river sediments and potentially bringing more PTEs contamination with the flood water, greatly influencing the contaminated status of the floodplain (Blöschl et al., 2017; Maggioni and Massari, 2018). The water inundating the floodplain contains dissolved matter (i.e. free ions, inorganic and organic complexes and uncharged molecules) as well as particulate matter (i.e. large organic and inorganic polymers, oxides, clay minerals and organic matter) (Kirk, 2004). The sediment loads travel at different rates due to their particle size, which reflects the texture of the river bed and bank (Malmon et al., 2004). Approximately 90% of PTEs load has been associated with sediment particles, with dissolved PTEs playing a comparatively minor role in pollutant transfer to floodplains (Ciszewski and Grygar, 2016). There have been many fluvial geomorphology studies showing how erosion and sedimentation have been influenced by climatic variability in the past (e.g. Lewin and Macklin, 2010; Macklin and Rumsby, 2007; Mullan et al., 2019), indicating that rivers are sensitive to climatic change (Arnell et al., 2015). Fluvial flooding is receiving increased scientific and political interest because of the potential impact that climate change may have on this type of flooding, with climate model projections showing an increased flood risk at a global scale (Pappenberger et al., 2012; Wilby et al., 2008).

In floodplains that are underlain by permeable deposits, increased rainfall causes groundwater to rise (leading to groundwater flooding), which can result from direct rainfall recharge, when the soil water storage potential is exceeded, as well as flow into the floodplain sediments from rivers with high water levels, and from areas inundated with fluvial flooding. However, good hydraulic connection between river and aquifer means that the aquifer can drain quickly as fluvial flood waters recess. Groundwater flooding in these settings is relatively short-lived compared with other groundwater flood settings, for example in chalk catchments (MacDonald et al., 2012).

With increased frequency of rainfall events predicted, it has become widely recognised that the storage of floodwater on floodplains can help to reduce the magnitude of a flood downstream. Thus, floodplains are useful for flood risk management (Acreman et al., 2003; Vink and Meeussen, 2007). As a result, floodplains may be deliberately managed to allow flooding to occur through engineered soakaways in order to protect an urban residential area (Lane, 2017; Wheater and Evans, 2009). It is important to understand the potential implications of these types of management practices on mobilisation of PTEs that may be associated with the sediments deposited on the floodplain during past flooding events.

2.1.3. Changes that floodplain soils undergo during and after inundation

Extreme rainfall events leading to flooding have generally been found to alter soil physical and chemical properties and influence biological processes (Harvey et al., 2019). The fluctuations between inundation and subsequent drying, associated with periodically flooded soils, are major drivers of spatial and temporal differences in soil properties that affect the biogeochemical processes taking place in floodplain soils (Schulz-Zunkel et al., 2015; Tockner et al., 2010). These changes include; a decrease in redox potential (E_H), which leads to, for example, reduction of iron (Fe) and manganese (Mn), which in turn can influence the soil pH (Rinklebe and Shaheen, 2017). Other processes affected include sulphur-cycling, changes to the presence of chelating agents such as dissolved organic carbon, mineralisation of POM and suppression of microbial activity (Poot et al., 2007; Puchalski, 2003; Schulz-Zunkel et al., 2015; Schulz-Zunkel and Krueger, 2009). Ibragimow, Walna, and Siepak (2013) showed, through analyses of fluvial samples before and after a flood, that the physicochemical properties (grain size, E_H, pH, POM, and calcium carbonate contents) as well as the total and available concentration of PTEs had changed. Harvey et al. (2019) found that after UK floods receded in the winter of 2013-14 there was a decrease in the soil bulk density, pH and available P. The flood was found to have had a negative effect on the overlying vegetation and caused a shift in the microbial community structure.

Inundation during a flooding event can carry PTEs dissolved in rising groundwater and potentially contaminated suspended sediment from upstream overbanking water, depositing this onto the floodplain during a flood (Acreman et al., 2003; Bednářová et al., 2015; Du Laing et al., 2009; Gröngröft et al., 2005; Junk et al., 1989; Rudiš et al., 2009; Tockner and Stanford, 2002; Weber et al., 2009). Subsequently, this deposition of suspended riverine sediments/POM by flood water results in the floodplain topsoil becoming a sink for PTEs (Du Laing et al., 2009; Frohne et al., 2011; Nshimiyimana et al., 2014; Overesch et al., 2007; Rinklebe et al., 2007; Visser et al., 2012; Zhao and Marriott, 2013). As a result, floodplain topsoil (uppermost 15cm) can often initially contain elevated concentrations of PTEs such as the metalloid; arsenic (As), and metals; chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn), but later due to post-depositional reactions with organic matter/other organic components the PTEs concentrations will vary (Adekanmbi et al., 2020; Ciszewski and Grygar, 2016; Hurley et al., 2017; Izquierdo et al., 2013; Jiao et al., 2014; Kelly et al., 2020). When laboratory experiments are undertaken on samples gathered from floodplain site, soils are collected as single or composite samples, air or oven dried and then homogenised, resulting in a loss of soil stratigraphy and therefore the potential differences in PTEs concentration with depth may be unaccounted for (Ciszewski and Grygar, 2016). Zhao and Marriott, (2013) looked at PTEs concentrations along a vertical profile and found that there were peak values at varying depths; affected by translocation and duration of inundation. The process of breaking up of soil samples for laboratory experiments will make interpretation of PTEs levels difficult. Kelly et al. (2020) took intact soil cores to overcome this and more closely reflect natural samples, they too found the duration of inundation influenced the fate of PTEs.

The biological health of floodplain soils is important as they act as an interface between terrestrial and aquatic environments, therefore playing an important role in maintaining the environmental quality of surface waters (Izquierdo et al., 2013; Stuart and Lapworth, 2011). Artificial or constructed wetlands have been used for flood and pollution control; storing and filtering excess water to protect rivers from various kinds of runoff e.g. high nutrient loads from farm land (Blackwell and Pilgrim, 2011; Ellis et al., 2003; Rizzo et al., 2018). An example of this technology is demonstrated at the Rothamsted Research North Wyke experimental farm (Pulley and Collins, 2019). Even if river and groundwater water quality improves due to the implementation of more stringent environmental policy, contaminated floodplains remain as a legacy of historic upstream pollution (Bradley and Cox, 1990; Förstner, 2004; Kowalik et al., 2004). With increased frequency and duration of flooding, there is the possibility that changes to soil properties and biogeochemical processes will ultimately lead to the mobilisation of PTEs from floodplain soils (Ciszewski and Grygar, 2016; González-Alcaraz and van Gestel, 2015). Therefore, historically contaminated floodplains may become a source of legacy pollution to the surrounding environment (Kelly et al., 2020; Pulchalski, 2003; Schulz-Zunkel and Krueger, 2009), as shown in Figure 2.1.

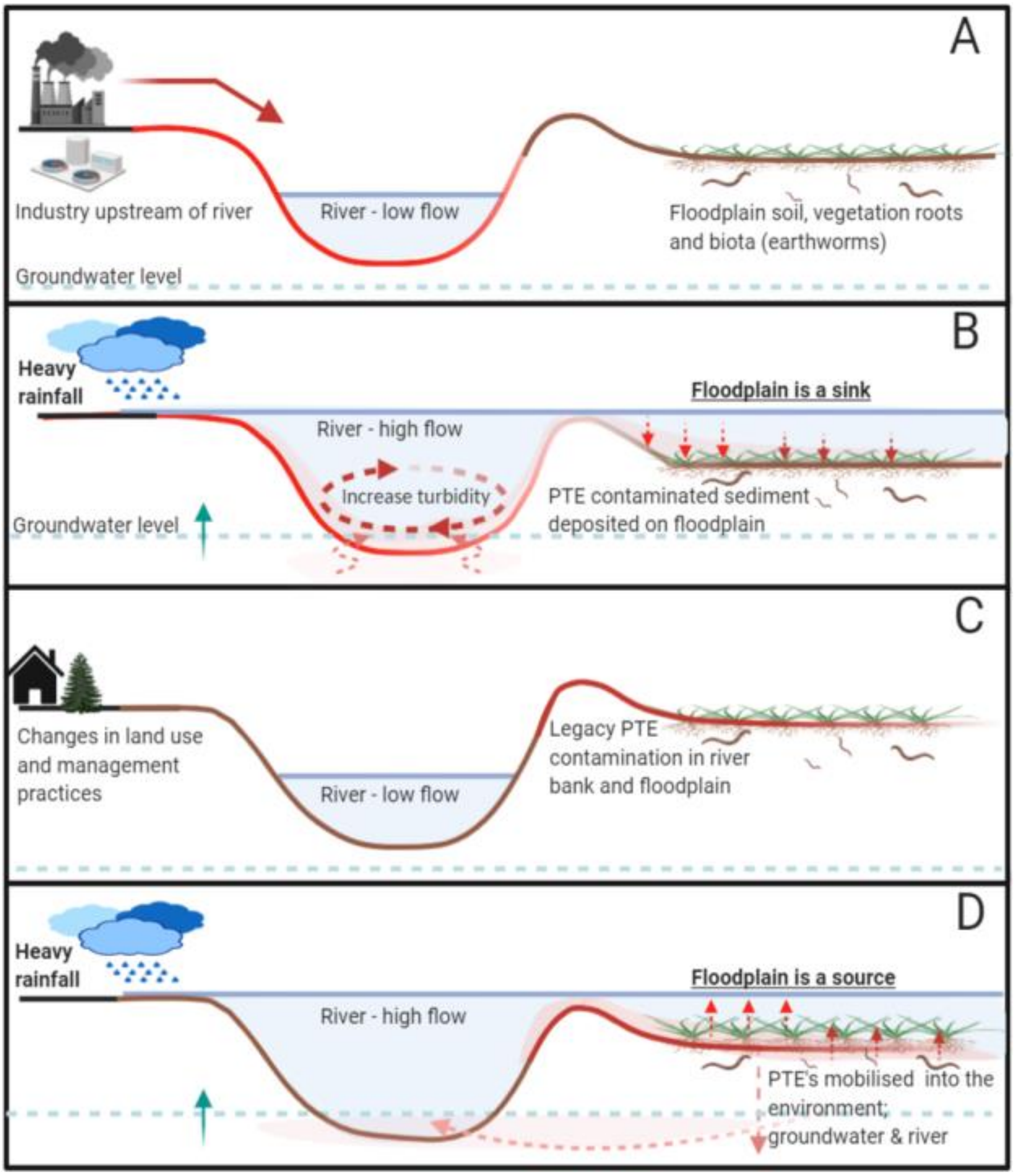


Figure 2.1: How floodplains may switch from being a sink of pollution to becoming a source of legacy pollution: *A) PTEs contaminated river sediment (red) due to industry in the catchment upstream, B) heavy rainfall influences the receiving catchment (increased river flow and groundwater level), resulting in flooding and the deposition of contaminated sediment onto the adjacent floodplain; dissolved contaminants may also reach the floodplain surface via rising groundwater, C) Later, the river is uncontaminated (brown) due to rising environmental quality standards, with legacy of PTEs contamination (red) in the river bank and floodplain soil, D) heavy rainfall results in flooding of the contaminated floodplain, mobilisation of the legacy PTEs by desorption and resuspended particulate matter into the surrounding environment and thus making them potentially available for uptake by vegetation and soil organisms, as well as pollutant transfer leaching into the overlying flood water, the groundwater, and ultimately the river. Created with BioRender.com.*

2.2 Impact of flooding on the mobility of potentially toxic elements in floodplain soil

2.2.1 PTEs in floodplain soil

Several PTEs are also essential nutrients that are required in low concentrations for healthy functioning and reproduction of microorganisms, plants, and animals, although may become toxic in high concentrations, these include; Cu, Cobalt (Co), Nickel (Ni), Vanadium (V), Zn, chlorine (Cl), Mn, Fe, boron (B), and molybdenum (Mo) (Adamo et al., 2014; Hooda, 2010; Wyszkowska et al., 2013). Other PTEs are non-essential and can cause toxicity even when they are found at low concentrations, these include; As, Pb, and mercury (Hg); (Adamo et al., 2014; Nriagu et al., 2007; Wuana et al., 2011; Wyszkowska et al., 2013). Cadmium (Cd) is generally considered a non-essential element to soil organisms, but it has been found to be beneficial to some microalgae (Xu et al., 2008) Chromium can be considered a micronutrient but its toxicity depends on its valence state (i.e. Cr (VI) is the more mobile and toxic form compared with Cr (III)). Redox potential therefore not only affects the mobility of PTEs, but also their toxicity (Lee et al., 2005; Shahid et al., 2017). The consequences of PTEs contamination of soils are rarely observed with immediate effect, rather they tend to cause delayed adverse ecological changes, due to the fact that PTEs are persistent in the environment for long periods, non-biodegradable and can only be bio-transformed through complex physico-chemical and biological processes (Chrzan, 2016; Czech et al., 2014; Hooda, 2010). PTEs cause adverse ecological effects on plants and organisms such as impacting their activity, growth rate/yield, metabolism and reproduction, causing symptoms of physiological stress and potentially death. The extent of the adverse effect depends on the exposure route (ingestion, dermal absorption or uptake of pore water) and time, resistance (related to residence time of the PTEs in the environment) and detoxification mechanisms of the plant or animal (Alloway, 2013a; Eggleton and Thomas, 2004; Ehlers and Loibner, 2006; Hooda, 2010; Pan et al., 2018; Shahid et al., 2017; Winger et al., 1998). Leaching of PTEs from the floodplain soil into the groundwater or river will also cause adverse effects to aquatic organism in these environments (Zia et al., 2018).

PTEs are either present naturally in the floodplain soil from the underlying or upstream geology and subsequent geogenic processes (e.g. weathering of parent material, emissions from volcanoes, forest fires) or introduced by anthropogenic sources, including solid and dissolved inputs from; aerial deposition, transport emissions, industrial, municipal and diffuse runoff from agricultural practices landfills and sewage treatment facilities (Alloway, 1995; Álvarez-Ayuso et al., 2012). PTEs can be adsorbed to colloidal suspended particulate material, transported in the river water and accumulate in the floodplain soil during inundation (Du Laing et al., 2009; Frohne et al., 2011; Peijnenburg et al., 2007; Rinklebe et al., 2007). PTEs have been found to be primarily associated with fine-grained clay or silt minerals and can reside in the floodplain for longer when compared with river sediments, as they are less likely to be susceptible to erosion (Lučić et al., 2019; Malmon et al., 2002). Contamination of the floodplain soil may result from a point source such as a sewage treatment facility, or from diffuse sources that have no specific point of discharge (e.g., agricultural applications). Impacts of diffuse pollution are difficult to predict as they can be affected by weather systems, meaning soils far from the source may be affected (Gregory et al., 2015; Neal et al., 1996). The anticipated changes to intense rainfall may result in increased delivery of diffuse pollution to rivers and groundwater (Arnell et al., 2015; Foulds et al., 2014b), particularly as contaminated floodplain soils may become a diffuse source of pollution themselves during a flooding event (Schulz-Zunkel and Krueger, 2009).

2.2.2. Influence of flooding on PTEs mobility

During a flooding event, biogeochemical processes occur in the floodplain soil at the oxic-anoxic interface and in the anoxic layers. The kinetics of these processes are of great importance because the location of the oxic-anoxic interface is subject to change due to fluctuating water table levels (Du Laing et al., 2009; Puchalski, 2003). In their review of trace metal behaviour in floodplain sediments, Du Laing et al. (2009) state that the spatial occurrence of processes affecting metal mobility and availability is largely determined by the topography of the floodplain. Remobilisation of PTEs from sediments into the overlying water column during a flooding event depends on the flood regime; the frequency of these intense floods which flush or remobilise contaminated material as well as the duration or alternation of flood with dry spells (Arnell et al., 2015; Foulds et al., 2014b; González-Alcaraz and van Gestel, 2015). Whilst research has suggested that the longer the flood duration, the greater the metal mobility (Shaheen et al., 2014a, 2014b), Stafford et al. (2018) suggest that even short periods of soil saturation can have an influence the solubility of PTEs.

There are conflicting results in the literature regarding the effect of flooding on the mobility of PTEs, expressed by changes in PTEs concentration (increase or decrease), in floodplain soils (Table SI-2.1). This may largely be the result of different site-specific conditions (e.g. soil pH, texture, mineralogy) or different laboratory set-ups (e.g. submerging soils in deionised water, or the use of inert gas to simulate the anoxic conditions of a flood), illustrating the complexity of the processes involved in mediating PTEs mobility in floodplain soils (Abgottspon et al., 2015; Du Laing et al., 2007; Frohne et al., 2011; Schulz-Zunkel et al., 2015). Many of the considerations in the literature are founded on research of soils or sediments in microcosm experiments, which often involves homogenising the soil samples, resulting in loss of natural soil structure, loss of roots and biota, short-exposure time to flood conditions, and the control of variable factors such as temperature and soil water conditions (Frohne et al., 2011; Rinklebe et al., 2010). Redox conditions are often simulated and controlled through additions of O_2, to increase E_H, and N_2, to lower E_H (Frohne et al., 2014, 2011; Schulz-Zunkel et al., 2015; Shaheen et al., 2016; Shaheen and Rinklebe, 2017). These differences make extrapolation of these laboratory-based findings to field situations difficult (Hooda, 2010).

A key factor in determining the fate and transport of PTEs is their chemical form which, in combination with environmental factors, can influence their mobility in the soil. The chemical form of an element is often referred to as its "speciation", "oxidation state", or "valence" (Rodgers et al., 2015; Wuana et al., 2011). There are important redox sensitive PTEs for which the oxidation state has a large influence on solubility and mobility. For example, Cr(VI) is more mobile than Cr(III), but As(V) is less mobile than As(III) (Frohne et al., 2015; Rinklebe et al., 2016a; Schulz-Zunkel et al., 2015; Shaheen et al., 2014b; Yang et al., 2015). Speciation of PTEs within the environment has a distinct influence upon their behaviour; specifically, reactivity, toxicity, mobility and bioavailability within the floodplain (Du Laing et al., 2009; Gambrell, 1994; Hooda, 2010; Rodgers et al., 2015). This understanding is important for predicting the environmental impact of contaminated soils, although we are only beginning to converge on consensus on how bioavailability or speciation soil tests can help with risk-assessments, while this is slowly introduced into legislation (Cipullo et al., 2018a; Naidu et al., 2015, 2008; Ng et al., 2015).

2.2.3. Changes to soil physical and chemical properties that influences PTEs mobility

Potentially toxic elements present in soils are often adsorbed to or protected within aggregates that are stabilised by organic matter. During a flooding event, these particles may be leached through the soil profile, or suspended in flood waters where they may be redistributed across floodplain soils, or be carried downstream by the river, potentially contributing to river pollution of the contamination of downstream floodplains. The solubility and therefore mobility of PTEs from the soils to the surrounding environment depends largely on the intrinsic soil physical and chemical properties (texture, availability of soil particulate surfaces and dissolved organic matter, salinity and the presence of Fe/Mn oxides, carbonates, phosphates and sulphides) and a range of variables that are directly affected by periodic inundation of the floodplain, including; soil pH, redox potential (E_H), dissolved organic carbon (DOC) and the valance of individual PTEs (Adewuyi and Osobamiro, 2016; Dawson et al., 2010; Du Laing et al., 2009; Frohne et al., 2015; González-Alcaraz and van Gestel, 2015; Lee et al., 2005; Puchalski, 2003; Rinklebe and Du Laing, 2011; Schulz-Zunkel and Krueger, 2009; Shaheen et al., 2016; Shaheen and Rinklebe, 2014; Steinnes, 2013). A conceptual model (Figure 2.2) has been produced based on our literature review (Table SI-2.1) as a way of visualising the various factors and processes influencing the solubility of PTEs in a floodplain soil.

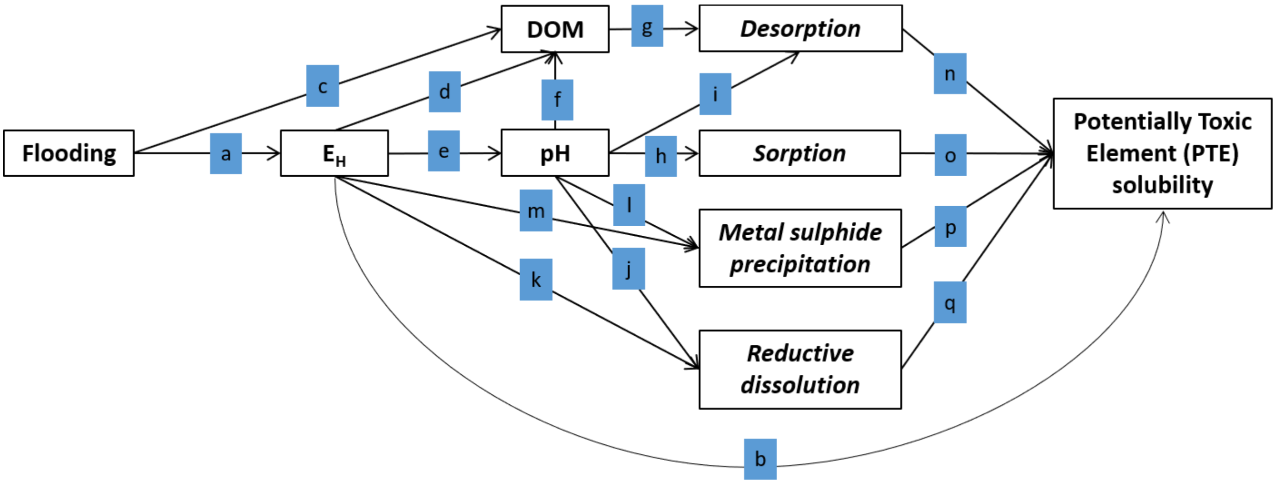


Figure 2.2: Conceptual model depicting the key processes influencing the solubility of Potentially Toxic Elements (PTEs) after a soil becomes flooded.
a) Oxygen is rapidly consumed by microbial and root respiration, decreasing the redox potential (E_H). b) Decreasing E_H can lead to redox sensitive elements (e.g. As and Cr) changing valence state, directly affecting solubility. c) Greater soil moisture brings dissolved organic matter (DOM) into solution. d) Reducing conditions (lower E_H) leads to the release of more DOM. e) Lower E_H results in the reduction of Fe and Mn, consuming protons (H^+) and increasing pH. f) an increase in pH often results in the release of more DOM. g) DOM acts as a chelating agent, forming soluble organo-metal complexes with PTEs desorbed from soil surfaces. h) as pH increases metal cations (e.g. Cu, Pb, Zn) are adsorbed on pH-dependent adsorption sites of particulate matter. i) as pH increases, anions and oxy-anions (e.g. As) are desorbed from pH-dependent adsorption sites. j) Dissolution of reducible Fe and Mn oxides is facilitated by increasing pH. k) Microbial reduction of Mn and Fe oxides increases their solubility and can cause reductive dissolution of co-precipitated PTEs. l) An increase in pH facilitates the precipitation of insoluble metal sulphides. m) Microbial reduction of sulphate results in the precipitation of metal sulphides. n) Release of adsorbed PTEs from soil surfaces increases PTEs solubility. o) Immobilisation of PTEs through adsorption processes reduces PTEs solubility. p) Reductive dissolution of PTEs associated with Fe and Mn oxides increases PTE solubility. q) Precipitation of PTEs as metal sulphides decreases PTEs solubility.

Soil physical, chemical and biological processes determine the mobility and redistribution of PTEs (Hooda, 2010). These processes include; sorption, desorption, dissolution and precipitation (Puchalski, 2003; Wijngaard et al., 2017). Subsequently, PTEs are redistributed into different geochemical fractions, associated with other soluble species, released from the soil matrix into the soil solution or pore water, and transferred through the ecosystem and food web to other terrestrial or riparian areas downstream from the floodplain; thus potentially becoming a risk to human and environmental health (Adamo et al., 2014; Adewuyi and Osobamiro, 2016; Baran and Tarnawski, 2015; Dang et al., 2002; Du Laing et al., 2009; Rinklebe et al., 2016a; Schulz-Zunkel et al., 2015; Shaheen et al., 2014a, 2014b; Sizmur et al., 2011b). Sorption processes that control PTEs mobility and bioavailability in soil are affected by the soil pH, redox and their interactions with other ions and substances present in soil solution (Antoniadis et al., 2018; Frohne et al., 2011; Ostergren et al., 2000; Violante, 2013).

Sorption processes are influenced by the changing conditions that flooding brings, particularly with regards to soil moisture content, temperature and redox potential. The mobility of PTEs in flooded soils is closely related to changes in redox potential which, in turn, is altered by flooding. This can have direct impacts on the mobility of redox sensitive PTEs (e.g. As and Cr). Inundation of soils with floodwater may indirectly affect PTEs mobility and speciation because it also influences, the population, community composition, and behaviour of invertebrates inhabiting the floodplain which, in turn, influence the mobility of PTEs through their burrowing and bioturbation behaviour. For example, earthworms are known to increase the mobility of PTEs due to passage through the earthworm gut (Sizmur et al., 2011b; Sizmur and Richardson, 2020) and their populations are supressed by flooding events (Plum and Filser, 2008; Kiss et al., in review). Bioturbation/bioirrigation behaviour by chironomid larvae has been found to increase oxygen uptake at the soil/sediment-water interface, promoting POM decomposition that results in the release of dissolved organic matter and subsequent release of PTEs (Y. He et al., 2019). Furthermore, the reduction of Mn and Fe can cause reductive dissolution of co-precipitated PTEs, and an increase in pH facilitates the precipitation of PTEs as insoluble sulphides. The mobility of PTEs can therefore increase or decrease due to the net effect of these processes (Figure 2.2). Which process dominates will depend primarily on the mineralogy of the soil.

The following sub-sections will explain how key soil physical and chemical properties are affected by flooding and how this influences PTEs mobility, followed by a discussion on the role of soil organisms and plants in mediating PTEs mobility in floodplain soils. Attention will be given to how each of these factors influence each other to distinguish direct and indirect impacts on PTEs mobility.

2.2.3.1 Soil texture and related properties

Soil texture is a stable property that refers to the physical composition of mineral fragments; sand, silt and clay and varies due to differences in underlying or upstream geology. The texture and related clay mineralogy reflect the particle/pore size distribution and overall soil surface area (Amacher et al., 1986) which, in turn, affects the soils' water holding capacity (WHC); the maximum quantity of water a soil can potentially contain, also known as the field capacity (Stürck et al., 2014). Therefore, soil physical properties play a role in flood duration because they determine the soils' ability to receive (via infiltration) and drain water during a rainfall event (Rinklebe et al., 2007). Clayey soils are likely to be saturated for longer than freely draining sandy soils (Sherene, 2010). Soil hydraulic (water retention and hydraulic conductivity curve) as well as thermal properties (thermal conductivity and heat capacity) affect the hydrothermal regime of the soil. Together these properties determine the ease in which water, and dissolved PTEs, moves through the soil pore continuum, how much water can be stored in the pore volume, and how soil temperature varies with depth. These properties are strongly dependent on soil texture, pore size distribution and mineralogy (Hillel, 1998; Tack et al., 2006; Thomas et al., 2016). Soil temperature affects the flow of water through the soil due to changes in viscosity and hence affects infiltration calculations (Gao and Shao, 2015; Prunty and Bell, 2005), so this is often corrected for when reporting hydraulic conductivity data (Thomas et al., 2016).

PTEs must be in the soluble phase or associated with colloids to be transported through the soil. The soil properties will play a part in the movement of PTEs into and out of the soil solution. Clay minerals and organic matter compounds have a large number of binding sites, so act as adsorption surfaces for PTEs in soils. The type of clay mineral present (kaolinite, illite, montmorrilonite etc.) will also affect the specific surface area (Meegoda and Martin, 2019; Tack et al., 2006). As a result, soils with high clay and silt (fine fractions) tend to retain higher amounts of PTEs, compared to course textured sandy soils (Sherene, 2010; Zhao et al., 1999).

2.2.3.2 Organic matter

Soil POM, along with the surfaces of clay particles and Fe and Al oxides, acts as a binding phase for PTEs due to the attraction of positively charged cations to negatively charged surfaces (Evans, 1989). Thus, dissolved organic matter raises the cation exchange capacity (CEC) of a soil, and is thus considered to be an important factor controlling PTEs distribution and mobility in floodplain soils and sediments (Baran and Tarnawski, 2015; Bufflap and Allen, 1995; Du Laing et al., 2009; Ehlers and Loibner, 2006). The mechanisms that bind the PTEs with particulate and dissolved organic matter include adsorption, complexation and chelation (Alvim Ferraz and Lourenço, 2000; Y. He et al., 2019; Selinus et al., 2005). Floodplains are subject to changing water table levels and occasional inundation that brings about associated changes in redox conditions. This can result microbially mediated soil POM degradation, either during prolonged periods of flooding or in the subsequent oxidising conditions when the flood recedes, which releases organically bound PTEs, such as As, Cu, Co, Cr, Ni, Pb, and Zn from the soil into the soil solution (Adewuyi and Osobamiro, 2016; Alvim Ferraz and Lourenço, 2000; Dang et al., 2002; Kalbitz and Wennrich, 1998; Koretsky et al., 2007; Rinklebe and Du Laing, 2011). Therefore, the extent to which flooding of soils results in the mobilisation of PTEs into solution is mediated by the proportion of the PTEs that are associated with soil POM, and the susceptibility of this organic matter to degradation (as a result of microbial activity (Fe(III) and Mn(IV)-reducing micro-organisms) under reducing conditions. The free ions that are then in solution are highly reactive with the solid phase and are thought to be a major determinant of bioavailability and causing the most significant biological effects (Bufflap and Allen, 1995; Dang et al., 2002; Dawson et al., 2010; Degryse et al., 2009; Lloyd, 2003).

2.2.3.3 Salinity

Salinity is proportional to the conductivity of a sample solution; which is a measure of its ability to conduct or carry electric current and depends on the presence of charged ion species (anions and cations) (Ander et al., 2016; de Souza Machado et al., 2018; De Vivo et al., 2008)). Increasing salinity in flood water is associated with an increase in major cations that compete with PTEs for sorption sites. This competition promotes PTEs desorption from the floodplain soil in the absence of sulphides and hence increases total PTEs concentrations in the soil pore water (Rinklebe and Du Laing, 2011). The presence of Ca-salts releases more PTEs into the soil solution compared with Na-salts that are less competitive for sorption (Du Laing et al., 2009; Hahne and Kroontje, 1973).

Changes in salinity may affect the soil physical properties and result in a destabilisation of the soil structure (Gregory et al., 2015). Increasing salinity of the water results in a decrease in the repulsive forces between particles, due to their charge, which makes them more like to aggregate together (by flocculation) which increases the deposition of sediments (along with the PTEs adsorbed to them) onto the floodplain. This process results in the floodplain becoming a sink for PTEs (Rinklebe and Du Laing, 2011). An extended flood duration, particularly when accompanied by low flow-rates (including stagnant water), results in sedimentation of fine grain sediment and organic matter that may have PTEs bound (Ciszewski and Grygar, 2016; Du Laing et al., 2009; Shaheen and Rinklebe, 2014).

2.2.3.4 Redox potential (E_H)

Waterlogging of soils generally results in a reduction in oxygen availability due to rapid consumption of oxygen by soil microbial activity and root respiration (Du Laing et al., 2007; Rinklebe and Du Laing, 2011) and because the dissolution of oxygen through water is many times slower than through air (Alloway, 1995; Du Laing et al., 2009; Frohne et al., 2015; Schulz-Zunkel et al., 2015). The soil microbial community (e.g. bacterial species such as *Thiobacillus ferroxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*) then uses alternative electron acceptors (such as nitrate, sulphate and Fe/Mn oxides), in anaerobic respiration, which results in a decrease in redox potential (E_H) (Maluckov, 2017) as the floodplain soils change from oxic ([O2]>30 µmol L^{-1}) to anoxic ([O2]<14µmol L^{-1}) conditions (Bellanger et al., 2004). Associated alkalinity generation drives increases in soil pH, a change which can be observed after a few days (Du Laing et al., 2007; Johnston et al., 2014; Karimian et al., 2017). Soil temperature has been found to dictate the rate and type of redox reactions; with soils at low temperatures (1 - 4 °C) requiring greater durations of saturation (20 days) before the onset of reducing conditions were seen, whereas soils at higher temperatures (above 9 °C) only required 2 days of saturation (Vaughan et al., 2009).

Redox potential has important effects on the speciation of As, Cu and Cr, as well as N, S, Fe, Mn, because these elements can exist in soils in more than one oxidation state (Selinus et al., 2005) and solubility depends on oxidation state. Copper solubility decreases after reduction from Cu (II) to Cu (I) under anaerobic near-neutral pH conditions and the presence of suitable electron donors, e.g. (Fe (II)) and sulphur compounds. Bacteria act as catalysts, actively involved in the reduction of Cu (II) to Cu(I), subsequently leading to sulphide precipitation (Cu_2S) (Simpson et al., 2000). However, other PTEs, such as Cd and Zn, are not observed to change valence state; their mobility can be affected as a consequence of redox dependent pH changes, complexation with organic matter or precipitation with Fe and Mn (hydr)oxides or sulphides (Du Laing et al., 2009; Frohne et al., 2011).) Shaheen et al. (2014a) demonstrated that sufficient time is needed for transformations between valence states to take place. For example, the oxidation of Cr from Cr (III) to the highly mobile Cr (IV) form was found to be a slow process. This means that with shorter flooding duration and quicker cycling between oxic and anoxic conditions, Cr mobility may be difficult to predict.

The presence of variable charge minerals, such as Fe and Mn oxides, phosphates, carbonates and sulphides provide a reaction surface for sorption processes, allowing PTEs to bind and become immobilised (Antoniadis et al., 2018; De Jonge et al., 2012; Sipos et al., 2014; Violante, 2013). Reducing conditions change the oxidation state of Fe and Mn, increase their solubility and may have indirect effects (known as reductive dissolution) on the mobility of associated metal cations (e.g. As, Cd, Cu, Ni, Pb, and Zn), releasing them from the solid phase to pore waters, depending on flood duration (Abgottspon et al., 2015; Ciszewski and Grygar, 2016; Du Laing et al., 2009; Frohne et al., 2011; Karimian et al., 2017; Rinklebe and Du Laing, 2011; Schulz-Zunkel et al., 2015; Shaheen et al., 2016, 2014b; Vaughan et al., 2009). Redox processes are a key factor for the reductive dissolution of Mn and Fe (hydr)oxides, these processes are often catalysed by microorganisms and result in the release of PTEs from the sediment (Du Laing et al., 2009; Frohne et al., 2011; Stafford et al., 2018; Yang et al., 2015). Relatively insoluble Fe(III) and Mn(IV) prevail under aerobic soil conditions providing sorption surfaces for many metals, whereas under anaerobic conditions Mn(IV) and Fe(III) are reduced to more soluble forms (Mn(II) and Fe(II)) with consequential dissolution of Mn and Fe hydrous oxides, co-sorbed PTEs ions (e.g. As, Cd, Cr, Ni and Pb), are released into soil solution (Simmler et al., 2017; Stafford et al., 2018; Yang et al., 2015). After inundation, Fe and Mn may re-precipitate as oxides and can bind (by desorption or co-precipitation) the trace metals back into the solid state (Ciszewski and Grygar, 2016; Davranche et al., 2011; Du Laing et al., 2009).

Decreasing of E_H can initiate microbial sulphate reduction and this can reduce the mobility of some PTEs (e.g. As, Cd, Cu, Cr, Ni and Pb) through coprecipitation of metal cations with sulphides

(Abgottspon et al., 2015; Borch et al., 2010; Weber et al., 2009). However, sulphur bearing minerals are known to be prone to change (metastable) which will influence the behaviour of associated PTEs under fluctuating E_H (Karimian et al., 2018). Yang et al., (2015) put mixed sediment samples into a laboratory culture tanks and found that microbially induced release of sulphur with subsequent As precipitation was more important for controlling As adsorption/desorption than reductive dissolution of Fe/Mn oxides. As the flood recedes, the floodplain soils undergo drying and aeration that change the conditions from anoxic back to oxic. The now oxic environment causes sulphides to be oxidised, which may release PTEs back into the pore waters (Abgottspon et al., 2015; Du Laing et al., 2007; Frohne et al., 2011). In addition to this, when exposed to oxygen and water, sulphides are oxidised to sulphates which leads to the formation of sulphuric acid thereby causing a decrease in pH and release of the PTEs (Emerson et al., 2017; Forstner and Wattman, 1981). Frohne et al. (2011) suggested that the mobility of Cd, Cu, Mn, Ni and Zn under oxidising conditions could be attributed to dissolution of sulphides and the resulting release of those metals. The extent to which the mineralogy of a floodplain soil is dominated by Fe/Mn oxides or sulphates may dictate whether PTEs are mobilised or immobilised during inundation, and the extent to which this phenomenon is reversed after floodwater recedes. The PTEs may re-adsorb onto soil organic matter, clays, and oxides, for example, so sulphide dissolution may not always correlate with increase PTE mobility.

2.2.3.5 <u>Soil pH</u>

pH is a measure of the hydrogen ion concentration and can also be referred to as the degree of acidity or alkalinity. The soil pH is affected by flooding because of a well-established correlation between soil pH and changing redox conditions; as a soil becomes flooded, this creates reducing conditions where (H^+ ions) are consumed (for example due to reduction of Fe and Mn oxides) and the pH increases (Rinklebe and Shaheen, 2017; Weber et al., 2009). When the flood recedes, oxidation processes produce protons and decrease the pH (Adewuyi and Osobamiro, 2016; Frohne et al., 2015, 2011; Rinklebe and Shaheen, 2017; Shaheen and Rinklebe, 2017). Furthermore, on exposure to the atmosphere, when flooding recedes, dissolved organic carbon (DOC) is converted to CO_2, which dissolves into pore water as carbonic acid, subsequently further reducing the soil pH (Peacock et al., 2015). However, this negative correlation between E_H and pH hasn't always been observed (Du Laing et al., 2009; Frohne et al., 2015). This is because the degradation of POM such as plant residues, by soil microbes, may increase the soil pH due to ammonification of the residue N (Xu et al., 2006).

As the pH changes, processes such as precipitation, co-precipitation and sorption/desorption of PTEs from organic matter or clay minerals occur, altering the chemical composition as well as reaction rates (Frohne et al., 2011). The soil pH plays an important role in mediating the mobility of PTEs and their availability for plant uptake, as the protons compete with metal cations for exchange sites on the surface of soils. Some of these exchange sites, particularly those associated with soil organic matter, are pH-dependent and thus only become deprotonated at high pH. A decrease in pH is generally accompanied by an increase in the mobility of most PTEs that are metal cations (e.g. Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) (Gröngröft et al., 2005; Sherene, 2010). Thus, as pH increases there is a subsequent decrease in the mobility of these PTEs (Giacalone et al., 2005). The extent to which PTEs mobility decreases in soils during flooding, due to a redox-induced increase in pH, is likely to depend on the proportion of PTEs in the soil that are associated with pH-dependent exchange sites) which are typically associated with soil organic matter) and the pH of the soil prior to the flooding event.

2.2.3.6 Dissolved organic matter (DOM)

The increase in pH of soil solutions with lower redox potential (reducing conditions) is often accompanied by a release of dissolved organic matter (DOM) from the soil into the soil solution, carrying with it any sorbed PTEs. Increasing DOM concentrations can subsequently form soluble organo-metal complexes (Abgottspon et al., 2015; Alvim Ferraz and Lourenço, 2000; Frohne et al., 2011). The presence of DOM in floodplain soils acts as a chelating agent which has a strong binding ability and increases the mobility of PTEs into pore waters and subsequently into river water or groundwater (Dawson et al., 2010; Du Laing et al., 2009; Shaheen et al., 2014b). Greater concentrations of DOM have been observed with decreasing $E_{H,}$ which may be due to supressed microbial carbon consumption under anoxic conditions (Frohne et al., 2015). Shaheen et al. (2014a) highlighted that increases in DOM associated with lower E_H may help to catalyse changes in the valence state of PTEs; for example, of Chromium (III) to (VI).

