

1 sediments, sec 1 • sediment quality and impact assessment • research article

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3 **Trace metals distribution in the bed, bank and suspended sediment of the Ravensbourne River and its**
4 **implication for sediment monitoring in an urban river**

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16

17 **Abstract**

18 **Purpose:** This study aims to identify a suitable sediment compartment for sediment quality monitoring by: (a)
19 studying the concentration of trace metals (Cd, Cu, Ni, Pb and Zn) in the bed, bank and suspended sediment compartments of the
20 Ravensbourne River to establish any differences in trace metal concentrations with compartment, (b) determining the
21 influence of sediment particle size fractions (<63 µm and 63µm - 2 mm), organic matter and mineralogy on any
22 differences, and (c) examining if metal concentration in each sediment compartment complies with the draft UK
23 sediment quality guidelines.

24

25 **Materials and methods:** Here we make a comparison of metal concentrations in the bed; bank and suspended
26 sediment compartments of the Ravensbourne River collected using different sampling techniques. We
27 distinguished between two particle size fractions – the <63 µm fraction (suspended, bed and bank sediment) and
28 the 63 µm – 2 mm fractions of bed and bank material with the aim of comparing concentrations between the two
29 fractions. Particle size analysis, metal speciation, organic matter content by loss on ignition and mineralogy using
30 X-ray diffraction were also carried out on each sediment compartment.

31

32 **Results and discussion:** The results showed variations in trace metals concentrations with sediment compartment
33 and with particle size. The mineralogical characteristics were comparable for all sediment compartments and the
34 relationships between organic matter content and metal concentrations were significant in the majority of the bank
35 sediment samples. There were no significant differences ($p>0.05$) in the concentrations of metals between the
36 suspended sediment and the <63 µm bed sediment fraction, but there was a significant difference ($p<0.05$)
37 between the suspended sediment and the <63 µm bank sediment fraction. There were also significant differences
38 between the concentrations of metals in the <63 µm and the 63 µm – 2 mm fractions. Generally, the Ravensbourne
39 River did not comply with the draft UK sediment quality guidelines for the metals analysed.

40

41 **Conclusions:** This study shows the importance of identifying a suitable sediment compartment to sample for
42 compliance with sediment quality standards. The bed and suspended sediments are the most widely used sediment
43 compartments for sediment monitoring, but collecting sufficient mass of the <63 µm sediment fraction for
44 monitoring presents a challenge for urban gravel bed rivers like the Ravensbourne River. It seems appropriate to
45 establish individual monitoring regimes for different rivers.

46

47 **Keywords** Sediment • Sediment compartments • Trace metals • Sediment quality

48 **1 Introduction**

49 The environmental significance of contaminated sediment is a focus of concern under the European Water
50 Framework Directive (WFD) (Bilotta and Brazier 2008; Bonnail et al. 2016; Perks et al. 2017) and widely
51 monitored using trace metals (Roig et al. 2016). River sediments are used as environmental indicators in river
52 monitoring and assessment of river quality (Kuusisto-Hjort and Hjort 2013; Han et al. 2014; Islam et al. 2015)
53 with higher levels of contaminants (trace metals) often reported in sediment compared to the overlying water
54 column (Gasperi et al. 2009; Atibu et al. 2013; Alves et al. 2014). Trace metals are persistent; bind easily to
55 river sediment, and could be a possible source of pollution when metals are released back into fluvial
56 systems. Presently in the UK, there are no mandatory sediment quality guidelines, however, the
57 Environment Agency have developed draft UK sediment quality guidelines using the Environment
58 Canada threshold effect level (TEL) and probable effects level (PEL) sediment quality guidelines
59 (Hudson-Edwards et al. 2008). There remain a number of challenges in sediment monitoring,
60 including identifying the most suitable sampling technique and the most appropriate sediment
61 compartment to sample (bed, bank or suspended sediment) for individual rivers (Crane 2003). River
62 systems are dynamic and the properties of their deposits are likely to vary with location and even
63 sediment compartment.

64

65 River bed, bank and suspended sediment can all be potentially used to monitor sediment environmental quality.
66 The question however is does it matter which sediment compartment (bed, bank and suspended sediment) is
67 monitored for sediment quality monitoring, and are there significant differences in the physical and chemical
68 characteristics of the bed, bank and suspended sediment sampled from the same river? Many studies have
69 focused on metal concentrations in the bed sediment (Jain et al. 2005; Fok et al. 2012; Islam et al. 2015; Hurley
70 et al. 2017), and / or in bed and suspended sediment (e.g. Jelodar et al. 2012; Kuusisto-Hjort and Hjort 2013;
71 Nazeer et al. 2014), and / or the bed and bank sediment (Grosbois et al. 2012). In fact, the bed sediment is
72 commonly used as a basis for monitoring trace metal concentrations in sediment and has been used in setting
73 sediment quality guidelines (SQG)/ sediment quality standards (SQS) in countries such as Canada, Australia, Italy
74 and the Netherlands (Burton 2002). The draft UK sediment quality guidelines are likely to be based on bed
75 sediment (Hudson-Edwards et al. 2008). However, the Fraunhofer Institute (2002) suggested that suspended
76 sediment should be measured and compared with environmental quality standards rather than bed or bank
77 sediment because suspended sediment retains and transports new contaminants whilst the residence time of
78 sediment in the river bed remains largely unknown. The Sediments in the Ravensbourne River are likely to retain
79 historical contaminants from long-lasting English industrial activities and persistent secondary contamination
80 associated with the urban environment. It is possible that not all locations on any river bed are suitable for

81 monitoring recent pollution as some locations are depositional, some are erosional and others will be stable
82 (Counihan et al. 2014); hence bed sediments were collected where deposition was observed to have occurred.
83 Significant differences in chemical composition would be expected between sites retaining only historical
84 pollutants and those with recently deposited sediments and these comparisons are reported in the results section.

85
86 Sediment particle size, organic matter and clay mineralogy are key factors commonly reported to affect metal
87 concentrations measured in sediment (Horowitz 1991; Luoma and Rainbow 2008; Bábek et al. 2015). The
88 variations in particle sizes of fluvial sediment are widely documented (Bábek et al. 2015; Matys Grygar and
89 Popelka 2016). Particle size accounts for more than 50% of the variation of trace metal concentration in river
90 sediment (Bábek et al. 2015) with metal concentration reportedly to increase with decreasing particle size (Zhao et
91 al. 2010; Yao et al. 2015; Maity et al. 2016; Yutong et al. 2016). For example, clay and silt tend to sequester high
92 concentrations of metals due to a commensurate increase in specific surface area. However, high concentrations of
93 heavy metals are also reported in sand fractions ($>63 \mu\text{m}$) (Lin et al. 2003). Organic matter substantially increases
94 the number of binding sites for metals and forms complexes with metal ion in sediment (Schumacher 2002; Luoma
95 and Rainbow 2008; Charriau et al. 2011). The loss on ignition (LOI) is widely accepted as a standard way of
96 measuring organic carbon content in both soils and sediments (Dean 1974; Heiri et al. 2001; Santisteban et al.
97 2004). Although clay minerals affect the ability of sediment to sequester trace metals, it is often in combination
98 with Fe, Mn amorphous oxides, and organic materials (Li et al. 2009; He et al. 2012; Chen et al. 2016). Several
99 studies have examined the relationship between trace metals and clay minerals such as smectite and kaolinite in
100 sediment (Vega et al. 2004; Zhang et al. 2004; Kim et al. 2007). For example, Chen et al. (2016) found metal
101 content to significantly correlate with kaolinite and illite concentration in surface sediment. The minerals
102 commonly found in most depositional environments include silicates, carbonates and clay minerals such as illite,
103 montmorillonite and kaolinite (Weaver 1956). The association of trace metals with kaolinite and other clay minerals
104 is likely due to the presence of Fe/Mn amorphous oxides and fine organic matter in fine aggregated sediment
105 fractions (Gilbert et al. 2009; Schaidler et al. 2014). It is widely documented that iron/manganese oxide and organic
106 material aggregates account for a significant proportion of metal sequestration in fluvial systems in comparison to
107 clay minerals (Li et al. 2009; Wang and Li 2011; Schaidler et al. 2014; Matys Grygar and Popelka 2016; Couture et
108 al. 2018).

