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The Effect of Flooding and Drainage Duration on the Release of Trace Elements from Floodplain Soils

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Abstract: Floodplains downstream of urban catchments are sinks for potentially toxic trace elements. An intensification of the hydrological cycle and changing land use will result in floodplains becoming inundated for longer durations in the future. We collected intact soil cores from a floodplain meadow downstream of an urban catchment and subjected them to an inundation/drainage cycle in the laboratory to investigate the effect of flood duration on trace element concentrations in the soil porewater. The porewater concentrations of Ni, Cr, and Zn increased, whereas Cu and Pb decreased with flood duration. All the Cr present in porewaters was identified as Cr(III). Copper concentrations increased after drainage but Pb mobility remained suppressed. Both pH and dissolved organic carbon (DOC) increased with flood duration but were lower in treatments that were drained for the longest duration (which were also the treatments flooded for the shortest duration). The porewater concentrations of Cr and Ni decreased after drainage to levels below those observed before inundation, mirroring the DOC concentrations. We concluded that the duration of floodplain inundation does have an influence on the environmental fate of trace elements but that flooding does not influence all trace elements in the same way. The implications of an intensification of the hydrological cycle over the coming decades are that floodplains may become a source of some trace elements to aquatic and terrestrial ecosystems. *Environ Toxicol Chem* 2020;00:1–12. © 2020 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Heavy metals; Soil chemistry; Climate change; Biogeochemistry; Porewater; Bioavailability

INTRODUCTION

The deposition of sediments on floodplain soils during a low flow velocity flooding event often results in floodplains becoming a sink for potentially toxic trace elements such as Ni, Cr, Cu, Pb, and Zn (Walling and Owens 2003; Overesch et al. 2007; Rinklebe et al. 2007; Du Laing et al. 2009; Hurley et al. 2017). These trace elements originate from solid and dissolved inputs from either the natural erosion of soils upstream or, particularly in urban catchments, anthropogenic sources of contaminants including transport emissions, industrial waste, mining, landfills, sewage treatment facilities, and diffuse runoff from fields impacted by agricultural applications or aerial deposition. Even if water quality improves as a result of

the implementation of more stringent environmental policy, contamination of downstream floodplains and waterways continues as a legacy of historic upstream pollution (Bradley and Cox 1990; Kowalik et al. 2003; Walling and Owens 2003).

Although there is some uncertainty regarding the effect that future climate change will have on river levels (Prudhomme and Davies 2009), increasing temperatures over the last 20 yr have led to an intensification of the hydrological cycle, with associated increases in intense rainfall and flooding events (Slingo et al. 2014; Watts et al. 2015). Climate model projections show an increased flood risk in many regions across Europe caused by an expected increase in the magnitude, duration, and frequency of fluvial flooding (Wilby et al. 2008; Blöschl et al. 2017). The effect of these climatic changes will be influenced by land management within individual catchments. Urbanization and the resultant creation of impermeable surfaces are of critical importance (Wheater and Evans 2009). Across Europe, increases in extreme precipitation have not always led to escalations in river flow (Madsen et al. 2014). However, drastic changes in management (e.g., a 50% expansion in forest cover) may be required to maintain the status quo in the face of future

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climate change scenarios (Reynard et al. 2001). As such, increased flooding is almost inevitable in some areas, particularly because many European governments are failing to incorporate future climate scenarios in their urban planning guidelines (Madsen et al. 2014).

Several authors have undertaken experiments *ex situ* that simulate flooding conditions and have observed that the inundation of floodplain soils remobilizes trace elements such as Ni, Cr, Cu, Pb, and Zn in the soil (Tack et al. 2006; Du Laing et al. 2007; Shaheen et al. 2014a, 2014b; Schulz-Zunkel et al. 2015; Izquierdo et al. 2017). Therefore, the effects that future climate and land-use change will have on flooding and hence trace element mobilization may turn floodplain soils into intermittent sources of pollution to rivers (Coulthard and Macklin 2003; Dennis et al. 2003). Elevated concentrations of trace elements in rivers may lead to failures to meet environmental quality standards such as those set by the European Union Water Framework Directive (Crane and Babut 2007). Furthermore, because floodplains are rich, fertile soils that support crop production and provide biodiverse natural habitats for plants and animals (Naiman et al. 1993), the mobilization of trace elements may have a detrimental effect on ecosystems, particularly on soil biota (Sivakumar and Subbhuraam 2005; González-Alcaraz and Van Gestel 2015, 2016). Therefore, understanding the factors that affect trace element concentrations and mobility in floodplain soils is environmentally important.

Several different mechanisms have been proposed to play a role in the alteration of trace element mobility in floodplains during inundation. As floodplain soils become inundated with water, oxygen is quickly depleted by soil organisms and roots, leading to a decrease in redox potential (E_h) and directly influencing the mobility of redox-sensitive trace elements such as As and Cr (Matern and Mansfeldt 2016). The reducing conditions create conditions conducive to reductive dissolution of some trace elements associated with Fe and Mn oxides (Tack et al. 2006) but may also lead to the precipitation of trace elements as sulfides (Borch et al. 2010) that are subsequently remobilized after flooding (Frohne et al. 2011). The consumption of H^+ during these redox processes results in an increase in pH (Rinklebe and Shaheen 2017), reducing the mobility of most cations; however, this is then followed by a decrease in pH because of oxidation processes consuming H^+ when the flood recedes, increasing trace element mobility again (Shaheen and Rinklebe 2017). An increase in dissolved organic matter (Grybos et al. 2009) that can form soluble metal organic complexes increasing trace element mobility is often observed (Grybos et al. 2007). Whether the mobility of individual trace elements is increased or decreased depends on which of the abovementioned processes dominate in a particular floodplain soil environment.