2.2.3.7 Temperature

As temperatures are predicted to increase as a result of climate change, they may become a factor that contributes to greater release of PTEs from the soil during a flood (Visser et al., 2012). Soils are affected by variations in air temperature which, in turn, affects the rate of biogeochemical processes during a flooding event, including decreasing redox potential and, ultimately, influences the rate and extent to which PTEs are released/ desorbed from POM into surface water and groundwater (Arnell et al., 2015; González-Alcaraz and van Gestel, 2015; Sánchez-Rodríguez et al., 2019; Shaheen et al., 2016; Stahl et al., 2013). Increases in temperature raise the ion activity in soil solution, and also make plants more active, which may lead to greater plant root uptake of soil water and dissolved/labile PTEs within this water (Sherene, 2010). Arsenic release from flooded soils was found to have temperature dependence, with As solubilisation increasing as temperature increased (Simmler et al., 2017; Visser et al., 2012). Temperature increases are attributed to a decrease in the water viscosity resulting in dissociation of molecules and a subsequent increase in the number of ions in the solution. For every degree Celsius increase in temperature there is an observed increase in electrical conductivity of 1.9% (Ander et al., 2016; Ma et al., 2011).

Many of the processes (e.g. redox reactions) described in the previous sections are microbially mediated and temperature dependent, and so the extent to which they affect the mobility of PTEs depends on their kinetics and the duration that floodplain soils are inundated. Changes in soil pH and DOM have been shown to exert a greater influence than E_H on the mobility of PTEs when considering shorter flood-dry cycles (Shaheen et al., 2014b, 2014a). However, Dang, Liu, and Haigh (2002) found that with increasing flood duration, more trace elements were transformed from inert phase to exchangeable fractions, increasing mobilisation. Soil redox processes are important for protecting environmental health; however, the kinetics and mechanisms remain poorly characterised and understood (Abgottspon et al., 2015; Borch et al., 2010; Pulchalski, 2003). Many of the studies reviewed in this manuscript undertook experiments in the laboratory at temperatures that are higher than the soil temperatures typically found *in-situ* at the location where the soil samples were collected, and so the rates at which reactions occur and the subsequent mobilisation of PTEs may be overestimated in these experiments. It is not possible to verify the extent of the overestimation, so more *in-situ* experiments are needed to investigate and provide quantification of the differences between laboratory and *in-situ* experiments.

Groundwater and river temperatures may have a strong effect on floodplain soil temperatures (Andersen, 2018). In warmer seasons they will generally be cooler than soil temperatures, but the opposite occurs in cooler seasons. Also, changes in soil moisture content, as a result of flood events, will affect the soil thermal properties such as thermal conductivity and heat capacity (Lu et al., 2007), thereby also affecting the spatial and temporal variation in the soils' temperature regime. A laboratory microcosm experiment with mining-contaminated topsoil and subsoil samples saturated for up to 41 days at temperatures ranging between 10-25°C, found that soil temperature increased the solubilisation of As, particularly in the topsoil when saturated for 1-2 weeks (Simmler et al., 2017). This means, for some PTEs, flooding during warmer seasons may result in greater mobilisation than flooding during cooler seasons. More seasonal field observations are required to understand the subtle interactions and feedbacks between soil moisture, floodwater temperature, and mobility of PTEs.

2.2.4. Soil biological processes that influence PTEs mobility

2.2.4.1 Soil organisms

Floodplain soils contain a great diversity of organisms that are known to contribute to the physical structure of the soil/sediment through bioturbation which influences the biogeochemical cycling of PTEs through oxygen diffusion, redox gradient and decomposition of dissolved organic matter (Classen et al., 2015; Y. He et al., 2019; Hooda, 2010; Selinus et al., 2005). As the soil pore spaces are filled with water, oxygen diffusion is low so microbial respiration relies on alternative electron acceptors (e.g. NO_3^-, Mn, Fe and S), resulting in reducing conditions (decreasing E_H) that simultaneously increase pH (Matern and Mansfeldt, 2016), and the changes to PTEs mobility (Figure 2.3) that are described in previous sections. Changes in the chemical speciation of PTEs can also occur due to microbial processes in reducing conditions, for example, sulphate reducing bacteria can methylate Hg in anoxic conditions (Ma et al., 2019).

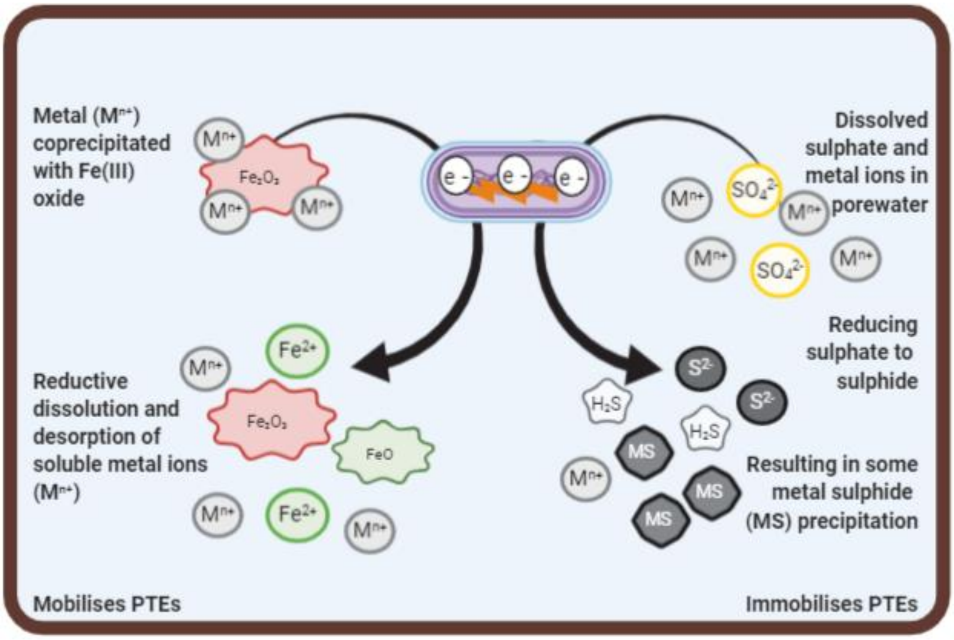


Figure 2.3: Soil microbial processes during inundation of floodplain soil influences mobility of PTEs; *(left-hand side) generic metals with valence state (denoted by M^{n+}) are coprecipitated to Fe oxides and are released due to reductive dissolution and (right-hand side) sulphate reduction (sulphate to sulphide) results in some metal (denoted by MS) precipitation, some of the metal (M^{n+}) remains in the pore water. Created with BioRender.com.*

PTEs that are present in floodplain soils are often protected within the soils' aggregates, which are stabilised by POM. However, inundation can stimulate the soil microbial community, which is sensitive to disturbance, accelerating the refractory organic matter mineralisation and destabilisation of aggregates, exposing and increasing the mobility of PTEs in the soil (Du Laing et al., 2009; Gall et al., 2015; González-Macé et al., 2016; Y. He et al., 2019; Rawlins et al., 2013). Tack et al. (2006) found that the drying of sandy soils caused an increase in soil solution metal concentrations, compared with the same soils maintained at field capacity. This observation was attributed to microbial effects, increasing the solubility of dissolved organic matter.

Flooding has been found to shift the soil biological community structure and function. These changes include a reduction of Gram-positive bacteria, mycorrhizal fungi and earthworms found under flooded conditions (Gregory et al., 2015; Harvey et al., 2019; Unger et al., 2009a). Harvey et al., (2019) found that flooding induced short-term alterations to soil microbial biomass but these changes did not persist in the long term; they concluded that temperate systems may be resilient to winter flood stress. The seasonal timing of floods influences the effect that flooding has on the soil microbial community, and so may result in different effects on, and recovery of, the soil microbial community. Sánchez-Rodríguez et al., (2019) subjected a UK agricultural grassland soil in an intact laboratory microcosm to flooding and found that summertime flooding (25°C), resulted in a loss of actinomycetes and arbuscular mycorrhizal fungi, and that these changes persisted post-flood. They expected microbial biomass to increase with flooding at higher temperatures, due to degradation of vegetation releasing labile carbon. However, they found that maintaining live roots and an active rhizosphere were more important for preserving the microbial community in grassland soils. Earthworms also play a role in increasing the mobility and availability of PTEs in floodplain soil through their activity causing changes to the soil microbial populations, pH, DOC or metal speciation (Sizmur et al., 2011b; Sizmur and Hodson, 2009) which in turn influences PTEs mobility as discussed in the above sections.

As the PTEs are released into the aqueous phase and mobilised in the environment, they present a potential risk to soil organisms (Ehlers and Loibner, 2006; González-Alcaraz and van Gestel, 2015). Soil organisms uptake PTEs via ingestion of polluted soil, food or pore water and/or via dermal uptake or absorption of soil water, with the soil water being the more important of the two pathways (Chrzan, 2016; Hobbelen et al., 2006; Sivakumar and Subbhuraam, 2005). Vijver et al. (2007) found that the frequency of flooding did not result in consistent changes in the internal PTEs concentrations of earthworms. Earthworms accumulate PTEs in their chloragogenous tissue and have a mechanism that allows them to regulate their internal PTEs concentrations, so when they are introduced to contaminated soils the earthworms reach an equilibrium and when they are returned to uncontaminated/”clean” soils they are able to detoxify and eliminate essential metals through excretion (e.g. Cu and Zn), but not non-essential metals (e.g. Cd and Pb) as detoxification processes involve sequestration within an inorganic matrix or organic ligand (Sizmur and Hodson, 2009; Spurgeon and Hopkin, 1999). While microbes can tolerate larger quantities of essential PTEs, in excess both essential and non-essential PTEs (e.g., Al, As, Cd, Hg, Pb, Zn) can adversely affect microbial communities by altering community structure and taxonomic richness; reducing the microbial biomass and lowering their enzyme activity which results in a decrease of soil diversity (Gadd, 2010; Gall et al., 2015; Wuana et al., 2011).

2.2.4.2 Plants

In many cases, PTEs are concentrated in the upper part of the soil profile where roots reside, meaning that increased mobility is likely to affect plants growing in floodplain soils. Wetland plants growing on inundated floodplain soils can also affect the mobility of PTEs because they are specially adapted to have air-filled tissues, or aerenchyma, which create patches of oxygenated soil around their roots, resulting in an increase in the volume of the oxic/anoxic interface and remobilising PTEs thus increasing their availability (Du Laing et al., 2009; Wright et al., 2017). However, in arable and pasture fields that are generally drier, flooding can cause crops to become stressed, as they are not adapted to wet soils. As oxygen levels decrease there is a build-up of carbon dioxide, methane and nitrogen gases that leads to the roots suffocating and dying (Hippolyte et al., 2012).

It is well established that symbiotic fungi, associated with plant roots, regulate the supply of micronutrients and reduce the uptake of non-essential PTEs by plants (Classen et al., 2015; Gadd, 2010; Tack, 2010). Plants, such as *Artemisia* and *Phalaris* species, on the floodplain excrete exudates during inundation which stimulates the activity of microbial symbionts in the rhizosphere, allowing PTEs to be taken up into the vegetation (Gall et al., 2015; Sullivan and Gadd, 2019; Violante et al., 2010; Xu et al., 2020). PTEs are often accumulated in plant root tissues and can sometimes be translocated into the plant shoots. However this is regulated in plants by the Casparian strip and therefore limited (Hooda, 2010; Nouri et al., 2009; Shahid et al., 2017). The uptake and accumulation of PTEs is element and plant-specific (Niu et al., 2007; Rinklebe et al., 2016a; Tack, 2010; Violante et al., 2010; Xu et al., 2020). The mobilisation and uptake of PTEs by plants may pose a potential environmental risk (Shaheen and Rinklebe, 2014). European floodplains are most commonly used as grassland for grazing cattle or hay production, whereas in other regions e.g. India, they are used for crops like rice, which raises concerns for possible pollutant transfer from the floodplain soil into the surrounding water bodies, then uptake and potential biomagnification of PTEs into the food chain (Martin et al., 2014; Overesch et al., 2007; Tóth et al., 2016a). However, the hyperaccumulation of PTEs by some plants (e.g. sunflower, mustard (Brassicaceae), alfalfa and Ricinus) has resulted in them being considered for phytoremediation of contaminated floodplain soils (Gall et al., 2015; Niu et al., 2007; Nouri et al., 2009; Shaheen et al., 2016; Violante et al., 2010).

Factors influencing plant uptake of PTEs include soil pH, electrical conductivity and the total concentrations of PTEs in the soil (Nouri et al., 2009). PTEs uptake also depends on the concentrations in the soil solution, governed by plant exudates and root-induced changes to pH and DOM (Gall et al., 2015). Quantifying the total content of PTEs transferred into the food chain via plants growing on contaminated soil is difficult (Gröngröft et al., 2005). The concentrations of PTEs found in floodplain plants are not always directly reflected in the PTEs content found in the soil, due to both physiological and biochemical differences between different plant species; for example, differences in the age of the plant biomass (seasonal trends in growth and therefore uptake of nutrients). Moreover, the rooting depth influences metal mobilisation/immobilisation and element specific uptake into the roots which also affects the transfer into the shoots(Chrzan, 2016; Overesch et al., 2007). Thapa et al. (2016) also demonstrated a change in semi-arid Australian floodplain vegetation productivity in response to flooding and drying cycles; flooding brings nutrients which increases net primary productivity. These changes in vegetation productivity could also initiate structural changes in floodplain vegetation communities in natural and semi-natural ecosystems (Overesch et al., 2007).

2.3. Summary and further research needs

2.3.1. Summary of current understanding

Floodplain soils downstream of urban catchments contain elevated concentrations of PTEs as a legacy of human activity and these PTEs could potentially be remobilised by future flooding events. A number of processes occur within the soil, ultimately determining PTEs fate. These processes include: sorption, desorption, complexation, precipitation and dissolution, transport of water and heat, and biological activity. The processes are influenced by the changing conditions that flooding brings particularly with regards to soil moisture content, temperature and redox potential. The mobility of PTEs in flooded soils is closely related to changes in redox potential which, in turn, is altered by flooding. These changes can have direct impacts on the mobility of redox sensitive PTEs (e.g. As and Cr). Furthermore, the reduction of Mn and Fe can cause reductive dissolution of co-precipitated PTEs, but the reduction of sulphate can result in the precipitation of PTEs as insoluble metal sulphides. Which of these processes dominates will depend on the mineralogy of the soil. PTEs precipitated as metal sulphides may oxidise after floodwaters recede and mobilise, accelerated by the pH reduction caused by production of sulfuric acid. There are important interactions between redox potential and other soil properties, such as soil pH, moisture content, POM, DOM, temperature, and salinity which also have a strong impact on PTEs mobility (Vaughan et al., 2009). Many of these reactions are microbially mediated, temperature dependent and the kinetics in real-world scenarios are poorly understood.

However, it seems that changes associated with alterations to pH and dissolved organic carbon are relatively fast, while changes to E_H are slower and only become apparent after extended periods of flooding. In many cases, PTEs deposited due to legacy pollution events are concentrated in the upper part of the soil profile, meaning that increased mobility is likely to affect plants growing in floodplain soils and potentially lead to contamination of the surrounding environment, including overlying surface waters.

2.3.2 Knowledge gaps and recommendations for future research

Floods are dynamic events that expose floodplain soils to water with rapidly changing flows, chemical composition, and sediment load. They can be difficult to predict, due to their different types (e.g. overbanking or groundwater flooding), and the high variation in their magnitude, duration, and frequency of recurrence. Therefore, chemical, physical and biological data from floodplain soils immediately before and immediately after a flooding event are often lacking. However these data would provide the necessary insights into the factors and processes involved in altering the mobility of PTEs during and after a real flooding event (Barber et al., 2017). The effect of flooding on PTEs mobility can be difficult to predict due to there being several factors (e.g. speciation, release through biological degradation and competitive action of other ions) or interactions between factors (e.g. changes in E_H caused degradation of POM) influencing PTEs mobility (Tack and Verloo, 1995).

Contamination of soil with PTEs receives most attention in highly contaminated urban, industrial, mining and waste disposal sites (Adamo et al., 2014; Resongles et al., 2015; Simmler et al., 2017; Wuana et al., 2011) with relatively little attention given to more ‘typical’ floodplains downstream of catchments with a history of urban and industrial development. Much of the work conducted to date (see Table SI-2.1) has been undertaken in Europe, America, Canada, China, Indonesia, Australia and New Zealand. Just over half of the studies cited in Table SI-2.1 were undertaken in Germany and Belgium (52%), with a particular research effort around the River Elbe and Wupper River in Germany (Du Laing et al., 2009; Förstner, 2004; Frohne et al., 2011; Overesch et al., 2007; Rennert et al., 2017; Rinklebe et al., 2013; Shaheen et al., 2017). However, research examining the relationship between PTEs mobility and flooding in other parts of the world that are expected to see an increase in the frequency and magnitude of flooding events, for example in Asia, Africa and India, is limited.

A number of factors were identified that contribute to whether the mobility of PTEs will increase or decrease during inundation of a floodplain, which may be interconnected or work in combination to affect PTEs mobility. As a result, different soils with differing mineralogy and thus different biogeochemical and physical properties, will likely respond differently to flooding. Individual studies tend to focus on one floodplain site. However, knowledge based on one river catchment may not be particularly useful for predicting the impacts of flooding at another site with different mineralogy and physical and chemical characteristics. A more fundamental mechanistic understanding is required to inform the development of predictive models. Therefore, more coordinated work encompassing multiple contrasting sites is required to understand the relative importance of key soil properties (e.g. mineralogy, POM, soil pH, texture; and how these affect derived soil properties such as hydraulic and thermal soil properties) on influencing the impact of flooding on the mobility of PTEs.

Many of the findings in the literature are based on research of soils or sediments in laboratory-based artificial flooding environments (Figure 2.4), which often involve; homogenisation of samples and removal of plant roots, short-exposure time for soil microorganisms and incubation under controlled conditions, such as temperature (often higher than *in-situ* temperatures) and soil water conditions (often wetting the samples with deionised water which is slightly acidic) (Frohne et al., 2011; Izquierdo et al., 2017; Rinklebe et al., 2010; Weber et al., 2009). This makes extrapolation of laboratory-based findings to field situations difficult (Hooda, 2010). Attempts to model the concentration of PTEs in floodplain pore waters have demonstrated the complexity of predicting how different variables such as soil moisture content and temperature interact and alter mobility (Rennert et al., 2017), with site or catchment-specific information being of great importance to establish and capture spatial differences sufficiently (Schulz-Zunkel et al., 2015). While much research undertaken in controlled conditions in laboratory microcosms is undoubtedly useful because independent replicates can be assigned to treatments without confounding variables (Figure 2.4), there is a clear research need for on-site experiments on the effect of flooding on PTEs mobility using real-time field-based observations that capture the kinetics of processes before, during, and after a flooding event under ambient temperatures and in geochemically contrasting soils.

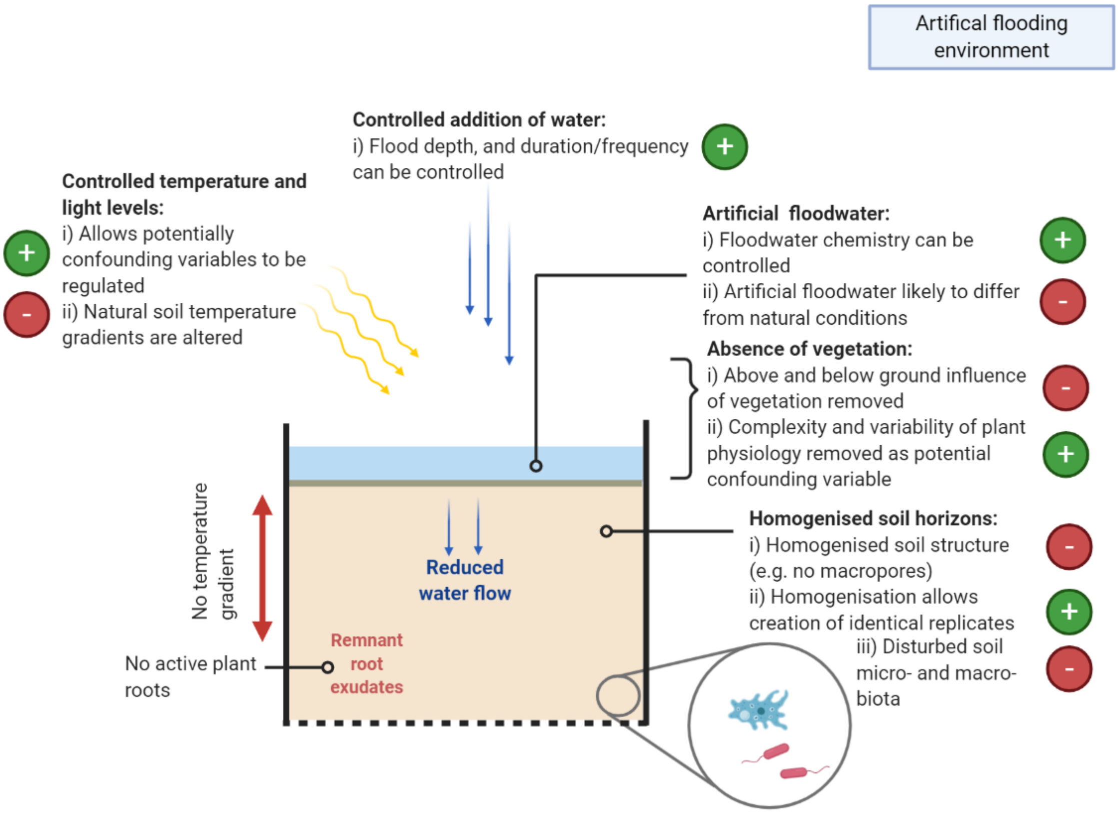


Figure 2.4: Strengths (+) and weaknesses (-) of laboratory-based studies for researching the impact of flooding on mobility of PTEs. Created with BioRender.com.

2.4. Chapter 2 Supplementary Material

One supplementary table is provided in Appendix 1:

Table SI-2.1: Summary of the findings of papers that report the impact of flooding on potentially toxic element (PTE) mobility.

Chapter 3

This chapter is formatted as a paper to be submitted to *Environmental Science: Processes & Impacts*.

Ponting, J., Verhoef, A., Watts, M.J., Al-Mousili, Layla, Dzimidowicz, Adam, Sizmur, T., (*In prep.*) Influence of floodplain topography on soil potentially toxic element concentrations. *Environmental Science: Processes & Impacts*

3.0. Abstract

During a flooding event, floodplains within urban catchments are flooded by river water containing elevated concentrations of dissolved and particulate potentially toxic elements (PTEs) such as arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). It can be difficult to distinguish between anthropogenically introduced contaminants and natural pre-existing background levels of contaminants in floodplain soils.

We sampled the Loddon Meadow floodplain site, adjacent to the Loddon River, south of Reading in Southeast England. Soil samples were collected from the site using a random stratified sampling method, digested in aqua regia and PTE concentrations determined using ICP-OES. The floodplain microtopography was characterised by creating a digital elevation model, with LIDAR imaging data. The distribution of PTEs across the floodplain were characterised by spatially plotting the PTE concentrations and performing geostatistical analysis (Kriging).

A significant positive correlation was found between floodplain elevation and soil contamination with some PTEs (Cr, Cu, Ni and Zn). Higher concentrations, particularly for Cr and Ni, were found in the centre of the floodplain where there is the lowest elevation. We infer that elevation is correlated with flooding (frequency and duration), therefore, the centre of the floodplain is where floodwater resides for the longest duration, PTE-contaminated sediments have the greatest opportunity to settle out of suspension, and this could explain why there are higher concentrations of some PTEs. Our findings are, therefore, strong evidence to suggest that the source of some of these PTEs in the floodplain soil samples of this urban catchment, is the river Loddon (and thus sources upstream in the Loddon catchment). It is likely that many floodplains downstream of urban catchments, particularly those with a history of industrial development, may harbour a legacy of PTEs that have been deposited with floodplain sediments. The use of this method of correlation between microtopography and PTE soil concentration, could be adopted in future studies for attributing the source of contaminants across a floodplain site.

Key words: Total PTEs, Sediment deposition, Flooding, Elevation, GIS, LIDAR, Kriging

3.1. Introduction

Riparian floodplains are flat lowland areas adjacent to rivers, that are subject to periodic overbanking of river water and fluctuating groundwater levels leading to a cycle of drying and flooding events (Acreman et al., 2003; Vijver et al., 2007; Vink and Meeussen, 2007; Weber et al., 2009). Rivers are important natural pathways transporting contaminated sediments (Famera et al., 2013). The inundation of floodplain land is important for flood risk management, acting as a buffer for flood water and also filtering nutrients and contaminants carried in the flood water (Lair et al., 2009; Stuart and Lapworth, 2011). Potentially contaminated sediment loads are deposited onto the floodplain topsoil during flooding events (Arnell and Lloyd-Hughes, 2014; Barber et al., 2017; Bednářová et al., 2015; Famera et al., 2013; Frohne et al., 2011; Vink and Meeussen, 2007). Floodplains have therefore been considered a sink for potentially toxic elements (PTEs) such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in urban and agricultural catchments (Capra et al., 2014; Greenwood et al., 2014; Marković et al., 2018; Pulchalski, 2003; Schulz-Zunkel et al., 2015; Sherene, 2010). However, it is sometimes difficult to differentiate between contaminants that have been anthropogenically introduced into the river and recently deposited on to the floodplain, and the natural background level of contaminants pre-existing in floodplain soils.

The topography of floodplains is usually slight, but can result in important hydrological (e.g. extent of flooding) and pedological (e.g. texture) differences across the floodplain (Förstner, 2004; Kuusisto-Hjort, 2009; Rinklebe et al., 2007). The rate of overbank sediment deposition varies between flood events both within and between different floodplain sites, due to the particle size (individual particles or aggregates) (Buchty-Lemke et al., 2019; Koiter et al., 2013; Nicholas and Walling, 1996). Spatial distribution of PTEs in floodplains with more complex microtopography may result in hotspots of PTEs concentrations, which can be more difficult to predict (Ciszewski and Grygar, 2016). Geographical information systems (GIS) and light detection and ranging (LIDAR) can be used to generate important information about floodplains, for example changing elevation (Elznicová et al., 2019; Ghoshal et al., 2010).

Concentrations of contaminants tend to decrease along the soil chronosequence (with depth); reflecting the deposition of anthropogenically contaminated sediments (aggradation) onto the soil surface (Bednářová et al., 2015; Zhao and Marriott, 2013). However, a number of studies from river and wetland soils/sediments show geochemical patterns that indicate the influence of human activities (i.e. industrial development, urban wastes and mining/mineral processing), in successive soil zones along the soil chronosequence, that subsequently reduce due to improved environmental quality standards (Davies and Lewin, 1974; Macklin et al., 1994; Zhang et al., 2016). River flooding and overbanking onto floodplains are still effective mechanisms of contaminant dispersal, that results in PTEs flux that can cause challenges to meet Water Framework Directive target goals relating to in-river conditions (Foulds et al., 2014a). Topsoil (c. 0-15cm) samples contain contamination that is representative of both anthropogenic sources as well as parent material contributions, whereas deeper soil (>30cm) samples capture historical anthropogenic sources of contamination (Ander et al., 2013). Anthropogenic contamination of floodplain soils in urbanised catchments originate from upstream sources, such as; waste from industrial activities, sewage and wastewater treatment, agricultural practices and atmospheric deposition (Ander et al., 2013; Arnell et al., 2015; Bowes et al., 2018; Groenenberg et al., 2012; Jiao et al., 2015; Palansooriya et al., 2020; Sherene, 2010; Wuana et al., 2011). Due to the persistent, toxic and non-biodegradable nature of PTEs, they remain in the environment and are regarded as a serious environmental concern (Bednářová et al., 2015; Nshimiyimana et al., 2014). While some PTEs are non-essential elements (e.g. As, Cr and Pb), others are essential micronutrients (e.g. Cu, Ni and Zn) and are required in low concentrations for biological functions, however in high concentrations they become toxic (Hooda, 2010; Strawn, 2018; Wuana et al., 2011). Some PTEs are naturally present in soils due to weathering of parent material (natural background levels), and deposited by other sources (e.g. volcano emissions, forest fires) (Álvarez-Ayuso et al., 2012; Ander et al., 2013; Jianfei et al., 2020). The PTEs may be associated with different soil minerals within the soil, depending on the parent material from which it was derived (Wragg and Cave, 2012). Guidance regarding ‘normal’ background contaminant levels arise from both natural geological variation and diffuse anthropogenic sources (Ander et al., 2013; McIlwaine et al., 2014). Concentrations of PTEs within soils are heterogenous and vary with time, so background concentrations are better considered as a range of values (Rothwell and Cooke, 2015).

The aim of this study was to identify whether floodplain elevation correlates with the spatial distribution of pseudo-total concentrations of PTEs, found in the floodplain soil. Our objective was to determine the source of PTEs to a floodplain site, using geospatial methods with spatially explicit elemental data and LIDAR imaging data.

3.2. Methodology

3.2.1. Field site

The field site used in this study is known as the Loddon Meadow and is part of the Loddon Floodplain Monitoring and Modelling Platform located to the south of Reading in Southeast England, United Kingdom, and is situated adjacent to the River Loddon. The Loddon River Valley is characterised as a flat valley of the River Loddon, a tributary of the River Thames; underlain by riverine alluvium and gravel deposits (Land Use Consultants, 2004). The Loddon catchment covers three counties; Berkshire, Hampshire and Surrey (area of 680km^2), has >20% urban and sub-urban land cover, with high population densities and has 210km of classified rivers and canals (EA, 1996; NRA, 1996). The discharge from wastewater treatment plants as well as runoff from roads through urbanised towns, are predominant diffuse sources of PTEs to the River Loddon, and are largely the reason for the River Loddons' moderate/poor status (Bowes et al., 2018; EA, 2020, 2012, 1999). The Loddon catchment has been described in detail in other published work (Kelly et al., 2020); explaining the extensive mineral extraction, historic landfill sites and other point sources (e.g. factories manufacturing engines, vehicles, agricultural equipment and alloy coatings for gas turbines). It is likely that all of these industries discharged effluent into the river upstream of the field site sampled in this study.

3.2.2. Soil sampling

A random stratified sampling method was used to locate 30 sampling sites across the Loddon Meadow floodplain (Figure 3.1). The randomised determination was performed by splitting each stratified grid square into grid subsets of 25 smaller squares, one sampling square was determined using Microsoft Excel random number generation function. Soil samples (100g) were collected using a stainless-steel auger to sample the topsoil (~3-15cm below the surface) from 30 locations across the floodplain. The samples were then analysed for 'pseudo-total' contents of PTEs by ICP-OES after digestion using the Aqua Regia method (ISO 11466, 1995; see section 3.2.1).

3.2.2.1. Aqua regia digestion and ICP-OES analysis

The soil samples were air dried, sieved using a 2mm mesh and weighed (1.5g). The weighed soil was transferred into a 100ml Kjeldahl digestion tube with 4 glass balls. Concentrated AnalaR hydrochloric acid (10.5ml) followed by AnalaR nitric acid (3.5ml) were added to the soil, mixed thoroughly and left overnight. The samples were placed in the digestion block on a heat of 50°C and then gradually increased to 140°C and left for 2 hours. The samples were removed from the digestion block and allowed to cool before filtering through prewashed (with a 2-3mls 0.5M nitric acid) 12.5cm diameter filter paper. The digested samples were filtered into a 100ml volumetric flask and made up to the 100ml mark using 0.5M nitric acid.

The digested samples were analysed using an Optima 7300 series inductively coupled plasma optical emission spectrometer (ICP-OES); this allowed the 'pseudo-total' metal concentrations (mg/kg) of PTEs (Cr, Cu, Ni and Pb) to be determined (Table SI-3.1), however the majority of As concentrations and all of the Cd concentrations were below the limit of detection. The limit of detection was derived by calculating 3x the standard deviation of blanks (n=10). Each batch of 30 samples was run alongside a triplicate of an uncontaminated soil (UCSS) internal reference material and we obtained the following recovery rates Cr (118%), Cu (90%), Ni (99%), and Pb (109%).

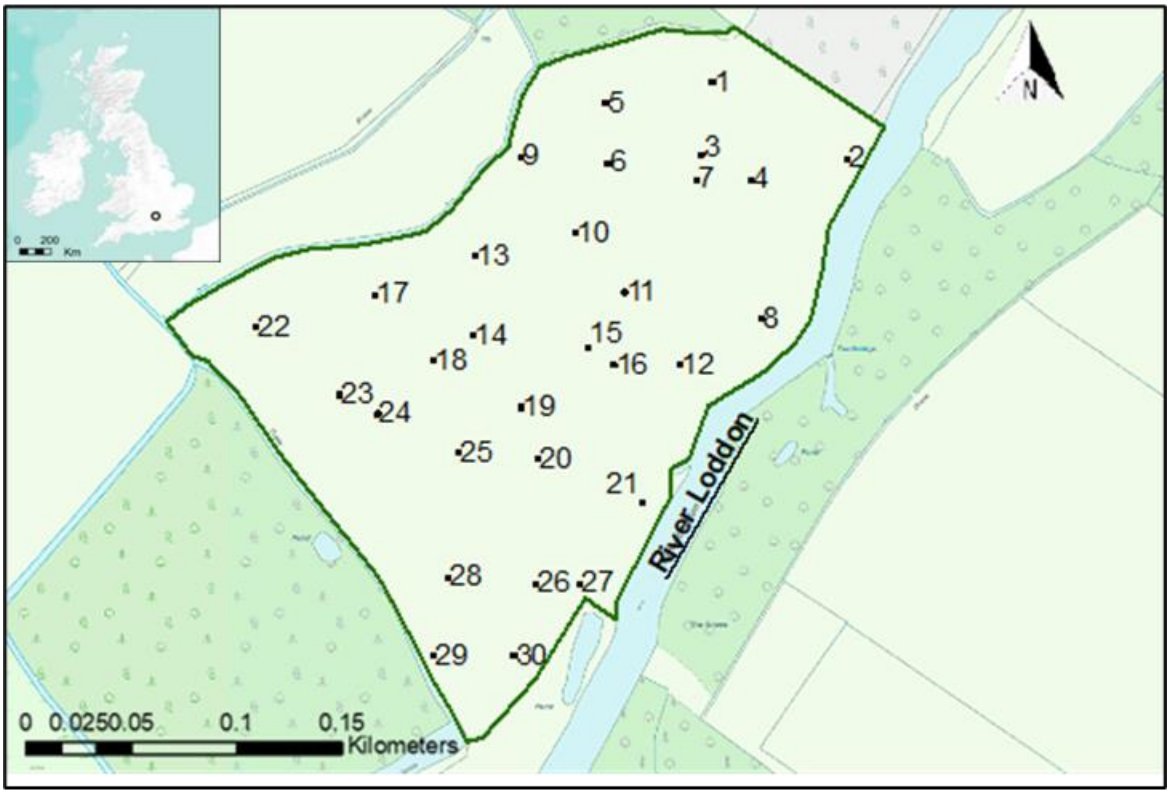


Figure 3.1: *The 30 sampling points located across the Loddon Meadow floodplain, identified through a stratified sampling grid.*

3.2.3. Mapping and statistical analysis

ArcMap 10.4 Geospatial Information System (GIS) software was used in this study to map and statistically analyse the Loddon Meadow floodplain site. Light detection and ranging (LIDAR) imaging data was imported from Digimap and, through an analytical 'hill-shade' tool, a digital elevation model (DEM; Figure 2) was created (Kokalj et al., 2011). The 'pseudo-total' PTE concentrations were added onto the GIS map and the spatial distributions across the floodplain interpolated using the Ordinary Kriging method (Ha et al., 2014; J. He et al., 2019; Webster and Oliver, 2007). Microsoft Excel was used to plot the correlation between the Loddon Meadow floodplain microtopography (elevation) and PTE concentrations in the soil. Regression analysis in Minitab 19.1.1 was used to determine the significance of the correlation.

3.3. Results

3.3.1. Floodplain microtopography

The digital elevation map (DEM) of the Loddon field site (Figure 1) clearly shows the higher elevation (around 40 metres above ordnance datum) in red and the lower elevation (around 38 metres above ordnance datum) in green. The red and white area/line directly adjacent to the River Loddon (labelled) shows the high elevation of the embankment between the river and the floodplain meadow. Drainage ditches to help with the flow of water during the flood and post-flood can be seen as low elevation (light green) lines in the North section of the floodplain.

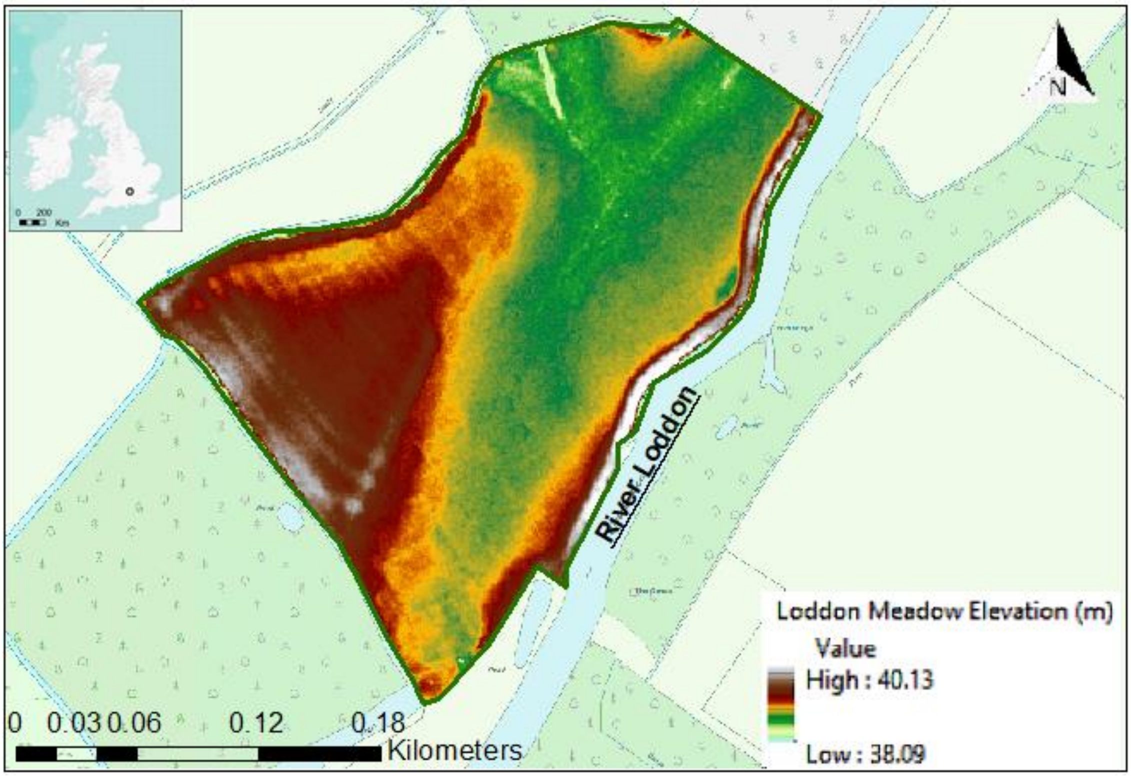


Figure 3.2: Elevation map of the Loddon Floodplain created using ArcMap 10.4 GIS software; the red areas are high elevation and the green areas are low elevation.