109
110 The sampling devices used in sediment (bed, bank and suspended sediment) monitoring vary depending on the
111 objective of the study (Mudroch and Azcue 1995). The Ravensbourne River in south London, UK was used to
112 explore challenges of sediment sampling and is located in a densely populated urban area. Good sediment sampling
113 programmes aim to collect samples that are representative of trace metal concentrations at the sampling site and

114 establish any variability in concentrations without disturbing the sediment (IAEA 2003; Simpson et al. 2005), even
115 during changes in environmental conditions such as storm events. In storm events, sampling the bed compartment
116 may be difficult or even impossible depending on the storm event and catchment characteristics. Sediment grabs are
117 commonly used for collecting bed sediments for chemical analysis (Liu et al. 2009; Liu et al. 2011; Ho et al. 2012;
118 Palma et al. 2015). The grab sampler is effective where sediment coring is problematic or impossible due to a
119 gravel or sandy substrate (Mudroch and Azcue 1995). A stainless steel grab sampler such as the Van Veen grab
120 is easy to use, portable, light weight and effective in shallow rivers and in particular generally retains the finest
121 sediment fractions. Hand scooping using a spoon or hand trowel is the most widely used method for sampling bank
122 sediment (Rotman et al. 2008; Juracek and Ziegler 2009), but is ineffective in flowing water as a result of losing
123 fine sediment. Several methods of sampling suspended sediment have been devised over the years such as the
124 integrated sampler (McDonald et al. 2010) and sediment traps (Hedrick et al. 2013). The Time Integrated Sediment
125 Tube Sampler (TISTS) described by Phillips et al. (2000), Russell et al. (2000) and McDonald et al. (2010)
126 provides an inexpensive and practical method of collecting representative suspended sediment samples. The TISTS
127 effectively samples active suspended sediment without disturbing the overlying water, and is best used where the
128 daily river flow is low. The deployment of multiple suspended samplers allows collection of sufficient mass of
129 sediment for physical and chemical analysis, especially where the river velocity and sediment concentrations are
130 low (Simpson et al. 2005).

131

132 This study aims to identify a suitable sediment compartment to sample for sediment quality monitoring by: (a)
133 studying the concentration of trace metals (Cd, Cu, Ni, Pb and Zn) in the bed, bank and suspended sediment
134 compartments of the Ravensbourne River to establish any differences in trace metal concentrations with
135 compartment, (b) determining the influence of sediment particle size fractions (<63 μm and 63 μm - 2 mm), organic
136 matter and mineralogy on any differences, and (c) examine if metal concentration in each sediment compartment
137 complies with the draft UK sediment quality guidelines.

138

139

140 **2 Materials and methods**

141 **2.1 Study area**

142 The Ravensbourne River is a tributary of the River Thames located in the heavily built-up area of South East
143 London (Fig. 1). It rises as a Chalk spring in Caesar's Well at Keston, and flows through London Boroughs of
144 Bromley, Greenwich and Lewisham before joining the River Thames at Deptford (Knight 1842; Lewisham
145 Council and Environment Agency 2010). The Ravensbourne River is about 17.4 km long and has a catchment area
146 of 180 km². The major tributaries that feed into the Ravensbourne are the Pool River, which joins the

147 Ravensbourne at Catford, and the River Quaggy which joins the Ravensbourne at Lewisham. There is a predictable
148 mix of historic and current industrial activity along the river e.g. breweries, chemical works (Barton 1992;
149 Lewisham Council and Environment Agency 2010; Talling 2011), as well as major and minor road arteries
150 adjacent to, and crossing, the river. The bedrock of the Ravensbourne consists mainly of sedimentary rocks
151 (London Clay Formation – silt and gravel) and superficial alluvial deposits which consist of clay, silt, sand and
152 gravel. The Ravensbourne River and its tributaries are one of the most culverted rivers in London flowing through
153 densely populated areas such as Lewisham and Catford (Barton 1992; Copas 1997). Like many urban rivers,
154 more than 50% of the Ravensbourne catchment is heavily modified by flood defence structures to protect
155 surrounding residential and commercial properties from flood events (Lewisham Council and Environment Agency
156 2010).

157

158 **2.2 Sampling location, river velocity and discharge measurement**

159 Sediment and water samples were collected from the Ravensbourne River at Ladywell Field (51.453793 N,
160 - 0.0186038 E, where the river was easily accessible) from January to December 2011 except for the months of
161 March and April (Fig. 1). The river discharge was measured at a fixed cross section of the river using an
162 electromagnetic current meter (SENSA) to measure velocity at a number of points across the stream. Computed
163 river discharges ranged between 83 and 490 L s⁻¹ except during a storm event when discharge reached 2370 L s⁻¹.
164 Further sediment samples were collected in May 2012 after a major storm event when the discharge had reduced to
165 490 L s⁻¹. The Ravensbourne River at Ladywell Field has a transect width of 5 m with an average depth of 0.4 m,
166 and the river bed consists mainly of medium to fine gravels.

167

168 **2.3 Sample collection and preparation**

169 Sediment samples were collected monthly from the bed, bank and actively transported suspended sediment.
170 The top 10 cm of sediment was collected from the bed and banks. Bed sediments were collected as composite
171 samples from the left, right and middle section of the river, and composite samples of the bank sediments were
172 collected from different sub samples of the bank. Suspended sediments were collected monthly in duplicate from
173 both sides of the river (Fig. 2) using time integrated sediment tube samplers (TISTS) as described by Phillips et al.
174 (2000) and Perks et al. (2017). Each TISTS sampler was installed horizontally at approximately 0.1 m above the
175 river bed at the sampling point, and fastened with cable ties to the wooden revetment along the river bank. A 5 L
176 Van Veen grab was used to sample bed sediment (United Nation Environment Programme 2006), and the bank
177 sediment was collected using a stainless steel hand trowel (Sekabira et al. 2010). All sediment samples were
178 transferred to labeled air-sealed transparent polypropylene bags immediately after collection. External sources
179 of contamination were avoided by using sediment samplers made of stainless steel and/ or plastic material

180 (Mudroch and Macknight 1994). Sediment samples were collected monthly between January and December (except
181 for the months of February and March), and storm samples for the bed, bank and suspended sediment were
182 collected in May 2012. Storm events were not common during the sampling year so storm samples were collected
183 in the following year in response to a major flood. The sediment samples were stored and transported to the
184 laboratory in the dark at 4 °C in an ice box (Palmer 1984; USEPA 2001). Prior to sieving, large debris, including
185 plant and gravel-sized material were carefully handpicked and removed from sediment samples. Sediment samples
186 were oven dried to a constant mass at 105 °C using a Gallenkamp oven and dry sieved into <63 µm and the 63 µm
187 – 2 mm fraction using stainless steel Endecotts laboratory test sieves (Tessier et al. 1979; Quevauviller 1998). The
188 sieves were thoroughly rinsed with distilled water and oven dried to avoid contamination between sample
189 preparations. Generally, the amount of suspended sediment and the <63 µm bed sediment fraction in the
190 Ravensbourne River was low and sediment mass obtained after drying and sieving were generally low in
191 comparison to sediment mass from the bank. All sediment samples were stored at room temperature in air-tight
192 plastic bags after drying and sieving and all analyses were carried out within three months of collection for dry
193 sediment samples (USEPA 2001).

194

195 **2.4 Analytical techniques**

196 All glassware used for sample analysis was of grade 'A' standard, and all reagents used were of analytical grade
197 (Aristar and AnalaR grade). High purity deionised water (18.3 MΩ) obtained from a Milli Q filtration unit was
198 used throughout. All equipment and apparatus were acid cleaned in 10% (v/v) nitric acid and rinsed with deionised
199 water prior to use. Working calibration solutions, blank calibration solutions, certified reference materials and an
200 independent/check analytical quality control solution were prepared and analysed alongside digested sediment
201 samples. Analyses were repeated on randomly selected samples throughout the experiments. Analyses of blank and
202 triplicate samples were used for total metal content. The calibration coefficient of the calibration line (linear fit)
203 was always better than 0.999 for all the analyses, and the equipment drift was within 10%. Triplicate
204 analysis of different samples indicated that most analyses had a reproducibility of about ±10%. The certified
205 reference material LGC 6187 for trace metal analysis was also within ±10% of the certified value (Table 1),
206 which was an acceptable experimental limit for reference materials (Holcombe 2009; Environment Agency
207 2016). The limits of quantification (LoQ) were 0.03 ppm, 0.02 ppm, 0.02 ppm, 0.05 ppm and 0.01 ppm for Cd, Cu,
208 Ni, Pb and Zn, respectively.