Previous research has involved *ex situ* laboratory studies of disturbed soils that have been dried and homogenized (Du Laing et al. 2007; Schulz-Zunkel et al. 2015; Shaheen et al. 2017), albeit with some limited exceptions (Shaheen et al. 2014a, 2014b). Homogenization removes important elements of soil architecture such as macropores, plant roots, and stones that are likely to have a particularly significant effect on the rhizosphere and the microbiology of the soil. This has a potential

knock-on effect on trace element concentrations in soil porewaters because, for example, microorganisms catalyze the reduction of Fe and Mn, a process central to the mobilization of some trace elements (Du Laing et al. 2009). A further limitation of many studies is that changes in mobility are often attributed to a change in the speciation of a redox-sensitive element (e.g., As or Cr) but this is mostly based on inference alone rather than actual measurements of speciation (Shaheen et al. 2014a; Rennert et al. 2017). In addition to being crucial to the understanding of trace element mobility, different species often have different levels of toxicity. For example, Cr(VI) is both more mobile and more toxic than Cr(III) (Hamilton et al. 2018).

Having identified a clear research need for studies of trace element mobility in undisturbed soils that directly measures the valence state of redox-sensitive elements such as Cr, we collected intact soil cores from a floodplain site downstream of an urban catchment in southern England to: 1) study the effect of flood duration on changes to trace element concentrations (of Cr, Cu, Zn, Ni, and Pb) and speciation of Cr(III) and Cr(VI) in the soil porewaters, and 2) suggest the mechanisms responsible for trace element mobility by measuring pH, dissolved organic carbon (DOC), Fe, and Mn.

MATERIALS AND METHODS

Site description and core sampling

Sixteen intact soil cores were collected in May 2017 from the Loddon Floodplain Monitoring and Modelling Platform, a floodplain meadow situated adjacent to the River Loddon (51°24'47.6"N, 0°55'10.6"W), a tributary of the River Thames to the south of Reading in southeast England (Figure 1A). The Loddon catchment is typical of an urban catchment in lowland England and stretches across the counties of Berkshire, Hampshire, and Surrey with a total area of 680 km². The bedrock of the catchment is primarily Paleogene sediments but the source of the Loddon catchment is on Cretaceous chalk deposits (British Geological Survey 2018). Soils within the catchment have Cr, Cu, Zn, Ni, and Pb concentrations ranging approximately from 30 to 100, 3 to 20, 10 to 135, 2 to 45, and 30 to 80 mg kg⁻¹, respectively (National Soil Inventory 2018).

Approximately 39% of the Loddon catchment consists of urban or suburban areas (Environment Agency 2014) and, as such, wastewater treatment plants and runoff from roads and other hard surfaces are likely sources of trace elements to the River Loddon. The majority of the water bodies that make up the Loddon and its tributaries are of moderate or poor status, largely because of discharges from wastewater treatment plants (Environment Agency 2014). Specific examples include the sewage treatment works at Basingstoke, Sherborne, and Sheffield, all of which lie upstream of the study site (Environment Agency 1999). A major tributary of the Loddon is the River Blackwater that passes through the highly urbanized towns of Camberley, Fleet, Aldershot, Farnborough, and Sandhurst that surround current or former military establishments (e.g., Royal Military College at Sandhurst, Deepcut Military Barracks, Army Staff College at Camberley, and Farnborough Airport), prior to its confluence with the River Loddon at Swallowfield. Some of