3.3.2. Characterising contamination on the floodplain

The soil concentrations of PTEs (Cr, Cu, Ni, Zn, As and Pb) are provided in Table SI-3.1. The distributions of Cr, Cu, Ni, and Zn, in the soil across the Loddon Meadow floodplain are represented in the maps in Figure 3.3(A-F) and summary statistics in Table 3.1. The relative standard deviation (RSD) is a useful indication of whether the data is homogenous (low RSD) or the result of anthropogenic sources (high RSD) (Mihailović et al., 2015). The concentrations of Cr (Figure 3.3A) and Ni (Figure 3.3C) closely relate to the microtopography of the floodplain shown in Figure 3.2. Higher concentrations of Cr and Ni were found in the centre of the floodplain, correlating with low elevation. The point circled in the Kriging map of Figure 3.3A is a sampling site located on the floodplain embankment and corresponds to data circled in the correlation plot of Figure 3.4A, that appeared to not fit the positive correlation otherwise found. This was a sampling point with high elevation but also a high Cr concentration in the soil sampled. An explanation for this result may be that the formation of the river embankment is likely to have come from dredging sediment from the River Loddon in the 60s or 70s. Therefore, the sample taken from the embankment was likely an example of the high concentrations found in the river sediment at that time. The strong, positive correlation can be seen in the scatterplots Figure 3.4A (Cr; R^2 = 58.95%, P<0.01) and Figure 3.4C (Ni; R^2 = 32.8%, P<0.01). The concentrations of Cu (Figure 3.3B) and Zn (Figure 3.3D) appear to be higher in the soils sampled closer to the River Loddon and lower in the soils sampled further from the river. A positive correlation can be seen in the scatterplots Figure 3.4B (Cu; R^2 = 12.38%, P=0.057) and Figure 3.4D (Zn; R^2 = 17.92%, P=0.02), showing (to a lesser extent than Cr and Ni) higher concentrations at low elevation and lower concentrations at high elevation.

Table 3.1: Summary statistics (e.g. Mean, Median, Standard Deviation (StDev), % Relative Standard Deviation (%RSD) to 3s.f.) for the PTEs (Cr, Cu, Ni and Zn (mg/kg)) found on the Loddon Meadow floodplain.

PTE	Min	Max	Mean	Median	StDev	%RSD
Cr	35.9	99.5	76.3	81.3	16.5	21.6
Cu	12.3	41.7	24.8	24.1	6.93	27.9
Ni	14.5	39.8	29.6	31.6	6.57	22.2
Zn	86.2	298	183	184	57.8	31.5

The distribution of pseudo-total concentrations of As and Pb did not show any relation to the microtopography of the Loddon Meadow floodplain; no correlations were found in the scatterplots (not presented). The As concentrations in the soil samples collected were predominantly below detection limit (DL = 34.42mg/kg), with only four sampling locations with concentrations above detection; therefore, finding a correlation between soil concentrations and floodplain microtopography was not possible (As; R^2 = 0%, P=0.837). The Pb concentrations, however, were above the DL (10.17mg/kg) and had a %RSD of 38.55, though we did not find a statistically significant correlation between Pb concentrations in the soil samples collected and floodplain microtopography (Pb; R^2 = 0%, P=0.419).

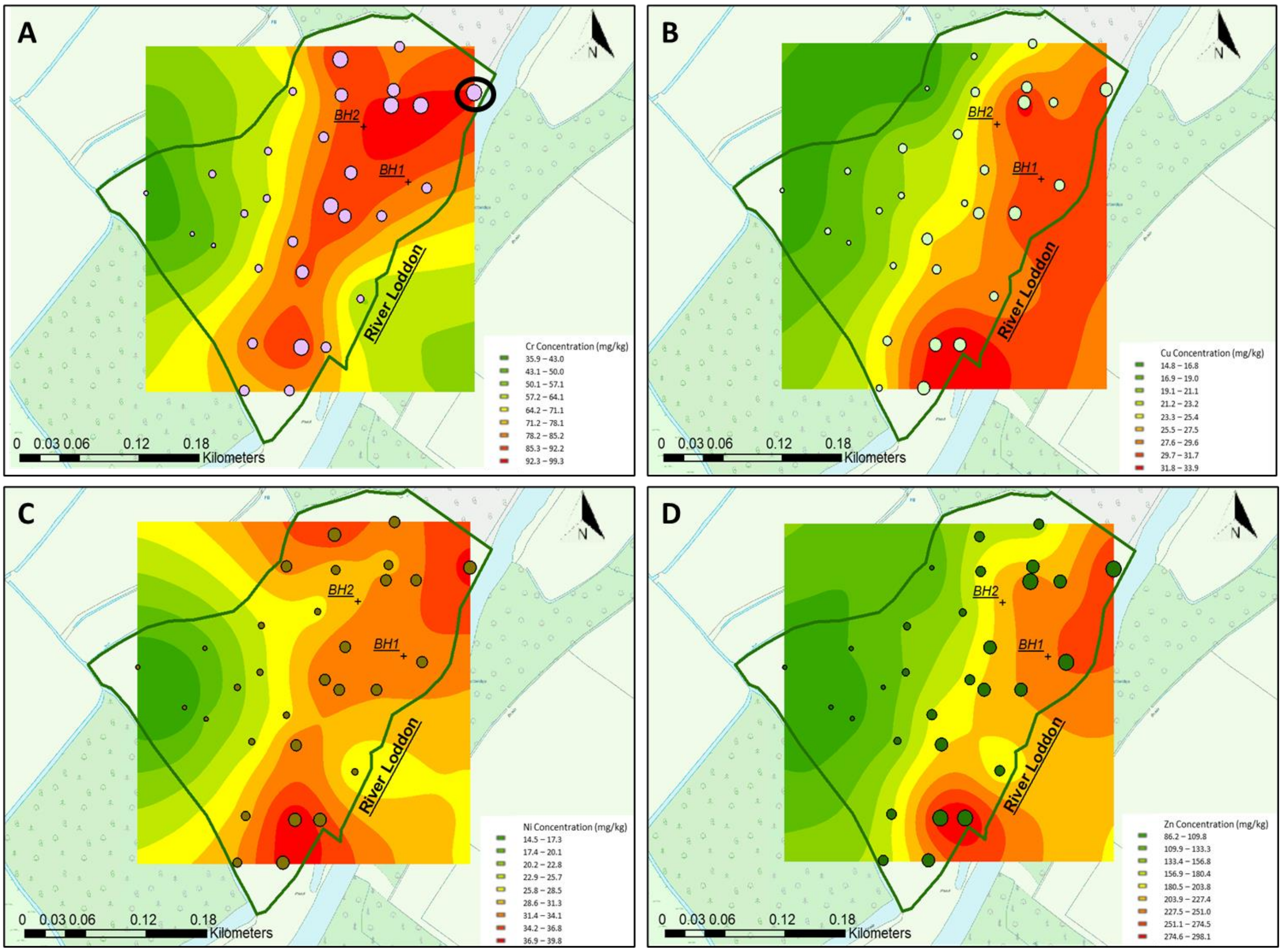


Figure 3.3: *Kriging maps for A) Chromium concentrations, B) Copper concentrations, C) Nickel concentrations, and D) Zinc concentrations, in the Loddon Floodplain, created using ICP-OES results from soil sampling data in the ArcMap 10.4 GIS software. The circled point in box A) is highlighting the location of the sample data that appeared to be an anomaly when considering the correlation between Chromium concentration and floodplain elevation.*

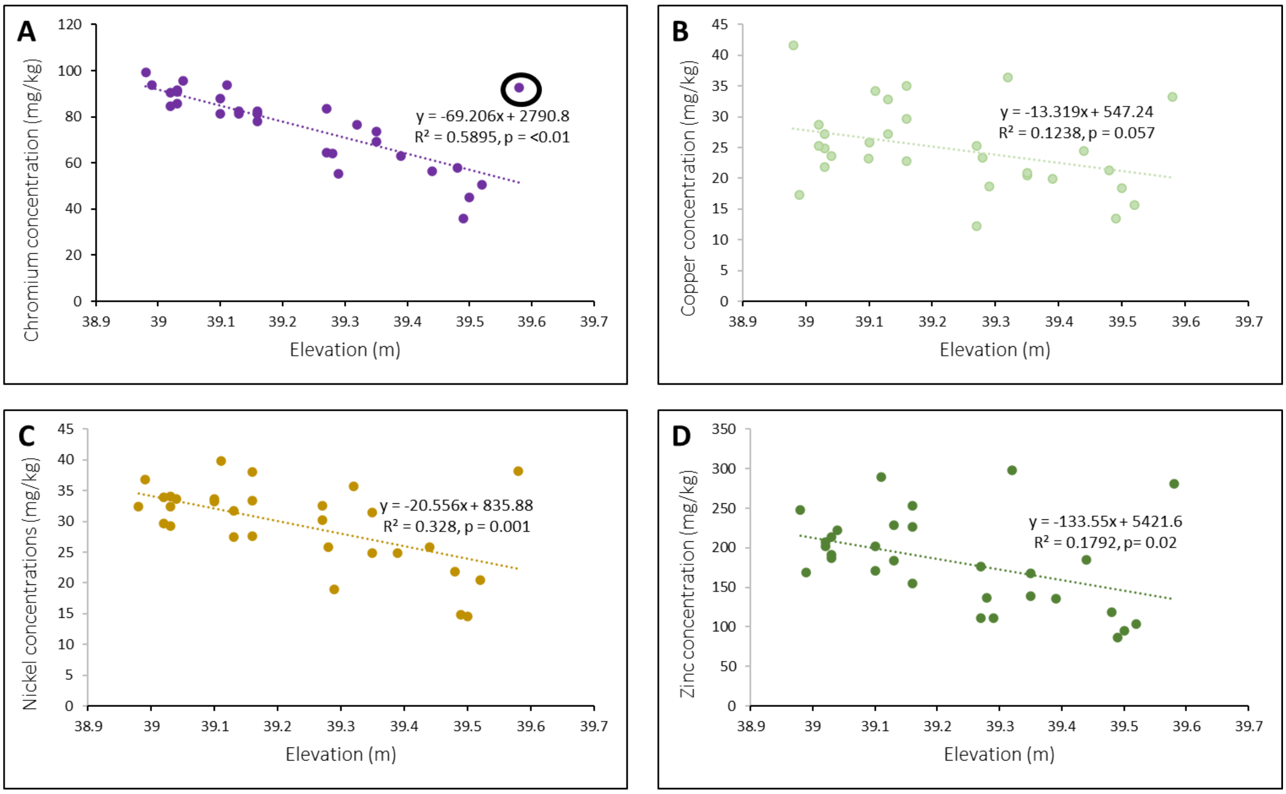


Figure 3.4: Relationship between elevation and pseudo-total soil concentrations of A) chromium, B) copper, C) nickel and D) zinc on the Loddon Meadow floodplain. The circled point in box A) is highlighting the sample data that appeared to be an anomaly compared to the other data points.

3.4. Discussion

Floodplains, such as those within the Thames Valley, have formed through the accumulation of sediment deposited adjacent to the river during flooding events (Bednářová et al., 2015). The River Loddon water quality has been affected historically by discharge from sewage treatment works, leachate from landfill in the catchment and metal plating industry (EA, 1996). The source of the contamination we have found on the Loddon Meadow floodplain (Cr and Ni, and to a lesser extent Cu and Zn) is likely to have originated from the factories such as the National Gas Turbine Establishment at Pyestock. This factory used Cu or Cu-alloy for the 'chill-plate' that the turbine mould was mounted onto, and used Ni- or Cr-base alloy coatings for the protection of gas turbine blades (Kelly et al., 2020; Northwood, 1972; Restall and Hayman, 1987). Where corrosion resistance was required; a composition of Ni, cobalt and iron, with Cr as the alloying ingredient made a 'superalloy' (Restall and Hayman, 1987). This study provides evidence that some PTEs found in the floodplain soil have been deposited by the river and thus upstream sources from the urban catchment, brought onto the floodplain when the river floods. The microtopography of the floodplain has an influence on the transport and deposition of contaminated sediments (Kuusisto-Hjort, 2009; Sweet et al., 2003) and direct effect on soil chemistry (Zhu et al., 2016). Although river pollution has declined as environmental quality standards have increased, historic contamination of river sediments may still act as a secondary contaminant source through transport and redistribution during flooding events (Bednářová et al., 2015; Förstner, 2004). Relatively course grained (sandy) sediments remain closer to the river source during overbanking compared to finer grained (clay) sediments, which travel further and only settle out of suspension when water is stagnant (Ghoshal et al., 2010). However, the distribution of PTEs across the floodplain may have also been a result of internal redistributions within the floodplain, as well as, or rather than, sedimentation from an upstream source. Effectively making it more difficult to establish the source of PTEs to the floodplain. Additional sampling of soils near to the floodplain but not affected by flooding, as well as soil sampling to a greater soil depth, may have helped with the overall conclusions about the effects of floodplain topography on soil PTE concentrations.

The geospatial methods used in this study make use of data from laboratory analysis of soil samples. There are other studies with this type of data that have used multivariate statistical methods (i.e. principal component analysis or cluster analysis (Davis et al., 2009; Hou et al., 2017; Jianfei et al., 2020; Lee et al., 2006; Manta et al., 2002; Micó et al., 2006; Wang et al., 2019)) as a classification tool to distinguish between natural and anthropogenic sources of PTEs. Isotope fingerprints combined with multivariate statistics have been used to identify the source of PTEs to air, soil and water (e.g. Pb isotope ratio analysis has been widely used) (Chen et al., 2018; Le Bot et al., 2011; Son, 2011; Wang et al., 2019). Geostatistical techniques (Kriging) have been used to create elemental distribution maps, showing 'hot-spots' of contamination (Ha et al., 2014; Hou et al., 2017; Jianfei et al., 2020; Li et al., 2004; Mihailović et al., 2015; Zhen et al., 2019). The use of GIS tools are important, not just for mapping but also interpretation of fluvial deposition processes, determining routes that PTEs are transported and possible source identification (Elznicová et al., 2019; Hou et al., 2017; Wang et al., 2019). The results of this study would suggest that by taking elemental analysis and mapping these results along with the elevation of the field site sampled; correlations found between the two can be used to infer contamination from the catchment compared with that of background levels in the soil. The benefits of using these techniques are they are low cost and within the capability of most environmental laboratories. These techniques have been used recently to find correlations between microtopography and soil physicochemical properties (e.g. clay, silt, bulk density, organic matter, electrical conductivity) (Ayele et al., 2019). There have been other studies that have also combined elemental/geochemical analyses and GIS techniques, (Elznicová et al., 2019; Famera et al., 2013; Grygar et al., 2016; Manta et al., 2002), however there are knowledge gaps around floodplains under near-natural conditions (Buchty-Lemke et al., 2019). The integration of GIS and geostatistical methods is valuable for understanding the distribution of PTEs in soils and of particular interest to policy makers and land use planning, source identification and risk mitigation (Hou et al., 2017).

3.5. Conclusions

This study has highlighted the correlation between floodplain microtopography and soil pseudo-total concentrations for some PTEs; with the key finding being that higher concentrations of Cr and Ni were found in the soils in areas of lower elevation. Concentrations of Cu and Zn were also in the soils at low elevation but more apparently, they were found in the soils located closer to the river; this may be due to the type of sediment (coarse grained) that they were bound to and brought onto the floodplain during overbanking. We infer that floodplain elevation is correlated with flooding (frequency and duration); where the low elevation areas are flooded more often and for longer periods of time and therefore allow PTE-contaminated sediment to settle out of suspension. These findings are, therefore, strong evidence to suggest that the source of Cr, Ni, Cu and Zn in the Loddon Meadow floodplain soil samples is deposition of contaminated sediments through overbanking of the River Loddon (and thus sources upstream in the Loddon catchment). There were no significant variations found for the concentrations of Pb across the floodplain, and this may suggest atmospheric deposition rather than deposition of river sediments during flooding, or alternatively that background Pb concentrations in the soils were higher than any anthropogenic input from deposited sediment.

The methods used in this study should be considered for characterising other floodplains sites across the UK. This will help to identify where legacy pollution has been deposited. Geospatially mapping contamination on floodplains shows how unevenly PTEs can be distributed in a landscape. It is important to quantify the extent of legacy pollution in floodplain soils, as these sites will become more important in the future for flood risk management.

3.6. Chapter 3 Supplementary Material

One supplementary table is provided in Appendix 2:

Table SI-3.1: Soil concentrations of Cr, Cu, Ni, Zn, As and Pb (mg/kg) at the 30 sampling points on the Loddon Meadow floodplain shown in Figure 1. Limit of detection (LOD) are also detailed.

Chapter 4

This chapter is formatted as a review paper to be submitted to Soil Systems Special Issue “Assessment and Remediation of Soils Contaminated by Potentially Toxic Elements (PTE)”.

Ponting, J., Verhoef, A., Watts, M.J., Sizmur, T., (*In prep.*) Analysis of cation and anion mobility in floodplain soils: A comparison of *in*-situ and *ex*-situ soil pore water extraction methods. *Soil Systems*

4.0. Abstract

When analysed, soil pore waters provide information on the chemical properties of the soil solution. This measure can be more useful than the total concentrations bound in the soil, as the mobile fraction is of higher environmental relevance and often assumed to be readily available for uptake by organisms. Chemical analysis of pore waters requires their separation from the soil while minimising any modification to the chemistry during the extraction process.

There is no consensus on the most appropriate method of extracting pore water from soil. Previous studies have concluded that centrifugation and Rhizon^{TM} samplers performed better than other pore water extraction methods, based on ease of use and reproducibility of concentrations measured. We therefore compared these two methods for extracting soil pore water; the centrifugation as an example of an *ex-situ* method and the Rhizon ^{TM} sampler as an example of an *in-situ* method. Criteria we have used for our comparison include: (1) the required soil moisture for ease of use, (2) the quantity of pore water yielded, (3) time, cost and reusability, (4) the pressure applied to the soil (and hence the size range of pores that the water is extracted from), (5) possible sources of contamination, and (6) concentrations of solutes in extracted pore water.

We highlight the strengths and weaknesses of *in-situ* Rhizon^{TM} samplers and *ex-situ* centrifugation as techniques for extracting pore water from soils, as well as comparing solute concentrations in the pore waters extracted by the two methods. The low pressure Rhizon^{TM} samplers (-93kPa) predominantly extract pore water from large pores (0.75μm), whereas the medium-high pressure centrifuge (1111kPa) extracts pore water from smaller pores (0.25μm). We did not, however, find significant differences in the concentrations of elements measured in pore waters extracted by the two methods.

We suggest that centrifugation is the preferred method when there are varying soil moistures, sampling time is limited, or when obtaining a homogenous sample is important to the investigators. The *in-situ* Rhizon^{TM} samplers are generally used in laboratory mesocosm experiments or when sampling remote locations where transit of field-moist soil samples to a laboratory is not feasible. Our

experience of using the Rhizon^{TM} samplers in-situ with no longer than 5 hours to equilibrate, often did not result in enough pore water volume being extracted. Other studies that have used the Rhizon^{TM} samplers in the field, have left them in place to equilibrate with the surrounding soil for at least 24 hours, but up to several days or weeks before pore water is extracted. It was not possible, in this study, to follow this procedure, however we suggest this is a necessary requirement.

Keywords; Soil solution, Rhizon^{TM} sampler, centrifugation, Potentially toxic elements

4.1. Introduction

4.1.1. Overview

Pore water is the water contained in voids (pores) within soil, sediment or rock. This liquid phase provides a medium in which solutes can desorb from the solid phase and react with one another. Solutes found in the pore water are referred to as being in the "mobile fraction" and so are of environmental importance because they are more bioavailable to organisms in the surrounding environment than chemicals in the solid phase (Di Bonito et al. 2008; Cipullo et al. 2018; Meers et al. 2006). Chemical analysis of pore waters can provide a more useful diagnostic tool for understanding the environmental fate of chemicals in the environment than total concentrations bound in the soil (Di Bonito et al. 2008; Schulz-Zunkel, Rinklebe, and Bork 2015; Tack and Verloo 1995). It is important to be able to separate the pore water from the soil matrix while ensuring minimal modification to the pore water chemistry (Steiner et al., 2018).

The pore water concentrations of solutes may vary depending on the pore water extraction method used. Variations in soil properties and conditions such as texture, structure, and moisture content have been given as reasons for why these differences may arise (Orlowski et al., 2016; Pulchalski, 2003; Rinklebe et al., 2007; Stuart and Lapworth, 2011; Weaver, 2014). The soil texture reflects the particle size distribution: the proportions of the constituent materials found within a soil sample, i.e., sand, silt and clay (Fraters et al., 2017; Sherene, 2010). The soil texture, together with soil organic matter, soil management, vegetation, and abundancy and activity of soil biota affect the soil structure; the way in which the individual particles, or their aggregates, are arranged, and the shapes, sizes and continuity of the pore spaces in between the particles. A sandy soil, with large relatively round particles, resulting in bigger pores, will drain more quickly after rainfall compared to a soil with a high clay content. Soils that are high in clay content have smaller pores that reduce the soil's hydraulic conductivity, compared to a sandy soil (but only when relatively wet; once the sandy soil has lost the water from its biggest pores its hydraulic conductivity will decrease rapidly) (Hillel, 1998; Ujile and Owhor, 2018). The type and amount of clay particles also plays a role in the binding of solutes, and thus their concentration in pore water (Giacalone et al., 2005; Sherene, 2010). Different soil types have different suitability for water storage for root uptake, and subsequent transpiration; with loamy soils having the largest amounts of available soil water. Hence, soil moisture constantly changes in soils; when pores that were filled with air fill with water, this changes the environmental conditions, often leading to the release of solutes from surfaces and into pore water (Bronstert, 2003; Ibragimow et al., 2013; Pulchalski, 2003; Schulz-Zunkel and Krueger, 2009; Stuart and Lapworth, 2011). The reverse occurs during dry-down (after rain) where the soil moisture decreases due to evapotranspiration and drainage, resulting in solute precipitation, retention and accumulation (Leitner et al., 2017; Schulz-Zunkel et al., 2015; Unger et al., 2009b).

There are several methods for extracting pore water from soil samples. These methods can be broadly divided into methods that either require: (i) the *in-situ* installation of a sampler within the soil volume of interest (e.g. Rhizon^{TM}, porous ceramic cups, dialysis) and equilibration prior to extraction by applying suction, or (ii) the removal of a subsample and *ex-situ* pore water extraction by exerting a force on it (e.g. centrifugation or squeezing). Previous comparisons of pore water extraction methods have focused on the extraction of pore water from generally saturated sediment samples, rather than soil samples (Brodecka-Goluch et al., 2019; Bufflap and Allen, 1995; Steiner et al., 2018; Winger et al., 1998; Wittke et al., 2020), and on sampling laboratory microcosms rather than field sampling (Ludwig et al., 1999; Meers et al., 2006; Orlowski et al., 2016; Shaheen et al., 2014b; Tiensing et al., 2001).

4.1.2. Rhizon^{TM} sampler

Rhizon^{TM} samplers (Rhizosphere Research Products, Wageningen, Netherlands) are composed of a thin porous, chemically inert hydrophilic polymer tube, capped with a Luer-lock which allows connection to a syringe (Dickens et al., 2007; Dubbin, 2004; Seeberg-Elverfeldt, 2005). The porous tube has a mean pore size of 0.15µm, therefore most colloids in the soil solution are expected to be excluded from the extracted sample, so filtering of the pore water samples is not necessary prior to analysis, which could be considered a benefit of using this method (Pan et al., 2016; Shotbolt, 2010). The Rhizon^{TM} sampler is inserted into the soil/sediment and the syringe creates a vacuum that extracts pore water (Figure 4.1B).

Rhizon^{TM} samplers have been used in many laboratory studies analysing soil pore waters extracted from soils in intact columns (Beesley et al., 2010; Clemente et al., 2010; Löv et al., 2017), artificially repacked pots/columns (Falcon-Suarez et al., 2014; Ma and Dong, 2004; Qasim et al., 2016) or sediment cores taken from the field (Brodecka-Goluch et al., 2019; Dickens et al., 2007; Du Laing et al., 2008; Schrum et al., 2012; Seeberg-Elverfeldt et al., 2005; Shotbolt, 2010; Steiner et al., 2018;

Wittke et al., 2020) but less so *in-situ* in the field (Clemente et al., 2008; Moreno-Jiménez et al., 2011). Where they have been used in the field, they tend to be installed permanently into the soil or sediment, vertically or horizontally; this allows for sampling in the same location over various sampling occasions. This semi-permanent installation also allows time for the Rhizon^{TM} samplers to settle (generally for a minimum of 2 weeks prior to pore water extraction), ensuring a good hydraulic contact with the soil (Beck et al., 2008; Beesley et al., 2010; Clemente et al., 2008; Di Bonito et al., 2008; Geibe et al., 2006; Schröder et al., 2008). Rhizon^{TM} samplers must be inserted into the soil or sediment completely to avoid air uptake through exposed sections, as this interferes with the vacuum produced by the syringe to draw the pore water from the sample (Wittke et al., 2020). The Rhizon^{TM} samplers are generally inserted into wet samples or moistened with ultra-pure water prior to sampling, as this helps to increase flow rate (Di Bonito et al., 2008; Wittke et al., 2020). The capillary pressure in the sampler needs to be lower than that of the water in the surrounding soil, to create tension and allow pore water to be actively drawn from the soil into the sampler (Di Bonito et al., 2008; Lajtha et al., 1999). The time required to sample depends on the soils unsaturated hydraulic conductivity (Di Bonito et al., 2008). It has been commented that Rhizon^{TM} samplers appear to sample water preferentially from more accessible pools, with a 'zone of influence' extending to a radius of around 5cm (this figure does not account for differences in hydraulic conductivity or porosity) from the porous sampler (Di Bonito, 2005; Di Bonito et al., 2008). It has also been found that if there is overlying water (in the case of flooding) then water is preferentially drawn from above the depth where the sampler is located, meaning no soil pore water may be extracted at all during a flood event (Steiner et al., 2018).

4.1.3. Centrifugation

Centrifugation is possibly the most widely used pore water extraction method, as it is relatively easy to use and equipment is generally available in most laboratories (Di Bonito et al., 2008; Lozano et al., 2020). Due to the destructive nature of the sampling required to remove soil from the field to extract pore water from, samples can only be taken once at exactly the same location (Geibe et al., 2006). The removal of the soil sample from the natural environment, for pore water extraction, can result in differences between the measured pore water composition and the true *in situ* pore water composition, due to changes in temperature and pressure after removal (Beck et al., 2007; Bufflap and Allen, 1995). *Ex situ* centrifugation works well when sample homogenisation is key to the experimental design (Di Bonito et al., 2008).

The centrifuge exerts a relative centrifugal force (RCF) on the soil, causing water to be drawn out from the sample, through holes in the centrifuge assemblage supporting the sample and into a collecting cup (Figure 4.1C). However, as the water migrates through the soil sample it will cause saturation of the soil at the base and this may cause an alteration to the chemical composition of the pore water (Di Bonito, 2005). The volume of pore water extracted by centrifugation is a function of the initial weight of the soil sample, the pore size distribution, degree of saturation, centrifuge dimensions and rotational speed (Di Bonito et al., 2008; Fraters et al., 2017). It is accepted that the faster the centrifuge spins, the smaller the pores that the water will be extracted from (Fraters et al., 2017; Geibe et al., 2006; Grieve, 1996; Reynolds, 1984). Hence, the pore water obtained through centrifugation may originate from small pores that have had longer contact time with the soil matrix, as it does not migrate easily (due to low hydraulic conductivity) (Geibe et al., 2006; Ujile and Owhor, 2018). When samples are centrifuged, fine particulate material may still be suspended in the pore water (Bufflap and Allen, 1995) so filtering is an important requirement. However, it should be noted that filtering the pore water will result in a loss of elements associated with the particulate matter, so subsequent pore water analysis is of the dissolved elements only (Bufflap and Allen, 1995; Di Bonito et al., 2008).

4.1.4. Comparing Rhizon^{TM} samplers with Centrifugation

A consensus for which pore water extraction method is optimal for sampling pore water in the field has not yet been reached due to all of the approaches having artefacts and drawbacks. For example; Rhizon samplers generally extract smaller volumes of pore water solution and centrifugation can result in potential pore water sample contamination (Bufflap and Allen, 1995; Steiner et al., 2018). Moreover, comparisons have revealed that considerable differences in the approaches lead to differences in the concentration of elements analysed when applied to the same samples (Steiner et al., 2018; Winger et al., 1998). Therefore, a pore water extraction method should ideally be selected *a priori*, to suit the needs of a particular research question.

The differences in the principles by which the Rhizon^{TM} sampler and centrifugation methods operate means that the pore waters extracted by each method may have a different composition from each other, because the Rhizon^{TM} samplers extract pore water from more accessible pools (macropores) and the centrifuge extracts water from a wider range of pore sizes (Bufflap and Allen, 1995; Di Bonito et al., 2008; Lajtha et al., 1999; Lorenz et al., 1994; Reynolds, 1984; Steiner et al., 2018). Nevertheless, centrifugation will still only extract a fraction of the total pore water as it samples more micropores, where the water is tightly held (Di Bonito et al., 2008; Lajtha et al., 1999). Somavilla, Dessbesell, & Dos Santos, (2017) compared centrifugation speeds for extracting pore water and concluded that even though only one pore water extraction method was used, the pore water concentrations differed because different energies had been applied to obtain the solutions. The distance of the sample from the centre of the centrifuge, the weight of the soil sample and its' initial water content will all affect the volume of pore water extracted (Di Bonito et al., 2008).

In this paper we compare the Rhizon^{TM} sampler, as an example of an *in-situ* method that uses low (negative; (-93kPa)) pressure to extract pore water, and centrifugation as an example of an *ex situ* method that uses medium-high centrifugal force (1111kPa) to extract pore water. We assessed whether these two methods result in different concentrations of solutes, including a range of elements, in pore water extracted from soils of a floodplain in the lower reaches of an urban catchment in Southeast England. We compared the usability of each method as well as the results of chemical analysis of the extracted pore water, including concentrations of anions, cations, pH, and dissolved organic carbon (DOC). Samples were collected on four occasions from three sampling points that were chosen to reflect the varying elevation across the floodplain, because elevation affects relative saturation.

This research aimed to investigate the practical differences between using Rhizon^{TM} samplers compared with centrifuging soil samples, to extract soil pore water from floodplain soils, as well as investigate whether the two sampling methods result in differences in the chemistry of the pore water extracted.

We hypothesised that *ex situ* centrifugation would extract higher concentrations of solutes than the *in situ* Rhizon^{TM} samplers because the higher pressure that is exerted on the soil sample will result in pore water extracted from a greater range of soil pore sizes, which we expect to have a higher ionic strength, owing to the lower volume-to-surface area ratio. We also expected that the centrifugation method would extract higher volumes of pore water (and more consistently) over the sampling period than the Rhizon^{TM} samplers. Finally, we expected that both methods would extract a greater volume of pore water from soils sampled from the lower elevation sampling point, which typically has a higher soil moisture (and therefore lower soil water suctions, i.e. less negative matric pressures) than soils sampled from the higher elevation sampling point, further away from the river. There is a direct relationship between pore diameter (d, µm) and matric potential (Ψm, kPa) as shown in the equation; $d = -300/\Psi m$ (Marshall and Holmes, 1988).

4.2. Methodology

4.2.1. Field site and sampling regime

Soil and pore water samples were taken on four sampling occasions during March-April 2018 from the Loddon Meadow floodplain pasture (part of the Loddon Floodplain Monitoring and Modelling Platform (LFMMP); SU 75141 68635, Figure 4.1A) situated adjacent to the River Loddon; a tributary of the River Thames, to the south of Reading, in Southeast England. This floodplain site has been previously characterised as having a silty loam soil texture, with the majority of particles <50 µm in size (Kelly et al., 2020). Three sampling locations were chosen across the field, one in an area of relatively high elevation (~40m above ordnance datum) where flooding is less likely for most of the year, the second in an area (~39m above ordnance datum) that floods but drains quickly, and the third in an area in the centre of the field with relatively low elevation (~38m above ordnance datum) that floods regularly and drains more slowly. A soil moisture probe (Pro-Check Decagon Device) was used to assess the soil moisture (%VWC; volumetric water content) at each location during each visit.

4.2.2. Pore water extraction

At each of the three locations; three Rhizon™ samplers (Rhizosphere Research Products, Wageningen, Holland), spaced 10 cm apart, were used to extract pore water *in situ* and the resulting pseudo-replicates combined into one composite sample. A wooden skewer was used to create a channel for the sampler to be inserted into the soil without damaging it. The sampler was then connected using polyethylene tubing and a Luer-Lock connector to a 25ml polypropylene syringe, which was drawn and kept in place with a wooden spacer, to create a vacuum in the barrel of the syringe and exert negative pressure on the soil (Figure 4.1B). The pore water extracted with the Rhizon™ sampler was filtered in this study using a Fisherbrand™ Sterile polyethersulfone (PES) single-use syringe filter (33mm diameter membrane with 0.45 µm pore size) into acid washed universal tubes in the field and stored in a cool box. The sampling was finished after 5 hours regardless of whether the sampler had extracted enough pore water to fill the barrel of the syringe, or not. Sampling time was an important consideration for deciding the right pore water extraction method and so the time it took to take the soil samples from across the Loddon Meadow floodplain was used as the maximum time for extraction using the Rhizon sampler, meaning the Rhizon samplers generally had between 2 and 5 hours to equilibrate. All Rhizon™ samplers had to be removed between visits, as the Loddon Meadow pasture field used for this study was intermittently grazed by livestock. Pore waters were returned to the laboratory and refrigerated (4°C) within 30 minutes of leaving the field site.

At the same three locations a composite soil sample was taken, about 30cm away from the Rhizon samplers, using a stainless-steel auger (5 pseudo-replicate soil samples from the topsoil (~10cm depth) put into one sample bag in a cool box) for later extraction of comparable pore water using centrifugation. On return to the laboratory, the soils were homogenised and 100g was weighed into custom made acid-washed Teflon centrifuge assemblages lined with a polyester mesh (Figure 4.1C; 6 assemblages per run) and placed into a Sorvall RC6+ Centrifuge set to centrifugal speed of 5,000rpm, which is an RCF of 3830 x g, for 1 hour. The extracted pore water was then filtered using a Fisherbrand™ Sterile PES single-use syringe filter (33mm diameter membrane with 0.45 µm pore size) into an acid washed universal tube and stored at 4°C prior to analysis.

The pressure applied by the centrifuge were calculated using the equation below (equation 4.1) (Di Bonito et al., 2008; Edmunds and Bath, 1976);

$$\mathrm{Pa} = \frac{\omega^2}{2\mathrm{g}} \text{ x } (\mathrm{r1}^2 - \mathrm{r2}^2) \tag{4.1}$$

where:

Pa = tension applied developed at a generic point r2 of column (cm water);

ω = angular velocity (rad sec^{-1});

g = gravitational constant (cm s^{-2});

r1 = distance from base of column to centre of rotation (cm).

The centrifuge revolutions per minute (rpm) was converted to angular velocity in a two-part calculation; the 5,0000rpm to rad/minute by multiplying by 2Pi, and then this was converted to rad/sec by dividing by 60 (Beaty, 2018). The pressure (Pa) is calculated in units of centimetres of water, this was converted to kilopascals (kPa) as 1 centimetres of water is equal to 0.0981kPa (Beaty, 2018). The distance from the base of the column (r1) for the centrifuge was 9cm.

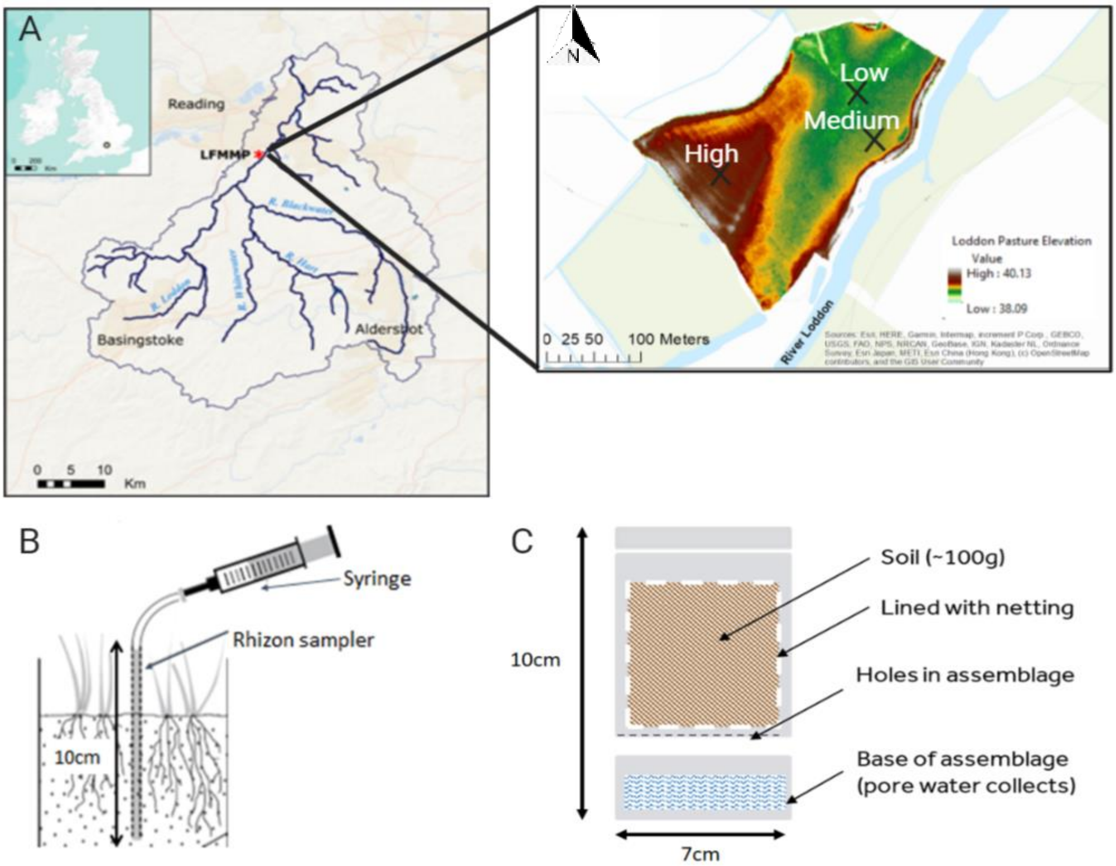


Figure 4.1 *A) Loddon Floodplain Monitoring and Modelling Platform (LFMMP) with surrounding catchment, and the floodplain meadow elevation map with the three sampling locations in the field labelled as "High" "Medium" and "Low" based on their elevation (created using LIDAR map data retrieved from Digimap and put into ArcGIS) B) Illustration of the Rhizon*^{TM} *sampler and C) illustration of the centrifuge assemblage.*

4.2.3. Environmental conditions

During the sampling period (March-April 2018) the environmental conditions were continually monitored. Daily rainfall was measured using a weather station installed at Reading University's campus grounds at a distance of approximately 6km from the study site; the daily average river levels were observed using the Environment Agency flow gauge located at Arborfield Bridge, 1.2 km upstream of the study site, and daily ground water level (GWL) was monitored using pressure transducers (one telemetered) installed in two boreholes located at the study site. During the fieldwork, the soil moisture was measured using a ProCheck, Decagon Device handheld meter which provided the volumetric water content (VWC), expressed as a percentage of the water held by the soil.

4.2.4. Laboratory analysis

A ‘Hanna’ pH meter was calibrated using pH 7 and pH 4 buffers at room temperature before further analysis of the pore water samples, washing the probe with ultrapure (>18.2 MΩ.cm) water between buffers and between samples. The pH meter was re-calibrated with the two buffers after 10 samples.