209

210 **2.4.1 Trace metal extractions and analysis**

211 Trace metals (Cd, Cu, Ni, Pb and Zn) were extracted from the bed (<63 µm and 63 µm - 2 mm), bank (<63 µm and
212 63 µm - 2 mm) and suspended sediment using aqua regia (1:3 v/v of concentrated HNO₃ and concentrated HCl)

213 after the method of the Environment Agency (2006). Sediment (1 ± 0.001 g) was weighed in triplicate into separate
214 50 mL Teflon tubes, 2.5 mL of concentrated HNO_3 and 7.5 mL of concentrated HCl were added to sediment in each
215 Teflon tube. The mixture was shaken and allowed to stand for 8 hours at room temperature. The solution was
216 placed in a heating block and heated at 60 °C for 10 minutes, 80 °C for 10 minutes, 100 °C for 10 minutes and
217 160 °C for 2 hours. The final solution was allowed to cool and made up to 50 mL with deionised water. The
218 solution was centrifuged at 3000 rpm for 15 minutes and analysed for the selected heavy metals using a Varian
219 VISTA PRO Inductively Coupled Plasmas Atomic Emission Spectrophotometer (ICP-AES). The results were
220 expressed in mg kg^{-1} dry weight.

221

222 **2.4.2 Particle size**

223 Sediment samples were pre-treated with 30% (v/v) hydrogen peroxide for 24 hours at room temperature to remove
224 organic matter following the method of Gray et al. (2010). Particle size was analysed with a Malvern MS2000
225 (Hydro 2000MU) Laser Diffraction Particle Size Analyser (Sperazza et al. 2004). The results were calculated on a
226 volume basis using the Mie theory and Malvern proprietary software. Mie's theory measures the light scattering
227 data obtained as light passes through or is being adsorbed by the particle. The theory is however based on spherical
228 properties. The obscuration rate ranged from 5 – 14% and the ideal range set out in the Malvern Mastersize manual
229 is between 3 and 20%. The specific surface area was computed with equivalent diameters to the volume of the
230 liquid displaced by the particles. This happens for every particle counted in the entire distribution and adds up to the
231 surface area of 1 g of sediment with the same particle size distribution. An assumed particle density is set at 1 g cm^{-3} ,
232 and the surface area is computed as $4/3 \pi r^3$, where r is the particle radius.

233

234 Approximately 2 ± 0.01 g of oven-dried sediment was weighed into 50 mL disposable centrifuge tubes and 20
235 mL of 30% (v/v) H_2O_2 was added to each tube. After the reaction was completed, the sediment residue (wet
236 sediment) was transferred into the Malvern sample dispersion unit (Hydro 2000) containing 600 mL of
237 ultrapure water produced by a reverse osmosis plant. The particle size results were expressed in μm for the d_{50}
238 (the median particle size distribution), and $\text{m}^2 \text{g}^{-1}$ for the specific surface area (total surface area of a sediment per
239 unit of mass).

240

241 **2.4.3 Organic matter content**

242 The total organic matter content in the sediment samples was determined by the percentage loss after
243 ignition (Donkin 1991; Heiri et al. 2001; Schumacher 2002). Porcelain crucibles were heated in a Griffin furnace
244 at 550 °C for 20 minutes to completely remove moisture. The crucibles were allowed to cool in desiccators.
245 Approximately 1.5 g of sediment was then placed into duplicate porcelain crucibles. The weight of the

246 crucibles and sediment was recorded, and the crucibles containing sediment were placed in the oven at 105 °C
247 for a minimum of 12 hours, allowed to cool in a desiccator and reweighed (A). The sediment + crucibles were
248 then placed in the furnace at 450 °C for 12 hours, allowed to cool and weighed (B). The loss on ignition (LOI %)
249 was calculated using the equation:

250

$$251 \quad LOI \% = \left\{ \frac{A - B}{A} \right\} \times 100$$

252

253 A = weight of crucible + sample after 105 °C for 12 hours

254 B = weight of crucible + sample after 450 °C for 12 hours

255

256 **2.4.4 Morphology and mineralogy**

257 The Scanning Electron Microscope is widely used in the study of sediment morphology, structure and chemical
258 composition (Swapp 2013). Scanning electron microscopy was carried out using a Carl Zeiss Ultra Plus Field
259 Emission SEM. Approximately 1 g of finely crushed selected bed, bank and suspended sediment samples
260 were mounted on an aluminum stub, and the electron beam produced by the electron gun was focused on the
261 sample and selected images were downloaded. The final image was projected on a screen from the detector.
262 Sediment mineralogy was analysed using the Enraf Nonius Powder X-ray Diffractometer coupled to INEL CPS
263 120 position-sensitive detector (PSD). Approximately 1 g of finely crushed and homogenised sediment sample
264 was carefully fixed onto the specimen holder and rotated around a fixed axis and X-ray diffraction intensities
265 recorded. Diffractograms were collected at 30 min (for phase identification) and 60 min (for quantitative
266 analysis). The X-ray diffraction data was calibrated using silver behenate (NIST SRM 640b) for low angle, and
267 silicon for a wider angle range. Clay mineral standards were run for named minerals that were identified as present
268 in initial data and the quantitative data was calculated from the modeled values of each mineral. The phase
269 identification was analysed using the STOE software which includes the ICDD (The International Centre for
270 Diffraction Data) Powder Diffraction Files (PDF) and a search- match programme for peak identification. The
271 quantitative data were expressed as weight percentage of the phase proportion of each clay mineral.

272

273 **2.5 Statistical analysis**

274 All statistical analyses were carried out using Microsoft Excel spread sheets, SPSS 20.0 and GraphPad Prism 5.1
275 Software. The normality (Gaussian) distribution of the data obtained for heavy metal concentrations in sediment
276 was analysed using the Shapiro-Wilk and Kolmogorov-Smirnov normality test due to its appropriateness for
277 small sample sizes (<50) (Chen 1971; Field 2001). The Spearman's rho test was used to measure correlations
278 between variables (sediment specific surface area and heavy metal concentrations, and heavy metal concentration

279 between compartments). Univariate analysis was used to calculate the mean and standard deviation of repeated
280 measures for each sample, and the non-parametric Kruskal-Wallis one way analysis of variance was used to
281 compare the difference in heavy metal concentration between sediment compartments (bed, bank and suspended
282 sediment).

283

284 **3 Results and Discussion**

285 **3.1 Particle shape, mass and size**

286 Sediment particles in the bed, bank and suspended sediment were irregularly shaped, non-spherical and varied
287 substantially in composition and size (Fig. 3). The bed sediment consisted mainly of gravel and the particle sizes of
288 the bed sediment were generally larger than those of the bank and suspended sediment samples. Suspended
289 sediment consisted mainly of silt, while the bank and bed sediment consisted mainly of silt/fine sand and silt/fine -
290 coarse sand/ gravel, respectively. Generally, the mass of suspended sediment and the <63 μm bed sediment
291 fraction were low compared to the bank sediment. The <63 μm sediment fraction constituted <1% (bed sediment)
292 and <10 % (bank sediment) of the total mass of sediment sampled monthly.

293

294 Sediment particle sizes showed variation with sampling time and sediment compartment (Table ESM_1 &
295 ESM_2). Particle size distribution in the bed sediment ranged from 11 μm – 221 μm , and 187 μm - 570 μm for
296 the <63 μm and 63 μm – 2 mm, respectively. The bank sediment ranged from 9 μm – 53 μm , and 100 μm – 191 μm for
297 the <63 μm and 63 μm – 2 mm. Particle sizes in the suspended sediment were generally below <63 μm except for the LM2
298 April sample (77 μm). The results indicated that the sieved <63 μm bed sediment fraction contained some coarse sediment
299 (>63 μm) (Table ESM_1 & ESM_2). Sieving defines the particle diameter of sediment as the length of the side of the square
300 hole of the mesh sieve through which the sediment particles can pass, whilst laser diffraction analyses sediment particle as a
301 function of its cross-sectional area of a sphere that displaces an equivalent volume of liquid (Allen 1990; Konert and
302 Vandenberghe 1997; Di Stefano et al. 2010). Discrepancies in results obtained for particle size analysis using dry sieving and
303 laser diffraction are also well documented (Polakowski et al. 2014; Rasmussen and Dalsgaard 2017). The sieving method
304 could have an effect on metal concentration in the <63 μm bed sediment fraction by possibly diluting metal
305 concentrations because of the larger particle size (>63 μm), as higher concentrations of metals were mainly
306 associated with the <63 μm in the sampling location. Wet sieving could be more effective in separating aggregates,
307 however, it is time consuming and there is a higher risk of sample contamination especially where large numbers of
308 samples are involved. Another possible reason for differences could be the shape of sediment particles passing
309 through the sieve mesh (Konert and Vandenberghe 1997; Blott and Pye 2006; Polakowski et al. 2014).