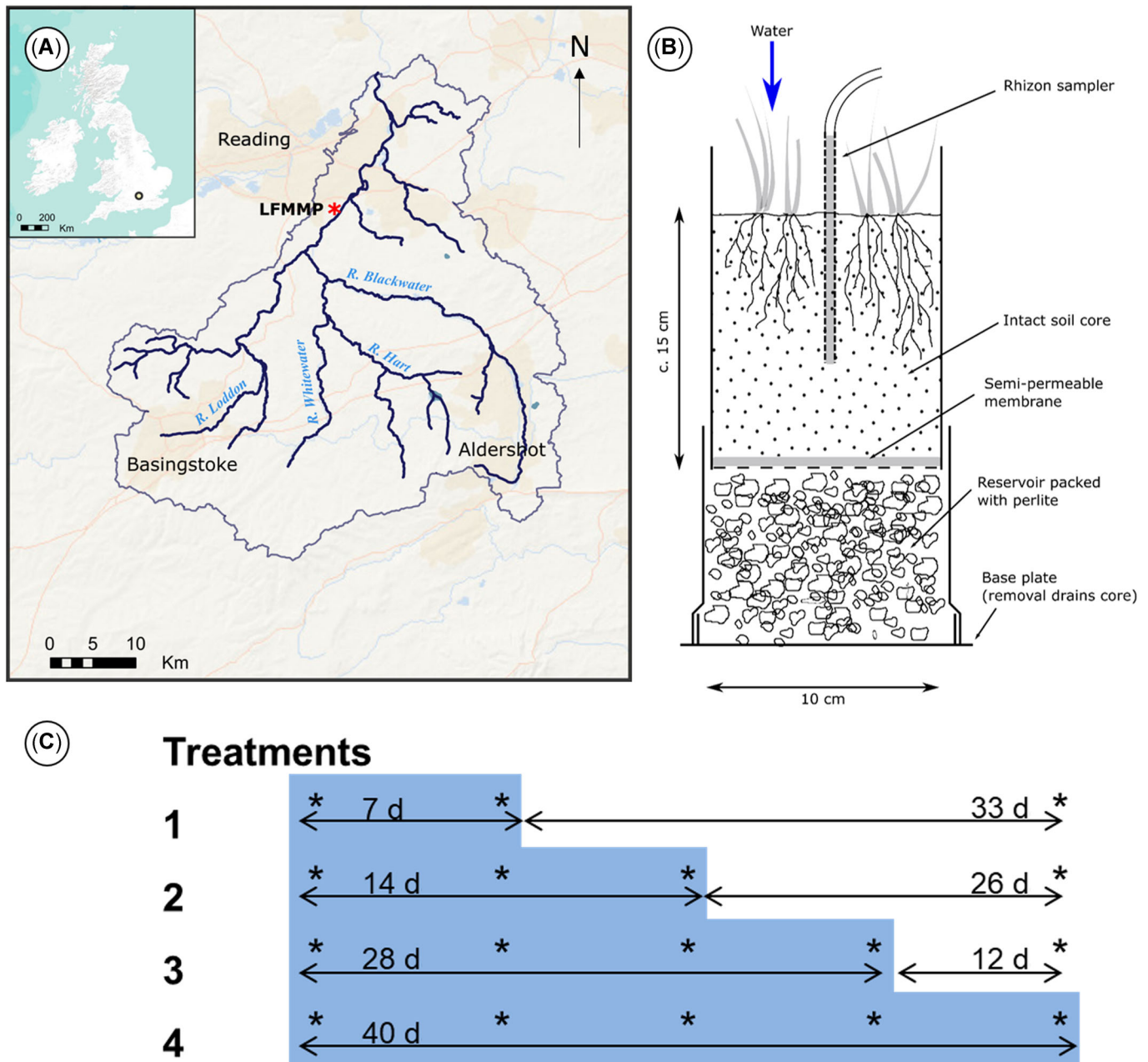


FIGURE 1: Experimental design. (A) Map of the Loddon catchment shows location of the Loddon Floodplain Monitoring and Modelling Platform (LFMMP) and major urban areas. Inset details the site within the United Kingdom (catchment outline and tributaries based on Environment Agency data). (B) Schematic cross section represents experimental setup. (C) Depiction of the flooding/drainage treatments for the 16 soil cores collected from the LFMMP. Shaded area identifies flood periods. Stars = identify sampling points.

the larger wastewater treatment plants in the catchment discharge into the River Blackwater. There has been extensive mineral extraction of gravels in the Blackwater Valley, particularly in the vicinity of Yateley and Eversley Cross—in part, the reason that there are dozens of historic landfill sites within the Loddon catchment (Environment Agency 2015). Other potential point sources of historic pollution to the River Loddon include a former paper mill at Arborfield; 2 factories—Thornycroft and Wallace & Stevens—that opened in the late 1800s and made engines, vehicles, and agricultural equipment in Basingstoke; and the former National Gas Turbine Establishment at Pyestock, near

Farnborough, where primary research into jet engines—such as the development and use of Al-, Ni-, and Cr-containing alloy coatings for the protection of gas turbines—took place during the 20th century (Northwood et al. 1968; Restall 1984). It is likely, in the past, that all these industries discharged effluent into the river upstream of our sampling location.

The concentrations of various anions and cations (including Cu and Zn) in the river have been the subject of ongoing weekly monitoring, with results covering the period from 2009 to 2013, recently published by Bowes et al. (2018). The highest concentrations of Cu and Zn were reported at sampling

locations downstream of catchments with the highest sewage treatment works' population density, with mean Zn and Cu concentrations of 5.9 and 2.7 $\mu\text{g L}^{-1}$, respectively. Unfortunately, this survey did not include other trace elements (e.g., Ni, Cr, and Pb) and, as such, a short sampling program was instigated to provide general context for the present study. Samples of river water were collected from 2 points adjacent to the Loddon Floodplain Monitoring and Modelling Platform at 4 time points covering a 1-mo period between October and November 2018. Water samples were filtered using a 0.45- μm cellulose nitrate syringe filter, and then acidified prior to storage and analysis via an Agilent 8900 inductively coupled plasma–mass spectrometer at the British Geological Survey. Dissolved organic carbon concentration was determined using a Shimadzu TOC-L analyzer. A summary of river water trace element concentrations is given in Table 1.

The soil type of the Loddon Floodplain Monitoring and Modelling Platform is a Gleysol (World Reference Base for Soil Resources) and the stratigraphy was observed in a soil pit and is typical of that found throughout the wider Thames Valley, with floodplain soil and fine sediment overlying flint-rich gravels (Sumbler 1996). Occasional chalk pebbles were found that were likely added as a soil amendment in the past—a common agricultural practice. The site frequently floods and it underwent prolonged flooding during the winter of 2013 to 2014. Cores were sampled from a 25 \times 25-m square area by forcing a 10-cm diameter plastic cylinder into the soil to a depth of approximately 15 cm. Previous research has shown that most trace elements are concentrated in the upper part of the soil profile (Shaheen and Rinklebe 2014; Ciszewski and Grygar 2016). A trowel was used to ease the insertion of the plastic cylinder into the soil and to minimize disturbance to the soil cores collected. The base of each core was sealed prior to transport back to the laboratory. Soil properties are provided in Table 2.

Experimental design

The base of each core was wrapped with a tough polypropylene semi-permeable membrane and inserted into an end section that acted as a reservoir and water-tight seal

(Figure 1B). The base plate of the end section could be removed to drain the core. The 16 cores were separated into 4 sets of 4 replicates, and each set was subjected to different periods of flooding ranging from 7 to 40 d (Figure 1C), after which the base of the core apparatus was removed to allow drainage. These durations of flooding encompass a range intended to reflect more common flooding events that might occur in a given year (up to 2 wk), as well as less common events such as the lengthy floods of 2013 through 2014 that might inundate the floodplain for more than 1 mo (Thorne 2014). Treatment 1 was flooded for 7 d and then drained for the remaining 33 d. Treatment 2 was flooded for 14 d and then drained for the remaining 26 d. Treatment 3 was flooded for 28 d and then drained for the remaining 12 d. Treatment 4 was flooded for all 40 d. Ultrapure ($>18.2 \text{ M}\Omega\text{cm}$) water was added to the cores each week as necessary to maintain a 1-cm head of water over the course of the flooding period; this water was added at least 24 h prior to sampling. Cores were kept in the dark at a constant temperature of 20 °C throughout. Soil porewater samples were taken according to the sampling regime depicted in Figure 1C using 20-mL polypropylene syringes and Rhizon samplers installed vertically into the cores to a depth of approximately 8 cm, such that the tip of each Rhizon sampler was located approximately halfway down each soil core (Figure 1B). Rhizon samplers were obtained from Rhizosphere Research Products, and consist of an inert porous polymer with a pore size of 0.15 μm (Knight et al. 1998). In most cases, syringes were filled gradually over the course of 1 h, leading to a withdrawal rate of c. 0.33 mL min^{-1} . Porewater was sampled from flooded cores only on days 0, 7, 14, and 28 and all cores were sampled on day 40 enabling us to quantify the change in trace element mobility over time in cores flooded for different durations (0, 7, 14, 28, and 40 d) and also identify changes in trace element mobility after they had been left to drain, each for different periods of time (0, 12, 26, and 33 d).