Sub-samples were diluted (typically by a factor of 4 or 10, depending on the volume of pore water obtained) and analysed for total organic carbon by subtracting inorganic carbon from total carbon measurements made on a Shimadzu TOC-L TOC analyser (Shidmadzu Scientific Instruments). The TOC analyser was calibrated with standards made from potassium hydrogen phthalate (total carbon) and sodium hydrogen carbonate and sodium carbonate (inorganic carbon) alongside a QC solution (TOIC 100) supplied by Reagecon Diagnostics Ltd, with an average recovery of 97%. Analysis of samples were carried out within 2 weeks of collection to avoid contamination from leaching of organic C from the plastic universal tubes. The detection limit (1.34mg/L) was calculated as 3 times the standard deviation of the TC 20ppm QC value for TOC (Table SI-4.1).

Sub-samples were diluted (typically by a factor of 4 or 10, depending on the volume of pore water obtained) directly into disposable Dionex tubes and run within one week of sample preparation on a Dionex DX-500 Ion Chromatograph (Thermo Scientific, US); to provide sequential determination of 7 anions: chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^-) and sulphate (SO_4^{2-}). Detection limits were calculated as 3 times the standard deviation of the QC solutions (Table SI-4.1).

To determine the concentration of cations, pore water samples were acidified at 2%, by volume, with concentrated nitric acid (HNO_3) as soon as possible after field sampling and analysed on an Optima 7300 inductively coupled plasma optical emission spectrometer (ICP-OES). At the start of the ICP-OES run, after calibration a QC solution containing 0.5 mg/L of Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, and Zn and a second QC solution containing 50 mg/L of As, both traceable to NIST SRM 1643e (trace elements in water) was run with recoveries of: 106% for As, 103% for Al, 99% for Cd, 102% for Co, 112% for Cu, 107% for Fe, 92% for K, 98% for Li, 105% for Mg, 106% for Mn, 98% for Na, 106% for Ni, 96% for Pb and 104% for Zn. The limits of detection for each element are provided in the appendix. Detection limits (Table SI-4.1) were calculated as 3 times the standard deviation of 10 measurements of the zero-calibration standard. If a low volume (below 5 ml) of pore water was extracted, priority was given to ICP-OES analysis, over TOC or Ion Chromatography.

4.2.5. Data analysis

The concentrations (cations, anions and TOC) in pore water extracted using the Rhizon^{TM} sampler and centrifuge were compared by quantifying how well they fit a one to one relationship (y=x) using MS Excel. Descriptive statistics as well as an outlier analysis (Grubbs' test), was performed on the data using Minitab 19.1.1 (Table 4.2) where the null hypothesis, that all data values come from the same normal population, was tested. Results that were found to be 'outliers' were not removed from any other analyses or the one to one plot, as the purpose of the Grubbs test was to allow another comparison of the results for the two methods. Principal Component Analysis (PCA) using PRIMER (version 7) was undertaken with the data classified by pore water extraction method (Rhizon^{TM} sampler and centrifuge) and elevation (high, medium and low). The data was normalised in PRIMER prior to the PCA and the output bi-plot used to compare the analytical results for the two methods. One-way Analysis of Similarities (ANOSIM) was performed to test for differences between the two extraction methods.

4.3. Results

4.3.1. Environmental conditions

The environmental conditions throughout the duration of the sampling period are shown in Figure 4.2 and reveal considerable variability of rainfall, river levels and ground water levels during the sampling period. A planned sampling trip on the 19th March was cancelled due to heavy snow fall. These conditions affected the soil moisture content over time (Table 4.1), which was a key criterion for comparison of the usability of the two pore water extraction methods. The groundwater table was slightly above ground level at the end of March/ beginning of April 2018, indicating a floodwater layer of around 10cm. Flooding only occurred at the lowest elevation sampling point, in the centre of the field and was most likely caused by a combination of heavy rainfall (see Figure 4.1C) and snow melt, increasing the groundwater level and river level.

The soil moisture/volumetric water content (VWC) differed considerably between the locations, with the location at medium elevation always exhibiting the highest soil moisture content (apart from on 9th April, when both locations had very similar VWC), and the high elevation location having the lowest water content. We would have expected the low elevation to always exhibit the highest soil moisture and this may reflect varying soil texture (not measured). For all locations, the VWC was highest on 9th April, particularly so for the low elevation location. This indicates that this location was affected by groundwater and/or river water, as seen in Figure 4.2A and B.

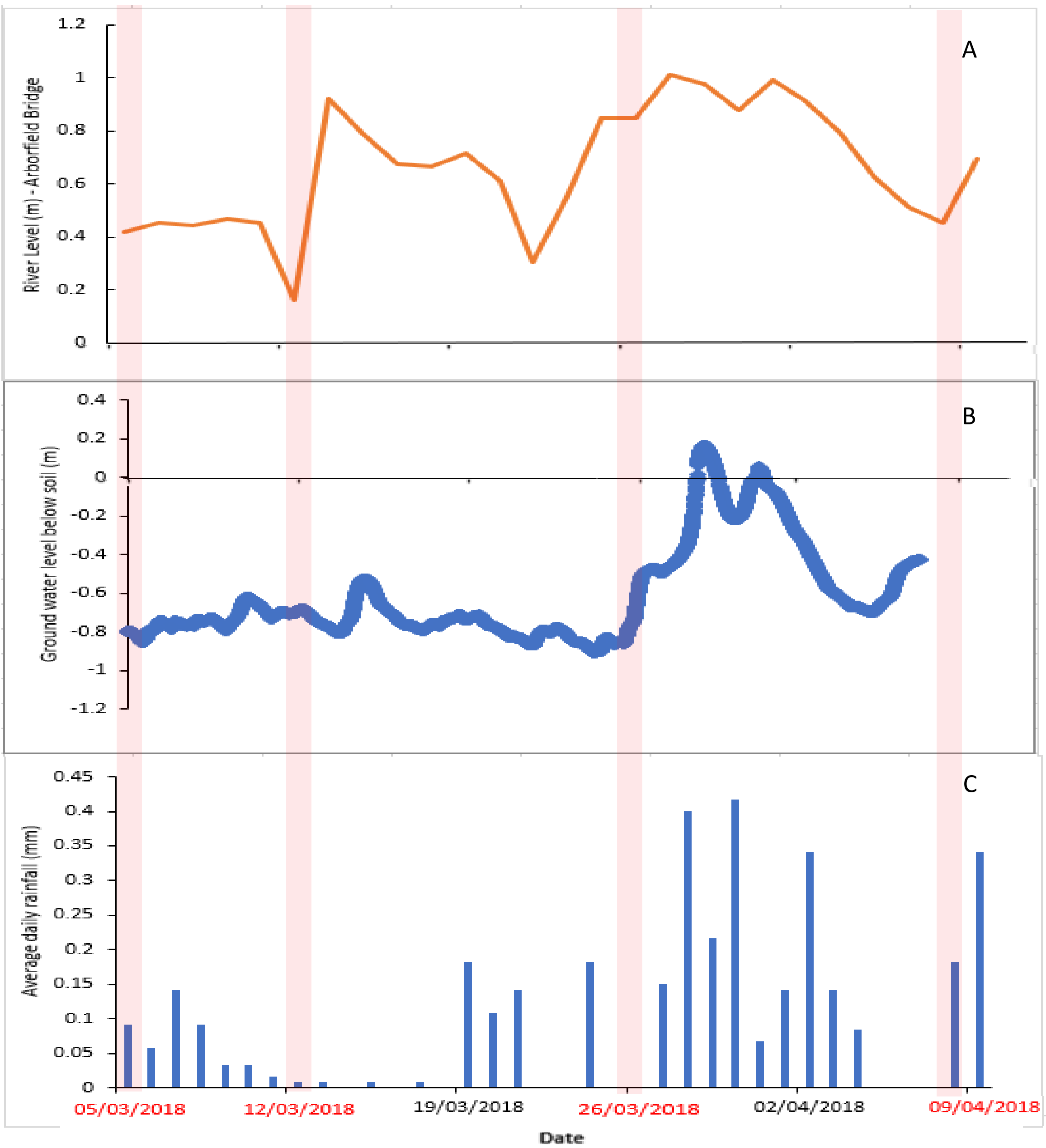


***Figure 4.2** Environmental conditions A) river level at Arborfield Bridge, 1.2 km upstream of the site, B) ground water level collected from a borehole located at the 'medium elevation' sampling point depicted in Figure 4.1A. and C) daily rainfall recorded at a weather station 6.3km from the site. The red vertical bars highlight when sampling occurred.*

Table 4.1: Soil moisture (volumetric water content; VWC, expressed as a percentage) at the three sampling location points (low, medium and high elevation) on the four sampling dates.

	Soil moisture (%VWC)			
Sampling point	05/03/2018	12/03/2018	26/03/2018	09/04/2018
Low	42.7	50.6	40.6	57.6
Medium	53.8	59.4	55.5	56.2
High	29.5	35.8	36.3	40.4

4.3.2. Pore water chemistry

The solute (cations, anions and TOC) concentrations measured in the pore waters extracted using the Rhizon^{TM} sampler and the centrifuge were compared (Figure 4.3) to assess the agreement between the results from the two methods. A fit forced through the origin, revealed that there is a significant 1:1 relationship between the Rhizon^{TM} sampler and centrifuge (R^2 = 79% and $P < 0.05$). Descriptive statistics and outlier analysis (Grubbs' test) results are presented in Table 4.2. The results show that the centrifuge was more consistent (the N values show the number of samples from each method) and also that the Rhizon^{TM} sampler has a greater number of data values outside the normal population ('outliers' total 5 compared to 2 for the centrifuge) i.e. the Rhizon^{TM} sampler had a bigger range of values compared with the centrifuge. No values were removed from the analysis as a result of them being highlighted in the Grubbs test as 'outliers'; the analysis was used as another way of comparing the two methods.

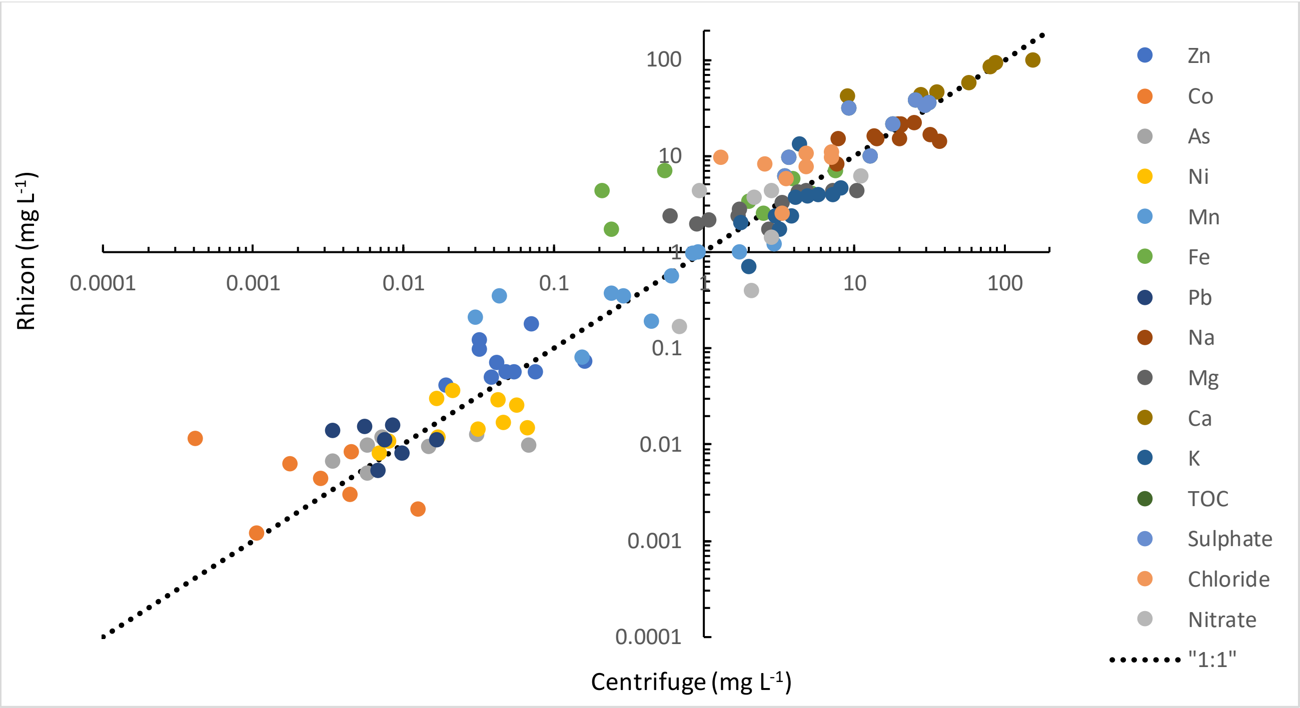


Figure 4.3 Concentrations of zinc, cobalt, arsenic, nickel, lead, iron, manganese, sodium, calcium, potassium, magnesium, total organic carbon (TOC), sulphate, chloride, fluoride and nitrate in the pore water samples extracted using Rhizon^{TM} sampler (x axis) and centrifuge (y axis) on a logarithmic scale. When the results are above the dotted 1:1 line, the concentrations were greater using the centrifuge and when they are below the dotted 1:1 line, the concentrations were greater using the Rhizon^{TM} sampler.

Table 4.2: Descriptive statistics and outlier analysis (Grubbs Test) results, comparing the results of pore water analyses from the Rhizon^{TM} sampler with the centrifuge for outlier results (values outside the normal population) in the pore water chemistry.

Variable	**PTE**	**N**	**Mean**	**StDev**	**Min (mg/L)**	**Max (mg/L)**	**Outliers**
Rhizon	As	7	0.019	0.024	0.0034	0.069	1
	Ca	7	64.8	49	9	155.4	
	Chloride	8	11.91	6.66	3.63	19.8	
	Co	9	0.0068	0.0072	0.00041	0.022	
	Fe	9	4.99	7.1	0.21	22.74	1
	K	11	4.38	2.008	1.76	8.13	
	Mg	11	3.53	3.053	0.59	10.49	
	Mn	11	0.75	0.88	0.03	2.94	1
	Na	11	19.87	9.16	7.62	36.82	
	Ni	10	0.032	0.021	0.0069	0.068	
	Nitrate	7	3.24	3.59	0.69	11.15	1
	Pb	7	0.0083	0.0042	0.0034	0.017	
	Sulphate	8	4.29	2.044	1.29	7.03	
	TOC	8	16.79	11.25	3.49	31.26	
	Zn	10	0.058	0.041	0.019	0.162	1
Centrifuge	As	11	0.0077	0.0031	0.0041	0.0123	
	Ca	11	60.88	26.34	24.88	98.18	
	Chloride	12	13.49	4.84	6.18	21.99	
	Co	11	0.0058	0.0047	0.0012	0.0165	
	Fe	11	4.51	2.058	1.56	7.06	
	K	12	3.94	3.16	0.69	13.13	1
	Mg	12	3.028	0.99	1.74	4.32	
	Mn	12	0.53	0.40	0.008	1.22	
	Na	12	16.8	4.08	8.08	22.32	
	Ni	12	0.018	0.0096	0.0053	0.016	
	Nitrate	12	3.01	1.97	0.017	6.15	
	Pb	12	0.012	0.0037	0.0053	0.016	
	Sulphate	12	7.43	2.98	2.05	11.06	
	TOC	12	21.34	11.32	6.22	37.58	
	Zn	12	0.079	0.039	0.042	0.18	1

A multivariate statistical analysis was used to establish the factors influencing the variability in the data set. The Principal Component Analysis (PCA) plot (Figure 4.4) shows that around 50% of the variability in the data was explained by the first two principal components; PC1 and PC2. The first principal component represents differences in pore water chemistry due to spatial and temporal variation in soil moisture; with samples from high elevation showing a negative loading on PC1. The second principal component represents differences in pore water chemistry due to the pore water extraction method; with the centrifuge having a positive loading on PC2. The ANOSIM sample statistic (R) value was close to zero (0.144) and so this indicates low separation between the Rhizon ^{TM} sampler and centrifuge. The spread of the data in the PCA plot is greater for the Rhizon™ sampler compared with the centrifuge results, which are more tightly grouped together. The spread of the Rhizon ™ sampler data is greater for the lower soil moisture areas (high and medium elevation), with the higher soil moisture at the low elevation resulting in less spread. This result will relate to the relative difficulty extracting enough pore water sample volume from the study site using the Rhizon ™ sampler. The data from the low elevation areas were true analytical results from the Rhizon ™ sampler, rather than the often-required use of ½ the detection limits for the high elevation areas that lacked the sample volume needed for analysis.

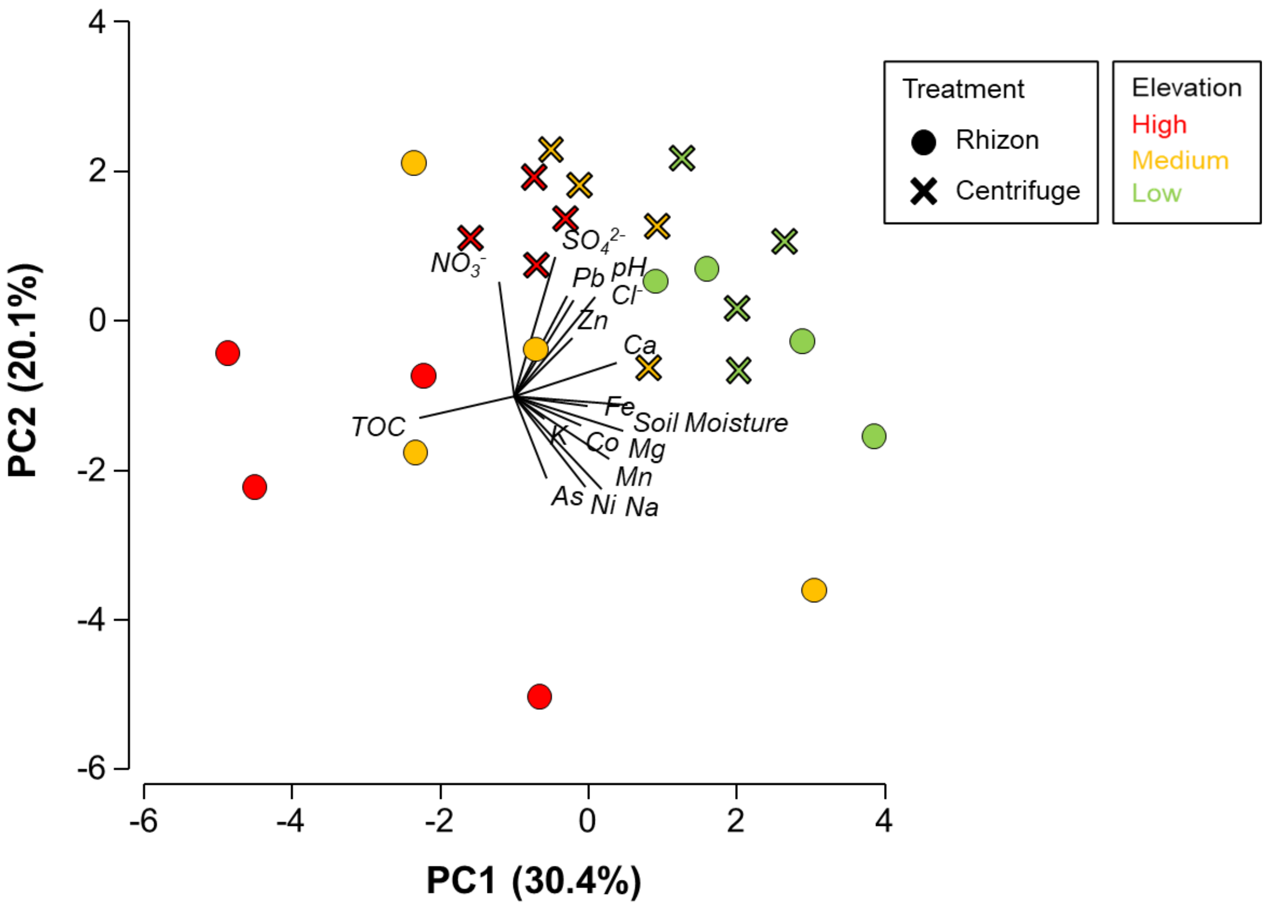


Figure 4.4 *Principal Component Analysis (PCA) biplot showing the pore water chemistry extracted using RhizonTM samplers (dot) and centrifugation (cross) and at the three elevations on the floodplain (high (red), medium (orange) and low (green)).*

4.3.3. Comparison criteria

There are advantages and disadvantages to using both the Rhizon™ samplers and centrifugation methods for the extraction of pore water, which is primarily why there has not already been a consensus reached for which method should be used. Table 4.3 provides factual information about both methods of pore water extraction based on some key criteria for comparison.

Table 4.3: Comparing key criteria for the two pore water extraction methods based on personal experience and information from literature (Bufflap et al. 1995; Di Bonito et al 2008; Geibe et al. 2006, Seeberg-Elverfeldt et al., 2005; Schrum et al 2011; Qasim et al., 2016, Yuan et al. 2019).

Criteria	**Rhizon™ Sampler**	**Centrifugation**
Disturbance	Minimal mechanical disturbance	Destructive sampling
Sampling depth	Generally top soil/upper portion of core is sampled where compaction is minimal	Can extract pore water from varying soil depths if necessary
Pressure applicable (calculated using equation 4.1)	Low; -93kPa	Medium to high; 1111kPa
Soil pore size sampled	0.75μm	0.25μm
Soil moisture required for ease of use	> ~50% VWC	> ~30%VWC
Pore water yielding efficiency, duration (for 10ml sample)	5+ hours (when soil moisture ~30%VWC), 1 hour (when soil moisture ~50% VWC) Inconsistent volume of sample	2-3 hours sampling regardless of soil moisture High-speed centrifuge 1 hour (typically 2 or 3 times) More consistent volume
Materials & possible contamination	Single-use sampler, acid washed tube/bottles artefacts Method eliminates many potential sources of artefacts present in ex-situ methods (due to temperature or pressure changes)	Stainless steel auger, plastic sampling bag, decon and acid washed Teflon centrifuge tube, acid washed tube/bottles. Movement of water due to pressure may change chemical composition
Environmental relevance	The sampler does not cause physical disturbance to soil meaning the same soils could be sampled over time	Centrifuge methods avoid the need for chemical reagents used for immiscible displacement/extraction
Cost of equipment	£10 per sampler; single use	£1,000-£4,000 for the high-speed centrifuge – reusable

4.4. Discussion

We found that the centrifugation method extracted more consistent pore water volumes, and hence yielded more reliably over the sampling period at the three elevations (and thus at varying soil moistures) on the floodplain. Centrifugation subsequently provided a more complete set of samples for analytical and statistical analysis than the Rhizon^{TM} samplers. It was more difficult to extract enough sample volume using the Rhizon^{TM} sampler, particularly for the "high" elevation sampling location, as the soil moisture was consistently lower (<50% VWC) in this area throughout the sampling regime. The time required for extracting pore water at this low soil moisture was considerably longer than the time required to collect soil samples from all of the locations, to take back to the laboratory for *ex-situ* centrifugation. This means, in this study, the Rhizon^{TM} samplers were allowed to equilibrate for no longer than 5 hours. Other studies have placed Rhizon^{TM} samplers in place for several days or weeks prior to sampling, to ensure a good contact with the soil and overcome this prolonged sampling time.

The two methods extract pore water in different ways, and from different pore sizes, due to the difference in pressure exerted on the soil (Scrum *et al*. 2011). The differences in the way that pressure is applied to the sample also affects processes that may alter the concentrations of elements in the pore water, including; precipitation or dissolution of carbonate minerals and ion exchange reactions with clay mineral surfaces (Wittke et al., 2020). During centrifugation, as the water migrates down through the soil sample whilst spinning, the soil at the base becomes saturated, which may cause changes to the chemical composition of extracted pore water (Di Bonito 2005). These differences in the methods raised the question of whether the concentrations of solutes (cations, anions and TOC) in the pore waters collected by the Rhizon^{TM} sampler or spinning soil in the centrifuge would therefore be significantly different from one another. The relatively low pressure Rhizon^{TM} samples predominantly extract the water-filled pore space of larger-sized pores (a suction of 200kPa is equivalent to a pore radius of 0.75μm), whereas the medium to high pressure of the centrifuge draws water out from smaller pores (a suction of ~600kPa is equivalent to a pore radius of 0.25μm). These smaller pores have a higher surface area to solution ratio, and this might mean that the partitioning of solutes between pore water and the soil surfaces is more likely to be in equilibrium (O'Geen, 2013; Vogel, 2000).

We did not observe that one method extracted pore water containing consistently higher concentrations of solutes (cations, anions or TOC) than the other. This was in agreement with another comparison that also found no significant differences between the methods (Geibe et al., 2006). There was a positive linear association between pore water extraction methods for all of the different solutes analysed in our samples; however, the relationship fit the 1:1 line particularly well for Mn, Mg, Ca, TOC, sulphate, chloride and nitrate. These are solutes that are generally present at higher concentrations in the soil pore water than trace elements (e.g. Zn, Co, As, Ni, Fe and Pb) for which a weaker relationship between Rhizon^{TM} and centrifuge pore water concentrations was observed.

The outlier and multivariate (PCA) analysis revealed that the Rhizon^{TM} samplers had a greater spread of pore water solute concentrations, with a greater number of the cations and anions having concentrations that fall outside of the normal range (outliers) compared with a much tighter, less variable spread in the data for analysis of pore waters extracted by centrifugation. Some variation can be explained by the soil moisture, which relates to the environmental conditions at each of the sampling positions (high, medium and low elevation). The Rhizon^{TM} samplers were more difficult to use and there were difficulties in extracting the volume of pore water required for analysis, particularly during sampling trips when soil moisture conditions were drier. For the PCA analysis, where a full complement of data with no gaps, is required for the analysis, therefore the use of ½ the detection limit was used for many of the Rhizon^{TM} sampler results due to low sample volume or (where there was enough volume to analyse) results below the limit of detection.

4.5. Conclusions

Extracting pore water from soils for analysis provides solute concentrations that are environmentally relevant. Therefore, having a full understanding of the strengths and weaknesses of pore water extraction methods in terms of practical application and analytical results is important. Chemical analyses of pore water sampled with Rhizon^{TM} samplers and centrifugation from floodplain soil have been compared in this paper. These findings have provided useful information about the usability of the two methods; their strengths and weaknesses regarding pore water volume extracted and potential sources of contamination.

Based on the literature, coupled with our sampling experience and analytical results from our sampling regime, we recommend centrifugation as a pore water extraction method when sampling over a long period of time, soil moisture is variable and sampling equipment cannot be permanently installed *in-situ*. This recommendation is in agreement with Mason, Bloom, Cappellino, Gill, & Benoit, (1998); Orlowski et al., (2016); and Winger et al., (1998) who all concluded in their papers that centrifugation was the recommended technique due to the ease of the method, the higher sample volumes collected and the consistently repeatable results. Di Bonito et al. (2008) suggested that centrifugation as a pore water extraction method is optimal when homogenisation of samples or obtaining a bulk solution is key to the experimental design. We too found that the centrifugation of soil collected from the floodplain provided more consistent pore water sample volume over the sampling period, at the three elevations on the floodplain, and this subsequently provided a more complete set of samples for laboratory analyses. Rhizon ^{TM} samplers have been used to extract pore water from soil whilst leaving the physical structure of the soil intact (Clemente et al., 2008; Qasim et al., 2016; Tiensing et al., 2001) which is why they were thought to be a promising alternative to the centrifugation method (Shotbolt, 2010). Clemente et al. (2008) comment on the surprisingly low number of studies using Rhizon^{TM} samplers in the field (Farley and Fitter, 1999; Geibe et al., 2006), despite many authors arguing that the Rhizon^{TM} samplers are a simple, powerful tool for pore water sampling (Schrum et al., 2012; Seeberg-Elverfeldt et al., 2005). We believe that this is because the Rhizon^{TM} method tends to work better when the sampler is allowed to settle for at least 2 weeks (Beck et al., 2008; Beesley et al., 2010). As it was not possible, in the instance of this study, to leave the Rhizon^{TM} samplers in the floodplain soil due to livestock grazing, this caused an increase in the sampling time and effort when using the Rhizon^{TM} samplers and also meant the time provided for samplers to equilibrate was not long enough. We found the Rhizon^{TM} samplers difficult to use when there was low soil moisture (long extraction time) as well as when there was flooding (inserting the sampler into the soil with standing water above the soil). It has also been suggested that sampling using the Rhizon^{TM} during flooding is not extracting sample that is representative of the soil pore water, this is an important consideration if sampling during a flood is required. The two pore water extraction methods have individual advantages and disadvantages and therefore the method should be chosen to suit the individual experimental design.

4.6. Chapter 4 Supplementary Material

One supplementary table is provided in Appendix 3:

Table SI-4.1: Limits of detection (LOD) for the solutes analysed in the pore water

Chapter 5

This chapter is formatted as a paper to be submitted to *Science of the Total* Environment

Ponting, J., Verhoef, A., Watts, M.J., Sizmur, T., (*In prep*). Field observations to establish the impact of fluvial flooding on potentially toxic element (PTE) mobility in floodplain soils. *Sci. Total Environ.*

5.0. Abstract

Climate change, coupled with land use change, means that rainfall amounts and rainstorm intensity in Europe and elsewhere are increasing, leading to widespread flooding. Inundation of river water during flooding deposits contaminated sediments onto the floodplain topsoil. Historically floodplains have been thought of as important sink for potentially toxic elements (PTEs). With increasing flood frequency and duration, it is important to understand the impact that further flooding may have on this legacy contamination.

Much of our current understanding of the impact of flooding on pollutant mobility comes from laboratory mesocosm studies; they have observed increased mobilisation with flooding. In this study we took a field-based approach, extracting soil pore waters by centrifugation of soils sampled on multiple occasions from multiple locations across a floodplain site, which lies adjacent to the River Loddon in southeast England.

Flooding did not influence the mobility of all PTEs in the same way. However, flooding generally decreased pore water PTE concentrations and we found significantly lower pore water concentrations of Cd, Cu, and Cr post-flood compared to pre-flood. The dominant process responsible for this observation was precipitation with sulphides, this occurred during the flood and as a result these PTEs were removed from the pore water post-flood. It is possible that there was dilution of PTEs in soil pore waters with groundwater and river water, which had considerably lower PTE concentrations.

The impact of flooding on the release and retention of PTEs in floodplain soils is the net effect of several key processes, occurring concurrently as a result of spatial variability. Therefore, we highlight the importance of understanding the dominant processes that drive mobility of individual PTEs on specific floodplains, so that site-specific predictions can determine the impact of future floods on the environmental fate of legacy contaminants.

Keywords; Fluvial flood, Groundwater flood, Legacy contaminants, Mobilisation, Microtopography, Pore water

5.1. Introduction

Floodplain soils are often contaminated with potentially toxic elements (PTEs) such as; arsenic (As), cadmium (Cd), cobalt, (Co), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), and zinc (Zn); these are generally released into the environment from anthropogenic sources (Álvarez-Ayuso et al., 2012; Förstner, 2004; Prabakaran et al., 2019; Rennert et al., 2017). Floodplains located in urban catchment areas are contaminated from sources including; wastewater/sewage treatment plants, factories using alloys, metal mining, landfills, and road surface runoff from tyre and brake emissions into the river (Hurley et al., 2017; Rowland et al., 2011; Stuart and Lapworth, 2011). The PTEs accumulate within the environment and are bio-transformed due to physico-chemical and biological processes with accumulating concentrations and transformed chemical states (Chrzan, 2016; Czech et al., 2014; Hooda, 2010). Soils have the ability to retain PTEs and their mobility is affected by pH, their concentration in the soil, cation exchange capacity, organic matter and inorganic interfaces, e.g. clays, metal oxides, metal carbonates and metal phosphates (Bradl, 2004; Stietiya, 2010). The mobilisation of PTEs in floodplain soils, even when at relatively low concentrations, may cause adverse ecological impacts for soil microorganisms, plants, and both terrestrial and aquatic fauna; affecting the function of their endocrine, nervous, and respiratory systems (J. He et al., 2019; Ortiz Colon, 2016; Tack, 2010; Tóth et al., 2016a). A decrease in the mobility of essential PTEs (e.g. Cu, Mn, Zn and Fe) that are also important micronutrients for plants, could result in deficiencies that impair plant function and reduce yields, as well as reduce soil productivity by altering the microbial community (Alloway, 2013b; Cornu et al., 2017; Palansooriya et al., 2020).

Climate and land management changes are contributory factors to current and predicted increases in flooding, largely because the effects of a greater intensity and duration of rainfall is exacerbated by urbanisation-driven land use and agricultural practices (O'Connell et al., 2007; Schober et al., 2020; Sparovek et al., 2002). Floodplains are important areas for flood risk management. However, these areas are also a potential environmental risk if flooding results in the remobilisation of legacy contamination from the soils (Ponting et al., 2021; Schober et al., 2020). When floodplain soils undergo inundation, PTE mobility can increase, or decrease, depending on the element (Abgottspon et al., 2015; Beesley et al., 2010; Rinklebe et al., 2016a), the floodplain topography (Ciszewski and Grygar, 2016; Du Laing et al., 2009) and the duration of flooding (Ciszewski and Grygar, 2016; Indraratne and Kumaragamage, 2017; Kelly et al., 2020; Shaheen and Rinklebe, 2014). Concentrations of dissolved PTEs may decrease during a flooding event, as a result of a 'dilution effect'; when an increased volume of water is present, and therefore a lower concentration of PTEs is observed. This increase in water volume and subsequent dilution, is not expected to affect the solubility of PTEs. Alternatively, PTE mobility can increase during a flooding event due to flushing of contaminated soil/sediment and subsequent mechanisms for release into solution (Resongles et al., 2015). We reviewed the literature on this topic and concluded that the mobility of PTEs in floodplain soils change during and after inundation due to the net effect of five key processes (Ponting et al., 2021): 1) soil redox potential for which decreases can directly alter the speciation, and hence mobility, of redox sensitive PTEs (e.g. As and Cr), 2) soil pH increase for which an increase usually reduces the mobility, through increased chelation of metal cations (e.g. Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}), 3) dissolved organic matter which can mobilise PTEs that are strongly bound to soil particles, 4) iron and manganese hydroxides undergoing reductive dissolution, thereby releasing adsorbed and co-precipitated PTEs, and 5) reduction of sulphate, which immobilises PTEs due to the precipitation of metal sulphides.

Much of our understanding about the influence of flooding on PTE mobility in floodplains has come from laboratory experiments undertaken in mesocosms; these report an increase in PTEs mobility, however, often involve short-exposure time and static temperature and soil water conditions (Frohne et al., 2011; Ponting et al., 2021; Rinklebe and Du Laing, 2011). The extrapolation of laboratory-based findings to field situations can be difficult; although this has been done in studies on mine impacted soils (Cadmus et al., 2016; González-Alcaraz and van Gestel, 2015; Hooda, 2010; Lynch et al., 2014; O'Connell et al., 2007; Simms et al., 2000; Small et al., 2015).

The aim of this study was to investigate the impact of flooding on the mobility of PTEs from floodplain soil downstream from an urban catchment by identifying changes to pore water PTEs concentrations pre-flood, during a flood event and post-flood. Our objective was to observe and understand the mechanisms by which PTEs are mobilised or immobilised during a flooding event and post-flood.

5.2. Methodology

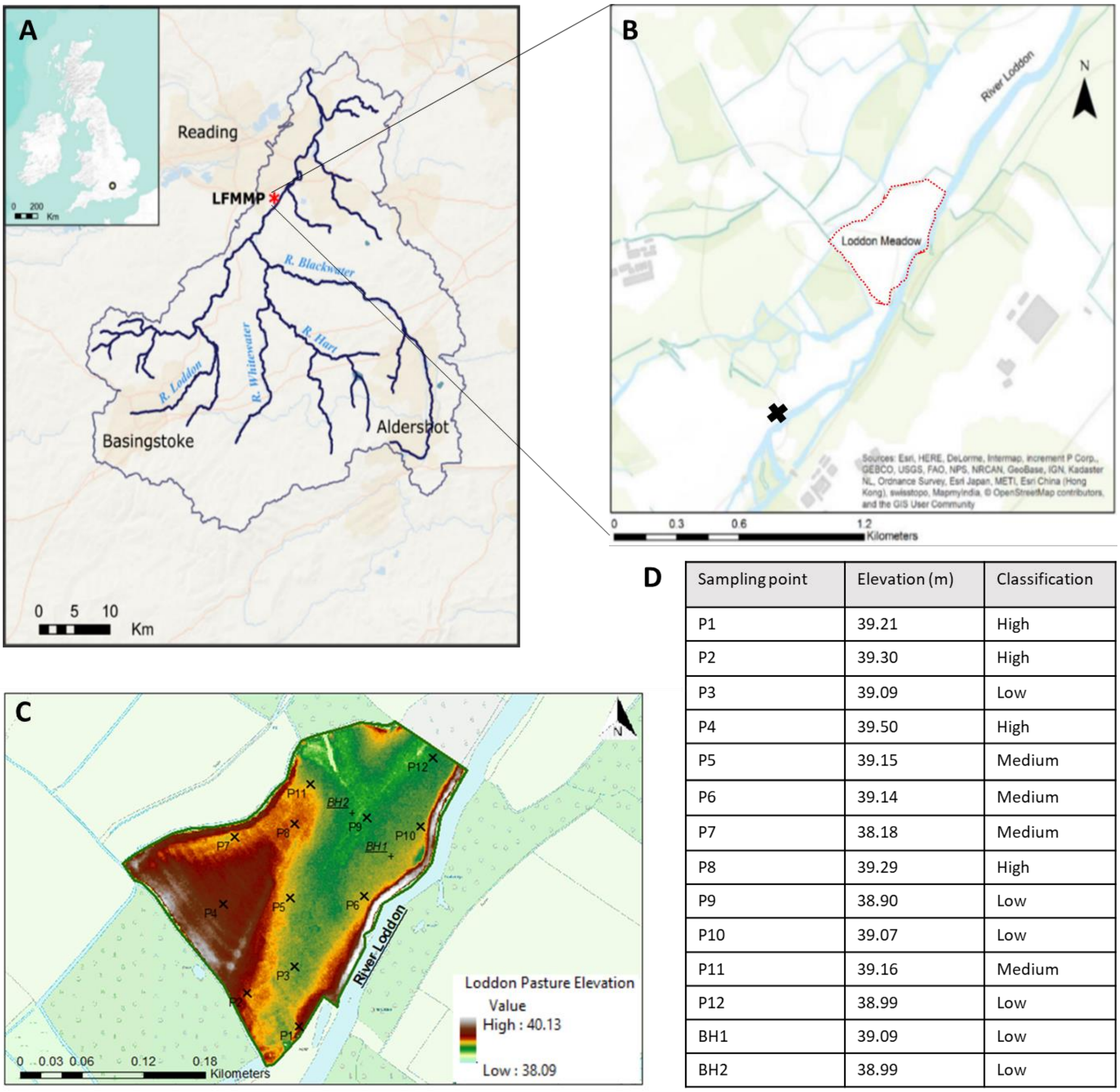
5.2.1. Site

The Loddon Meadow site used in this study is a floodplain downstream of a lowland urban catchment in England and is part of the Loddon Floodplain Monitoring and Modelling Platform. The Loddon Meadow is located adjacent to the River Loddon; a tributary of the River Thames, to the south of Reading, in southeast England, United Kingdom (Figure 5.1A and B; 51º24'47.6" N, 0º55'10.6" W). The Loddon Catchment contains sub-urban, agricultural and semi-natural grassland areas (EA, 1996). The dominant land covers (34,030ha) are arable land and improved grassland (The Wildlife Trusts Hamshire & Isle of Wight, 2003). The underlying geology is predominantly clay, silt, sand, and gravel sediments, with chalk in the upper reaches. The soil texture at the Loddon Meadow site have been previously classified as silty loam using laser granulometry method (Kelly et al., 2020). Under the original Soil Survey of England and Wales classification the soils were classified as argillic gley soil (soil series 0841b, Hurst), (Cranfield University, 2021). The Soil Survey of England and Wales classifications have been correlated and reclassified using the World Reference Base, 2006 Tier 1 Version as a Gleysols. Indeed, the soils on the site are classified as being influenced by surface water/groundwater and categorised as Floodzone 3 (high probability of flooding; Figure SI-1). The Loddon Meadow is a floodplain that generally floods annually with the extent and frequency of flooding depending on interrelated environmental conditions (i.e. precipitation, river and groundwater levels, and soil moisture stores).