310

311 The bank sediment had the highest specific surface area of 1.31 $\text{m}^2 \text{g}^{-1}$ compared to the bed (1.12 $\text{m}^2 \text{g}^{-1}$) and

312 suspended sediment ($1.02 \text{ m}^2 \text{ g}^{-1}$) (Table ESM_1). These variations in particle sizes and SSA are important for
313 sediment monitoring especially if sediment quality is to be based on a specific sediment fraction. For example,
314 using the $<63 \mu\text{m}$ for sediment monitoring would favour the use of bank sediments because collecting sufficient
315 $<63 \mu\text{m}$ bed/suspended sediment mass for laboratory analysis poses a challenge in gravel bed rivers with low
316 sedimentation rates such as in the Ravensbourne River. Similarly, using the $63 \mu\text{m} - 2 \text{ mm}$ fraction for sediment
317 monitoring will tend to omit the significant contribution of heavy metals from the $<63 \mu\text{m}$ fraction (Lin et al. 2003).
318 It is not clear what particle size has been used in setting most sediment guidelines (O'Connor 2004), however the
319 commonly used particle sizes reported in the literature for sediment analysis are the $<63 \mu\text{m}$ fraction (Rodrigues
320 and Formoso 2006; Simpson et al. 2011) and the $<2 \text{ mm}$ fraction (Karlsson et al. 2010; Bartoli et al. 2012). The <2
321 mm fraction is currently promoted by environmental geochemists (Frančišković-Bilinski and Cukrov 2014; Palleiro
322 et al. 2016; Tiquio et al. 2017). Perhaps the best option would be to delineate a fraction that incorporates particle
323 sizes from $<63 \mu\text{m}$ to 2 mm for analysis and setting quality standards by sieving sediment through a 2 mm sieve.

324

325 **3.2 Organic matter**

326 The suspended sediment had higher percentages of organic matter compared to the bed and bank sediment (Table
327 ESM_3). Organic matter in the bank sediment was more than twice and about 6 times greater than that in the
328 bed sediment for the $<63 \mu\text{m}$ and $63 \mu\text{m} - 2 \text{ mm}$ sediment fraction, respectively. Generally, the $<63 \mu\text{m}$ particle
329 fraction mirrored higher organic matter content compared to the $63 \mu\text{m} - 2 \text{ mm}$ fraction. Organic matter content
330 ranged from 0.6% ($63 \mu\text{m} - 2 \text{ mm}$ bed sediment) to 22.1% (suspended sediment). There were significant
331 differences ($p < 0.0001$) in organic matter content between each of the sediment compartments. There was a
332 statistically significant relationship between organic matter and metal concentration only in the bank sediment but
333 not in the other sediment compartments (Fig. 6). The number of binding sites produced by organic matter is
334 dependent on the type of organic acid. For example, fulvic organic materials have a larger binding surface
335 compared to lignin (Luoma and Rainbow 2008). However, in most sediment, the number of binding sites is not
336 only influenced by organic matter content, but also by the presence of iron oxides and clay minerals (Schneider et al.
337 2014).

338

339 **3.3 Mineralogy**

340 The most common minerals present in the sampled sediments were quartz, illite, muscovite, calcite, kaolinite,
341 dolomite, montmorillonite and goethite. Clay mineral distributions followed a similar pattern for each sediment
342 compartment (Fig. 4) with only minor differences (Table 2). The dominant clay minerals in the non-storm
343 suspended sediments were illite-smectite (56 – 63%), muscovite (9 – 11%) and kaolinite (3 - 6%). The dominant
344 minerals in the bed sediment were illite-smectite (39%), muscovite (5%) and calcite (5%). The dominant minerals

345 in the bank sediment were illite-smectite (51%), Muscovite (5%), calcite (4%) and kaolinite (3%). Kaolinite appears
346 to be more visible in the suspended sediment (Fig. 4), consisting up to 6% of the total minerals (Table 2). Calcite
347 was associated more with the bed and bank sediment, with up to 4% for the <63 μm bed sediment and 3% for the
348 <63 μm bank sediment. Muscovite was mainly associated with the suspended sediment. Clinocllore (up to 3% in
349 suspended sediment) and goethite (0.2 %) were present in all sediment compartments (Table 2) but were not visible
350 in graphs for X-ray diffraction (Fig. 4). This might be due to their low content or poor crystallinity or a combination
351 of the two (Chen et al. 2016).

352
353 Clay minerals have different binding characteristics depending on surface areas and surface charges (Horowitz
354 1991; He et al. 2012). However, trace metals tend to sorb mainly on nano-crystalline Fe-oxides (Plathe 2010;
355 Frančičković-Bilinski et al. 2014) and organic matter (Charriau et al. 2011). The mineralogy (illite-smectite, muscovite,
356 calcite, kaolinite, dolomite and goethite) of each sediment compartment are commonly associated with urban
357 environments; consisting of fine particles of natural origin from soils and dust mixed with trace metals from cars,
358 anticorrosive pigments and car batteries. However, the proportion of clay minerals in each sediment compartment
359 differed (Table 2). This suggests that each sediment compartment could behave differently when it comes to metal
360 sequestration. For example, Helios Rybicka et al. (1995) investigated the adsorption behavior of Cd, Cu, Pb, Zn and Ni on
361 clay minerals including illite and montmorillonite, the results indicated that smectites had the highest enrichment of all
362 metals except Pb ions which were enriched on illite. In this study, the concentrations of Pb in bank sediment were high
363 compared to the bed and suspended sediment. However, the proportion of illite-smectite, were highest in the suspended
364 sediment (63%) compared to bed (39%) and bank (51%). Particle size fraction could also be a contributory factor in high
365 Pb concentrations in bank sediment because the bank sediment had the highest specific surface area of $1.31 \text{ m}^2 \text{ g}^{-1}$
366 compared to the bed ($1.12 \text{ m}^2 \text{ g}^{-1}$) and suspended sediment ($1.02 \text{ m}^2 \text{ g}^{-1}$).

367

368 **3.4 Trace metal concentrations in the different sediment compartments**

369 The concentrations of metals varied with the trace metal, particle size (Table 3), sediment compartment and
370 sampling period (Fig. ESM_5). Zinc had the highest concentration of all the metals in the bed, bank and
371 suspended sediment samples, whilst Cd was mainly detected in the bank sediment and below the limit of
372 quantification in some of the bed and suspended sediment samples. The bank sediment retained higher
373 concentrations of metals compared to the bed and suspended sediment. For example, the concentration of Pb in the <63
374 μm bank sediment ranged from 514 mg kg^{-1} – 821 mg kg^{-1} , compared to the <63 μm bed and suspended (Left monthly) sediment
375 which ranged from 150 mg kg^{-1} - 555 mg kg^{-1} , and 92 mg kg^{-1} – 368 mg kg^{-1} , respectively. A similar pattern of metal distribution was
376 recorded for Zn and Cd in the bed, bank and suspended sediment. However, Cu tended to be more associated with the bed and
377 suspended sediment whilst Ni remained largely unchanged. The larger concentrations of risk elements in banks could be a consequence

378 of more severe historical pollution now exposed by bank erosion. The Ravensbourne has historically served as a source of energy (e.g.
379 water mills) and also industrial production such as ship building, cutlery factories, gas works, brewing and chemical works (Barton
380 1992; McCartney and West 1998; Lewisham Council and Environment Agency 2010; Tailing 2011).

381

382 The $<63\ \mu\text{m}$ fraction was used in comparing metal concentration in different sediment compartments. The results only show significant
383 differences in Pb concentration between the bank and suspended sediment using the $<63\ \mu\text{m}$. Pb in bank sediment could be
384 linked to historic anthropogenic pollution from sources such as chemical works, construction works, erosion from
385 cultivated areas, atmospheric deposition and building of flood defence structures that all could have contributed to
386 contaminated sediments deposited on the river bank (Taylor and Owens 2009; Lewisham Council and Environment
387 Agency 2010). The infiltration of banks by polluted river water could also have brought in more pollution to the
388 bank (Matys Grygar et al. 2013). Whilst the differences in concentration may suggest that the bank sediment may
389 be unrepresentative of the sediments in the water course itself, that is, the bed and suspended sediment; polluted
390 bank sediments represent a potential future threat and are also important for examining the pollution status of
391 fluvial system. If analyses of suspended and/or bed sediment reveal pollution, banks should be sampled to identify
392 possible pollution source(s) of sediment and associated heavy metal contaminants that could enter the river as a
393 result of bank erosion, migration of reactive risk element species, or transported to rivers during flood events
394 (Gellis and Noe 2013; Theuring et al. 2013). Arguably, in the case of sampling pollution in the Ravensbourne
395 sediment, it might be suggested that the bank sediment could be excluded from the sampling regime when
396 establishing compliance with any sediment standards. However, sampling the bank sediment may be an important
397 prelude to designing remediation techniques and controlling pollutant ingress from sources in very close proximity
398 to the channel and which are directly connected to the river at times of high discharge.