Laboratory analysis

Soil characterization. Soil samples taken from the same area, to be representative of the soil in the cores, were air dried and sieved to $<2 \text{ mm}$ prior to analysis. Particle size analysis was conducted on the soil matrix using a Malvern Mastersizer

TABLE 1: Water samples taken from the River Loddon adjacent to the study site from October to November 2018^{a,b}

Sampling Date	DOC (mg L^{-1})	pH	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)	Zn ($\mu\text{g L}^{-1}$)
22 Oct. 2018	NA	7.35	99.1	7.60	0.11	0.22	4.24	2.70	22.7
22 Oct. 2018	NA	7.56	90.8	9.30	0.10	0.19	4.27	3.10	6.40
5 Nov. 2018	7.85	6.65	15.0	8.30	<0.2	5.59	4.31	8.10	10.0
5 Nov. 2018	5.25	7.38	17.0	7.60	<0.2	0.31	4.36	9.80	23.8
12 Nov. 2018	8.28	7.08	68.0	45.1	0.30	0.30	3.33	6.00	8.00
12 Nov. 2018	8.16	7.21	80.0	41.3	0.30	0.34	3.24	8.30	6.10
19 Nov. 2018	6.57	7.5	25.0	18.9	0.20	0.13	4.13	7.10	12.7
19 Nov. 2018	8.73	7.55	31.0	15.7	<0.2	0.12	4.12	2.40	6.80
Mean	7.47	7.29	53.24	19.23	0.20	0.90	4.00	5.94	12.06
Standard deviation	1.31	0.31	34.88	15.39	0.10	1.90	0.45	2.87	7.24

^aSamples were filtered using a 0.45- μm filter before storage and analysis.

^bData are shown for dissolved organic carbon (DOC), pH, and a selection of major and trace elements that were the focus of the present study. NA = not applicable.

TABLE 2: Soil characterization^{a,b}

Texture (laser granulometry)			Pseudo total metal concentrations (aqua regia)									
%Clay	%Silt	%Very fine sand	%Fine sand	pH	Ni (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Mn (mg kg ⁻¹)	Fe (mg g ⁻¹)	Al (mg g ⁻¹)
0.17	61.67	28.64	9.52	5.32	33.9 (80–90%)	90.5 (80–90%)	25.2 (60–70%)	84.8 (30–40%)	202.4 (90+%)	479	57.8	53.9

^aKey properties (texture, pH, and pseudo total metal concentration) of the 2-mm sieved soil collected (0–15 cm) from the Loddon Floodplain Monitoring and Modelling Platform and used in this experiment.

^bPseudo total metal concentrations are compared with those in the UK Soil Observatory database, and their concentrations expressed (in parentheses) as a percentile rank relative to all of the values given in the *Advanced Soil Geochemical Atlas of England and Wales* (National Soil Inventory 2018).

3000 laser granulometer, with soil samples first disaggregated and dispersed using sodium hexametaphosphate and a small rubber pestle. The pH was determined in a soil–water suspension after shaking with water for 15 min at a 1:10, w/v ratio based on BS7755-3.2 (British Standards Institution 1995a). Pseudo-total concentrations of trace elements were determined using a PerkinElmer Optima 7300 series inductively coupled plasma–optical emission spectrometer after digestion at 140 °C in aqua regia, based on BS7755-3.9 (British Standards Institution 1995b).

Porewater analysis. All equipment used for sampling, storage, and analysis of samples was acid washed in 3% HCl overnight prior to use to prevent contamination, given the low concentrations of trace elements in the porewater. The porewater pH was determined immediately after sampling by utilizing a Hanna pH meter. Two buffer solutions (pHs 4 and 7) were used to calibrate the probe and to check for drift. Samples were then filtered with 0.45- μ m cellulose nitrate syringe filters. Subsamples of porewater (2 mL) for DOC analysis were diluted (\times 10) and stored at 4 °C prior to analysis. Dissolved organic carbon concentrations were determined using a Shimadzu TOC-L analyzer by subtraction of inorganic dissolved carbon from total dissolved carbon, with standards made from potassium hydrogen phthalate (total carbon) and sodium hydrogen carbonate and sodium carbonate (inorganic carbon). Subsamples of porewater (4 mL) for analysis of trace element concentrations were diluted (\times 2) and acidified using concentrated nitric acid and stored at 4 °C prior to analysis. Samples were analyzed with a PerkinElmer Optima 7300 series inductively coupled plasma–optical emission spectrometer for Zn and major elements (Al, Ca, Fe, Mn, Mg, K, and Na) but several trace elements of interest were below the detection limits (Cr, Ni, Cu, and Pb). Therefore the samples were subsequently also analyzed with a Thermo Scientific iCAP Q inductively coupled plasma–mass spectrometer for these elements.

Chromium speciation. Subsamples of porewater were kept sealed from the atmosphere and frozen within 6 h and in most cases within 2 h, depending on the rate of sample extraction, and stored prior to analysis. Speciation analysis of Cr(III) and Cr(VI) was conducted according to a variation of the method described by Palumbo-Roe et al. (2017) and summarized in the present study. The Cr(III) in the samples was complexed with 15 mM EDTA (0.5-mL sample was added to 0.5 mL 30 mM EDTA) by heating at 70 °C for 1 h. These were then injected into a high-performance liquid chromatograph connected to an inductively coupled plasma–mass spectrometer (Agilent 7500 series); the mobile phase consisted of 5 mM EDTA, 40 mM NH₄NO₃, and 0.05 mM C₄H₁₁NO₃, corrected to pH 7 using nitric acid. This allowed separation of Cr(VI) and Cr(III) into 2 separate peaks, with the concentration determined using the peak area for each species. Further method refinement was undertaken and is discussed in Supplemental Data, Figure S1.