There are multiple current and historic sources of contamination to the river from within the catchment, including effluents from wastewater sewage treatment plants, chrome alloy plating industries, landfills situated on previous gravel extraction sites, contaminated runoff from urbanised areas, and military establishments (Kelly et al., 2020). The Loddon Meadow floods intermittently during the winter and occasionally during the summer. Flooding prior to this study was likely to have occurred in April 2018 (Figure SI-2). The extent of flooding is closely linked to the microtopography(soil surface level variation) and elevation of different parts of the floodplain (Figure 5.1C) (Moser et al., 2007; Schumann et al., 2019; Szabó et al., 2020). The characteristics of the Loddon Meadow soils are provided in Table 5.1, including pH, organic matter and (pseudo) total concentrations (further detailed in Table SI-5.1).

Table 5.1: Soil properties averaged across the Loddon Meadow floodplain site, number of measurements (n) is provided and the +/- standard deviation.

Soil properties	Average on Loddon Meadow floodplain
pH (n=132)	6.53 +/- 0.51
OM (%) (n=120)	16.82 +/- 3.89
(pseudo) total As (mg/kg) (n=12)	13.49 +/- 3.73
(pseudo) total Cd (mg/kg) (n=12)	0.56 +/- 0.28
(pseudo) total Co (mg/kg) (n=12)	13.54 +/- 2.41
(pseudo) total Cu (mg/kg) (n=12)	25.92 +/- 8.73
(pseudo) total Cr (mg/kg) (n=12)	35.85 +/- 12.49
(pseudo) total Ni (mg/kg) (n=12)	21.39 +/- 4.57
(pseudo) total Pb (mg/kg) (n=12)	67.02 +/- 31.05
(pseudo) total Zn (mg/kg) (n=12)	137.46 +/- 40.16



Sampling point	Elevation (m)	Classification
P1	39.21	High
P2	39.30	High
P3	39.09	Low
P4	39.50	High
P5	39.15	Medium
P6	39.14	Medium
P7	38.18	Medium
P8	39.29	High
P9	38.90	Low
P10	39.07	Low
P11	39.16	Medium
P12	38.99	Low
BH1	39.09	Low
BH2	38.99	Low

Figure 5.1; *Map of the study site and sampling locations; A) the Loddon Floodplain Monitoring and Modelling platform (LFMMP) showing the regional context (south of Reading in southern England) and the position within the Loddon catchment, B) the local context of the Loddon Meadow site along the northern margin of a section of the River Loddon, with 'X' depicting the location where river water samples were taken upstream from the floodplain, C) a digital elevation model created using Lidar data from Digimap EDINA and hillshade processing in ArcGIS showing the microtopography of the study site. The sampling points P1-14 are shown alongside two boreholes; BH1 and BH2 where groundwater was sampled, and D) a table of sampling points, elevation (metres above ordnance datum) and classification of the locations into 'high', 'medium' and 'low' elevation.*

5.2.2. Sampling

The data used in this paper was collected through the period of December 2018 to March 2019; pre-flood, during the flood, and post-flood. The flood event occurred due to high groundwater levels and overbanking of the River Loddon. There were 5 sampling visits before the flood (pre-flood), one visit during the flood (towards the end of approximately a one-week flood) and 5 sampling visits after the flood (post-flood). Soil properties pre-flood, during the flood and post-flood are presented in Table SI-5.2. All equipment used for soil sampling, storage of pore water samples, and subsequent analysis of samples was acid washed in 3% HCl overnight prior to use, to prevent contamination from the equipment to the pore water samples.

5.2.2.1 Soil samples

The 12 sampling locations used throughout the sampling regime (Figure 5.1C) were selected by creating a Fishnet grid (5m x 5m) in ArcGIS and taking the centre of the grid as the sampling point. The coordinates were put into a Garmin eTrex 10 handheld GPS logger to ensure that the same sampling locations were used during repeat visits. The elevation was determined by creating a digital elevation model using LIDAR data from Digimap and hillshade processing in ArcGIS showing the microtopography of the study site (Figure 5.1C). These sampling locations represent varying elevations in metres above ordnance datum (Figure 5.1D).

At each sampling location, 5 soil samples were collected from an approximately 1m^2 area using a stainless-steel auger to consistently sample the top 30cm of floodplain soil; these 5 samples were combined into 1 composite sample and stored in a cool box before return to the laboratory. Homogenised (~100 g) samples were placed into a centrifuge at 5,000 rpm (RCF 3830 x g) for 1 hour to extract pore water samples (Di Bonito et al., 2008; Sizmur et al., 2011a). Soil pore waters were extracted to determine the free ion concentrations as these are considered the bioavailable metal pools (Hooda, 2010). Analyses conducted on the pore water samples included elements using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), anions using Ion Chromatography (IC), and dissolved organic carbon using the Non-Purgeable Dissolved Organic Carbon (NPOC) method. Details of these analyses are provided below.

5.2.2.2 Environmental conditions

Daily measurements of river levels are monitored by the Environment Agency at Arborfield Bridge, approximately 1.2 km upstream of the Loddon Meadow floodplain site; these data were accessed remotely (https://riverlevels.uk/loddon-arborfield-and-newland-arborfield-bridge#.X7udX2j7SUk). This information, combined with the knowledge that the Loddon Meadow site has an elevation of between 38 and 40 m above ordnance datum, was used to plan sample collections around the flood event (Figure 5.2A). When the river level is around 41.19m or higher, flooding is likely to occur. On the 6th sampling trip (11/02/2019) the floodplain was inundated; this was the only observed flooding event during the sampling period of this study.

River water samples were collected with a Nalgene bottle on a pole from a bridge located upstream of the floodplain (Figure 5.1B) at two time points (8am and noon) on each sampling day during the period between November 2018 and March 2019. The water samples collected were transported in a cool box back to the laboratory and then were filtered using a 0.45 µm cellulose nitrate syringe filter and acidified prior to storage in the fridge and further analyses for elements (ICP-MS), anions (IC) and dissolved organic carbon (NPOC), as described below.

There are two boreholes located on the Loddon Meadow Floodplain (Figure 5.1C); borehole 1 (BH1) is located closest to the River Loddon and borehole 2 (BH2) is located in the ‘low’ elevation centre of the floodplain (Figure 5.1C). Daily measurements of the groundwater levels were monitored remotely using an IMPRESS submersible water pressure transmitter sensor installed in BH1, connected to an Isodaq Frog RXi-L GPRS-8-channel data logger; the data was accessed via Timeview Telemetry (© 2017 Isodaq Technology, Hydro International), whereas a BaroTROLL sensor was installed in BH2, that required manual downloading and processing. Furthermore, the groundwater levels in the boreholes were regularly ‘dipped’ manually to allow for correction of the automatically recorded groundwater levels, where required. A BaroTROLL stored in the housing of the ‘Frog’ datalogger measured atmospheric pressures; these data were also regularly downloaded to correct the BaroTroll data obtained in BH2. This barometric correction was not necessary for the IMPRESS sensor. The groundwater levels were above the ground level on two occasions during this sampling (between the 2nd and 3rd sampling visit and during the 6th sampling visit) and the groundwater levels were within the top 30cm of the soil profile during the 9th and 10th sampling visits (Figure 5.2B).

Groundwater samples were collected from BH1 and BH2 on each sampling day during the period between December 2018 and March 2019. An acid-washed 1m plastic tube with 60ml syringe was used to create a vacuum to draw water up from the borehole. The first sample drawn up was used to wash the 500ml Nalgene sample bottle and then discarded. The groundwater samples collected were transported back to the laboratory in a cool box and then were filtered using a 0.45 µm cellulose nitrate syringe filter. Groundwater samples were then analysed for elements (ICP-MS), anions (IC) and dissolved organic carbon (NPOC), as described below.

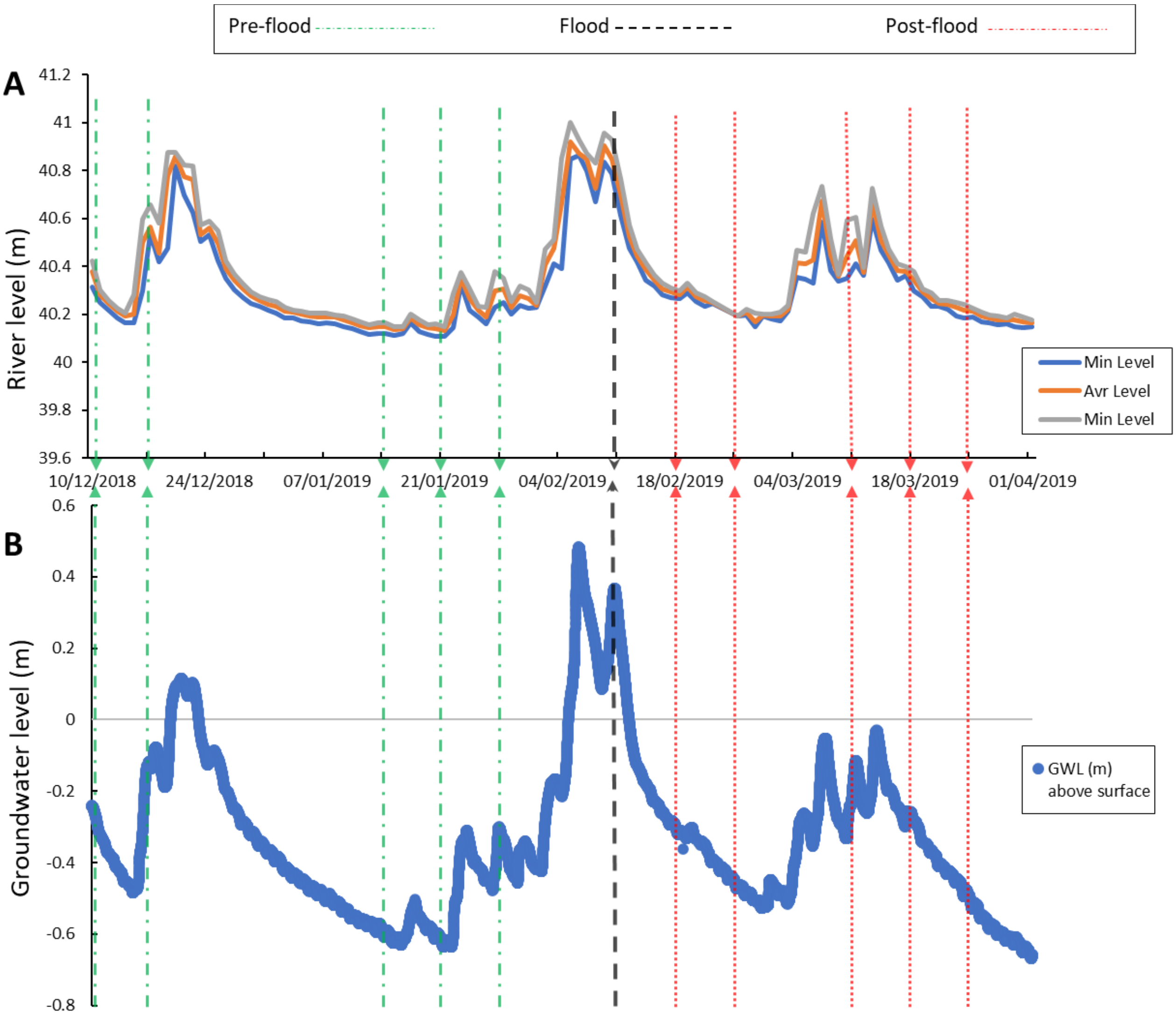


Figure 5.2; *A) Hydrograph showing River Loddon level (m above ordnance datum, where stage datum is 40m) at Arborfield Bridge river level station upstream from the Loddon Meadow floodplain; during the sampling period, B) Groundwater level (m relative to soil surface) averaged from the boreholes on the floodplain. The dot and line green arrows show five sampling dates pre-flood, the dashed line black arrow shows the one sampling date during the flood and the dotted line red arrows show the five sampling dates post-flood.*

5.2.3. Analysis

5.2.3.1 Laboratory analysis

5.2.3.1.1 Soil samples

Moisture and organic matter were determined by mass loss after overnight heating to 105°C and loss on ignition at 500°C, respectively.

The (pseudo) total concentrations of PTEs in soil samples collected from the floodplain were found through soil digestion by reverse aqua regia method using the MARS 6 microwave digestion system followed by ICP (OES and MS) analysis (Sizmur et al., 2019). Each batch of 30 samples was run alongside a replicate of an in-house reference material (SS 51) that is traceable to a Channel sediment certified reference material (BCR 320 R); we obtained the following recovery rates for As (64%), Cd (81%), Co (106%), Cu (97%), Cr (86%), Ni (86%), Pb (86%), and Zn (92%).

5.2.3.1.2 Water samples; soil pore water, river water and groundwater

The soil pH, and redox potential were determined immediately following sampling using a Hanna 9125 pH/ORP meter. For the pH reading, two buffer solutions (pH 4 & 7) were used to calibrate the probe and to check for drift, after every 10 samples. For the redox potential, the probe was checked using a redox check solution before measurements on the samples were taken. Measurements were only taken when the redox check solution reading was +476 mV.

Electrical conductivity (EC) is a measure of the proportion of anions and cations in the solution (De Vivo et al., 2008). In addition to EC being part of the experimental data, it was also used to help identify the correct dilutions required for Ion Chromatography (IC) analysis. The samples were allowed to equilibrate to approximately room temperature prior to taking this measurement. For the conductivity, a check solution was made using KCL 0.746g in 1L; this solution has a known conductivity (1411 µs) and so was used to check the probe prior to measurement on the samples.

All samples were frozen after pH, redox and EC analysis, and then shipped in batches to the British Geological Survey (BGS), Keyworth via courier for further laboratory analysis. The dissolved organic carbon (DOC) content was measured with a Shimadzu TOC-L using the NPOC method. The groundwater and river water samples were analysed without dilution as there was a greater sample volume than that collected for the pore waters. All samples were acidified to remove inorganic carbon prior to measurement of DOC with a non-dispersive infrared gas analyser. The limit of detection for the Shimadzu TOC-L and NPOC instrument was 0.5mg/L. A blank check was run before any samples to avoid contamination within the machine. Standards were made from potassium hydrogen phthalate (total carbon) and sodium hydrogen carbonate and sodium carbonate (inorganic carbon) and DOC calculated as the difference between these measurements.

The concentrations of aluminium (Al), calcium (Ca), potassium (K), nitrate (NO_3^-), phosphorus (P) and sulphur (S) were measured in 200 µl sub-samples by Ion Chromatography (IC) on a Dionex AS-AP. Low sample volumes meant dilution was necessary, the dilution was based on the conductivity reading (i.e. twofold dilution for samples with a conductivity 200-500 µs and fivefold dilution for samples with a conductivity 500-800 µs).

The PTE concentrations were analysed via an Agilent 8900 Inductively coupled plasma mass spectrometer (ICP-MS). All of the samples were acidified with 1% HNO_3 and 0.5% HCl prior to analysis. The detection limits for the PTEs; As, Zn, Cr, Ni, Cu, Cd and Pb are shown in Table SI-5.3.

5.2.3.2 Statistical analyses

Data analysis was performed using Microsoft Excel 2019 (descriptive statistics) and SAS software version 9.4 (Linear Mixed effects Mode; LMM). The LMM takes into account the repeated sampling temporally (specific pattern) and spatially (the spatial scatter chosen at random). All of the response (dependent) variable values were log-transformed due to the fact that pore water PTE concentrations followed log-normal distributions. The model also included explanatory factors as model effects; elevation, distance to river, treatment (pre-flood, during the flood or post-flood), soil moisture (proxy for flooding/groundwater level), organic matter, soil pH, redox, conductivity, DOC, as well as pore water concentrations of; Fe, Mn, Al, Ca, K, NO_3^-, P and S.

The percentage change in concentration of each PTE and explanatory factors during (equation 5.1) or post-flood (equation 5.2), compared to pre-flood, was calculated as follows;

$$\%\Delta C_{df} = \frac{C_{df} - C_{bf}}{C_{bf}} \times 100 \tag{5.1}$$

$$\%\ \Delta C_{af} = \frac{C_{af} - C_{bf}}{C_{bf}} \times 100 \tag{5.2}$$

Where:

C_{df} = concentration during the flood

C_{bf} = concentration before the flood (pre-flood)

C_{af} = concentration after the flood (post-flood)

Principal Component Analysis (PCA) using PRIMER (version 7) was undertaken with the data classified by the position on the floodplain (sampling position; P1-14) as well as by elevation ('high' (39.50m - 39.21m), 'medium' (39.18m – 39.14m), and 'low' (39.09m – 38.90m) which was classified prior to analysis (Figure 5.1D) and by time ('pre-flood', 'flood' and 'post-flood'). The data was normalised in PRIMER prior to the PCA and the output visualises the dataset and allows subsequent interpretation of correlations found between variables in the dataset. ANOSIM; a one-way ANOVA was used to test spatial and temporal differences in the dataset by comparing the treatment levels (pre-flood, flood, and post-flood), elevation (high, medium, and low) and the treatment and elevation combined. ANOSIM generates an R value between -1 and 1; where zero represents the null hypothesis, a negative value indicates greater variability within the treatment than between different treatments, and a positive value indicates the amount by which the treatments differ.

Concentrations of Cu and Zn found in the river and groundwater were higher than expected, when considering the Water Framework Directive (WFD) and UKTAG recommended concentrations. We conducted an outlier (Grubbs) test and the high 'outlier' data (2x standard deviation from the mean) were removed from the dataset.

5.3. Results

5.3.1. Pore water concentrations

The Loddon Meadow floodplain is not heavily polluted (Table 5.1, Table SI-5.1) with concentrations ranging within natural levels (Rawlins et al., 2012). Therefore, this study investigates whether a flooding event on a typical floodplain downstream of an urban catchment could alter the concentrations of PTEs in soil pore waters. The (pseudo) total concentrations of the PTEs are geospatially mapped across the Loddon Meadow (Figures SI-5.3 to SI-5.10).

During the flood, mean pore water concentrations of As ($p=0.887$), Cu ($p=0.141$), Cr ($p=0.113$), Ni ($p=0.657$) and Zn ($p=0.539$) were lower than pre-flood concentrations, whereas the mean concentrations of Cd ($p=0.738$), Co ($p=0.352$) and Pb ($p=0.781$) increased during the flood, compared to pre-flood concentrations; calculated using equation 5.1 (Figure 5.3A). However, none of the PTE concentrations in pore waters were statistically significantly different during the flood, compared to pre-flood ($p>0.05$). When looking at the explanatory variables (Figure 5.3B), we found higher mean pore water concentration of Mn ($p=0.244$) and lower mean pore water concentrations of Fe ($p=0.074$), Al ($p=0.052$), DOC ($p=0.002$), P ($p<0.01$), S ($p=0.514$), NO_3^- ($p=0.405$), Ca ($p=0.907$), Mg ($p=0.108$) and pH ($p=0.716$) during the flood, compared to pre-flood.

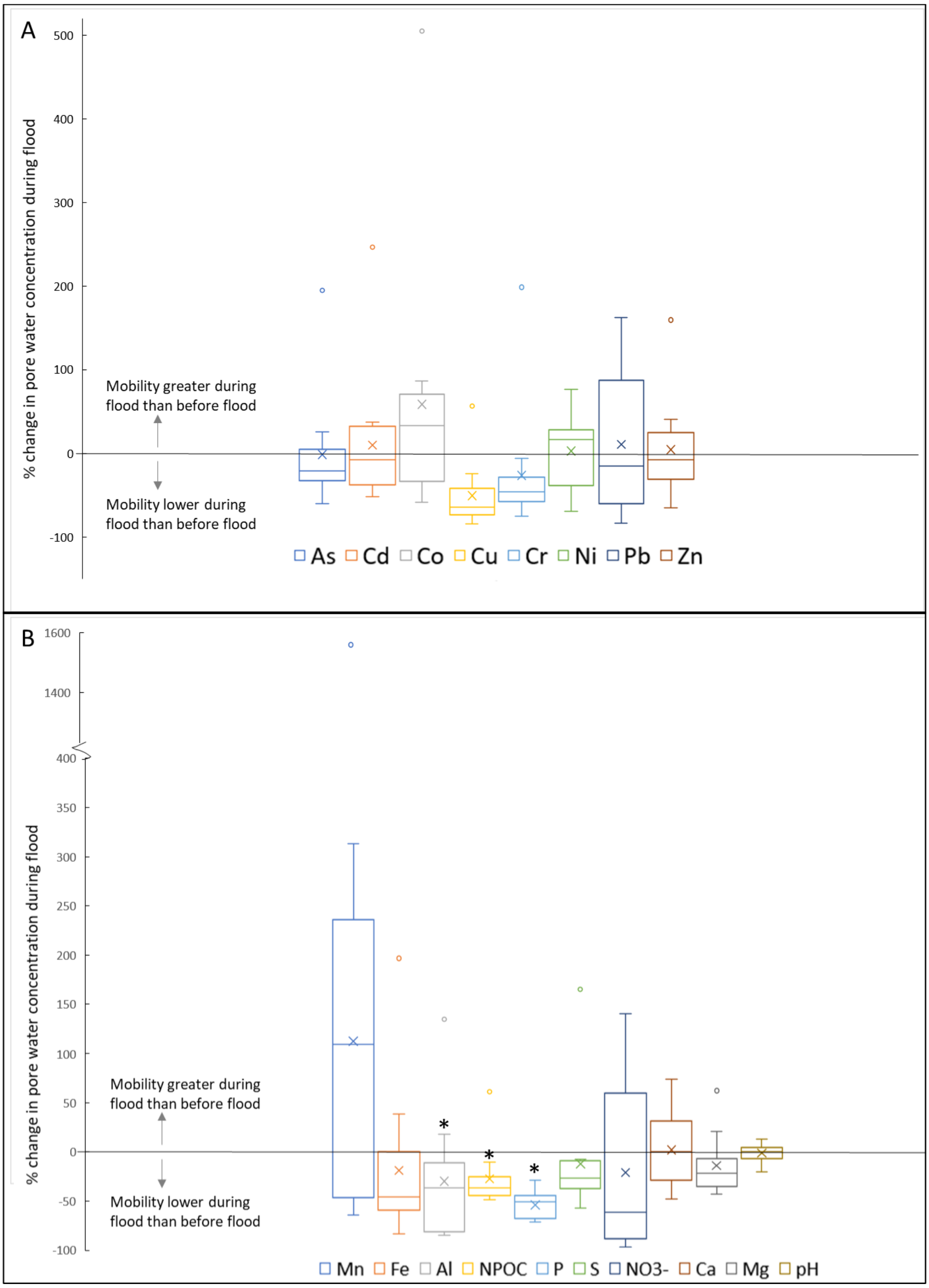


Figure 5.3; *% change in pore water concentration during flood for A) PTEs and B) key explanatory variables. The % change increase or decrease is in relation to the averaged concentration (N=12) found pre-flood. Box and whisker plots show the distribution of data into quartiles (box) and variability outside of the upper and lower quartiles (whiskers). The 'outlier' results (outside of the normal range of values i.e. 1.5 times the inter-quartile range below the 1st quartile of 1.5 times above the 3rd quartile) are represented as dots. The 'x' denotes the mean value and the line across the box is the median value. The * denotes significant differences in concentration (p<0.05).*

Post-flood mean pore water concentrations of As ($p=0.091$), Cd ($p<0.01$), Cu ($p=0.011$), Cr ($p=0.001$), Pb ($p=0.067$) and Zn ($p=0.231$) were lower than pre-flood concentrations, whereas the post-flood mean concentrations of Co ($p=0.626$) and Ni ($p=0.194$) were greater than pre-flood concentrations; calculated using equation 5.2 (Figure 5.4A). When looking at the explanatory variables (Figure 5.4B), we found the mean Mn pore water concentrations remained higher when the floodwater had receded post-flood ($p=0.335$), compared to concentrations pre-flood. The soil pH slightly increased ($p=0.433$), meaning that the H^+ ion concentrations decreased, post-flood, compared to pre-flood. The mean pore water concentrations of the other explanatory variables (Fe ($p=0.335$), Al ($p=0.067$), DOC ($p=0.021$), P ($p<0.1$), S ($p=0.013$), NO_3^- ($p=0.009$), Ca ($p=0.017$), Mg ($p=0.018$)) were lower post-flood compared to concentrations pre-flood.

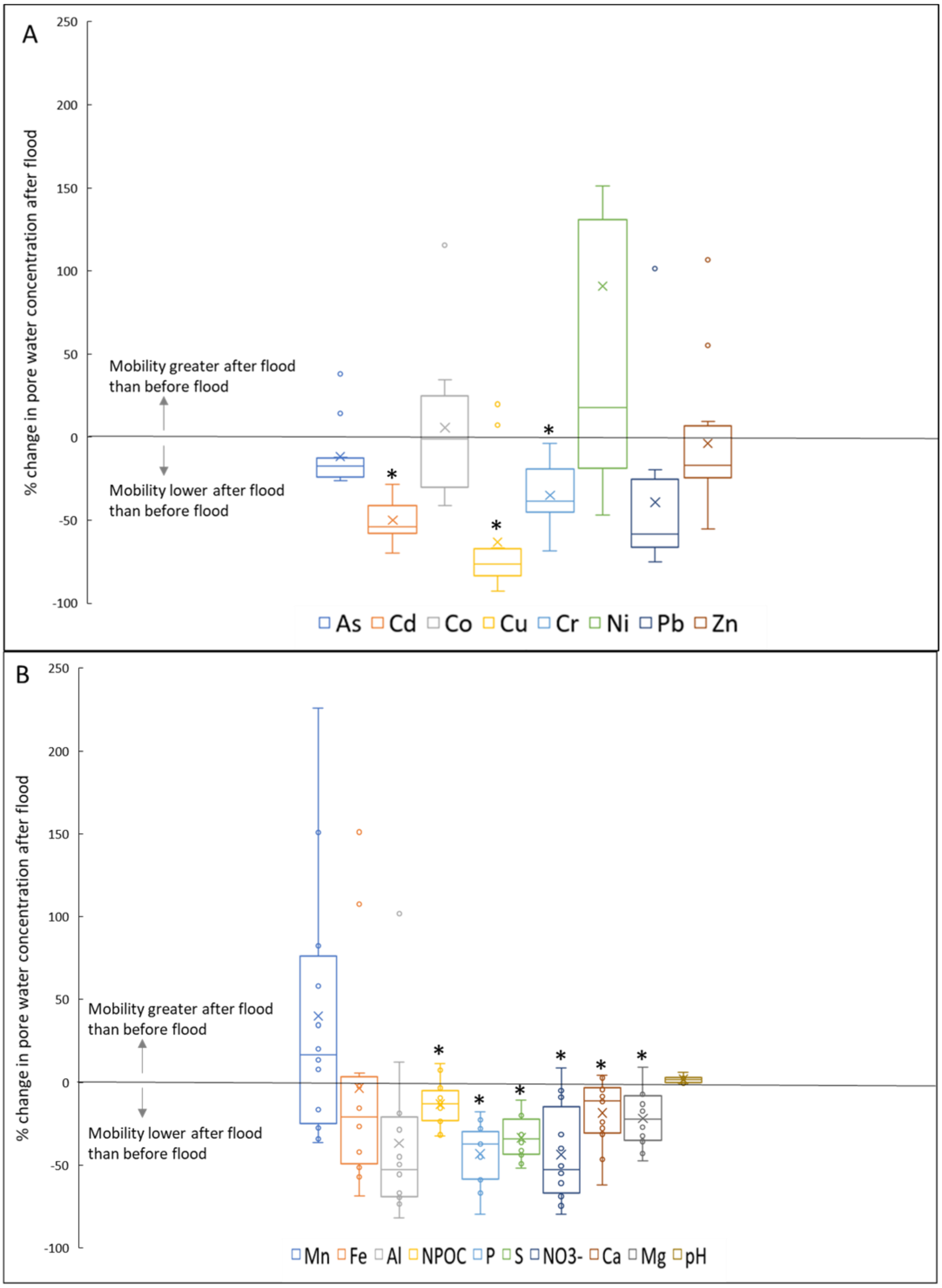


*Figure 5.4; % change in pore water concentration after flooding (post-flood) for A) PTEs B) key explanatory variables. The % change increase or decrease is in relation to the averaged concentration (N=12) found pre-flood. Box and whisker plots show the distribution of data into quartiles (box) and variability outside of the upper and lower quartiles (whiskers). The 'outlier' results (outside of the normal range of values i.e. 1.5 times the inter-quartile range below the 1st quartile of 1.5 times above the 3rd quartile) are represented as dots. The 'x' denotes the mean value and the line across the box is the median value. The * denotes significant differences in concentration ($p<0.05$).*

Temporal (pre-flood, during the flood, post-flood) and spatial (high, medium, low elevation) factors influenced the pore water chemistry on the floodplain (Table SI-5.4 Analysis of Similarities (ANOSIM)). When the temporal and spatial treatments were combined and the influence on pore water chemistry considered, the flooding event (during the flood) appeared to remove the differences in pore water chemistry seen across the three elevations. These factors were considered in greater detail in the Principal Component Analysis (PCA; Figure 5.5). Pore water samples collected pre-flood tended to have a positive loading on PC1 (x axis of Figure 5.5), while samples collected during or post-flood have a negative loading. Pore water samples collected from low elevation locations tended to have a negative loading on PC2 (y axis of Figure 5.5), while pore water samples collected from medium and high elevation locations tended to have a positive loading. Therefore, we conclude from the biplot (Figure 5.5) that time (pre-flood, flood and post-flood) is represented on PC1 and location/elevation (high, medium and low) is represented on PC2. These two principal components (PC1 and PC2), combined, explain 35% of the variability in the dataset. The PCA also identified organic matter, pH, redox and conductivity as important factors explaining the variability in the pore water chemistry.

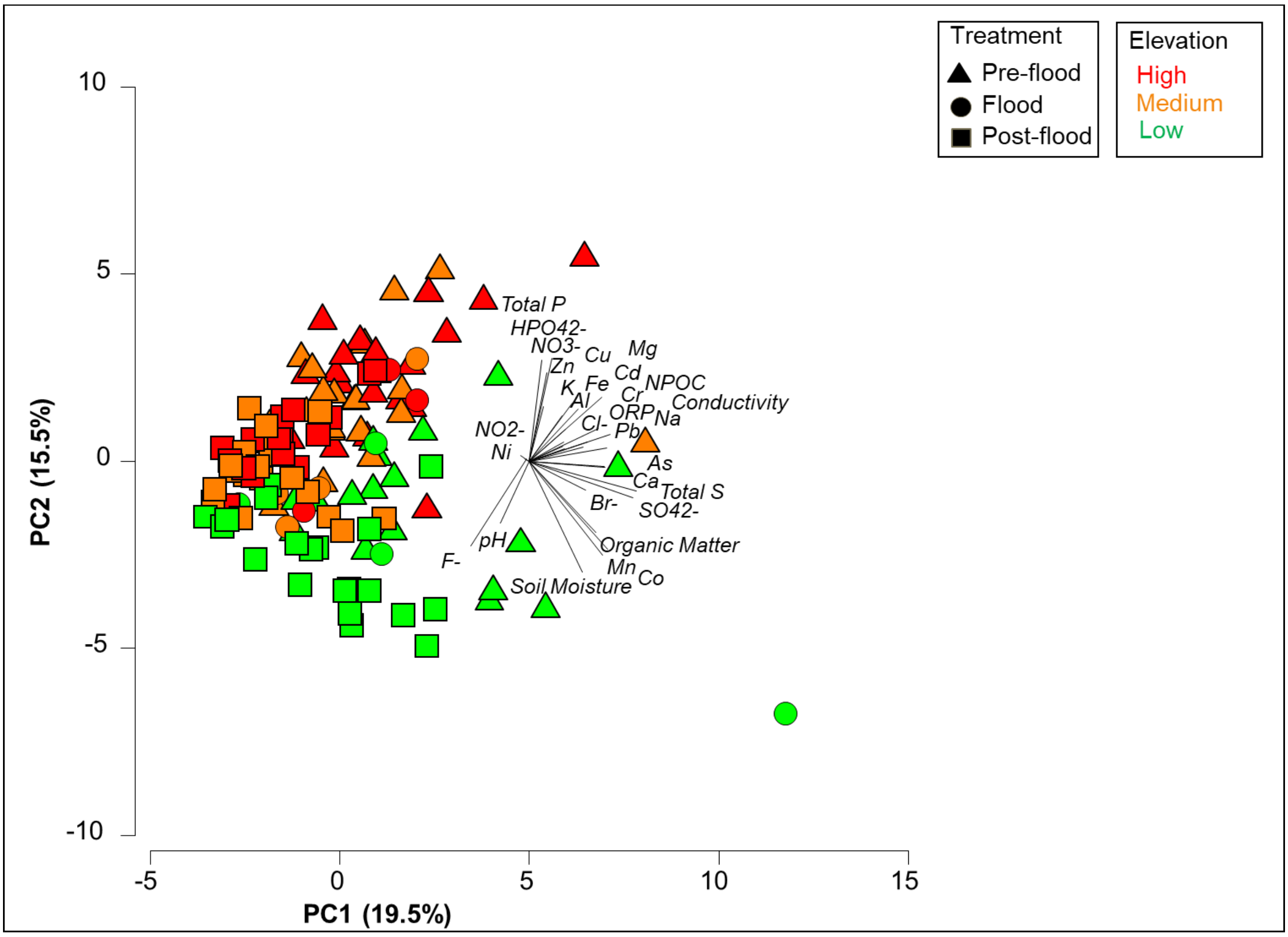


Figure 5.5*; Principal Component Analysis (PCA) biplot, reflecting correlation between PTEs and other explanatory variables at three time points (pre-flood, during flooding and post-flood) and at three elevations on the floodplain (high, medium and low).*

The results of Linear Mixed effects Modelling (LMM) are shown in Table 5.2. The explanatory variables contributing the influence of flooding on each individual PTE are discussed below element by element using a combination of the % changes in pore water concentrations and PCA and LMM statistical outputs to help determine the key process(es) involved in the mobility of each PTE.

Table 5.2; Results of mixed model (LMM) analysis; the numbers reported here are the fixed effects ‘estimate’ which means that for every 1 unit increase in an explanatory variable there is either a positive or negative change in PTE concentration in µ/L. The effect size significance (p value) is indicated by * denoting <0.05, ** denoting <0.01 and *** denoting <0.001.

Response variable (PTE)	**During flood concentration compared to pre-flood**	**Post-flood concentration compared to pre-flood**	**Explanatory variables (fixed effects ‘estimate’) & effect size**														
			Elevation	Soil moisture	OM	pH	Redox	Conductivity	DOC	Fe	Mn	Al	Ca	K	P	S	NO_3^-
Arsenic	Decrease	Decrease	0.05	0.002	0.02	-0.001	-0.001	0.00003	0.01 ***	0.00002	0.001 ***	0.0004 ***	-0.006 ***	0.00002	0.37 *	0.004	0.002 *
Cadmium	Increase	Decrease	0.47	0.0001	0.03	-0.125	0.0003	0.00035	-0.008	1.909	0.002 ***	0.00003	-0.00009	0.009	1.29 ***	-0.0005	0.003
Cobalt	Increase	Increase	-0.04	0.009 *	-0.009	0.049	0.0015	0.0006	0.011 ***	0.00006	0.004 ***	0.0006 ***	-0.00571 *	-0.008	-0.22	-0.004	-0.004 **
Copper	Decrease	Decrease	-0.08	0.0003	0.035	-0.296 *	-0.0056	0.0012	0.012	0.00029 *	-0.002 *	0.00026	0.00224	0.0528 ***	-0.346	-0.0133	-0.006 *
Chromium	Decrease	Decrease	0.046	-0.0103 ***	0.048 ***	-0.091	-0.0061 ***	-0.0011 *	0.009 *	0.00008	0.002 ***	0.0007 ***	0.00097	-0.0083	0.115	-0.0023	0.003 *
Nickel	Decrease	Increase	-1.4153 *	-0.0132	0.021	-0.017	-0.0003	0.0003	0.008	-0.00006	0.00004	0.0005	0.0043	-0.0201 *	0.0421	0.0011	0.409
Lead	Increase	Decrease	-0.2305	0.0107	0.0051 ***	-0.299 ***	0.0024	0.00005	-0.0008	0.00019	0.00142 *	0.00103 ***	-0.0124 ***	0.0029	1.1025 ***	0.0119	0.003
Zinc	Decrease	Decrease	0.8387	-0.0019	0.0037	-0.079	0.0001	0.00136	-0.0074	0.00017	-0.00052	-0.00024	0.0128	0.0149	0.1624	-0.008	-0.003

5.3.1.1. *Arsenic*

The mean pore water concentrations of As were found to decrease (albeit not statistically significantly) both during the flood and post-flood (Table SI-5.5). A significant positive correlation was found between As and DOC, this could be due to pH having a similar effect on both As and DOC solubility (both decreased during and post-flood). Alternatively As pore water concentrations could have been affected by the reduction of As(V) to As(III) during anoxic conditions.

The Mn concentrations were generally found to increase during the flood and post-flood (Table SI-5.6). However, Figures 5.3 and 5.4 show a range of values where Mn sometimes increased and sometimes decreased post-flood. Manganese has a negative loading on PC2 (Figure 5.5), so higher concentrations were found at low elevation. The correlation found between As and Mn relates to the floodplain elevation; therefore, it is possible that there is reductive dissolution of Mn oxides (and a few As oxides) in the surface soils of the lower elevation sampling points (Figure SI-5.3) due to high groundwater levels (Figure 5.2B).

Finally, a significant positive correlation was found between As and P pore water concentrations. However, rather than this being an explanatory variable it is likely that these elements are affected by the same processes (DOC complexation and reductive dissolution of Fe oxides), since phosphate is chemically very similar to arsenate (Strawn, 2018).

5.3.1.2. *Cadmium*

The mean Cd pore water concentrations were found to increase during the flooding and subsequently decreased (significantly) post-flood (Table SI-5.5). There is a strong positive correlation between Cd and Mn, and this is a significant variable in the LMM (Figure 5.5, Table 5.2). They both have a positive loading on PC1 (pre-flood, during the flood, post-flood; Figure 5.5), reflecting greater pore water concentrations pre-flood. The increase in concentrations found for both Cd and Mn during the flood provides evidence for reductive dissolution of Mn oxides and release of Cd into the soil solution, particularly at the low elevation sampling points (Figure SI-5.4). The concentrations of Cd in the soil were low (Table 5.1, Table SI-5.1) and therefore adsorption processes were likely controlling (im)mobility (Van Groeningen et al., 2020). In the pH range found during this study (average 6.53; Table 5.1) Cd would not be very mobile; its divalent form is soluble but can form complexes with organics and oxides (Mulligan et al., 2001).