399

400 There were no significant differences in trace metal concentrations between the bed ($<63\ \mu\text{m}$ fraction) and the
401 suspended sediment samples (Table 3). This however differs significantly with the $63\ \mu\text{m} - 2\ \text{mm}$ bed sediment
402 fractions. It may be useful when designing a sampling programme for sediment monitoring using the $<2\ \text{mm}$
403 sediment fraction to sample both suspended and bed sediment initially, with the aim of first confirming similarities
404 in metal concentration and ultimately reducing sampling to the bed or to samples obtained from integrated tube
405 samplers only. Significant differences in metal concentrations between suspended and bed sediment would probably
406 require a continuation of sampling from both compartments. However, the challenge of collecting sufficient
407 sediment mass for physical and chemical analysis favours sampling of the bed sediment instead of the suspended
408 sediment in rivers like the Ravensbourne. The sampling of gravel bed rivers to ensure sufficient mass of the $<63\ \mu\text{m}$
409 sediment fraction for analysis is likely to require the collection of a relatively large number of sub-samples from
410 different sections of the river bed. Certainly, the bed and suspended sediment are the most widely used sediment

411 compartments for sediment monitoring (Lee et al. 2003) and similar results are often reported for the concentration
412 of metals in both compartments (Davide et al. 2003). The argument that suspended sediment measures the most
413 recent influx of metals in a river (Fraunhofer Institute 2002) may be appropriate as part of the monitoring of water
414 quality but this might fail to establish the reality of potential exposure of benthic organisms. Suspended sediments
415 are effective for studying recent contaminant and short term chemical variability but the bed sediment is the
416 sediment compartment that benthic organisms are likely be exposed to for longer periods of time (Horowitz 1995;
417 Crane 2003).

418
419 The concentrations of trace metal in sediment is a function of particle size distribution (Zhou et al. 2015) and metal concentrations in
420 this study were highly correlated with particle size (Fig. 5). The results show significant differences in metal concentrations between the
421 sediment fractions (<63 μm and 63 μm – 2 mm), including metal concentrations between the suspended sediments (<63 μm) and the
422 63 μm – 2 mm sediment fractions of the bed and bank sediment. This however varies with specific metal and higher concentrations of
423 metals were often associated with the small particles sizes (<63 μm). The <2 mm (i.e. <63 μm + 63 μm - 2 mm) sediment fraction
424 may be the most appropriate particle size fraction to sample for a standardized and widely applied sediment monitoring programme for
425 determining compliance with EQSs both for gravel and non-gravel bed sediment (Palleiro et al. 2016; Tiquio et al. 2017). There were
426 strong correlations between metals concentrations and SSA in all sediment compartments (except for Cu and Ni in the suspended
427 sediment), possibly indicating that other factors could be significant in controlling these metal concentrations in suspended sediment
428 (Fig. 5). Metal concentrations are also known to be influenced by factors such as sediment source, mineralogy, the presence of iron
429 oxides, clay minerals, weathering and the geochemical characteristics of the sediment sources (Bábek et al. 2015). The correlation of
430 LOI % with metal concentration was only significant in the bank sediment (Fig. 6). The unknown concentrations of common reference
431 elements such as Al, Fe, and Ti considerably limit evaluation of risk element concentrations in individual compartments, in particular in
432 evaluation of grain-size effects.

433
434 Clearly, sediments in the Ravensbourne River at the sampling site do not comply with the UK draft sediment
435 quality guidelines (Table 3). The concentrations of metals in all sediment compartments reflect a combination of the
436 natural geochemical background, anthropogenic impacts, possibly mixing effects of contaminant sources and
437 erosion of topsoil within the Ravensbourne catchment as often reported in literature (Luoma and Rainbow 2008).
438 Similarly, data obtained from the British Geological Survey (BGS) showed similar levels of metal concentrations in
439 the <2 mm topsoil fraction in local soils (BGS Personal Communication, 12/12/12) (Fig. ESM_4). Although, the
440 characteristics of the topsoil differs from the river sediment; a similar pattern of metal concentration was observed
441 in both. The dominant metals (Zn, Pb and Cu) retained in all sediment compartments were also the dominant metals
442 found in local topsoils by the BGS and relatively abundant in nature.

443

444 **3.5 Variations in metal concentrations in the integrated tube samplers**

445 The concentrations of metals in each of the integrated tube samplers positioned differently along the river did
446 not differ significantly ($p>0.05$) . It appears that for a shallow river with low flow like the Ravensbourne, and
447 providing the sampling area is in a straight stretch of river, the positioning of the integrated tube samplers makes no
448 significant difference to the physical and chemical characteristics of the suspended sediment collected. Similar
449 result was also reported by Perks et al. (2017) for the Esk catchment in Northern England, UK, where the location
450 of integrated tube samplers was not significant in the determination of organic matter content and particle size.
451 This may be different if the sampling location was on a bend and the river velocity was higher on the outside of the
452 bend than the inside of the bend or where the river increased was extremely wide. The most important factor for
453 sediment monitoring is the concentration of suspended sediment in the river which determines if sufficient
454 suspended sediment mass can be sampled for analysis. Low concentrations (small mass) of sediment could result in
455 inhomogeneity, where one grain of sediment sample could result in marked differences in the sediment
456 characteristics (Horowitz 1995). The variation of metal concentration in replicate sediment samples is clearly seen
457 in the results obtained for metal concentrations in the suspended and bed sediment (Table 1). Low concentrations of
458 suspended sediment may not be unusual in urban rivers such as the Ravensbourne River, suggesting that multiple
459 deployments of tube samplers may be necessary in order to obtain sufficient material for analysis or that the
460 samplers should remain in situ for longer periods of time. The low concentration of suspended sediment trapped in
461 the time integrated tube samplers could also have been a consequence of the sampling frequency and Horowitz
462 (2003) suggested that hydrological-based sampling instead of calendar-based sampling could reduce error
463 associated with estimating sediment concentrations. Monthly sampling of a shallow low flow river such as the
464 Ravensbourne may often provide insufficient sediment mass for reliable metal analysis. Sampling annually or
465 biannually might allow enough time to collect sufficient sediment (Simpson et al. 2005). However, this may not
466 reflect the variation of metal concentrations in sediment over shorter periods of time, and of the potential pulsed
467 levels of metal exposure to biota.

468

469 **3.6 Storm effect on metal concentration in the bed, bank and suspended sediment**

470 Storms affect sediment characteristics for quality monitoring. Storm events reportedly increase the transportation of
471 sediment and remobilization of trace metals in an urban river system (Smith et al. 2003; Palanques et al. 2006;
472 Horowitz et al. 2008; Barańkiewicz et al. 2014; Ramos et al. 2015; Ciszewski and Grygar 2016). In historically
473 polluted rivers, storms may enhance pollutant fluxes; however, in rivers polluted rather recently the storms may
474 have the opposite impact. The effects of a storm on the concentration of metals in all sediment compartments varied
475 in this study (Table 4). The results indicated Cd was enriched in both suspended and bank sediment. This might imply
476 that Cd was a significant contaminant washed in from urban surfaces during the storm. The likely sources of Cd in

477 rivers with storm events are run-off from road deposited sediment from materials detached from brake linings and
478 cigarette butts (McKenzie et al. 2009; Zafra et al. 2011). The bank sediment constitutes a pathway for sediment
479 transportation to rivers especially during storm events, with sediment deposition increasing as run-off velocity
480 decreases. In such cases, sampling the bed sediment only might result in the neglecting contaminants in other
481 sediment compartments. Therefore, sampling only the bed sediment or bed/suspended sediment as is often done in
482 monitoring campaigns, might miss out important routes for sediment transport to rivers during storm events. It
483 might be appropriate to sample the suspended and possibly the bank sediment in addition to bed sediment
484 compartment after storm events as part of any sediment monitoring regime.