Quality control. Data quality was ensured by running a series of blanks and standards when conducting laboratory analyses,

particularly DOC, ordinary elemental analyses using inductively coupled plasma–optical emission spectrometry and inductively coupled plasma–mass spectrometry, and chromium speciation analyses (details are provided in the Supplemental Data). After inductively coupled plasma calibration, an independently sourced quality control solution was analyzed and the run rejected if analysis of this quality control solution was outside $\pm 10\%$ of the expected value. Where sample quantity and analysis time allowed, replicates were also used to test the consistency of analyses. Aqua regia digestion of soils was determined alongside an in-house reference soil traceable to certified reference material, BCR-143R. Recoveries were 100% for Ni, 118% for Cr, 91% for Cu, 109% for Pb, and 120% for Zn.

Statistical analysis

All statistical analyses were conducted using Minitab software Ver 17. A one-way analysis of variance was conducted to determine whether there were significant differences in trace element concentration in porewaters drawn from soils that had been flooded or drained for different periods of time, with post hoc Tukey comparisons used to identify significantly different ($p < 0.05$) groupings. Multiple linear regression models were created for individual trace elements to explore how much the variation in trace element molar concentrations could be explained by using the molar concentrations of H^+ , DOC, Fe, and Mn as possible explanatory variables. Models were created using forward selection with an alpha level of 0.25.

RESULTS AND DISCUSSION

Ni and Cr mobility increases with flood duration and is primarily influenced by DOC. The effects of inundation and drainage influenced the mobility of different elements in different ways. The effects of inundation and drainage impacted Ni and Cr mobility similarly, with a significant ($p < 0.05$) increase in mobility with increasing flood duration up to 28 d of inundation (Figure 2), a finding observed by previous authors (Shaheen et al. 2014a, 2014b; Schulz-Zunkel et al. 2015). This increase was followed by a slight decrease after 40 d of inundation. The samples that were drained for the longest period of time (which were also the treatments flooded for the shortest duration) had mobile Ni and Cr concentrations that were at a level lower than those observed prior to inundation (Figure 2), indicating that the influence of flooding on Ni and Cr mobility in this floodplain soil is transient. Nickel and Cr are both used as alloys (Northwood et al. 1968; Restall 1984; Wallinder et al. 2006). Therefore the Ni and Cr in these soils may have originated from the same source but the precise origin remains uncertain.

The pattern of increased Cr and Ni mobility with flood duration and lower mobility after drainage is mirrored in the DOC concentrations that also significantly ($p < 0.05$) increased with flood duration during the first 28 d, followed by lower concentrations in the drained soils than observed during

inundation (Figure 3). Shaheen et al. (2014a) also found DOC concentrations that increased with flood duration. There is a well-established relationship among redox potential, soil pH, and DOC. Soil pH increases under reducing conditions (Rinklebe et al. 2016) because of the consumption of protons during reducing processes (Frohne et al. 2011; Frohne et al. 2015). This effect was found in our experiment because the soil pH increased during the time that cores were inundated (Figure 3). The increase in the pH of soil solutions with decreasing redox potential is often accompanied by a release of DOC and the formation of soluble organo-metal complexes (Grybos et al. 2009). There were strong significant ($p < 0.05$) positive correlations between DOC and both Ni ($R^2 = 0.781$) and Cr ($R^2 = 0.520$) but only a weak significant ($p < 0.05$) negative correlation between the concentrations of H^+ and Ni ($R^2 = 0.102$). Whereas the positive relationship between DOC and Ni or Cr is intuitive because Cr^{3+} and Ni^{2+} cations bind with organic ligands in solution, the negative relationship between H^+ concentration and Ni is counter-intuitive because one might expect fewer protons (higher pH) to create less competition for binding sites on soil surfaces and a lower mobility of Ni in solution (Gonnelli and Rinella 2013). It can therefore be inferred that the primary influence of pH on Ni and Cr mobility in these soils is indirect because of a pH-induced increase in DOC. Nevertheless, the molar concentrations of both DOC and H^+ can be used as explanatory variables in a multiple linear regression model (Figure 4) that explains 80% and 59% of the variation in the Ni and Cr data, respectively.

Cr in porewater is Cr(III) and its redox state is not influenced by inundation. The results obtained from Cr speciation analysis indicate that there is no Cr(VI) present in the porewater (Supplemental Data), and that all the Cr present is shown to be Cr(III), which is both less mobile and less toxic. A possible explanation for this is that the DOC in the porewater acts as an electron donor, aiding in the reduction of Cr(VI) to Cr(III) (Shaheen et al. 2014a). As demonstrated in the spike experiment conducted as part of the present study (Supplemental Data, Figure S2), it is possible for this process to be observed during sample preparation. In samples where Cr(VI) was spiked, all Cr(VI) was reduced to Cr(III) prior to analysis, a process accelerated by heating. Chromium(VI) was not immediately reduced to Cr(III) on short timescales without heating, and thus it can be assumed that the Cr present when the soil porewater was sampled was also likely to be Cr(III).