A significant positive correlation was found between Cd and P concentrations in pore water; they both have a positive loading on PC2, reflecting greater pore water concentrations at high elevation (Figure

5.5) and they both decreased post-flood (Table SI-5.5 and SI-5.6). This relationship may suggest an immobilisation of Cd by precipitation with phosphate. It is thought that Cd can be retained in the solid phase while precipitating as carbonate, hydroxide, phosphate or sulphide (Van Groeningen et al., 2020). However, phosphate fertilisers also contain trace amounts of Cd, so rather than this being an explanatory variable, the positive correlation we found may just infer the existence of a source of Cd in this floodplain soil from agricultural land in the catchment.

5.3.1.3. *Cobalt*

The Co pore water concentrations were found to increase (albeit not significantly) during the flood and post-flood (Table SI-5.4). The mobility appears to be strongly linked to that of Mn (Table SI-5.6); as Co has a high affinity for Mn oxides. Cobalt and Mn concentrations in pore waters significantly positively correlate with each other (LMM; Table 5.2); they both have a positive loading on PC1 (pre-flood, during the flood, post-flood) and negative loading on PC2 (elevation; Figure 5.5). Therefore, when Mn oxides were reductively dissolved the concentrations of both Mn and Co increased in pore water (Figure 5.3 and 5.4), particularly in the low elevation sampling points pre-flood (Figure SI-5.5), likely influenced by the high groundwater levels (Figure 5.2B).

5.3.1.4. *Copper*

The Cu pore water concentrations were found to decrease both during the flood and (significantly) post-flood (Table SI-5.5). The LMM identified pH as a significant explanatory variable influencing Cu mobility, with a negative correlation found (Table 5.2). The pH did increase slightly post-flood (albeit not significantly) and this may have increased the Cu sorption, resulting in strong binding to soil mineral and organic matter surfaces and low concentrations in the pore water.

There was a significant positive correlation between Cu and Fe (LMM; Table 5.2) and these are both positively loaded on PC1 and PC2 (Figure 5.5) meaning greater pore water concentrations pre-flood and at high elevation. The Cu may have been adsorbed to Fe oxides and a release of Cu pre-flood (Figure SI-5.6) may be explained by an increase in Fe in solution resulting in reductive dissolution when the ground water levels were high (within the top 30cm of soil; Figure 5.2B).

5.3.1.5. *Chromium*

The Cr pore water concentrations were found to decrease both during the flood and (significantly) post-flood (Table SI-5.5). During flooding the soil moisture increased and this was found to have a significant negative correlation with Cr (LMM; Table 5.2), possibly linked to reducing conditions.

Chromium is a redox-sensitive element and so the reducing/oxidising conditions may have an influence on the speciation and therefore (im)mobility.

There was a positive correlation between Cr and DOC and this was a significant positive variable in the LMM (Table 5.2). They both have a positive loading on PC1 (pre-flood, during the flood, post-flood; Figure 5.5) meaning greater concentrations were found pre-flood. The concentrations of Cr and DOC were both decreased during the flood and post-flood, meaning that Cr may have been removed from the pore water solution due to the reduction in DOC.

Despite the overall Cr pore water concentrations being found to decrease, a significant positive correlation between Cr and Mn concentrations (LMM; Table 5.2) may explain why there were high Cr concentrations in the pore waters collected pre-flood (Figure SI-5.7), as they both had a positive loading on PC1 (Figure 5.5). Therefore, reductive dissolution of Mn oxides may have released Cr into the pore waters.

5.3.1.6. *Nickel*

The Ni pore water concentrations decreased during the flood and then increased post-flood (Table SI-5.5). However, the LMM does not provide strong evidence for why we observed changes in Ni mobility. Spatial and temporal variations did not appear to explain the changes in Ni concentrations found (Figure SI-5.8). It is possible that Ni was released during reductive dissolution of oxides, however there were insufficient sulphides formed to precipitate it to a significant degree. The precipitation of Cu and Zn with sulphides would be preferential to the Ni sulphide formation. Therefore, the Ni mobility remained high post-flood, before Fe and Mn oxides reform. In soil solution, Ni generally occurs as the free ion (Ni^{2+}) which is stable and forms strong associations to redox sensitive species and dissolved organic ligands (e.g. carboxylic acids, amino acids and fulvic acids) (Rinklebe and Shaheen, 2017).

5.3.1.7. *Lead*

The Pb pore water concentrations were found to slightly increase during flooding and subsequently decreased (albeit not significantly) post-flood (Table SI-5.5). There was a positive correlation between Pb pore water concentrations and soil organic matter; the Pb mobility was likely controlled by desorption and dissolution processes during the flood, with adsorption and removal from the solution post-flood due to the slight increase in pH. There was a significant positive correlation between Pb and Mn concentrations (LMM; Table 5.2) and these have a positive loading on PC1 (pre-flood, during the flood, post-flood; Figure 5.5); so reductive dissolution could explain the increased pore water concentrations pre-flood (Figure SI-5.9).

There was also a significant positive correlation between Pb and P. They both had a positive loading on PC2 (elevation; Figure 5.5) so there may have been immobilisation of Pb from pore waters due to precipitation of Pb phosphates, a stable mineral substance, removing it from pore water solution post-flood (Andrunik et al., 2020).

5.3.1.8. *Zinc*

The Zn pore water concentrations decreased (albeit not significantly) during the flood and post-flood (Table SI-5.5). However, the LMM does not provide evidence for why we observed this, with no significant correlations with explanatory variables. The Zn and Cu pore water concentrations appear to correlate and therefore the mechanisms controlling the mobility of Cu may also explain the mobility of Zn (Shaheen et al., 2014a). For example, the influence of pH on sorption and complexation with DOC. We found Zn pore water concentrations to increase on one sampling occasion pre-flood and one sampling occasion post-flood, across the whole floodplain (Figure SI-5.10), which suggests there are mechanisms to release Zn into the pore water that have not been established through the explanatory variables measured in the study.

5.3.2. Concentrations in the river and ground water

The PTE concentrations in the river water (Table SI-5.7) and groundwater (Table SI-5.8) are generally orders of magnitude lower than the pore water PTE concentrations from the floodplain soil. Most of the PTE concentrations did not significantly change over time in the river water (Figure 5.6A) or groundwater (Figure 5.6B). However, in the river water samples we found higher mean concentrations during the flood and reduced concentrations post-flood for Cd ($p=0.003$), Co ($p=0.001$), Cr ($p=0.041$) and Pb ($p<0.01$), which may provide some evidence against the dilution effect (increased volumes of river water resulting in a lower concentration of PTEs through dilution) in the river during the flood event (Figure 5.2A). In the groundwater samples we found higher mean concentrations of Co ($p=0.052$) during the flood and post-flood compared to pre-flood. There were also high groundwater levels post-flood (within the top 30cm of the soil; Figure 5.2B); this would have caused (near-) saturated conditions in the surface soil, partly due to the capillary fringe being of a significant size in this soil, due to the soils relatively high clay content and related pore-size distribution. Therefore, the groundwater levels may have influenced the soil pore water concentrations through reduction processes, despite there being no observable flooding above the ground. The high groundwater levels may have caused a release of Co from the floodplain soil into the pore waters with subsequent leaching downwards into the groundwater.

From this analysis, we conclude that PTEs in the river and groundwater were not at high enough concentrations to have significantly increased the concentrations we observed in floodplain soil pore waters. An increase in the concentrations of PTEs observed in the pore water samples during the flooding event or post-flood were more likely due to release from the floodplain soil than brought in during the inundation of river water or via rising groundwater levels. The low concentrations combined with the increased water volume during the flooding might result in dilution of the soil pore water PTE concentrations; explaining the decreased concentrations found during flooding.

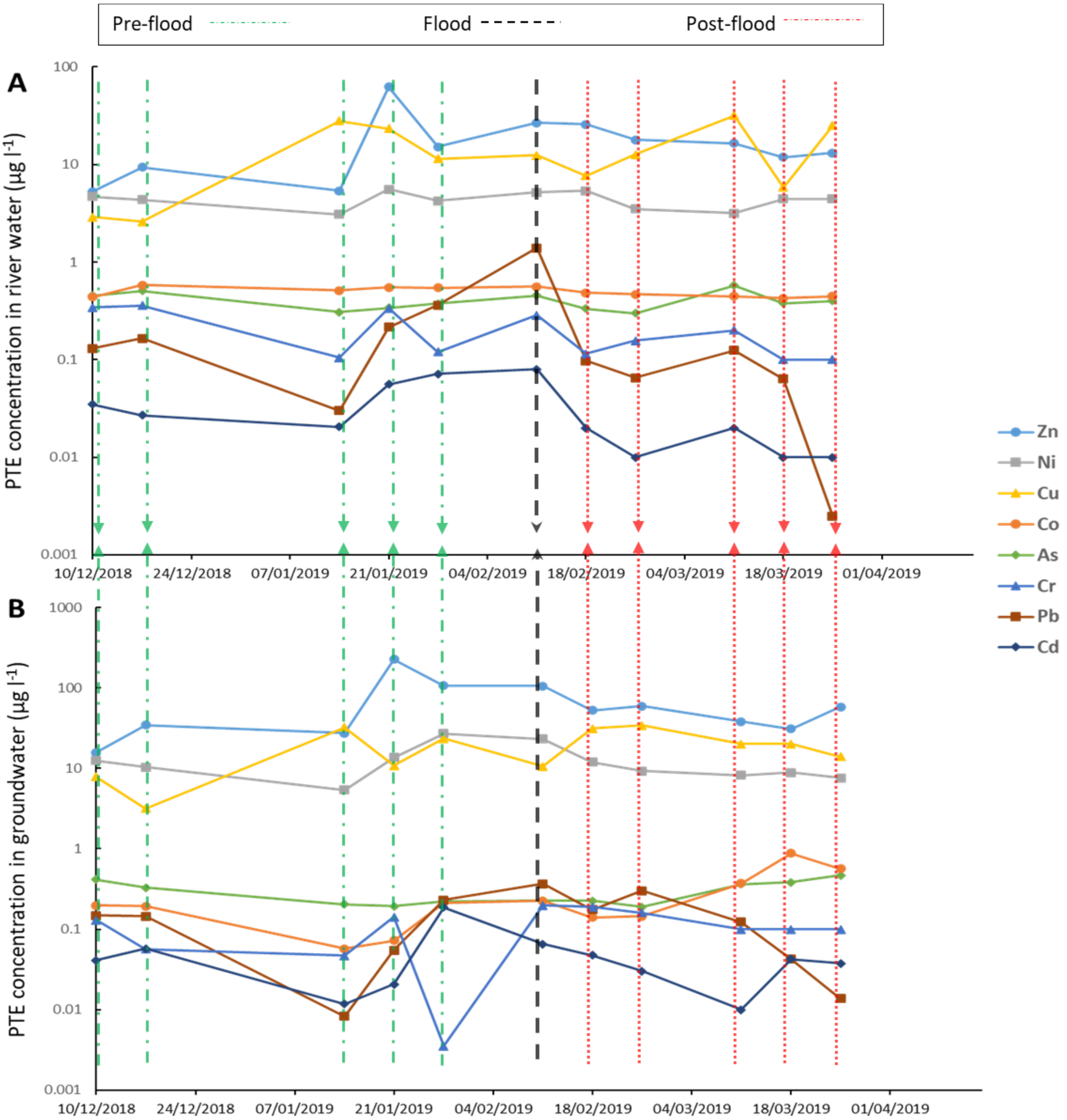


Figure 5.6; *A) PTE concentrations in the river water (µg l^{-1}) and B) PTE concentrations in the ground water (µg l^{-1}). The dot and line green arrows show five sampling dates pre-flood, the dashed line black arrow shows the one sampling date during the flood and the dotted line red arrows show the five sampling dates post-flood.*

5.4. Discussion

Flooding did not influence the mobility of all the PTEs in the floodplain soils in the same way. There were also differences found in mobilisation during the flood and post-flood. Overall, there were higher concentrations of PTEs found in pore waters collected pre-flood and lower concentrations found in the pore waters collected during the flood, and significantly lower concentrations post-flood. The latter might be due to a dilution effect where incoming floodwater with low concentrations of PTEs decreases the PTE concentrations in the soil pore waters. The temporal comparisons (pre-flood, during the flood, and post-flood) provides evidence to suggest that the influence of a flooding event on PTE mobility continues after the floodwaters recede.

Overall, there were higher concentrations of PTEs found in the pore waters collected at low elevation than at the medium or high elevations, so we can infer that the microtopography (a proxy for flood duration) is an important factor influencing the mobility of PTEs. The entire floodplain sampled for this study was inundated during the flooding event and we found that this meant the differences in PTE pore water concentrations due to elevation (microtopography) were not observed at this time point, likely due to mixing in the floodwater. The changes in concentrations of individual PTEs over time and across the floodplain may be explained due to a net effect of five key processes: redox potential, soil pH, complexation with dissolved organic matter, Fe/Mn reductive dissolution and sulphate reduction (Ponting et al., 2021). The contribution of each of these will be discussed in turn in the sections below.

5.4.1. Soil redox potential

The soil redox potential is directly affected by flooding because water fills the pore space, reducing the concentration of dissolved oxygen, which is exhausted by organisms. Pore water Cr concentrations decreased during the flood and post-flood, and were found to be linked to redox potential; this observation was expected as Cr is a redox sensitive element (Frohne et al., 2015; Lee et al., 2005; Trebien et al., 2011). Reducing conditions can also immobilise and sequester Cr through reductive precipitation mechanisms (Matern and Mansfeldt, 2016). However, speciation analysis to see whether Cr (III) or Cr (VI) was present in the pore water samples was not conducted, Cr (III) is the more stable form and tends to occur in soils with high OM. A separate study on the same floodplain site found that pore water samples contained only Cr (III) (Kelly et al., 2020). Furthermore, DOC may act as electron donor to reduce Cr (VI) to Cr (III) (Maranguit et al., 2017; Zhang et al., 2017) and DOC was generally high at all sampling points, across the floodplain.

5.4.2. Soil pH

Soil pH is an inverse logarithmic expression of the H^+ ion concentration in aqueous solution. During flooding the pH is known to increase due to H^+ ions being consumed (Mohamed and Paleologos, 2018). This study found the pH increased slightly after the floodwater recedes post-flood. The pH increase might be due to the amount of exchangeable Ca, Mg and K (Wood et al., 2004). The size of the increases in pH may be dependent on flood duration (Kashem and Singh, 2001) and therefore the slight increase that we observed may suggest that the flooding had not been long enough to significantly alter pH. If the pH had increased to very alkaline conditions, this could have resulted in increasing mobility for most of the PTEs (Król et al., 2020). During flooding events, H^+ ions are available for consumption in processes such as the reduction of Fe and Mn. The concentrations of H^+ were lower post-flood (increase pH) which suggests that these processes took place in our study. The changes in pH were found to be significantly associated with the decreased pore water concentrations of Cu and Pb, which suggests the pH rise may have aided adsorption mechanisms or precipitation with P (Andrunik et al., 2020; Cirelli et al., 2009; Koupai et al., 2020; Zia-ur-Rehman et al., 2015). We found significant associations of As, Cd and Pb with P. Therefore these PTEs may have precipitated as metal phosphates resulting in decreased bioavailability (Andrunik et al., 2020; Van Groeningen et al., 2020; Zia-ur-Rehman et al., 2015). In weakly acidic to neutral pH soils, as sampled on the Loddon Meadow (Table SI-5.2), clay minerals and Fe(III)/Mn(II) oxides are also important mineral sorbent phases for PTEs e.g. Cd (Van Groeningen et al., 2020).

5.4.3. Dissolved Organic Matter

Organic matter is an important site of PTE retention in soils. However, due to complexation by soluble organic matter, the addition of dissolved organic matter in soil solution can also act as a chelating agent and therefore be associated with mobilisation of PTEs (Beck et al., 2008; Grybos et al., 2009; Newsome et al., 2020; Sherene, 2010). The higher the concentration of DOC in the soil solution, the greater the pore water concentration of PTEs that bind with DOC in solution. The composition of DOC is complex due to microbial decomposition/degradation processes of organic substances (e.g. root exudates) in soil (Antoniadis and Alloway, 2002). We found As concentrations, which decreased both during the flood and post-flood, to be correlated with DOC. This observation supports the notion that arsenate (As(V)) was the dominant form in the floodplain pore waters because it has a greater affinity for sorption to soil minerals (Indraratne and Kumaragamage, 2017; Williams et al., 2011). We did not find a significant association between As pore water concentrations and redox potential, so this flooding event might not have been long enough for reduction from As(V) to As(III) to occur and subsequently increase the mobility of As in the floodplain soils. We also found Cr concentrations decreased both during the flood and post-flood, which was correlated with soil organic matter and DOC. As DOC will change over time, but soil organic matter does not (in the timescale of this sampling), the correlation with DOC is likely to relate to temporal changes whereas the correlation with soil organic matter is likely to relate to spatial differences. This finding suggests that as there was less DOC in solution the equilibrium between the solid and liquid phase for Cr shifts towards the solid phase (i.e. the pore water has less capacity to contain Cr because there is less DOC in solution) (Di Bonito et al., 2008; Icopini and Long, 2002; Wuana et al., 2011).

5.4.4. Reductive dissolution of Fe and Mn oxides

An increase in concentrations of Fe and Mn were found in the soil pore water during flooding, comparable to the increases reported in studies across a range of soil types (Amarawansha et al., 2015; Du Laing et al., 2007; Indraratne and Kumaragamage, 2017; Stafford et al., 2018). It was found that the increase in concentration was much higher for Mn than for Fe, as was also found by Indraratne and Kumaragemage (2017). Reductive dissolution appears to be a predominant process for the mobilisation of PTEs in this study; releasing adsorbed As, Cd, Co, and Pb into the pore waters; particularly at the low elevation sampling points, even if the net effect of multiple mechanisms during the flood or post-flood was to reduce the pore water concentrations of these elements. The process of reductive dissolution is bacterially-induced and has been reported to have an effect on As mobilisation, releasing the mobile form of As during a flood but also immobilising it due to co-precipitation post-flood when oxic conditions return (Chowdhury et al., 2018; Frohne et al., 2011). The Cd and Pb concentrations during the flooding were also likely controlled by desorption and dissolution processes, influenced by the reducing conditions of the flood and association with Mn oxides (Frohne et al., 2011; Furman et al., 2007; Stafford et al., 2018).

In flooded soils Mn(II) is often the major cation in the soil solution and has therefore been expected to compete with PTE cations (e.g. Cd(II) and Zn(II)) for adsorption to mineral surfaces (Van Groeningen et al., 2020). Post-flood, during aeration of the soil, Fe(II) is oxidised by O_2 much more rapidly than Mn(II); this means that Mn can persist for prolonged periods and continue to act as a competing cation with PTEs, or form new Mn-containing solid phases that leads to a net increase in the sorption of PTEs e.g. Cd (Van Groeningen et al., 2020). Dissolution of Co has been closely linked to that of Mn (Beck et al., 2010; Newsome et al., 2020); when Mn oxides are reductively dissolved, Co is released into the solution (Cornu et al., 2009; Shaheen et al., 2016). There has been an evaluation of the effect that competition with Co for ion exchange sites has on Cr. It is thought that increasing Co concentrations, coupled with a decreasing availability of surface area for precipitation as the dissolution of Mn occurs, results in lower Cr(III) adsorption to Mn oxides. This subsequently results in lower Cr(VI) formation which would have increased the Cr mobility (Shaheen et al., 2016; Trebien et al., 2011). Studies on PTEs are commonly focused on a single metal, but they occur simultaneously in the environment and so an understanding of interactions is an important consideration (Aprile et al., 2019).

5.4.5. Precipitation of metal sulphides

Flooded soils can result in immobilisation of PTEs through precipitation with insoluble sulphides (Bunquin et al., 2017; Du Laing et al., 2009; Indraratne and Kumaragamage, 2017; Lair et al., 2009). The concentration of S in the pore water (all total S was found to be sulphate when compared using regression analysis (R^2=98.08%, $p<0.01$)) decreased during the flood and (significantly) post-flood; suggesting that there was sulphate reduction to sulphide occurring during this study. The S concentrations negatively correlated with Cd, Cu and Cr (albeit not significantly; Table 5.2). These PTEs significantly decreased post-flood and therefore it is possible that they have precipitated with sulphides during the flood and removed from the pore water post-flood. When aerobic conditions return, sulphides can be oxidised by microbes resulting in soluble PTEs (e.g. Cd and Zn) being released (Emerson et al., 2017; Lynch et al., 2014). This may explain some increased concentrations of these elements in the pore waters in the lower elevation a number of weeks after the floodwater recedes post-flood (Figure SI-5.4 and SI-5.10), but not enough to prevent the overall finding that PTE concentrations decreased post-flood, compared to during the flood.

5.4.6. River water and Groundwater concentrations

We measured the concentrations of PTEs in the river water and these concentrations were found to be orders of magnitude lower than in the pore water samples. Although these samples are a snapshot of the concentrations in the river at the time of sampling, they suggest that the concentrations of PTEs that were found in the pore waters were most likely concentrations originating from the floodplain soil, rather than being deposited onto the floodplain during the flood event. The top 30 cm of soil was sampled for this study and the groundwater levels (Figure 5.2B) were within the top 30 cm during pre-flood (2nd sampling visit before flooding) and post-flood (3rd sampling visit after flooding) at the location of boreholes. Therefore, reduction mechanisms may have taken place in the soil prior to flooding or continued after the water aboveground recedes.

There were greater concentrations of Pb, Ni and Cr measured in the groundwater during the flood and greater concentrations of Co post-flood, compared to pre-flood. Therefore, the Loddon Meadow floodplain may have released contaminants into the groundwater, which is an environmentally sensitive media (Kotuby-Amacher and Gambrell, 1988), especially because river water and groundwaters are highly connected in floodplain areas. The PTEs concentrations will depend strongly on the flow between the river and groundwater; at times the river is feeding the groundwater and other times it is the other way around.

5.5. Conclusions and environmental relevance

Floodplain soils have long been considered a sink for contamination discharged into rivers through sedimentation during flooding events (Capra et al., 2014; Marković et al., 2018; Schulz-Zunkel et al., 2015; Sherene, 2010). This study has provided field-based evidence of the effect of flooding on the mobility of PTEs from floodplain soils, and the results suggest that there were no significant increases in PTEs mobility during the flooding, and therefore no evidence to support the idea that floodplains become a source for PTEs due to flooding events. This is an interesting result because evidence from laboratory mesocosm studies have suggested there is potential for mobilisation of PTEs as a result of flooding (Frohne et al., 2011; Izquierdo et al., 2017; Rinklebe et al., 2010; Weber et al., 2009). The overall concentrations of PTEs decreased during the flooding and this may be due to dilution effect from river water inundation and high groundwater levels (Balaban et al., 2019).

There were differences in the concentrations of PTEs in soil pore waters observed across the floodplain; this may suggest that a number of different processes influencing mobility are acting at the same time across a spatial area. The groundwater level at times during this study was high (within the top 30cm of the soil) without there being a groundwater flood above the surface; this will have influenced processes such as reductive dissolution (releasing Mn and PTEs into pore water) particularly at sampling points at lower elevation areas of the field. The flooding event observed in this study inundated the entire floodplain, and we found flooding removed the variation in pore water concentrations that was otherwise found due to microtopography. We show that the influence of a flooding event on PTE mobility continues after the floodwaters recede post-flood. A significant reduction in mobility of Cd, Cu and Cr was found post-flood and this was due to an increase in pH, a reduction in DOC, and the precipitation of metal sulphides.

This study highlights the need for more field-based studies to monitor soil pore waters from floodplains pre-flood, during the flood, and post-flood because the impact of flooding on mobility of PTEs may not be as clear-cut and consistent as laboratory studies have previously indicated. The impact of flooding on PTE mobility is likely to be the result of a net effect of multiple processes occurring simultaneously, so while we have observed some increases to PTEs mobility, the overall net effect was found to be a decrease in concentrations because immobilising processes were dominant (i.e. precipitation and adsorption). Soil type and composition will have an important influence on the dominant processes influencing mobility of PTEs (Golia et al., 2019). For example; Endisols have high amounts of sand and high electrical conductivity resulting in increased availability of PTEs, whereas Vertisols have high clay content, which allows for adsorption of PTEs, but also have high pH which is associated with ion exchange (Alloway, 2013a; Golia et al., 2019). Further field monitoring, collecting data pre-flood, during a flood and post-flood, of different soil types on floodplains or lowland settings, is required to support modelling exercises that would improve predictive capabilities.

5.6. Chapter 5 Supplementary Material

The following can be found in Appendix 4:

Figure SI-5.1: Environment Agency Flood Map for the Loddon Meadow
Figure SI-5.2: Levels from 1st January 2018 to 1st April 2019 to show river and ground water levels
Table SI-5.1: Soil pseudo-total (aqua regia) concentrations for the sampling points across the Loddon Meadow floodplain site.
Table SI-5.2: Soil properties; moisture organic matter and pH across the Loddon Meadow floodplain pre-flood (averaged 5 sampling visits), during the flood and post-flood (averaged 5 sampling visits).
Table SI-5.3: Detection limits for PTEs using ICP-MS
Table SI-5.4: Analysis of similarities (ANOSIM) a one-way ANOVA testing 1) the treatment levels (pre-flood, flood and post-flood) and 2) elevation and 3) treatment with elevation from Principal Component Analysis (PCA).
Table SI-5.5: Summary statistics for the concentrations of PTEs (µg l^{-1}) found in the floodplain soil pore water during the sampling regime
Table SI-5.6: Summary statistics for the concentrations of explanatory variables (µg l^{-1}) found in the floodplain soil pore water during the sampling regime
Table SI-5.7: Summary statistics for the concentrations of PTEs (µg l^{-1}) found in the river water
Table SI-5.8: Summary statistics for the concentrations of PTEs (µg l^{-1}) found in the ground water
Figure SI-5.3: Arsenic concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.4: Cadmium concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.5: Cobalt concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.6: Copper concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.7: Chromium concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.8: Nickel concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.9: Lead concentrations map series, total soil concentrations, pre-flood, during the flood and post flood
Figure SI-5.10: Zinc concentrations map series, total soil concentrations, pre-flood, during the flood and post flood

Chapter 6

6.0. General discussion

6.1. Overview

The purpose of this PhD research was to investigate the mechanisms influencing the mobility of potentially toxic elements (PTEs) in floodplain soil pre-flood, during a flood and post-flood. Flooding is a global environmental risk, that is likely to be exacerbated by climate change and land-use change. With human populations increasing worldwide; there has become increasing pressure for housing globally, meaning there will be more housing developments on or near to what was designated floodplain land (Bowes et al., 2018; McLean and Watson, 2009; Pappenberger et al., 2012). This land-use change will increase the number of people experiencing flooding and could make them receptors to contaminated waters. Contamination of soils with PTEs has received most attention in highly contaminated areas and, as such, this research chose to examine relatively uncontaminated floodplain soils as a way to demonstrate whether these areas could, in practice, become a source of legacy PTEs in the future. The principle, in theory, was that floodplain soils contain legacy contaminants from the catchments' industrial past, and that, as the impact of climate change will increase the intensity and duration of flooding events in the future, these areas of land may change from a sink to a source of PTEs to the wider environment (Ponting et al., 2021).

Insufficient data (e.g. chemical, physical and biological) prior to flooding of a floodplain area was determined to be a limitation to our current knowledge of how flooding influences PTE mobility because this data would help to identify mechanisms responsible for changes observed during the flood and post-flood (Barber et al., 2017). Much of the research evidence to date had come from laboratory studies, rather than field-based observations (Hooda, 2010; Ponting et al., 2021). This affects the overall understanding of mechanisms involved in mobilisation of PTEs, due to the controlled conditions used in these studies (e.g. often higher temperatures than in-situ and use of deionised water for flooding) (Frohne et al., 2011; Izquierdo et al., 2013). Extrapolation of results from laboratory studies to the field has posed some difficulties; as such, this research used a field-based approach. There could be greater environmental impacts from flooding on floodplain sites that are more highly contaminated with legacy contamination.

6.2. Main findings

The individual site characteristics were found, in the literature, to have an important influence on the mobility of PTEs; so detailed mapping of the floodplain elevation and the (pseudo) total PTEs concentrations was conducted early in this research (Chapter 3). Although slight, the (micro)topographical features of the Loddon Meadow floodplain, used as the sampling site in this PhD, were found to influence the deposition of some PTEs (e.g. Cr, Cu, Ni and Zn). The correlations between the floodplain elevation and soil concentrations suggest that these contaminants are found in the soil as a result of deposition of contaminated sediment originating upstream. Higher concentrations were found either in the centre of the floodplain at lowest elevation (Cr and Cu) or closer to the river (Ni and Zn). These differences may be the result of the size of the sediment particles, as larger particles fall from the floodwater and deposit on the topsoil faster than smaller particles that may have then fallen from the floodwater in the centre of the floodplain where flood waters remain for longer durations. This provides evidence that there may be two potential sources of PTEs; with Cr and Cu bound to fine sediment and Ni and Zn bound to coarse sediment.

Extracting pore water from the floodplain soil was instrumental for this PhD research because the pore waters contain the fraction that is mobile and more readily available to the uptake by crops (either agricultural or in natural vegetations) or soil organisms (Cipullo et al., 2018a; Römkens et al., 2004). Sampling pore water chemistry therefore provides the best indication of the bioavailable PTEs; mobilised due to their association with soluble species or released from the soil matrix during flooding (Ibragimow et al., 2013; Selim, 2013). The methodology for extracting pore waters from the soil was also thought to impact the results of chemical analyses because different methods may extract pore water from different pores, which may have different chemical compositions. Preliminary work (Chapter 4) comparing two different extraction methodologies (*in-situ* Rhizon^{TM} samplers and *ex-situ* centrifugation) did not find significant differences in the analytical results, despite the pressure exerted on the soil samples between the two methods being different by orders of magnitude. However, the usability of the methods through varying soil moistures, resulted in the *ex-situ* centrifugation being chosen as the extraction method for the winter sampling conducted (Chapter 5); in which soil pore waters were extracted pre-flood, during a flood and post-flood. Flooding was found not to influence the environmental fate of all PTEs (As, Cd, Co, Cu, Cr, Ni, Pb and Zn) in the same way; we actually found significantly lower concentrations of Cd, Cu and Cr post-flood, compared to pre-flood. It was found that Cr and Cu behave similarly during the flooding and post-flood; they may also have a common source (upstream from the catchment) and subsequent distribution of fine sediments across the floodplain caused by river water inundation (Chapter 3). Therefore, it is possible that the source of these PTEs to the floodplain influences the impact that flooding has on their mobility. An important take-home from this research was that the impact of flooding on PTEs mobility is the net-effect of multiple processes, so while we observed some processes to increase the pore water concentrations of PTEs (reductive dissolution of Mn oxides) in some areas (generally in the lower elevation areas) of the floodplain, the overall net affect was a decrease in pore water concentrations because other processes (e.g. precipitation with sulphides) were dominant. This highlighted again the influence of (micro)topographical features of the floodplain site. It is important to understand the dominant processes that drive mobility of individual PTEs on specific floodplains so that site-specific predictions can be made on the impact of future floods on the environmental fate of legacy contaminants.

6.3. Further research needs

The duration of flooding is thought to influence PTE mobilisation due to the length of time taken for key processes to take place, particularly redox mediated processes. It is therefore difficult to predict which PTEs might be mobilised into the soil pore water as a result of any given flooding event (during the flood or post-flood). This research study is specific to the soils of the Loddon Meadow floodplain in the Southeast of the UK (classified as silty loam) and only captures a single, relatively short-duration, flooding event; this somewhat limits the extent to which the conclusions can be extrapolated to other sites and seasons. Therefore, sampling that captures multiple floods over multiple seasons would provide valuable insights into the impacts of increased flooding frequency and intensity on the mobility of PTEs. Further work would still be required to continue the field-based sampling approach of floodplain sites across different soil types; as this will affect soil structure and the ability to hold or release PTEs during flooding (Schneider et al., 2016; Shaheen et al., 2013) and also at different times of the year; as summer flooding may result in differences to mobilisation due to different ambient temperatures that will influence these processes (Simmler et al., 2017). The use of sediment traps would help to further consider whether the impact of flooding on the mobility of these elements is influenced by their source. These investigations would benefit from analysing PTE speciation as this would provide a greater understanding of the changes to PTEs mobility and toxicity to receptors.

The conceptual model created as part of the literature review (Chapter 2; (Ponting et al., 2021)) should be used in future work to aid building a model with predictive capability for assessing the impact of flooding on the mobility of PTEs. Predicting the biogeochemical processes that influence the mobilisation of PTEs will become increasingly important for environmental health and risk assessment, particularly as climate change is likely to mean increased frequency and duration of flooding that directly impacts redox reactions (Borch et al., 2010). Attempts to model the concentration of PTEs in floodplain pore waters have demonstrated the complexity of predicting how different soil properties interact to alter mobility (Rennert et al., 2017). Statistical (empirical) modelling relates pore water concentrations to total concentrations and would be site specific whereas process-based modelling “multi-surface models”, describe processes and interactions between pore waters and reactive surfaces and could be combined with hydrological models already in the literature (e.g. the SWAP model: Soil-Water-Atmosphere-Plant system) (Groenenberg et al., 2012). Observations on uptake by organisms e.g. plants, worms and microbes living in periodically inundated floodplain soils may improve models that already predict uptake in aerobic conditions (Vink and Meeussen, 2007). This would also help to further understanding of the extent that mobilisation and higher concentrations of phytoavailable contaminants have on plants ability to function (Deverel et al., 2011). Consideration of how the duration of flooding affects these receptors would also be beneficial, as it has been found that some uptake of PTEs (e.g. As) by floodplain vegetation was enhanced during longer submersion time (Overesch et al., 2007). The interconnectedness of stresses posed by climate change and by environmental contaminants on human and ecological health exemplify the need for increased interdisciplinary discussion and research to examine the potential impacts (Wenning et al., 2010).

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Chapter 7

7.0. Activities

This chapter showcases the additional activities undertaken during the PhD including co-supervising a number of BSc and MSc projects, presenting work at various conferences as well as successful collaboration with other researchers that has resulted in publication.

7.1. Co-supervising

During the PhD period, a number of MSc and BSc research projects in the Department of Geography and Environmental science have been supported, including:

2016-17

MSc Research Project Student Tom Kelly: The effect of flood duration on the release of PTEs in floodplain soils from the Loddon catchment

2017-18

MSc Research Project Student Koji Wantanabe: Rare Earth Elements in the Loddon Catchment

2018-19

MSc Research Project Student Nurul Diyana Binti Mohamad Basiron: Rare Earth Elements (REEs) in Rivers of The Loddon Catchment

MSc Research Project Student Rachel Blissett-Lyne: The impact of extreme rainfall on the mobilisation of potentially toxic elements

2019-20

BSc Dissertation Project Student Danielle Page: An Investigation into the Impacts of Flooding on the Deposition and Accumulation of Heavy Metals on the Loddon Floodplain

BSc Dissertation Project Student Ruoyao Wang: Evaluation of the Effects of Soil Flooding on the Mobility of Potentially Toxic Elements using Meta-analysis

7.2. Research presentations

Research from this PhD has been presented via poster and oral presentation at a number of conferences and events, including;

PICO presentation (vPICO) at the virtual EGU General Assembly, April 2021: Impact of fluvial flooding on potentially toxic element mobility in floodplain soils

MSc Environmental Pollution Lecture at Reading University, March 2021: Impact of fluvial flooding on potentially toxic element mobility in floodplain soils

Invited Seminar (online) at University of York, February 2021: Impact of climate change on environmental pollution

Poster presentation at the British Society of Soil Science Annual Meeting, September 2019: Impact of extreme rainfall events on the mobility of potentially toxic elements in floodplains

Poster presentation at the Loddon Observatory Showcase event, September 2019: Mobility of Potentially Toxic Elements in Floodplain Soil – A Comparison of Two Pore water Extraction Methods

Poster presentation at the British Geological Survey Science Festival, June 2019: Impact of extreme rainfall events on the mobility of potentially toxic elements in floodplains

Oral presentation at Royal Society of Chemistry meeting #EnvChem2019: Advances in Environmental Chemistry, October 2019: Mobility of Potentially Toxic Elements in Floodplain Soil – A Comparison of Two Pore water Extraction Methods

Oral presentation at the Loddon Observatory Showcase event, September 2018: Impact of extreme rainfall on mobility of PTEs in floodplain soil

Poster presentation at the British Society of Soil Science Annual Meeting, September 2018: Influence of Floodplain Topography on Soil Chromium Concentrations

Poster presentation at a Royal Society of Chemistry meeting on 'The geochemistry and mineralogy of contaminated environments', June 2018: Influence of Floodplain Topography on Soil Chromium Concentrations

Poster presentation at the British Geological Survey Science Festival, June 2018: Influence of Floodplain Topography on Soil Chromium Concentrations

7.3. Co-authored Publications

During the PhD period, a number of relevant publications have arisen through collaboration with students at the University of Reading and University of York. These are listed below with the specific contribution that was made to each paper.

Kelly, T.J., Hamilton, E., Watts, M.J., **Ponting, J**. and Sizmur, T., 2020. The effect of flooding and drainage duration on the release of trace elements from floodplain soils. *Environmental Toxicology and Chemistry*, 39(11), pp.2124-2135. DOI 10.1002/etc.4830
https://setac.onlinelibrary.wiley.com/doi/full/10.1002/etc.4830

Jessica Pontings' Contribution; Field sampling, writing, editing drafts, providing additional data of river concentrations.

Kiss, T.B., Chen, X., **Ponting, J**., Sizmur, T. and Hodson, M.E., 2021. Dual stresses of flooding and agricultural land use reduce earthworm populations more than the individual stressors. *Science of The Total Environment*, 754, p.142102. DOI 10.1016/j.scitotenv.2020.142102
https://www.sciencedirect.com/science/article/pii/S004896972035631X?dgcid=author

Jessica Pontings' Contribution; Field sampling, creation of elevation maps using GIS, editing and providing feedback on drafts.

Appendices

Appendix 1. Supporting information for Chapter 2

This supporting information contains:

- Table SI-2.1 Summary of the findings of papers that report the impact of flooding on potentially toxic element (PTE) mobility.
- Reference list for Table SI-2.1.