485
486 Another possible reason for the lack of Cd enrichment in bed sediment could be that the first flush of contaminants
487 had been transported beyond the sample point and had not penetrated the gravel matrix as it was already full of
488 sediment (Quek and Förster 1993; Taylor and Owens 2009; Kellagher 2012) or due to sediment dilution effect from
489 overlying waters (Dawson and Macklin 1998). It is often reported that storm events after a dry period are
490 significant sources of heavy metals in the aquatic environment (Quek and Förster 1993; Ramos et al. 2015); this
491 however tends to reduce when the storm event is preceded by days of low rainfall as is the case of the storm sample
492 collected for this study.

493

494 **4 Conclusions**

495 This study clearly shows that the concentrations of metals varied with sediment particle size and sediment
496 compartment sampled, and that the selection of the sediment compartment to use in any sampling depends on the
497 aim of the monitoring program. The bed and suspended sediment are the most widely used sediment compartments
498 for sediment monitoring, but collecting sufficient mass of the $<63 \mu\text{m}$ sediment fraction for monitoring
499 posed a challenge for urban gravel bed rivers like the Ravensbourne with very low sediment concentrations. The
500 wider particle size range of $<2 \text{ mm}$ appears to be the most suitable sediment fraction for trace metal monitoring
501 purposes as it gives enough sample mass for analysis. This study also showed that sampling the bed sediment has
502 more advantages compared to sampling the suspended or bank sediment although the bed samples did not appear
503 to retain the high Cd concentration found in suspended and bank sediments. It is the sediment compartment that
504 not only provides habitat for benthic organisms, but also has the advantage of providing sufficient mass of sediment
505 from gravel-bed and low-flow rivers in a shorter time period than suspended sediment. Revising the
506 sampling frequency from the commonly used monthly sampling to either annually or biannually might be helpful
507 in collecting sufficient mass of suspended sediment from rivers with low velocity using the time integrated
508 suspended sediment sampler. This, however, will miss any fluctuations in metal concentrations with time in
509 sediment and the effects of long term sediment storage of sediment in the tube samplers has yet to be fully

510 investigated. Sampling bed sediment is likely to provide a more time focused assessment of fluctuations in metal
511 concentrations and allow identification of concentrations that exceed environmental quality standards (EQSs)
512 over short time frames.

513

514 The concentration of heavy metals in the bed, bank and suspended sediment of the Ravensbourne River exceeded
515 the draft UK sediment quality guidelines for most of the sampling periods. It is likely that many urban rivers
516 exceed these guidelines. Inevitably, any guidelines should reflect the vulnerability of benthic organisms to
517 sediment bound metals but will have to confront the reality of existing sediment metal concentrations. Further
518 study would also be required to compare the chemical and physical properties of the bed, bank and suspended
519 sediment in other urban rivers with that obtained in the Ravensbourne River.

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800 **Table 1** The average (\pm standard deviation) concentrations of metals in the sediment compartments (n=10) and
 801 surrounding soils

Sediment		Cd, mg kg ⁻¹	Cu, mg kg ⁻¹	Ni, mg kg ⁻¹	Pb, mg kg ⁻¹	Zn, mg kg ⁻¹
	LOQ	0.03	0.02	0.02	0.05	0.01
Bed	<63 μ m	2.0 \pm 1.3	187.0 \pm 55.9	31.3 \pm 8.1	275.0 \pm 114.0	444.0 \pm 136.0
	63 μ m - 2 mm	0.8 \pm 0.2	30.3 \pm 1.9	10.6 \pm 1.9	85.0 \pm 55.0	127.0 \pm 33.4
Bank	<63 μ m	4.6 \pm 1.3	180.7 \pm 24.2	41.2 \pm 3.8	637.0 \pm 87.0	718.0 \pm 77.8
	63 μ m - 2 mm	2.1 \pm 0.7	67.0 \pm 8.5	17.2 \pm 1.2	259.0 \pm 33.9	293.6 \pm 26.7
Suspended	LM1	2.7 \pm 1.8	181.0 \pm 103.0	36.6 \pm 5.9	211.0 \pm 99.7	535.0 \pm 269.0
	LM2	2.9 \pm 1.9	167.0 \pm 79.3	34.8 \pm 9.7	206.0 \pm 101.0	487.0 \pm 272.0
	RM1	2.3 \pm 1.4	147.0 \pm 66.8	35.1 \pm 11.9	161.0 \pm 76.1	309.0 \pm 117.0
	RM2	2.6 \pm 1.7	160.0 \pm 52.9	35.6 \pm 9.7	201.0 \pm 66.5	424.0 \pm 138.0
UK TEL^a		0.6	36.7	18.0	35.0	123.0
UK PEL^b		3.5	197.0	35.9	91.3	315.0
Concentration in top soils ^c		0.8	86.4	30.0	398.0	331.0
Certified reference value		2.7	83.6	34.7	77.2	439.0
Experimental value		2.5 \pm 0.2	80.8 \pm 11.4	32.3 \pm 3.7	771.0 \pm 5.3	428.4 \pm 52.4
Certified recovery (%)		91.5	96.6	93.2	91.9	97.6

(Source for sediment quality guidelines: Hudson-Edwards *et al.*, 2008)

802 **a** TEL: Threshold effect level; draft freshwater sediment quality guidelines, **b** PEL: Probable effects level ; draft freshwater sediment quality

803 **c** Source from the British Geological Survey (Personal Communication)

804 **Table 2** The percentage phase proportion of minerals in July 2011 and May 2012 (storm) samples (n=2)

	Quartz, %	Illite-Smectite, %	Muscovite, %	Clinchlore, %	Calcite, %	Kaolinite, %	Dolomite, %	Goethite, %
July 2011								
Left monthly 1 (LM1)	21.3	62.0	10.4	3.1	0.6	4.5	0.5	0.2
Left monthly 2 (LM2)	20.6	56.1	10.7	3.2	1.3	6.1	1.9	0.2
Right monthly 1 (RM1)	21.7	63.4	8.5	1.6	0.6	3.0	1.0	0.2
Bed <63 μ m	48.1	39.2	4.8	1.4	4.5	1.4	0.4	0.2
Bed 63 μ m- 2 mm	82.4	9.4	4.4	1.3	1.1	1.3	0.0	0.2
Bank <63 μ m	34.5	51.2	5.1	1.5	3.6	2.9	0.9	0.2
Bank 63 μ m- 2 mm	67.7	25.5	0.9	1.4	2.8	1.3	0.3	0.2
May 2012 (storm sample)								
Left after storm1	21.0	68.9	3.3	1.6	1.9	1.6	1.0	0.7
Left after storm 2	19.8	70.3	3.3	1.6	1.9	1.6	1.0	0.5
Right after storm 1	13.4	71.3	3.3	3.3	3.3	1.6	3.0	0.8
Right after storm 2	13.5	69.8	3.4	3.3	4.6	1.6	3.0	0.8
Bed <63 μ m	41.1	36.6	13.3	2.8	2.2	2.7	0.9	0.4
Bed 63 μ m- 2 mm	62.1	23.4	1.8	0.3	1.6	2.5	8.0	0.4
Bank <63 μ m	39.3	44.7	6.1	3.0	3.0	2.9	0.6	0.5
Bank 63 μ m- 2 mm	68.4	20.2	1.8	2.6	1.3	2.5	3.2	0.0

(See figure 2 for tube sampler deployment).