Chromium(VI) is far less common in the environment than Cr(III); when present in elevated concentration, it is often assumed to be of anthropogenic origin (Saha et al. 2011) because most free Cr in natural soils is present as Cr(III) (Gonnelli and Renella 2013). Nevertheless, a natural origin for the Cr in the Loddon catchment cannot be assumed. Although there is limited previous data with which to make a comparison, a similar result was obtained by Palumbo-Roe et al. (2017); they sampled porewaters in a heavily contaminated streambed in Glasgow, Scotland, United Kingdom. Similar to the present study, no Cr(VI) was detected in the sediment porewater

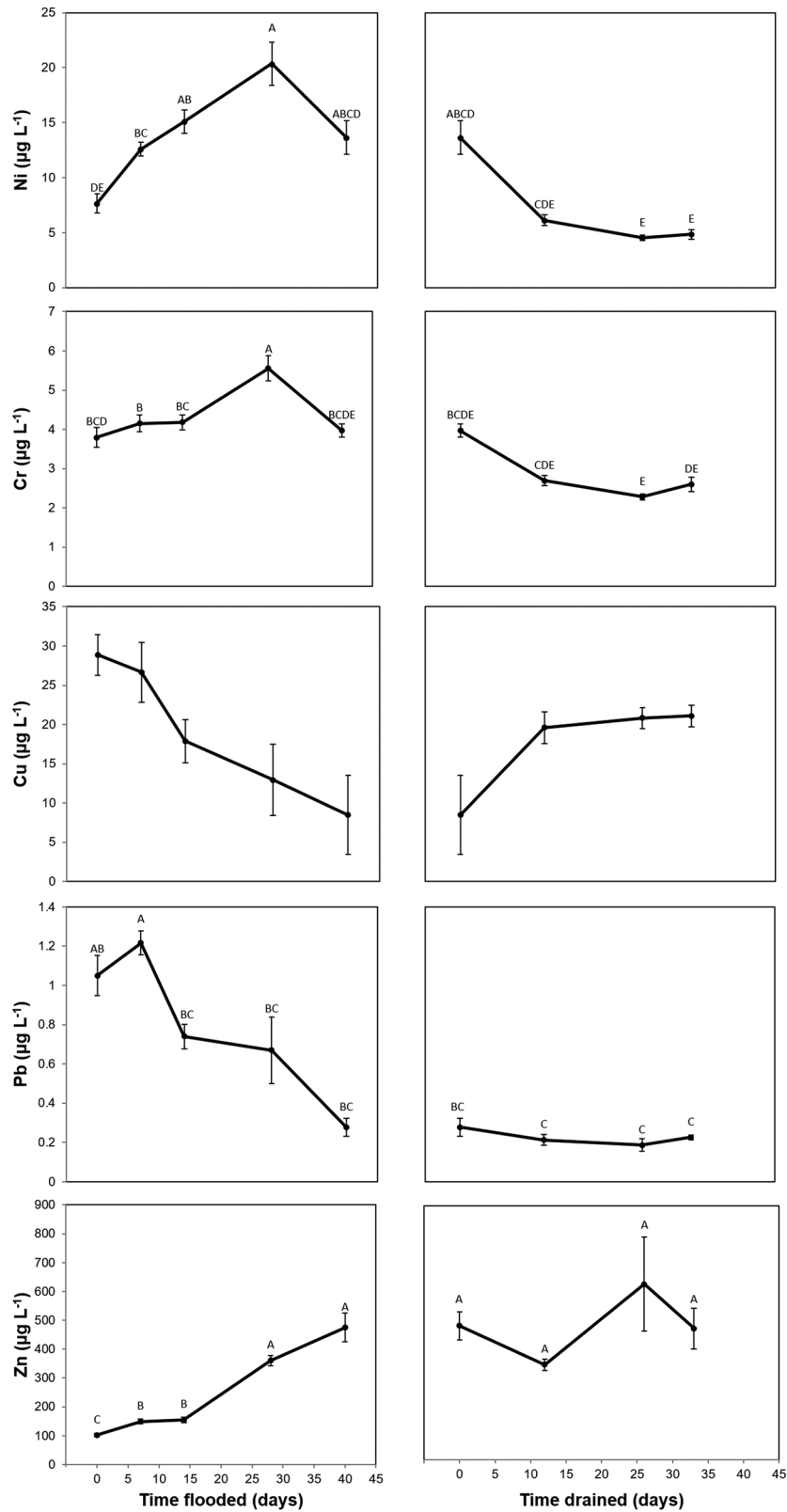


FIGURE 2: Concentrations of Ni, Cr, Cu, Pb, and Zn in soil porewater sampled from cores for 0, 7, 14, 28, and 40 d after flooding and for 0, 12, 26, and 33 d after draining. The experimental treatments from which these data are drawn are provided in Figure 1C. Error bars represent standard errors of the mean. $N = 4$. One-way analysis of variance indicated that the flooding/drainage regime significantly ($p < 0.01$) affected the porewater concentration of each metal except Cu. Letters above data points are Tukey pairwise comparisons for each metal (across 2 graphs) at the 95% level. Data points with the same letter, or no letter, are not significantly different from each other.

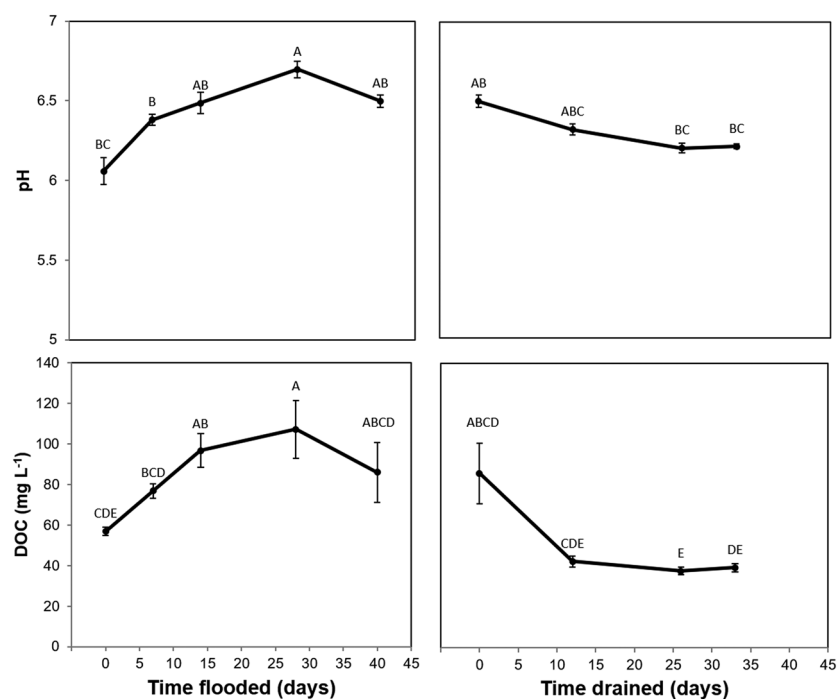


FIGURE 3: pH and concentrations of dissolved organic carbon (DOC) in soil porewater sampled from cores for 0, 7, 14, 28, and 40 d after flooding and for 0, 12, 26, and 33 d after draining. Error bars represent standard errors of the mean. $N = 4$. One-way analysis of variance indicated that the flooding/draining regime significantly ($p < 0.001$) affected both parameters. Letters above data points are Tukey pairwise comparisons for each parameter (across 2 graphs) at the 95% level. Data points with the same letter are not significantly different from each other.

despite the fact that Cr(VI) was found in the overlying water column.