Table SI-2.1: Summary of the findings of papers that report the impact of flooding on potentially toxic element (PTE) mobility

PTEs	Mobility of PTEs	Observations that may explain the result	Sample	Duration	Temperature	Lab or Field	Study Location	References
Arsenic	Increase	Microbially mediated Fe(III) reduction, raised pH and released Fe(II) which was associated with mobilisation of As (peaked after 14-28 days)	Homogenised Fe-rich soils saturated with deionised water	up to 91 days	25±1 °C	Lab Perspex columns	East Australia	(Burton et al., 2008)
	Increase	Associated with increasing Fe-concentrations. Reduction of As(V) to more soluble As(III).	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm system	Germany	(Schulz-Zunkel et al., 2015)
	Increase	Highest concentrations with high flow flooding. High temporal variation.	River water from former mining watershed	Two flood events; 2 days each		Field-based 24-hour automatic samplers	SE France	(Resongles et al., 2015)
	Increase	Related to changes in Eh/pH, co-precipitation with Fe oxides and release of dissolved aromatic carbon compounds	Fresh water marsh sediment cores taken			Automated biogeochemical microcosm system	USA	(Shaheen et al., 2016)
	Increase	After 20 days reductive dissolution of As-bearing Fe(III)- oxyhydroxides main cause for high solubilisation. High Mn concentrations inhibited As solubilisation while higher temperatures increased As solubilisation	Mining-impacted homogenised floodplain topsoil (0-20cm) and subsoil (20-40cm)	up to 41 days	10˚C, 17.5˚C and 25˚C	Lab anoxic polypropylene tube microcosm	Bulgaria	(Simmler et al., 2017)
	Increase	With decreasing E_H, more As was released into pore water and this also increased with flooding duration	Calcareous, uncontaminated agricultural soils, composite samples	8 weeks	20 ± 5 °C	Lab Incubation study	Canada	(Indraratne and Kumaragamage, 2017)
	Increase during flood and decrease after	Mobility under reducing conditions due to reduction of Fe (hydr)oxides releasing As. Reduction of arsenate to arsenite enhances As mobility.	Homogenised eutric fluvisol soil from grassland	22 days (2011) 61 days (2014)		Lab automated (redox) microcosm system	Germany	(Frohne et al., 2014, 2011)

		Mobility decreases with oxidation and rising Eh indicating co-precipitation with Fe oxides.						
	Increase then decrease	Initially reductive dissolution of Fe oxides increased desorption of As releasing As(III) from sediments but then in the middle/later stages reductive dissolution of Fe oxides promoted adsorption, As was also co-precipitated with sulphur generating insoluble sulfo-arsenide compounds.	Mixed sediment samples with cultivated microbes	45 days	4 ˚C	Lab culture tanks	China	(Yang et al., 2015)
	Variable	Dependent on flood duration. Increase soluble concentrations under reducing conditions during long-term flooding. Mobilisation in oxidising conditions during short-term flooding	Composite surface soil sample from flood channel (old river bed) used as cattle pasture	Long-term (94 days) short term (21 days) flooding		Lab 70cm high soil monolith with lysimeter	Germany	(Shaheen et al., 2014b)
Cadmium	Decrease	Role of Fe oxides, soil solution concentrations may significantly depend on previous soil moisture conditions; dried soils had higher concentrations than field capacity and saturated treatment	8 soils with range of pH and clay content, flooding with deionised water	35 days; 14 days treatment (D, F or S) then 21 days field capacity	Between 18 and 22 °C	Greenhouse study; pot treatments (dried (D), field capacity (F) and saturated (S))	Belgium	(Tack et al., 2006)
	Decrease during flood and increase after	Formation and re-oxidation of sulphides	Polluted over-bank sediment, top 20cm homogenised soil flooded with acidified deionised water	96 days	Between 15 and 25 ˚C	Lab green-house set up, 5 flooding regimes	Belgium	Du Laing et al. 2007
	Decrease	Attributed to the interaction with DOC, Mn and sulphide precipitation	Homogenised eutric fluvisol soil from grassland	22 days		Lab automated (redox) microcosm	Germany	(Frohne et al., 2011)
	Decrease	Under reducing conditions, and decreased pH, also controlled by DOC, Fe, Mn and SO_4^{2-} Liming soil samples immobilised Pb under dynamic redox conditions	Contaminated soil (eutric fluvisol) samples and sugar beet factory lime + soil sampled	Soils incubated for year pre - experiment		Lab automated (redox) microcosm	Germany	(Shaheen and Rinklebe, 2017)

	Variable	Salinity enhanced Cd mobility (during first 20 days), however sulphide precipitation immobilises Cd independent of salinity (from day 20-50)	Flooded homogenised sediments with different salinities (dissolving NaCl in deionised water)	250 days	15-25 ˚C	Lab set up	Belgium	(Du Laing et al., 2008)
	Variable	Dissolved Cd increased during first 3 days of flooding driven by reductive dissolution of Fe(III) and Mn(IV, III) (hydr)oxides but then dropped due to sulphate respiration	Contaminated homogenised gleyic fluvisol floodplain soil submerged with synthetic river water	52 days	~23 ˚C	Lab microcosm	Germany	(Weber et al., 2009)
	Variable	Rapid release, peaking after 6 days flooding with decreasing concentrations after due to colloid aggregation	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
	Variable	Initial release after water saturation of oxidised soil Co-precipitation with sulphides forming less soluble CdS	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm	Germany	(Schulz-Zunkel et al., 2015)
	Variable	Solubility of soil Cd sensitive to initial increases in soil moisture following periods of soil drainage but not sensitive to short-term saturation (3 days) Soil pH and organic matter appear to influence Cd phytoavailability	Kereone (allophanic): fine sandy loam and topehaehae (gley): sandy clay loam soils	(F) 3 days, drained for 11 (NF) 70% field capacity for 7 days	Ambient air temp 0.1 ˚C to 21.7 ˚C	Lab pot trial; flooded (F) and non-flood (NF)	New Zealand	(Stafford et al., 2018)
	Increase	Highest concentrations with high flow flooding High temporal variation	River water from former mining watershed	Two flood events; 2 days each		Field-based 24-hour automatic samplers	SE France	(Resongles et al., 2015)
	Increase	Related to changes in Eh/pH, co-precipitation with Fe oxides and the release of dissolve aromatic carbon compounds	Fresh water marsh sediment cores taken			Lab automated (redox) microcosm	USA	(Shaheen et al., 2016)

Chromium	Decrease	Under reducing conditions and decreased pH, also controlled by DOC, Fe, Mn and SO_4^{2-}	Flooding of soil (eutric fluvisol) samples			Lab automated (redox) microcosm	Germany	(Shaheen and Rinklebe, 2017)
	Decrease	Attributed to the interaction with DOC, Mn, precipitation of sulphides and strong absorption to Fe(hydr)oxides. In reducing conditions relatively immobile Cr(III) dominates.	Homogenised eutric fluvisol soil from grassland	22 days (2011) 61 days (2015)		Lab automated (redox) microcosm	Germany	(Frohne et al., 2015, 2011)
	Variable	Increased with increasing duration of flooding but lower after drainage	Intact soil cores from floodplain subjected to different flooding (with ultrapure water)/drainage regimes in the laboratory	40-day experiment; 4 treatments of flooding (7, 14, 28 and 40 days)	20°C constant temperature	Lab incubation of soil cores	UK	(Kelly et al., 2020)
	Variable	Dependent on flood duration; increase soluble concentration under reducing conditions (reduction of Cr(VI) to Cr(III) in short-term flooding enhanced by increase in DOC in long-term flooding, mobilised in oxidising conditions during short-term flooding	Composite surface soil sample from flood channel (old river bed) used as cattle pasture	Long-term (94 days) short term (21 days) flooding		Lab 70cm high soil monolith with lysimeter	Germany	(Shaheen et al., 2014b)
	Increase during flood and decrease after	Correlation with Fe/Mn concentration but stronger correlation with Ca	Polluted over-bank sediment, top 20cm homogenised soil flooded with acidified deionised water	96 days	Between 15 and 25 °C	Lab green-house set up, 5 flooding regimes	Belgium	Du Laing et al. 2007
	Increase, remained constant then decreased	Dependent on Sulphur, absorption to Fe(hydr)oxides and interaction with DOC. Constant amount of dissolved Cr suggest high amount of Cr(III) in soil solution with oxidisation to Cr(VI) at start and end of experiment	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm	Germany	(Schulz-Zunkel et al., 2015)

	Increase	Available Cr may increase along with $CaCO_3$ content Total Cr strongly correlated with coarse and medium grained sediment and OM	Homogenised surface (0-30cm) fluvial sediments before and after real flood event	More than 28 days flood at highest water level	Room temperature	Field sampling lab extraction with 0.01M $CaCl_2$	Poland	(Ibragimow et al., 2013)
	Increase	Dissolution of Fe and Mn oxide minerals, thereby allowing release of associated Cr. Fluvisols showed high potential mobility of Cr compared with Gleysols. Gleysols had higher metal mobility during longer flooding duration.	Homogenised soil comparing fluvisols and gleysols	Number of days flooding in two years provided	Room temperature	Field sampling periodically flooded area, lab fractionation	Germany	(Shaheen and Rinklebe, 2014)
	Increase	Correlated with release of Fe and Mn by reductive dissolution of oxyhydr(oxides), Forming oxyanions (CrO_4^{2-}) in oxidised form or superficially sorbed in reduced form (Cr(III))	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
Cobalt	Decrease	Attributed to precipitation of metal sulphides and association with DOC	Homogenised eutric fluvisol soil from grassland	61 days		Lab automated (redox) microcosm	Germany	(Frohne et al., 2014)
	Decrease	Under reducing conditions and decreased pH, also controlled by DOC, Fe, Mn and SO_4^{2-}. Liming soil samples immobilised Co under oxic conditions, however mobilised it under reducing conditions	Contaminated soil (eutric fluvisol) samples and sugar beet factory lime + soil sampled	Soils incubated for year pre - experiment		Lab automated (redox) microcosm	Germany	(Shaheen and Rinklebe, 2017)
	Increase	After 2 days flooding, followed by stabilisation at high level at days 6 - 22. Correlated with release of Fe and Mn by reductive dissolution of (oxyhydr)oxides	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
	Increase	Related to solubility of Fe, Mn and DOC. Reductive dissolution of Fe/Mn	Fresh water marsh sediment cores taken			Lab automated (redox) microcosm	USA	(Shaheen et al., 2016)

		oxides, Fe^{2+} displaces Co from exchange sites						
Copper	Decrease	Decreased with increasing duration of flooding but concentrations were higher in those drained for longest time	Intact soil cores from floodplain subjected to different flooding (with ultrapure water)/drainage regimes in the laboratory	40-day experiment; 4 treatments of flooding (7, 14, 28 and 40 days)	20°C constant temperature	Lab incubation of soil cores	UK	(Kelly et al., 2020)
	Decrease	Role of Fe oxides, soil solution concentrations may significantly depend on previous soil moisture conditions; dried soils had higher concentrations than field capacity and saturated treatment	8 soils with range of pH and clay content, flooding with deionised water	35 days; 14 days treatment (D, F or S) then 21 days field capacity	Between 18 and 22 °C	Lab greenhouse study; pot treatments (dried (D), field capacity (F) and saturated (S))	Belgium	(Tack et al., 2006)
	Decrease	Gradual decline, depletion of dissolved cu accompanied by major transformations in solid-phase Cu (e.g. Cu(II) bound to OM or Cu_xS precipitates	Contaminated homogenised gleyic fluvisol floodplain soil submerged with synthetic river water	52 days	~23 °C	Lab microcosm	Germany	(Weber et al., 2009)
	Decrease	Attributed to the interaction with DOC, Mn and precipitation of sulphides, high affinity with OM	Homogenised eutric fluvisol soil from grassland	22 days (2011) 61 days (2014)		Lab automated (redox) microcosm	Germany	(Frohne et al., 2014, 2011)
	Decrease	After the flood in 2010 there was a decrease in actual available and total Cu concentrations Total contents strongly correlated with participation of coarse-grained sediments	Homogenised surface (0-30cm) fluvial sediments before and after real flood event	More than 28 days flood at highest water level	Room temperature	Field sampling lab extraction with 0.01M $CaCl_2$	Poland	(Ibragimow et al., 2013)
	Decrease	Mobility during oxidising conditions due to dissolution of sulphides. Fluvisols showed high potential mobility of Cu compared with	Homogenised soil comparing fluvisols and gleysols	Number of days flooding in two years provided	Room temperature	Field sampling periodically flooded area, lab fractionation	Germany	(Shaheen and Rinklebe, 2014)

		Gleysols. Gleysols had higher metal mobility during longer flooding duration						
	Decrease	During reduced phase less mobile CuS may be formed	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm	Germany	(Schulz-Zunkel et al., 2015)
	Decrease	Relatively high pH and metal-sulphide precipitation	Homogenised eutric fluvisol soil samples			Lab automated (redox) microcosm and sequential extraction	USA, China and Indonesia	(Rinklebe et al., 2016b)
	Decrease	Flooding and decrease in E_H decreased Cu concentration; reduced forms of Cu may form insoluble Cu^+-humic acid complexes, reduction of Cu^{2+} with subsequent complexation/ precipitation may also play a role; particularly CuS precipitation	Calcareous, uncontaminated agricultural soils Composite samples	8 weeks	20 ± 5 °C	Lab incubation	Canada	(Indraratne and Kumaragamage, 2017)
	Decrease during flood and increase after	Formation and re-oxidation of sulphides	Polluted over-bank sediment, top 20cm homogenised soil flooded with acidified deionised water	96 days	Between 15 and 25 ˚C	Lab green-house set up, 5 flooding regimes	Belgium	Du Laing et al. 2007
	Variable	Rapid release peaks after 2 days flooding, showed a peak after 2-6 days followed by decrease because of colloid aggregation and formation of metal sulphide colloids with the onset of sulfate reduction	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
Lead	Decrease	Decreased with increasing duration of flooding and concentrations were consistently suppressed after drainage	Intact soil cores from floodplain subjected to different flooding (with ultrapure water)/drainage regimes in the laboratory	40-day experiment; 4 treatments of flooding (7, 14, 28 and 40 days)	20˚C constant temperature	Lab incubation of soil cores	UK	(Kelly et al., 2020)

	Decrease	Under reducing conditions and decreased pH, also controlled by DOC, Fe, Mn and SO_4^{2-}. Liming soil samples immobilised Pb under dynamic redox conditions.	Contaminated soil (eutric fluvisol) samples and sugar beet factory lime + soil sampled	Soils incubated for year pre - experiment		Lab automated (redox) microcosm	Germany	(Shaheen and Rinklebe, 2017)
	Variable	Rapid release peaking 6 days flooding with decreasing concentrations after, strongly dominated by colloidal fraction, Then onset of sulphide reduction	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
	Variable	Peaked at 10 days then declined slowly, due to affinity of Pb to bind to Fe and Mn oxy-hydroxides. Slowly rising pH enhanced re-absorption and competitive sorption with Zn^{2+}, Mn^{2+} and Fe^{2+}	Topsoil (0-15cm) homogenised samples from pasture land	10, 21 and 42 days	20˚C	Lab incubation mesocosm	UK	(Izquierdo et al., 2017)
	Increase	Dissolved Pb increased during first 3 days of flooding driven by reductive dissolution of Fe(III) and Mn(IV, III) (hydr)oxides	Contaminated homogenised gleyic fluvisol floodplain soil submerged with synthetic river water	52 days	~23 ˚C	Lab microcosm	Germany	(Weber et al., 2009)
	Increase	Strong binding ability and co-transport of Pb with DOC	Gley and peat soil cores, porewater and stream water collected	3x sampling dates, 2 days each (Jul-Sept)		Field sampling of soil cores, porewater and stream water	UK	(Dawson et al., 2010)
	Increase	Highest concentrations with high flow flooding High temporal variation	River water from former mining watershed	Two flood events; 2 days each		Field-based 24-hour automatic samplers	SE France	(Resongles et al., 2015)
Nickel	Decrease	Microbially mediated Fe reduction released Fe(II). Formation of acid-volatile sulphide (AVS) slowed Fe(II) mobility and strongly immobilised Ni	Homogenised Fe-rich soils saturated with deionised water	up to 91 days	25±1 °C	Lab Perspex columns	East Australia	(Burton et al., 2008)

		through co-precipitation, after 49 days.						
	Decrease	Attributed to the interaction with DOC, Mn and precipitation of sulphides	Homogenised eutric fluvisol soil from grassland	22 days (2011) 61 days (2014)		Lab automated (redox) microcosm	Germany	(Frohne et al., 2014, 2011)
	Variable	Increased with increasing duration of flooding and concentrations were lower after drainage	Intact soil cores from floodplain subjected to different flooding (with ultrapure water)/drainage regimes in the laboratory	40-day experiment; 4 treatments of flooding (7, 14, 28 and 40 days)	20°C constant temperature	Lab incubation of soil cores	UK	(Kelly et al., 2020)
	Increase	Consistent with Fe/Mn oxidation and reduction	Polluted over-bank sediment, top 20cm homogenised soil flooded with acidified deionised water	96 days	Between 15 and 25 °C	Lab green-house set up, 5 flooding regimes	Belgium	Du Laing et al. 2007
	Increase	Dissolved Ni concentration tripled during first 15 days of flooding, driven by reductive dissolution of Fe(III) and Mn(IV, III) (hydr)oxides	Contaminated homogenised gleyic fluvisol floodplain soil submerged with synthetic river water	52 days	~23 °C	Lab microcosm	Germany	(Weber et al., 2009)
	Increase	After the flood in 2010 there was a decrease in actual available and total Cd concentrations increased insignificantly	Homogenised surface (0-30cm) fluvial sediments before and after real flood event	More than 28 days flood at highest water level	Room temperature	Field sampling lab extraction with 0.01M $CaCl_2$	Poland	(Ibragimow et al., 2013)
	Increase	Interactions with DOC, pH Fe/Mn oxides and sulphur control solubility	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm	Germany	(Schulz-Zunkel et al., 2015)
	Increase	Correlated with release of Fe and Mn by reductive dissolution of oxyhydr(oxides)	Carbonatic homogenised topsoil flooded with artificial river water	14 sampling days over 40 days		Lab microcosm purged with N	Switzerland	(Abgottspon et al., 2015)
	Increase	Decreasing E_H increased Ni concentration in pore water, Ni exists as free ionic Ni^{2+}, reductive dissolution of Fe/Mn oxyhydroxides	Calcareous, uncontaminated agricultural soils Composite samples	8 weeks	20 ± 5 °C	Lab incubation	Canada	(Indraratne and Kumaragamage, 2017)

		results in displacement of Ni^{2+} by Fe^{2+} and Mn^{2+} from exchange sites						
Zinc	Decrease	Role of oxides of Fe and Mn, soil solution concentrations may significantly depend on previous soil moisture conditions; dried soils had higher concentrations than field capacity and saturated treatment	8 soils with range of pH and clay content, flooding with deionised water	35 days; 14 days treatment (D, F or S) then 21 days field capacity	Between 18 and 22 °C	Greenhouse study; pot treatments (dried (D), field capacity (F) and saturated (S))	Belgium	(Tack et al., 2006)
	Decrease	Microbially mediated Fe reduction released Fe(II). Formation of acid-volatile sulphide (AVS) slowed Fe(II) mobility and strongly immobilised Zn through co-precipitation after 49 days	Homogenised Fe-rich soils saturated with deionised water	up to 91 days	25±1 °C	Lab Perspex columns	east Australia	(Burton et al., 2008)
	Decrease	After the flood in 2010 there was a decrease in actual available and total Zn concentrations Total contents strongly correlated with participation of coarse-grained sediments	Homogenised surface (0-30cm) fluvial sediments before and after real flood event	More than 28 days flood at highest water level	Room temperature	Field sampling lab extraction with 0.01M $CaCl_2$	Poland	(Ibragimow et al., 2013)
	Decrease	Attributed to the interaction with DOC, Mn and sulphide precipitation	Homogenised eutric fluvisol soil from grassland	22 days (2011) 61 days (2014)		Lab automated (redox) microcosm	Germany	(Frohne et al., 2014, 2011)
	Decrease	Precipitation with sulphides Fluvisols showed high potential mobility of Zn compared with Gleysols. Gleysols had higher metal mobility during longer flooding duration	Homogenised soil comparing fluvisols and gleysols	Number of days flooding in two years provided	Room temperature	Field sampling periodically flooded area, lab fractionation	Germany	(Shaheen and Rinklebe, 2014)
	Decrease	Under reducing conditions and decreased pH, also controlled by DOC, Fe, Mn and SO_4^{2-}. Liming soil samples immobilised Zn under oxic conditions however mobilised it under reducing conditions	Contaminated soil (eutric fluvisol) samples and sugar beet factory lime + soil sampled	Soils incubated for year pre - experiment		Lab automated microcosm system - adding O_2 to increase Eh and N_2 to lower Eh	Germany	(Shaheen and Rinklebe, 2017)

	Variable	Interactions with DOC, pH Fe/Mn oxides control solubility. Concentrations increased with increasing Fe-concentration. During reduced phase less mobile ZnS may be formed	Homogenised alluvial gley / eutric gleysol soil	85 days		Lab automated (redox) microcosm	Germany	(Schulz-Zunkel et al., 2015)
	Variable	Depending on C amendment due to pH (negative correlation) and competition with Fe^{2+} after 42 days	Topsoil (0-15cm) homogenised samples from pasture land	10, 21 and 42 days	20 °C	Lab incubation mesocosm	UK	(Izquierdo et al., 2017)
	Increase	Highest concentrations with high flow flooding High temporal variation	River water from former mining watershed	Two flood events; 2 days each		Field-based 24-hour automatic samplers	SE France	(Resongles et al., 2015)
	Increase	Increased with increasing duration of flooding and concentrations remained elevated after drainage	Intact soil cores from floodplain subjected to different flooding (with ultrapure water)/drainage regimes in the laboratory	40-day experiment; 4 treatments of flooding (7, 14, 28 and 40 days)	20°C constant temperature	Lab incubation of soil cores	UK	(Kelly et al., 2020)
	No consistent trend	Dissolved Zn concentration remained relatively constant indicating that it was sorbed in reduced soil or partly incorporated in carbonate precipitates	Contaminated homogenised gleyic fluvisol floodplain soil submerged with synthetic river water	52 days	~23 °C	Lab microcosm	Germany	(Weber et al., 2009)
	No consistent trend	Correlated negatively with pH and Ca and positively with Al	Calcareous, uncontaminated composite agricultural soil samples	8 weeks	20 ± 5 °C	Lab incubation	Canada	(Indraratne and Kumaragamage, 2017)

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Appendix 2. Supporting information for Chapter 3

This supporting information contains:

- Table 3.1. Soil concentrations of Cr, Cu, Ni, Zn, As and Pb (mg/kg) at the 30 sampling points on the Loddon Meadow floodplain shown in Figure 1.

Table SI-3.1: Soil concentrations of Cr, Cu, Ni, Zn, As and Pb (mg/kg) at the 30 sampling points on the Loddon Meadow floodplain shown in Figure 1. Limit of detection (LOD) are also detailed.

Point	Cr	Cu	Ni	Zn	As	Pb
LOD	**1.52**	**0.58**	**3.15**	**1.17**	**34.42**	**10.17**
1	81.20	23.19	33.32	170.71	<LOD	61.00
2	92.61	33.25	38.14	280.97	36.11	96.78
3	84.44	28.71	29.74	207.78	<LOD	104.20
4	95.70	23.60	33.63	222.02	51.12	73.79
5	93.74	17.31	36.80	168.72	<LOD	63.60
6	85.66	24.87	29.20	191.76	<LOD	84.98
7	99.45	41.67	32.36	247.53	<LOD	107.52
8	81.31	29.72	33.38	253.46	<LOD	92.82
9	64.55	12.27	32.53	111.41	<LOD	22.67
10	82.44	22.79	27.57	155.09	44.98	82.53
11	90.52	25.24	33.94	202.44	<LOD	84.79
12	81.25	32.84	31.78	228.58	39.31	86.73
13	64.24	23.42	25.80	137.24	<LOD	49.14
14	62.88	19.98	24.92	135.77	<LOD	56.71
15	91.73	21.80	34.10	187.49	<LOD	79.94
16	90.80	27.15	32.40	213.78	<LOD	94.79
17	55.12	18.70	18.97	111.48	<LOD	52.81
18	57.92	21.31	21.89	119.06	<LOD	46.20
19	82.26	27.16	27.51	184.12	<LOD	83.42
20	87.74	25.78	33.72	201.54	<LOD	78.55
21	56.50	24.51	25.81	184.66	<LOD	61.04
22	35.91	13.44	14.89	86.22	<LOD	38.30
23	45.06	18.37	14.51	94.86	<LOD	30.92
24	50.41	15.65	20.52	103.72	<LOD	184.20
25	69.26	20.49	24.83	138.75	<LOD	62.87
26	93.62	34.22	39.82	289.53	<LOD	106.18
27	76.67	36.34	35.77	298.50	<LOD	87.22
28	83.41	25.34	30.19	175.87	<LOD	77.26
29	73.47	20.94	31.44	167.80	<LOD	93.57
30	77.84	35.06	38.00	226.40	<LOD	78.87

Appendix 3. Supporting information for Chapter 4

This supporting information contains:

- Table SI-4.1: Limits of detection for the solutes analysed in the pore water

Table SI-4.1: Limits of detection (LOD) for the solutes analysed in the pore water

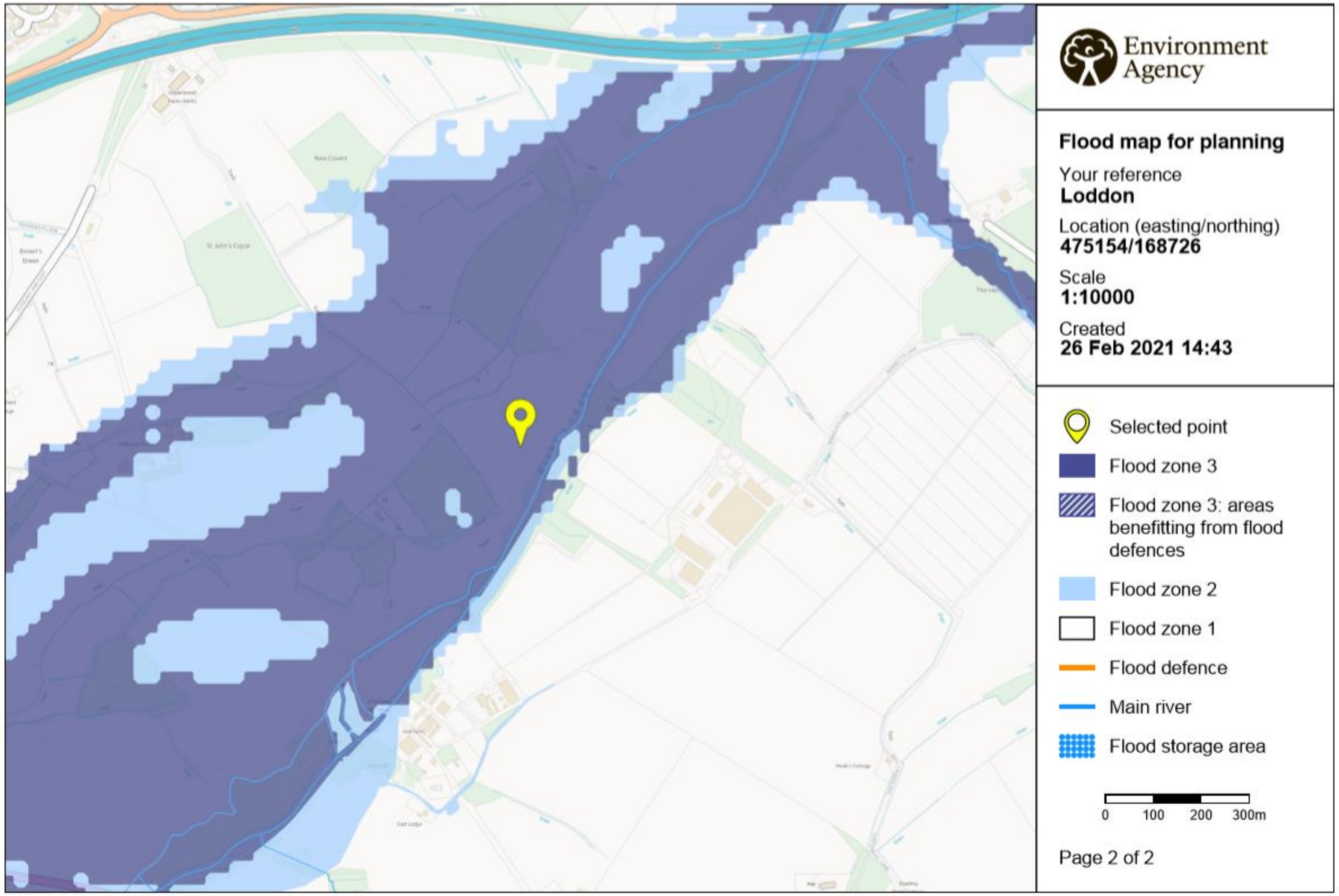
PTE	**LOD (mg/L)**	**Method**
Zn	0.0043	ICP-OES
Co	0.00011	ICP-OES
As	0.0017	ICP-OES
Ni	0.003	ICP-OES
Mn	0.000043	ICP-OES
Fe	0.00089	ICP-OES
Pb	0.0014	ICP-OES
Na	0.017	ICP-OES
Mg	0.000022	ICP-OES
Ca	0.0061	ICP-OES
K	0.056	ICP-OES
TOC	1.34	TOC
Sulphate	0.56	Dionex
Chloride	0.27	Dionex
Nitrate	0.38	Dionex

Appendix 4. Supporting information for Chapter 5

This supporting information contains:

- Figure SI-5.1: Environment Agency Flood Map for the Loddon Meadow
- Figure SI-5.2: Levels from 1st January 2018 to 1st April 2019 to show river and ground water levels
- Table SI-5.1: Soil pseudo-total (aqua regia) concentrations for the sampling points across the Loddon Meadow floodplain site.
- Table SI-5.2: Soil properties; moisture organic matter and pH across the Loddon Meadow floodplain pre-flood (averaged 5 sampling visits), during the flood and post-flood (averaged 5 sampling visits).
- Table SI-5.3: Detection limits for PTEs using ICP-MS
- Table SI-5.4: Analysis of similarities (ANOSIM) a one-way ANOVA testing 1) the treatment levels (pre-flood, flood and post-flood) and 2) elevation and 3) treatment with elevation from Principal Component Analysis (PCA).
- Table SI-5.5: Summary statistics for the concentrations of PTEs (µg l-1) found in the floodplain soil pore water during the sampling regime
- Table SI-5.6: Summary statistics for the concentrations of explanatory variables (µg l-1) found in the floodplain soil pore water during the sampling regime
- Table SI-5.7: Summary statistics for the concentrations of PTEs (µg l-1) found in the river water

- Table SI-5.8: Summary statistics for the concentrations of PTEs (µg l-1) found in the ground water
- Figure SI-5.3: Arsenic concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.4: Cadmium concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.5: Cobalt concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.6: Copper concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.7: Chromium concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.8: Nickel concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.9: Lead concentrations map series, total soil concentrations, pre-flood, during flood and post flood
- Figure SI-5.10: Zinc concentrations map series, total soil concentrations, pre-flood, during flood and post flood



Flood map for planning

Your reference
Loddon

Location (easting/northing)
475154/168726

Scale
1:10000

Created
26 Feb 2021 14:43

Page 2 of 2

Figure SI-5.1: Environment Agency Flood Map for the Loddon Meadow, accessed from https://flood-map-for-planning.service.gov.uk/summary?easting=475154&northing=168726 with the Loddon Meadow as the selected point.

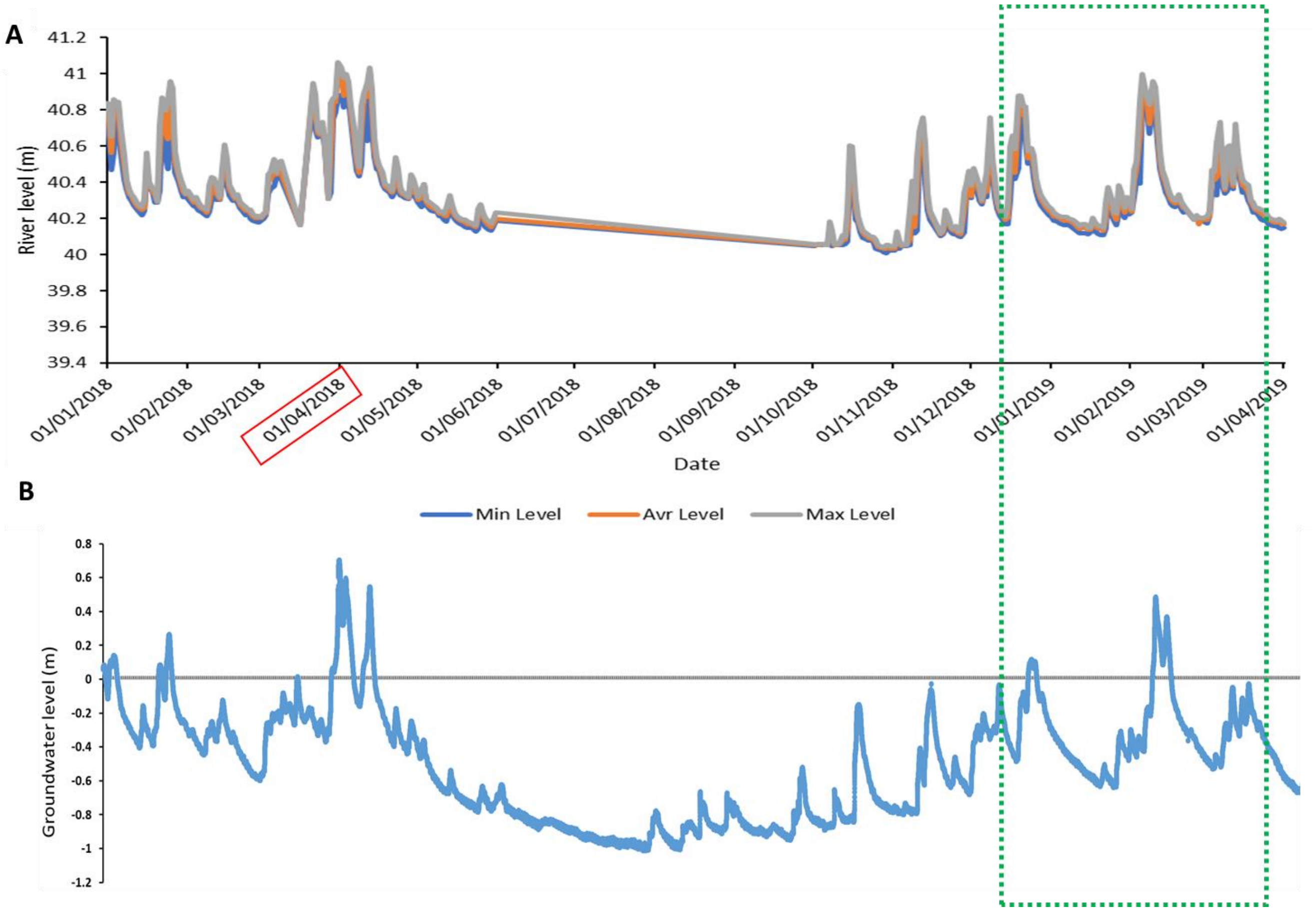


Figure SI-5.2: *Levels from 1st January 2018 to 1st April 2019 to show the A) River Loddon level (m above ordnance datum, where stage datum is 40m) at Arborfield Bridge river level station upstream from the Loddon Meadow floodplain, and B) Groundwater level (m relative to soil surface) averaged from the two boreholes on the Loddon Meadow floodplain. The red box around the date ('01/04/2018') shows the likely previous flooding period (based on river and groundwater levels) prior to the flooding event described in this study (green dotted box).*

Table SI-5.1: Soil pseudo-total (aqua regia) concentrations of PTEs for the sampling points across the Loddon Meadow floodplain site.

Sample point	**As (mg/kg) ICP-MS**	**Cd (mg/kg) ICP-MS**	**Co (mg/kg) ICP-OES**	**Cu (mg/kg) ICP-OES**	**Cr (mg/kg) ICP-OES**	**Ni (mg/kg) ICP-OES**	**Pb (mg/kg) ICP-OES**	**Zn (mg/kg) ICP-OES**
P1	16.24	0.68	14.13	31.16	40.45	24.36	61.59	143.76
P2	7.84	0.16	12.66	16.84	25.51	18.08	37.884	102.87
P3	8.84	0.22	12.67	28.93	39.61	23.22	83.0	153.0
P4	14.86	0.66	8.75	21.09	21.4	15.04	25.50	84.90
P5	11.8	0.3	14.94	37.49	49.88	25.68	94.60	152.30
P6	15.45	0.48	16.32	26.95	33.93	21.58	83.23	161.52
P7	16.34	0.8	11.28	13.62	21.29	17.95	29.71	83.19
P8	11.72	0.46	14.9	32.29	45.10	25.34	73.96	136.28
P9	13.70	0.74	13.11	35.33	50.37	24.23	126.40	172.35
P10	16.62	0.71	14.96	11.59	15.04	13.14	31.12	98.46
P11	19.76	1.13	11.3	22.12	36.84	20.12	68.65	139.66
P12	8.68	0.39	17.44	33.74	50.82	27.95	88.54	221.20

Table SI-5.2: Soil properties; moisture, organic matter and pH across the Loddon Meadow floodplain pre-flood (averaged 5 sampling visits), during the flood. and post-flood (averaged 5 sampling visits).

	Pre-flood (N=60)					**Flood (N=12)**					**Post-flood (N=60)**				
	Minimum	**Maximum**	**Mean**	**Skewness**	**St. Dev**	**Minimum**	**Maximum**	**Mean**	**Skewness**	**St. Dev**	**Minimum**	**Maximum**	**Mean**	**Skewness**	**St. Dev**
Soil Moisture	40.76	138.48	73.28	0.65	21.52	54.17	123.83	82.77	0.73	17.65	41.60	121.68	73.68	0.61	23.45
Organic Matter	10.39	28.98	17.79	0.32	3.81	12.06	24.05	15.69	1.33	3.41	10.24	24.85	15.70	0.58	3.82
pH	4.80	7.42	6.49	-1.01	0.55	4.75	7.25	6.41	-1.20	0.71	5.57	7.28	6.60	-0.65	0.40

Table SI-5.3: Detection limits for PTEs using ICP-MS.

PTE	**Detection Limit batch 1 (sampling 5-10; Dec-Feb) µg L−1**	**Detection Limit batch 2 (sampling 11-15; Feb-Mar) µg L−1**
Ni	0.4	0.006
Co	0.03	0.03
As	0.04	0.04
Zn	0.6	0.6
Cd	0.009	0.02
Cu	0.3	0.09
Pb	0.03	0.05
Cr	0.07	0.2

Table SI-5.4: Analysis of Similarities (ANOSIM) a one-way ANOVA testing 1) the treatment levels (pre-flood, flood and post-flood) and 2) elevation and 3) treatment with elevation from Principal Component Analysis (PCA). ***** denotes significant result (P <0.05 where the P value is calculated as the significance level/100).

Groups	ANOSIM (R) Statistic	Significance Level %
1) pre-flood, flood	0.131	12
1) pre-flood, post-flood	0.192	0.1 *****
1) flood, post-flood	0.277	1 *****
2) high, low	0.185	0.1 *****
2) high, medium	0.011	11.5
2) low, medium	0.145	0.1 *****
3) pre-flood; high - low	0.131	0.1 *****
3) flood; high - low	-0.031	60
3) post-flood; high - low	0.398	0.1 *****
3) pre-flood; low - medium	0.131	0.3 *****
3) flood; low - medium	-0.021	57.1
3) post-flood; low - medium	0.28	0.1 *****

Table SI-5.5: Summary statistics for the concentrations of PTEs (µg l^{-1}) found in the floodplain soil pore water during the sampling regime.

PTE	**Pre-flood (N=60) concentrations (µg l-1)**						**Flood (N=12) concentrations (µg l-1)**						**Post-flood (N=60) concentrations (µg l-1)**					
	Min	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**	**Min**	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**	**Min**	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**
As	0.85	3.42	2.03	1.47	1.34	0.50	0.75	4.49	2.95	1.42	1.16	1.01	0.71	2.20	0.67	1.28	1.20	0.33
Cd	0.12	0.81	0.69	0.36	0.37	0.17	0.13	0.95	1.42	0.38	0.34	0.24	0.09	0.63	3.04	0.18	0.16	0.08
Co	0.41	6.22	2.68	1.32	0.97	1.00	0.44	10.72	3.31	2.09	1.40	2.75	0.47	4.44	1.12	1.49	0.90	1.10
Cu	8.90	3123.50	4.25	211.92	28.20	496.86	17.50	413.20	1.60	107.37	37.80	129.47	9.50	397.92	3.47	49.20	23.93	78.47
Cr	1.21	10.20	2.67	2.83	2.40	1.70	0.62	7.10	2.89	1.94	1.58	1.71	0.78	4.00	1.15	1.81	1.60	0.75
Ni	7.90	87.20	2.97	20.12	14.40	15.87	9.23	39.35	1.46	18.65	17.19	8.29	8.04	448.53	6.77	32.06	19.13	57.21
Pb	0.63	13.75	1.57	3.67	2.90	2.39	0.70	8.92	0.66	3.92	2.60	2.92	0.46	21.50	5.07	2.29	1.50	2.94
Zn	22.10	2442.30	1.98	433.15	222.55	584.47	143.60	658.40	0.29	387.68	375.45	158.98	75.40	1259.90	1.37	354.22	269.40	266.96

Table SI-5.6: Summary statistics for the concentrations of explanatory variables (µg l^{-1}) found in the floodplain soil pore water during the sampling regime.