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Table 3 The Kruskal-Wallis test (two-way ANOVA using the Bonferroni method) for metal concentration in the bed, bank and suspended sediment compartments of the Ravensbourne River

Sediment compartments	Cd	Cu	Ni	Pb	Zn
LM1 vs. LM2	ns	ns	ns	ns	ns
LM1 vs. RM1	ns	ns	ns	ns	ns
LM1 vs. RM2	ns	ns	ns	ns	ns
LM1 vs. <63 µm bed	ns	ns	ns	ns	ns
LM1 vs. <63 µm bank	ns	ns	ns	*	ns
LM2 vs. RM1	ns	ns	ns	ns	ns
LM2 vs. RM2	ns	ns	ns	ns	ns
LM2 vs. <63 µm bed	ns	ns	ns	ns	ns
LM2 vs. <63 µm bank	ns	ns	ns	*	ns
RM1 vs. RM2	ns	ns	ns	ns	ns
RM1 vs. <63 µm bed	ns	ns	ns	ns	ns
RM1 vs. <63 µm bank	ns	ns	ns	***	**
RM2 vs. <63 µm bed	ns	ns	ns	ns	ns
RM2 vs. <63 µm bank	ns	ns	ns	**	ns
<63 um bed vs. <63 µm bank	ns	ns	ns	ns	ns
LM1 vs. 63 µm- 2 mm bed	ns	***	***	ns	***
LM1 vs. 63 µm- 2 mm bank	ns	ns	*	ns	ns
LM2 vs. 63 µm- 2 mm bed	*	***	***	ns	**
LM2 vs. 63 µm- 2 mm bank	ns	ns	ns	ns	ns
RM1 vs. 63 µm- 2 mm bed	ns	**	**	ns	ns
RM1 vs. 63µm- 2 mm bank	ns	ns	ns	ns	ns
RM2 vs. 63 µm- 2 mm bed	ns	**	**	ns	**
RM2 vs. 63 µm- 2 mm bank	ns	ns	ns	ns	ns
<63 um bed vs. bed 63 µm- 2 mm	ns	***	*	**	**
<63 um bed vs. 63 µm- 2 mm bank	ns	*	ns	ns	ns
63 µm- 2 mm bed vs. <63 um bank	***	***	***	***	***
63 µm- 2 mm bed vs. 63 µm- 2 mm bank	ns	ns	ns	**	ns
<63 um bank vs. 63 µm- 2 mm bank	*	*	***	ns	**

* Significant at p<0.05, **significant at p<0.01, ***significant at p<0.001, ns - not significant, LM - Left monthly, RM - Right monthly (see figure 2 for tube sampler deployment).

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Table 4 The mean (\pm standard deviation) concentrations of metals in storm samples (n=3)

Storm samples	Cd	Cu	Ni	Pb	Zn
LOQ	0.03	0.02	0.02	0.05	0.01
<63 μ m bed	<	161.9 \pm 7.9	26.0 \pm 1.4	178.4 \pm 6.9	324.7 \pm 6.7
63 μ m - 2 mm bed	<	38.1 \pm 14.5	12.3 \pm 0.0	70.0 \pm 14.3	108.0 \pm 12.0
<63 μ m bank	33.8 \pm 0.8	170.8 \pm 2.7	43.6 \pm 1.0	617.3 \pm 6.9	679.4 \pm 5.8
63 μ m - 2 mm bank	13.8 \pm 0.5	63.3 \pm 2.1	17.2 \pm 1.3	243.0 \pm 4.5	265.3 \pm 1.7
LM1	15.2 \pm 1.6	215.9 \pm 19.6	34.5 \pm 3.5	257.9 \pm 25.2	623.7 \pm 56.8
LM2	20.1 \pm 0.6	281.4 \pm 4.3	43.5 \pm 0.5	348.2 \pm 3.1	879.0 \pm 8.6
RM1	20.8 \pm 0.6	275.9 \pm 6.3	43.0 \pm 1.1	327.4 \pm 6.0	830.7 \pm 7.7
RM2	19.2 \pm 2.1	260.0 \pm 3.4	40.9 \pm 0.8	332.1 \pm 2.3	740.3 \pm 7.4

LOQ – Limit of quantification, LM - Left monthly suspended tube sampler, RM - Right monthly suspended tube sampler (see Figure 2)

Figures

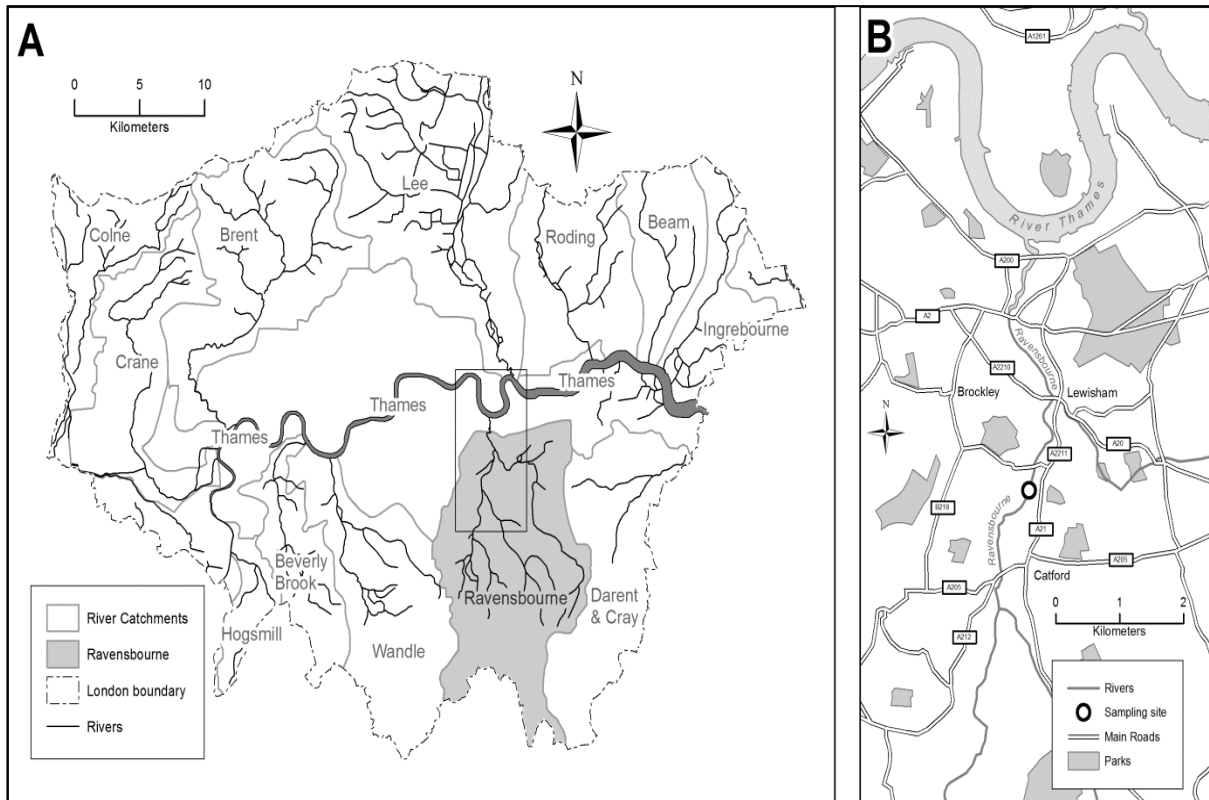
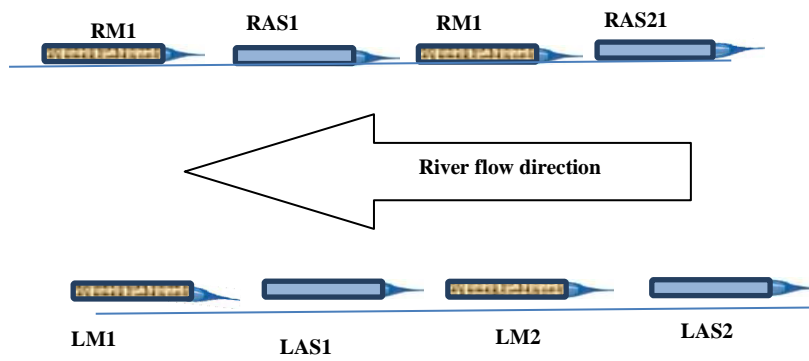
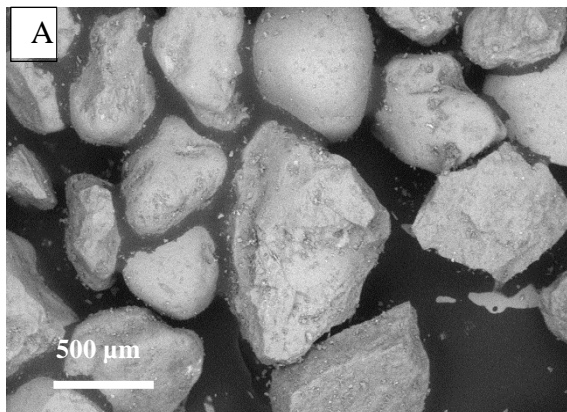


Figure 1 The Ravensbourne River in London, (a) Catchment area (b) Sampling location