The mobility of Cu and Pb decreased with flood duration despite increases in DOC.

The concentration of Cu and Pb measured in porewater decreased with flood duration (significantly [$p < 0.05$] for Pb but not for Cu; Figure 2). However, whereas the mobility of Cu increases with drainage duration, Pb mobility remained suppressed regardless of the duration of drainage; note that the soils drained for the longest period of time were the ones that were flooded for the shortest period of time. Copper and Pb did not positively correlate with DOC. In fact, there was a slight significant negative correlation ($p < 0.05$; $R^2 = 0.154$) between molar concentrations of Cu and DOC. This observation is somewhat surprising because both Cu and Pb have a strong affinity for organic ligands and are usually found primarily bound to DOC in solution (Sizmur et al. 2011), much more so than Ni or Cr. Therefore, the higher concentrations of DOC observed during flooding might be expected to carry Cu and Pb into solution and lead to higher Cu and Pb concentrations in porewater. However, a multiple linear regression model indicated that 61% of the variation in Cu porewater concentration could be explained by concentrations of DOC and Fe alone, whereas 54% of the variation in Pb concentration in porewater could be explained by concentrations of H^+ , DOC, Fe, and Mn (Figure 4). These models indicate that DOC positively influences Cu and Pb mobility, whereas Fe negatively influences Cu and Pb mobility.

A possible reason for lower concentrations of Cu and Pb in porewater after inundation may be because of precipitation

with sulfides to form insoluble metal sulfides (Abgottsson et al. 2015) that are very stable under reduced conditions but increase in solubility after aeration (Hesterberg 1998). Reducing conditions can cause microbial sulphate reduction and this can actually limit the mobility of some trace elements through coprecipitation with sulfides (Weber et al. 2009; Borch et al. 2010; Abgottsson et al. 2015). As the flood recedes, the floodplain soils undergo drying and aeration that change the conditions from anoxic back to oxic. The now oxic environment may have caused sulfides to be oxidized, thereby releasing Cu into the porewater (Du Laing et al. 2007; Frohne et al. 2011; Abgottsson et al. 2015).

Factors influencing greater Zn mobility during and after inundation remain unknown.

In contrast with the results of Du Laing et al. (2007) and Shaheen et al. (2014b), flooding did not decrease the concentration of Zn in the porewater, and Zn concentration steadily and significantly ($p < 0.05$) increased as the duration of inundation increased. However, there were no significant differences in Zn mobility in cores that were drained for different periods of time despite the fact that these treatments were also flooded for different periods of time. Shaheen et al. (2014b) found that the behavior of Zn closely matched that of Cu; however, in this experiment flooding had the opposite effect on Zn from what it had on both Cu and Pb. Unlike Cu and Pb, the majority of Zn in soil solutions is found to be a free ion, rather than bound to organic or inorganic ligands (Sizmur et al. 2011). The multiple linear regression model (Figure 4) indicated that only 42% of the variation in Zn porewater concentrations could be explained by DOC and Fe