PTE	**Pre-flood (N=60) concentrations (µg l-1)**						**Flood (N=12) concentrations (µg l-1)**						**Post-flood (N=60) concentrations (µg l-1)**					
	Min	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**	**Min**	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**	**Min**	**Max**	**Skewness**	**Mean**	**Median**	**St. Dev**
Al	34.00	2251.00	3.41	313.60	191.00	339.08	35.00	557.00	1.35	195.00	160.50	147.59	22.00	851.00	1.69	196.23	126.50	181.55
Mg	1.10	6.47	1.83	2.41	2.28	0.99	1.25	2.71	-0.03	1.99	1.98	0.56	1.10	3.29	0.85	1.82	1.76	0.53
Mn	5.70	400.70	3.42	42.59	18.90	69.65	4.30	699.10	3.31	109.53	48.40	188.08	5.30	348.30	1.52	68.40	22.05	84.90
Fe	144.30	4548.50	3.18	863.42	739.95	664.32	150.80	1213.00	0.42	595.62	546.35	360.50	181.40	2783.90	1.56	759.77	530.80	565.32
NO3-	3.73	288.15	2.23	70.33	64.15	46.60	1.27	183.43	1.10	54.15	25.03	57.90	0.06	100.89	0.55	37.89	37.00	25.42
P	0.11	1.10	0.08	0.55	0.55	0.24	0.13	0.50	1.31	0.25	0.25	0.10	0.06	0.72	0.43	0.32	0.31	0.16
S	6.50	37.35	1.60	14.59	11.95	7.31	5.93	34.75	1.94	12.59	8.55	8.82	5.61	22.97	2.10	9.43	8.14	3.74
Cl-	9.67	442.61	6.32	37.48	26.02	57.24	21.25	43.80	0.74	30.95	27.36	7.64	11.95	74.22	1.44	27.47	24.26	11.25
Na	12.70	37.10	1.15	19.99	19.65	4.76	13.60	22.70	0.04	18.18	17.60	3.36	9.60	27.60	0.34	17.03	16.30	4.17
K	0.25	50.09	4.98	3.57	1.29	7.26	0.21	11.08	3.43	1.40	0.54	3.06	0.23	43.00	4.76	3.31	1.30	7.48
Ca	24.70	200.00	5.13	45.52	39.15	23.51	20.20	71.70	0.37	44.91	42.40	13.97	21.00	54.40	0.42	35.59	33.75	9.21

Table SI-5.7: Summary statistics for concentrations of PTEs (µg l^{-1}) found in the river water.

PTE	Pre-flood (N=10) concentrations (µg l-1)						Flood (N=2) concentrations (µg l-1)						Post-flood (N=10) concentrations (µg l-1)					
	Min	Max	Skewness	Mean	Median	St. Dev	Min	Max	Skew	Mean	Median	St. Dev	Min	Max	Skewness	Mean	Median	St. Dev
As	0.29	0.545	0.56	0.39	0.38	0.081	0.45	0.47	*	0.46	0.46	0.014	0.29	0.73	2.31	0.39	0.36	0.13
Cd	0.0045	0.101	0.97	0.042	0.034	0.03	0.05	0.11	*	0.08	0.08	0.042	0.01	0.02	0.48	0.014	0.01	0.0052
Co	0.43	0.605	-0.64	0.53	0.54	0.054	0.55	0.58	*	0.56	0.56	0.018	0.41	0.49	-0.16	0.45	0.46	0.029
Cu	2.1	53	2.1	10.32	6.6	11.71	7.8	22	*	12.4	9.9	6.48	4.5	42.15	0.93	15.86	7.3	12.91
Cr	0.09	0.55	0.81	0.25	0.18	0.17	0.28	0.29	*	0.29	0.29	0.0071	0.01	0.2	-0.19	0.11	0.11	0.075
Ni	3	8.1	1.62	4.39	4.23	1.6	5.11	5.3	*	5.20	5.20	0.14	3.04	6.98	1.17	4.18	3.52	1.41
Pb	0.015	0.455	0.86	0.18	0.15	0.13	0.71	2.09	*	1.39	1.39	0.98	0.025	0.15	0.47	0.082	0.08	0.034
Zn	3.5	89.9	3.94	13.31	7.75	15.81	10.5	43.3	*	26.73	14.35	12.5	7.7	64.8	3.18	17.07	14.35	12.5

Table SI-5.8: Summary statistics for concentrations of PTEs (µg l^{-1}) found in the ground water during the sampling regime.

PTE	Pre-flood (N=10) concentrations (µg l-1)						Flood (N=2) concentrations (µg l-1)						Post-flood (N=10) concentrations (µg l-1)					
	Min	Max	Skewness	Mean	Median	St. Dev	Min	Max	Skew	Mean	Median	St. Dev	Min	Max	Skewness	Mean	Median	St. Dev
As	0.19	0.61	0.61	0.27	0.21	0.1	0.13	0.33	*	0.23	0.23	0.14	0.1	0.7	0.7	0.33	0.29	0.18
Cd	0.005	0.21	1.32	0.06	0.024	0.07	0.05	0.08	*	0.07	0.07	0.02	0.01	0.08	0.5	0.03	0.03	0.03
Co	0.05	0.33	0.75	0.15	0.1	0.10	0.15	0.31	*	0.23	0.23	0.11	0.08	1.05	0.8	0.42	0.32	0.32
Cu	1	58.2	2.23	11.93	9.3	12.21	6.6	15.2	*	11.94	14	4.66	3.7	86	2.1	24.9	18.1	23.19
Cr	0.004	0.21	0.4	0.08	0.09	0.07	0.15	0.25	*	0.2	0.2	0.07	0.004	0.32	1.1	0.13	0.1	0.08
Ni	5.2	27.9	0.78	13.87	11.57	8.58	11.3	35.2	*	23.2	23.2	16.9	5.79	18.08	1.7	9.21	8.62	3.67
Pb	0.002	0.23	-0.03	0.12	0.13	0.08	0.27	0.47	*	0.37	0.37	0.15	0.003	0.57	2.3	0.13	0.07	0.17
Zn	7.1	336.5	2.79	51.6	20.6	67.92	80	119.8	*	106.2	112.5	18.01	9.9	102.1	0.85	47.67	44.3	20.9

Figure SI-5.3: Arsenic concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.

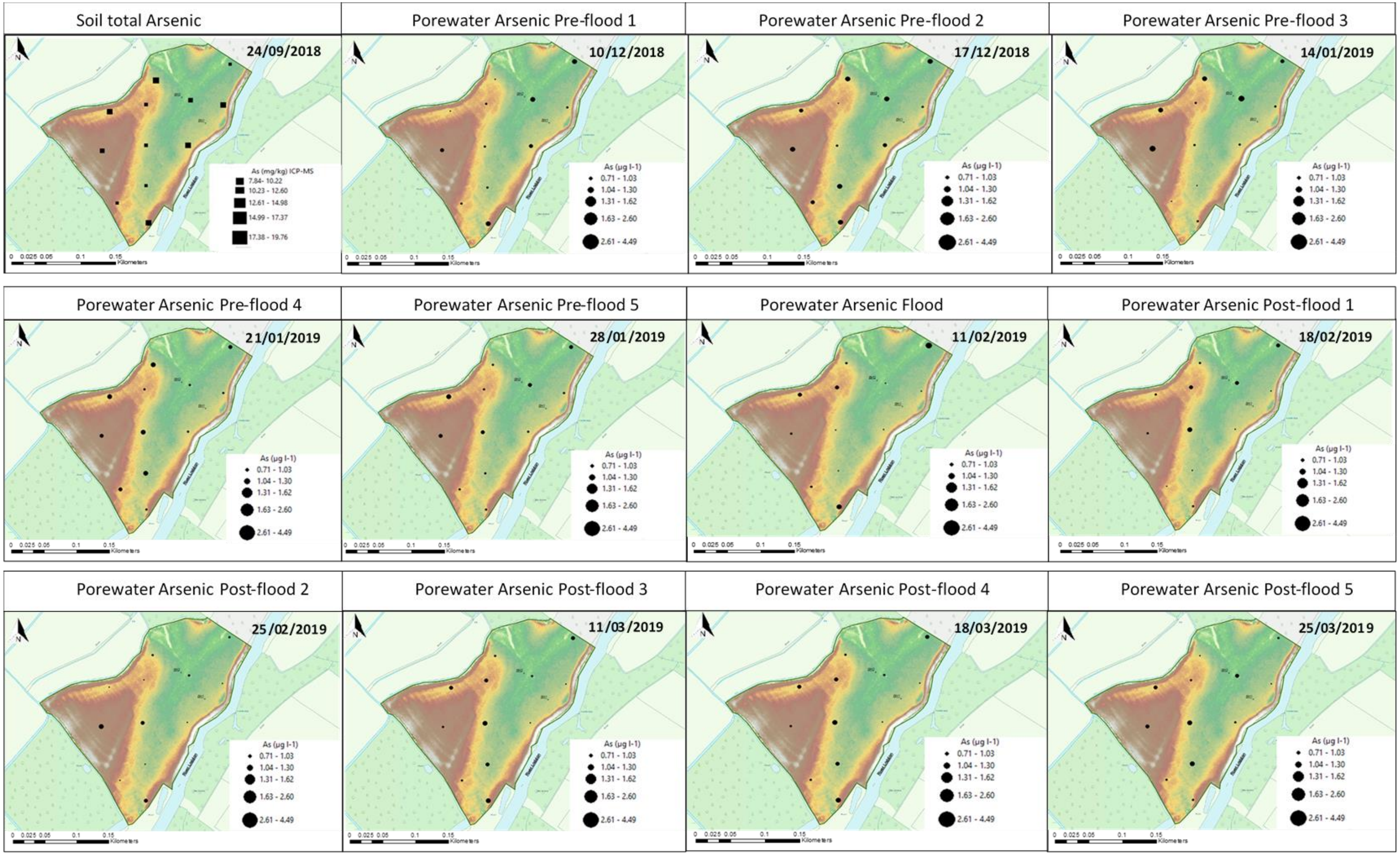
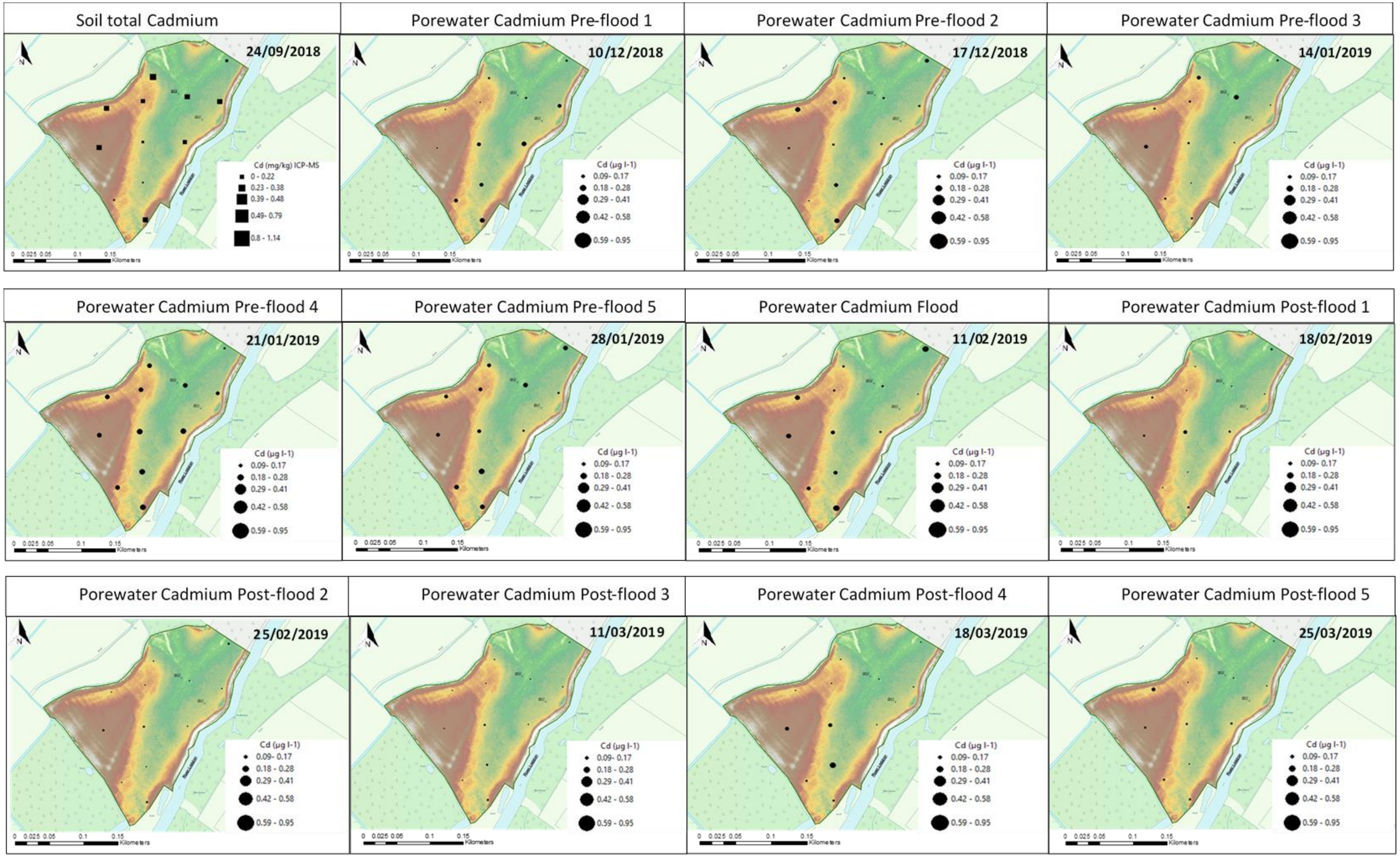


Figure SI-5.4: Cadmium concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.



Soil total Cadmium 24/09/2018

Porewater Cadmium Pre-flood 1 10/12/2018

Porewater Cadmium Pre-flood 2 17/12/2018

Porewater Cadmium Pre-flood 3 14/01/2019

Porewater Cadmium Pre-flood 4 21/01/2019

Porewater Cadmium Pre-flood 5 28/01/2019

Porewater Cadmium Flood 11/02/2019

Porewater Cadmium Post-flood 1 18/02/2019

Porewater Cadmium Post-flood 2 25/02/2019

Porewater Cadmium Post-flood 3 11/03/2019

Porewater Cadmium Post-flood 4 18/03/2019

Porewater Cadmium Post-flood 5 25/03/2019

Figure SI-5.5: Cobalt concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.

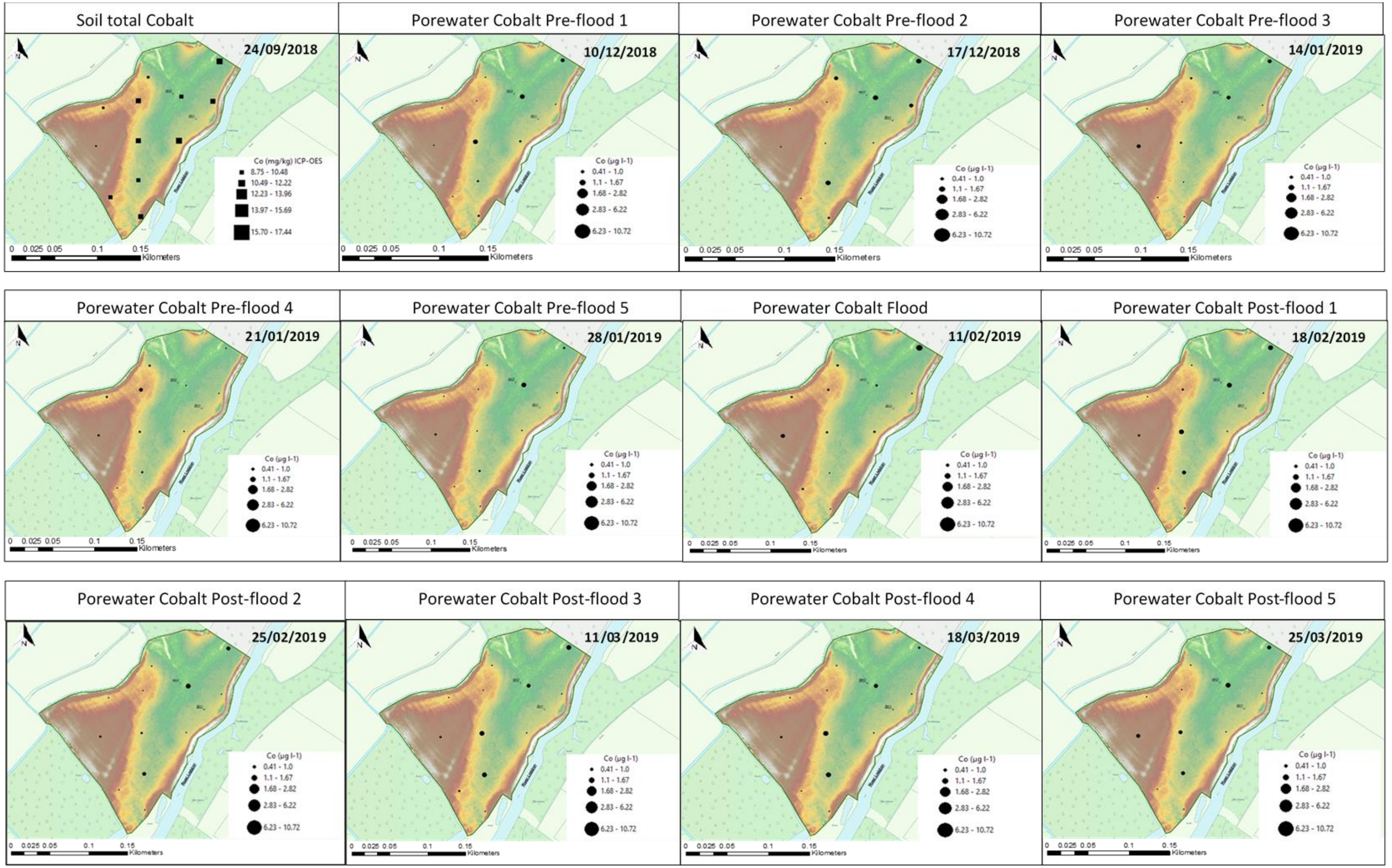
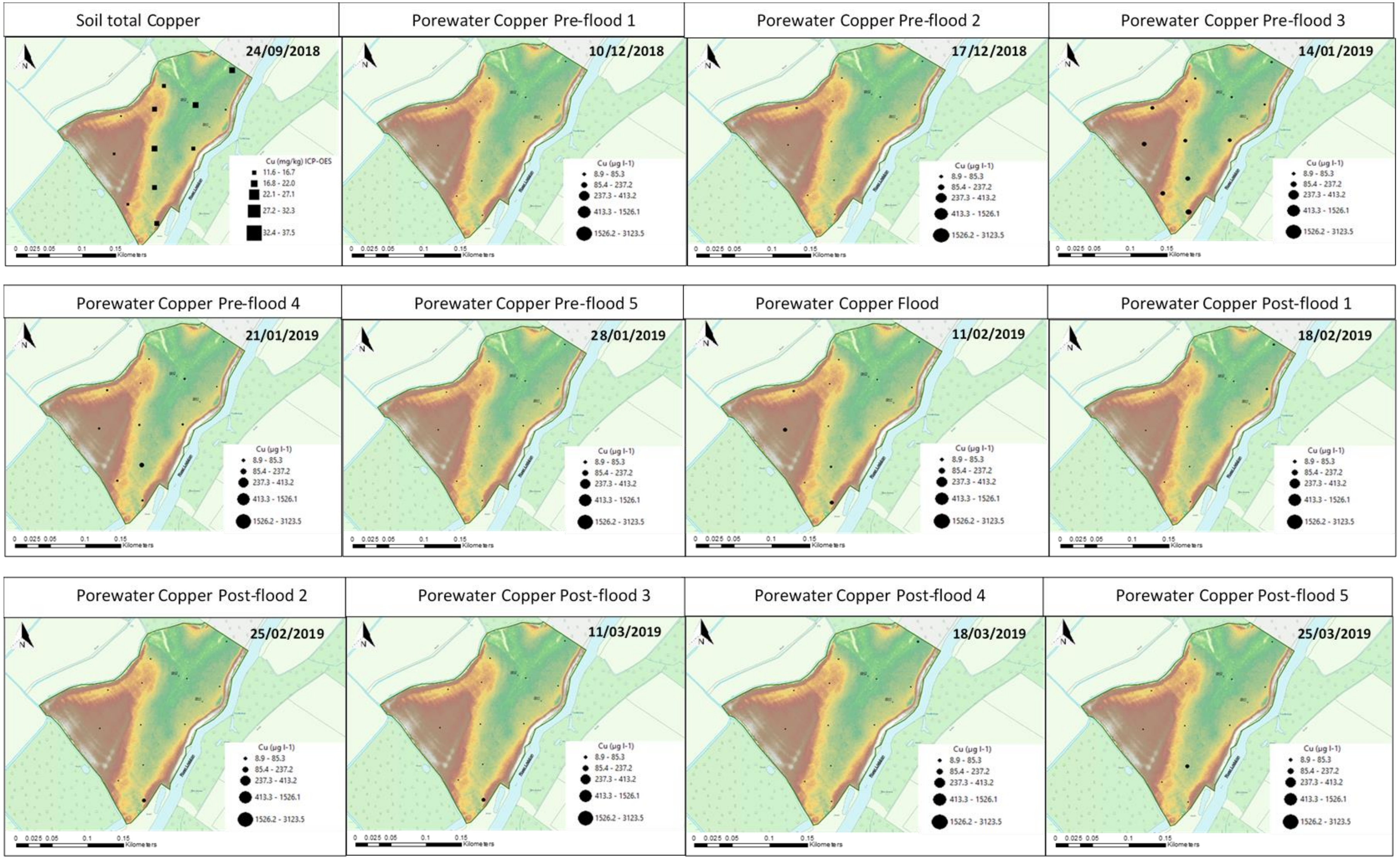


Figure SI-5.6: Copper concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.



Soil total Copper

Porewater Copper Pre-flood 1

Porewater Copper Pre-flood 2

Porewater Copper Pre-flood 3

Porewater Copper Pre-flood 4

Porewater Copper Pre-flood 5

Porewater Copper Flood

Porewater Copper Post-flood 1

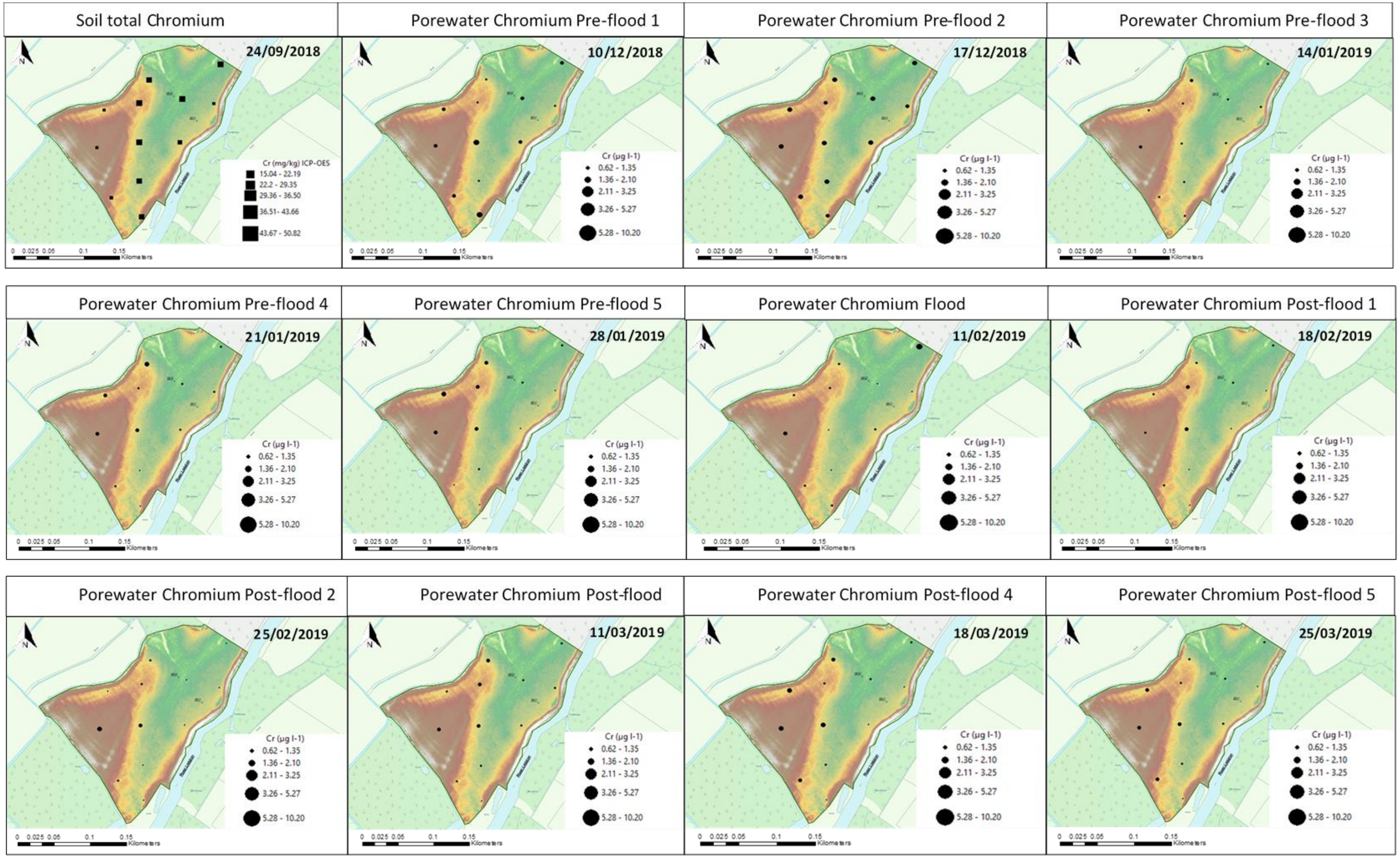
Porewater Copper Post-flood 2

Porewater Copper Post-flood 3

Porewater Copper Post-flood 4

Porewater Copper Post-flood 5

Figure SI-5.7: *Chromium concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.*



Soil total Chromium 24/09/2018

Porewater Chromium Pre-flood 1 10/12/2018

Porewater Chromium Pre-flood 2 17/12/2018

Porewater Chromium Pre-flood 3 14/01/2019

Porewater Chromium Pre-flood 4 21/01/2019

Porewater Chromium Pre-flood 5 28/01/2019

Porewater Chromium Flood 11/02/2019

Porewater Chromium Post-flood 1 18/02/2019

Porewater Chromium Post-flood 2 25/02/2019

Porewater Chromium Post-flood 11/03/2019

Porewater Chromium Post-flood 4 18/03/2019

Porewater Chromium Post-flood 5 25/03/2019

Figure SI-5.8: Nickel concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.

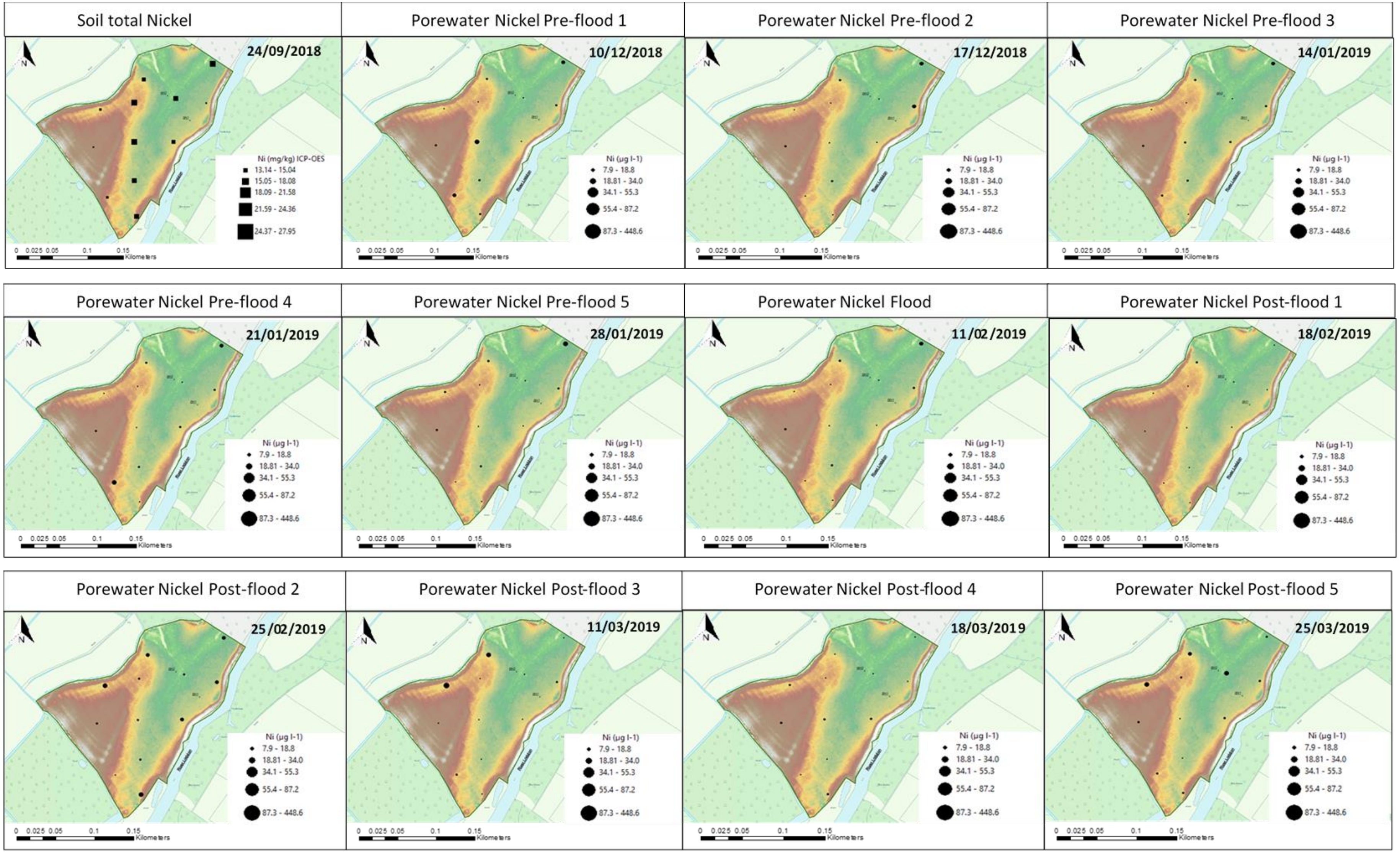


Figure SI-5.9: Lead concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.

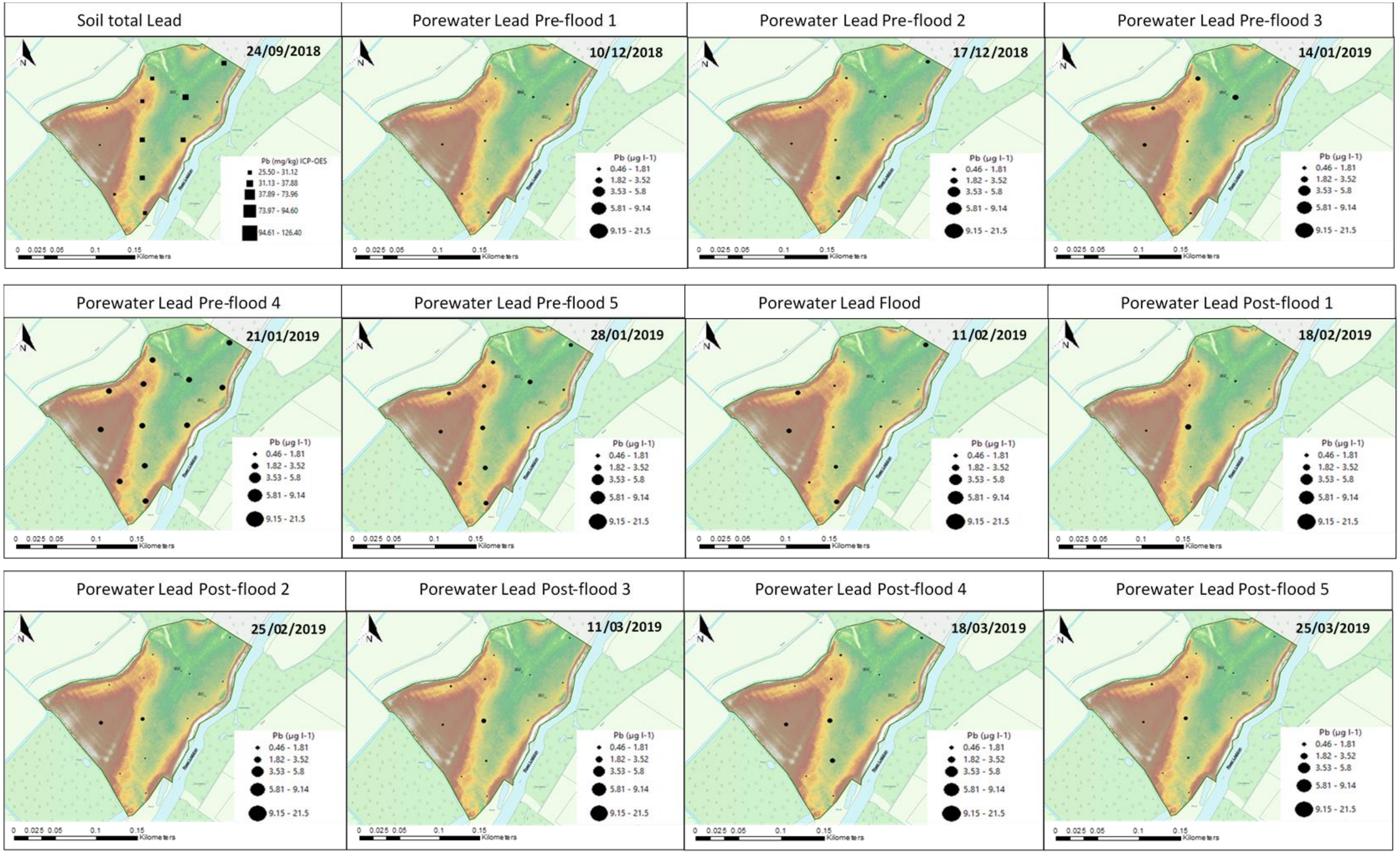
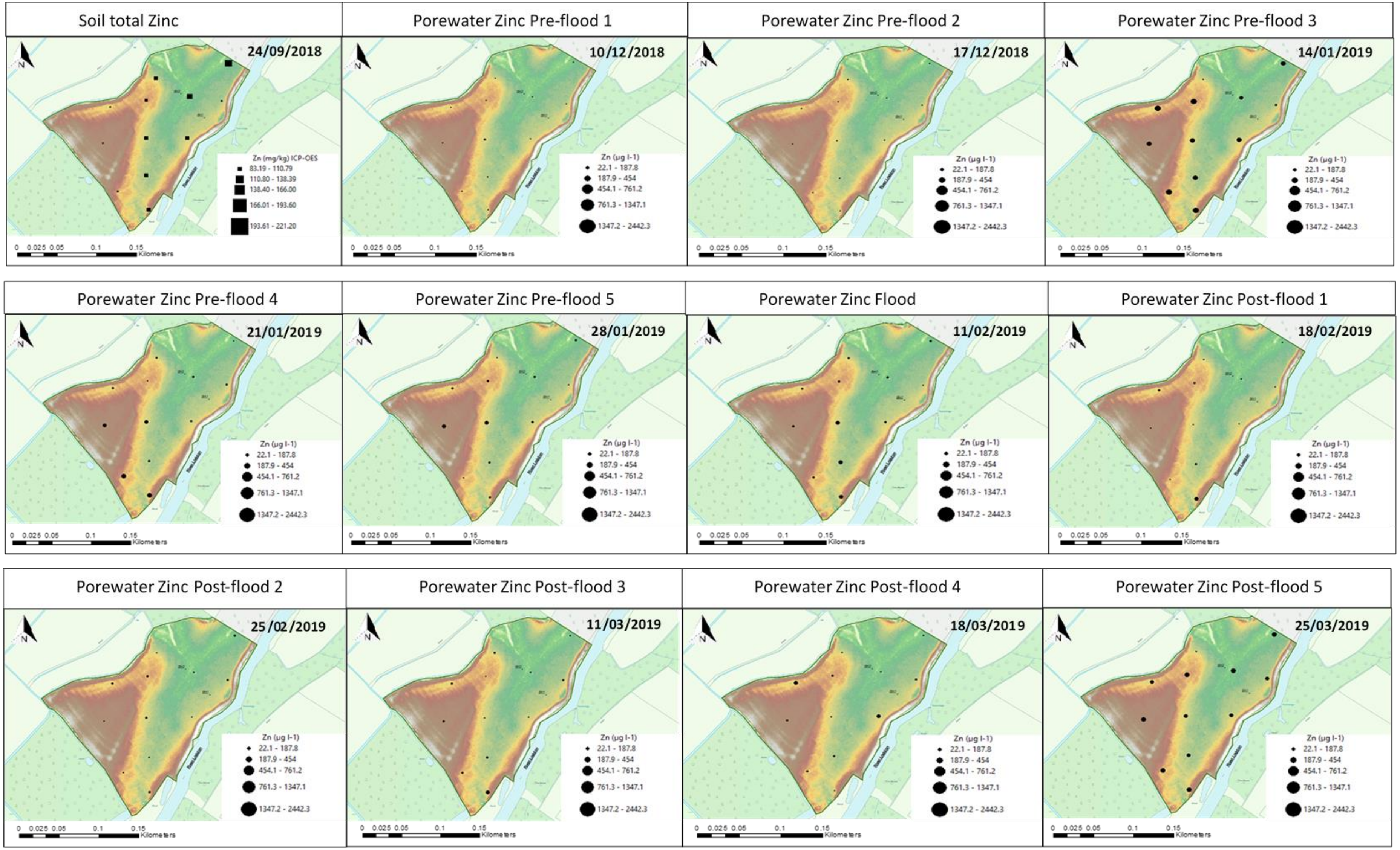


Figure SI-5.10: *Zinc concentrations map series, total soil concentrations, pre-flood, during the flood and post flood.*



Soil total Zinc 24/09/2018

Porewater Zinc Pre-flood 1 10/12/2018

Porewater Zinc Pre-flood 2 17/12/2018

Porewater Zinc Pre-flood 3 14/01/2019

Porewater Zinc Pre-flood 4 21/01/2019

Porewater Zinc Pre-flood 5 28/01/2019

Porewater Zinc Flood 11/02/2019

Porewater Zinc Post-flood 1 18/02/2019

Porewater Zinc Post-flood 2 25/02/2019

Porewater Zinc Post-flood 3 11/03/2019

Porewater Zinc Post-flood 4 18/03/2019

Porewater Zinc Post-flood 5 25/03/2019

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