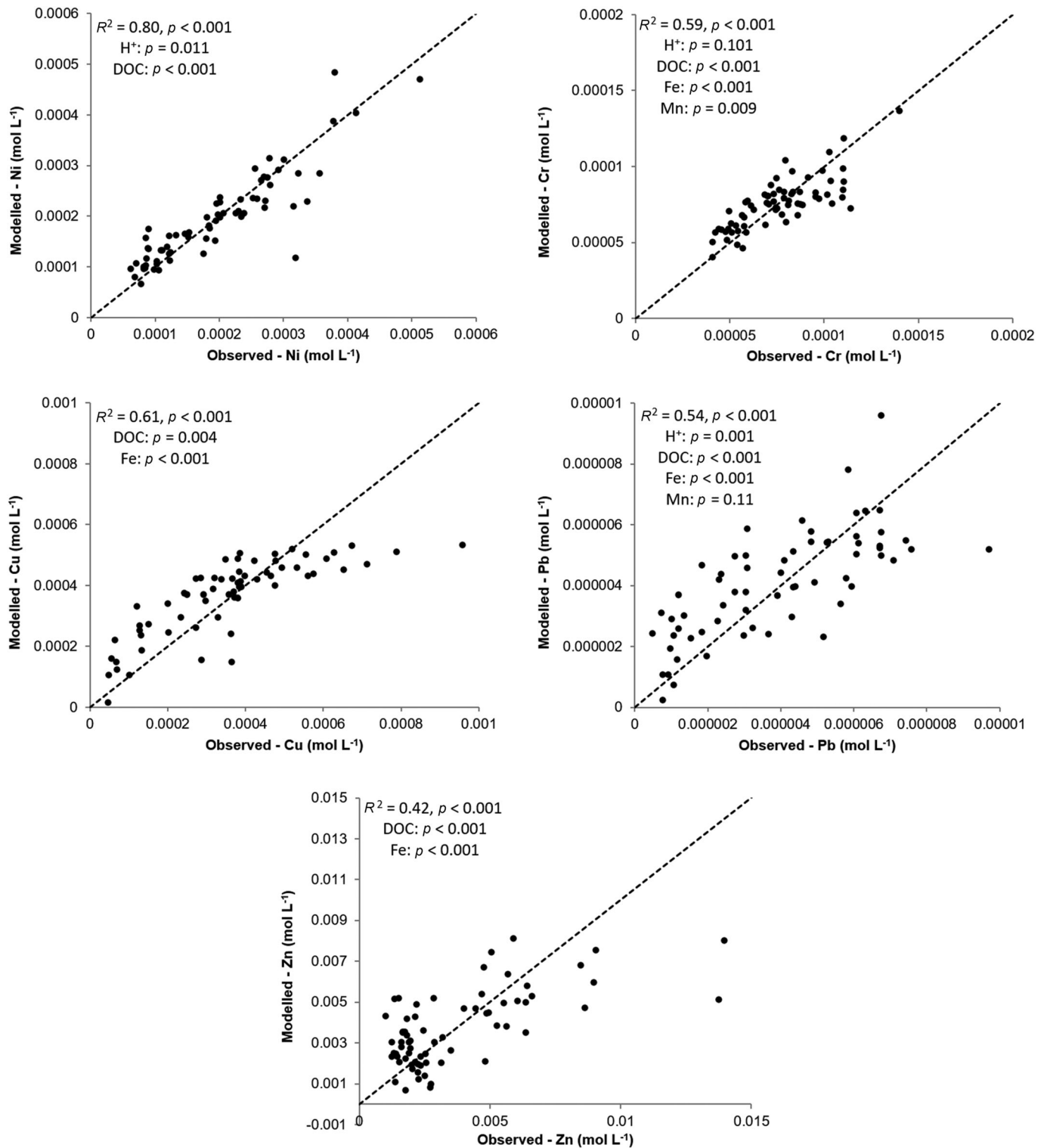


FIGURE 4: Molar concentrations of Ni, Cr, Cu, Pb, and Zn in porewater collected from both flooded and drained cores (all experimental data) plotted against modelled concentrations predicted using multiple linear regression models created using the same data. Models were created using forward selection with an alpha level of 0.25 with pH, dissolved organic carbon (DOC), Fe, and Mn as possible explanatory variables. All variables included made a significant ($p < 0.05$) contribution to explaining the variation in the data. 1:1 lines are shown for comparison.

concentrations; nevertheless, there was a relatively poor relationship between the modelled and observed values, indicating that a major factor influencing Zn mobility was not taken into account.

Implications of our findings. Because the present study used intact soil cores, porewater concentrations were likely to more closely reflect those that might be found in the natural environment rather than soil samples that were sieved,

homogenized, and assigned to experimental units (Adekanmbi et al. 2020). However, it is still unclear how well the conditions in the intact cores really do reflect the natural environment, and work is underway to make observations on the impact of a real flooding event on trace element mobility in the field at this site. Concentrations of Zn found in the porewaters collected in this experiment were above English environmental standards for freshwater (Department for Environment, Food and Rural Affairs 2015) and well above the defined ambient background concentration for the River Thames ($2.5 \mu\text{g L}^{-1}$; Peters et al. 2012). These concentrations of Zn were also an order of magnitude higher than concentrations found in the River Loddon by the present study (Table 1) and by Bowes et al. (2018), even at the start of the experimental inundation of the soil cores. Similarly, concentrations of Cr and Ni were an order of magnitude higher in the porewater of flooded soil cores than in the water samples obtained from the River Loddon by the present study (Table 1). This indicates that during (and after) a flooding event, the floodplain soil may become a net source of Zn and other trace elements to the river at a concentration that may contribute to exceedance of environmental quality standards. It is likely that the United Kingdom may experience more intense, short-duration, extreme rainfall events in the future (Chan et al. 2014), which may lead to more frequent flooding events magnified by land use change (e.g., soil sealing) and land use practices that favor inundation over infiltration.

The present study investigated soil porewater concentrations and further work is required to establish whether high concentrations of trace elements such as Zn, relative to those found in rivers such as the Loddon, will translate into elevated concentrations in watercourses during periods of floodplain inundation. However, previous work conducted elsewhere in the United Kingdom suggests that this is a definite possibility. Neal et al. (1996) measured trace element concentrations in the upper reaches of the River Swale in Yorkshire, England, United Kingdom (a historic center for Pb and Zn mining and processing) during periods of high and low flow. The concentrations of some trace elements (e.g., B, Ba, and Sr) in the river water decreased during periods of high flow and thus the sources of these trace elements were attributed to point sources that become diluted. However, some elements (e.g., Mo, Cu, and Cr) showed no increase and others (e.g., Zn, Ni, and Pb) had higher concentrations in river water during periods of high flow and were therefore attributed to diffuse sources in the catchment (Neal et al. 1996). These observations lend support to the notion that extreme weather events that cause inundation of floodplains may result in the remobilization of historically deposited trace elements to the water column and an increase in trace element concentrations in rivers.

CONCLUSIONS

Our observations support the hypothesis that the duration of floodplain inundation does have an influence on the environmental fate of trace elements and that future changes in the duration of flooding events will change the biogeochemical

cycling of these elements. However, inundation did not influence the mobility of all the trace elements in the same way. Porewater concentrations of both Ni and Cr increased with increasing duration of flooding but were lower after drainage. Copper and Pb concentrations in porewater decreased with flood duration; however, whereas Pb concentrations were consistently suppressed after drainage, Cu concentrations were higher in the treatments that were drained for the longest time period (which were also the treatments flooded for the shortest duration). Zinc mobility increased with flood duration and remained elevated after drainage. Therefore, based on our observations, the Loddon Floodplain Monitoring and Modelling Platform becomes a net source of Ni, Cr, and Zn to the water column during a flooding event but becomes a net sink of Cu and Pb. These differences highlight the importance of understanding the factors influencing the solubility and mobility of individual trace elements at a given site to predict the impact that increased duration of flooding may have on their environmental fate in the soil and their potential to affect river water quality.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at <https://doi.org/10.1002/etc.4830>.

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Data Availability Statement—Data, associated metadata, and calculation tools are accessible from the corresponding author (t.sizmur@reading.ac.uk) and on figshare (<https://doi.org/10.6084/m9.figshare.11295701>).

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