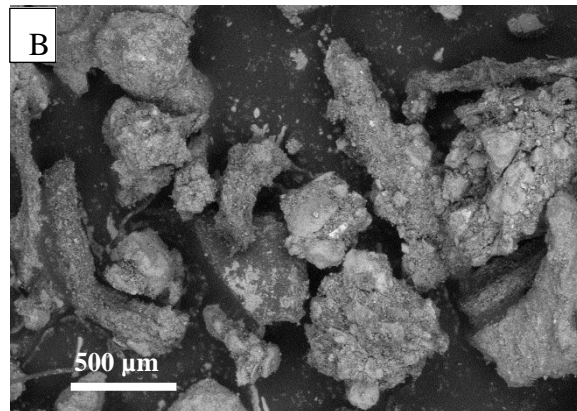


LM – left, sampled monthly, **RM** – right, sampled monthly, **LAS** – left, sampled after storm, **RAS** – right, sampled after storm

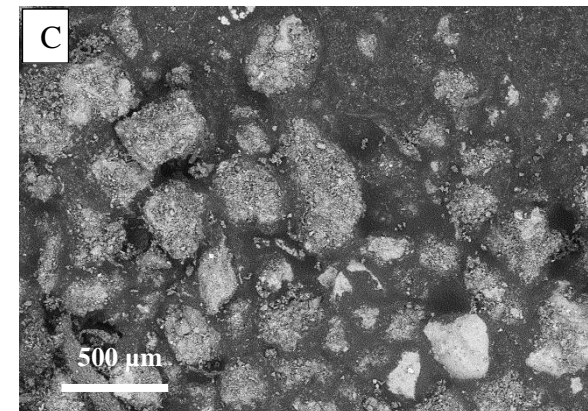
Figure 2 Layout of the time integrated suspended sediment tube samplers placed on opposite sides of the Ravensbourne River



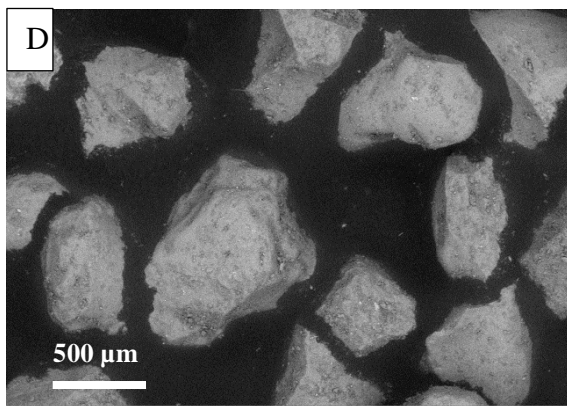
Bed 63 μm - 2 mm January 2011



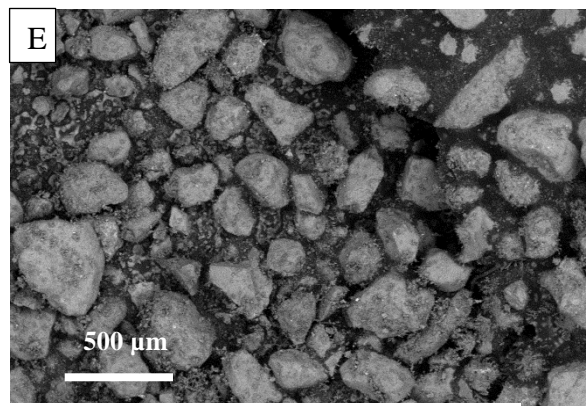
Bank 63 μm - 2 mm January 2011



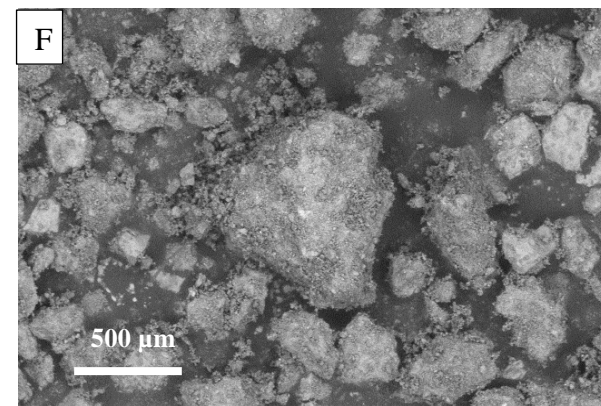
Suspended sediment January 2011



Bed 63 μm - 2 mm April 2011



Bank 63 μm - 2 mm April 2011



Suspended sediment April 2011

Figure 3 The shape and arrangement of particles in the 63 μm - 2 mm bed, 63 μm - 2 mm bank and suspended sediment for January 2011 and April 2011 (a) Bed January 2011 (b) Bank January 2011 (c) Suspended sediment January 2011 (d) Bed sediment April 2011 (e) Bank sediment April 2011 (f) Suspended sediment April 2011

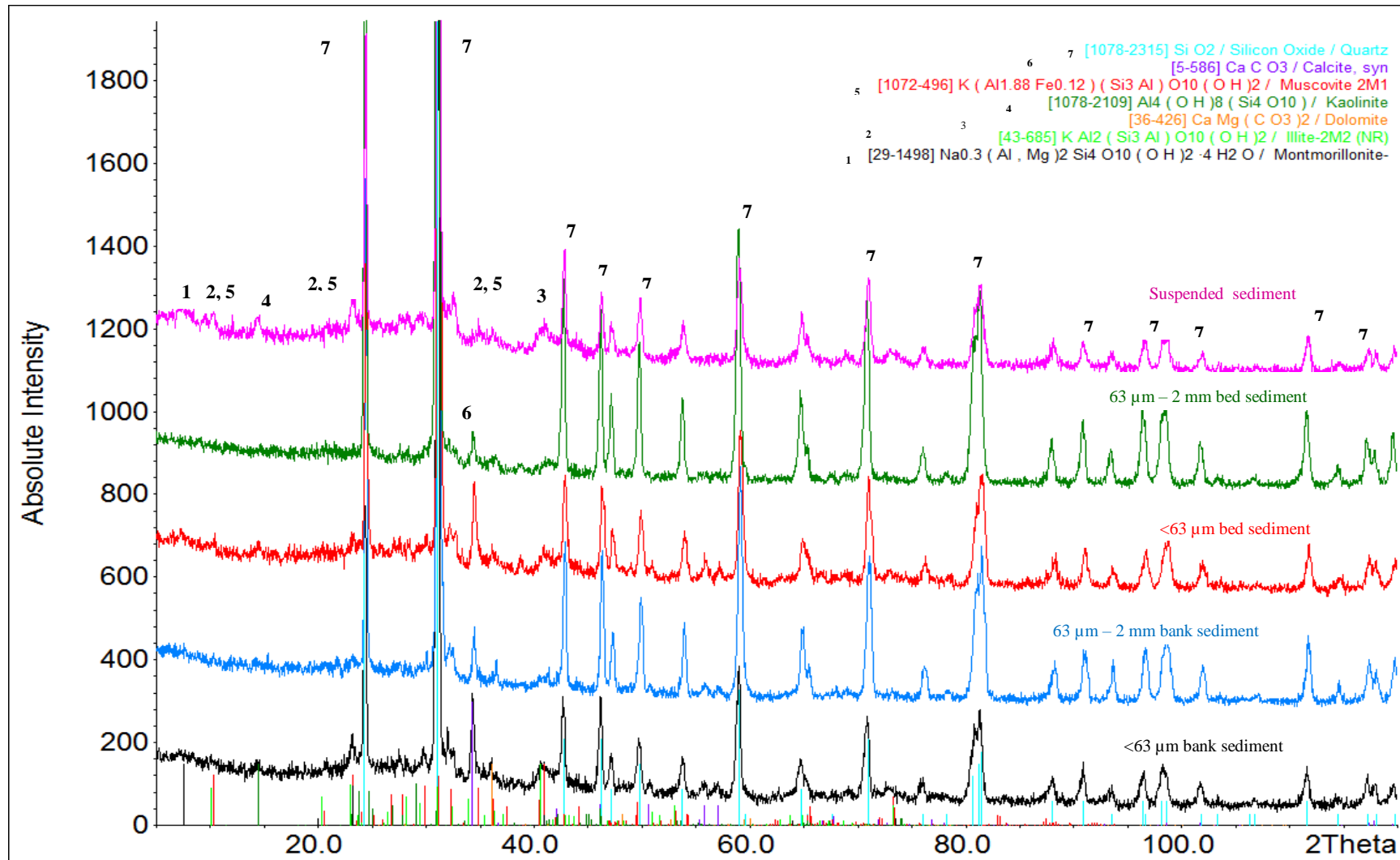


Figure 4 Mineral compositions by X-ray diffraction of the bed, bank and suspended sediment compartments for the month of July 2011

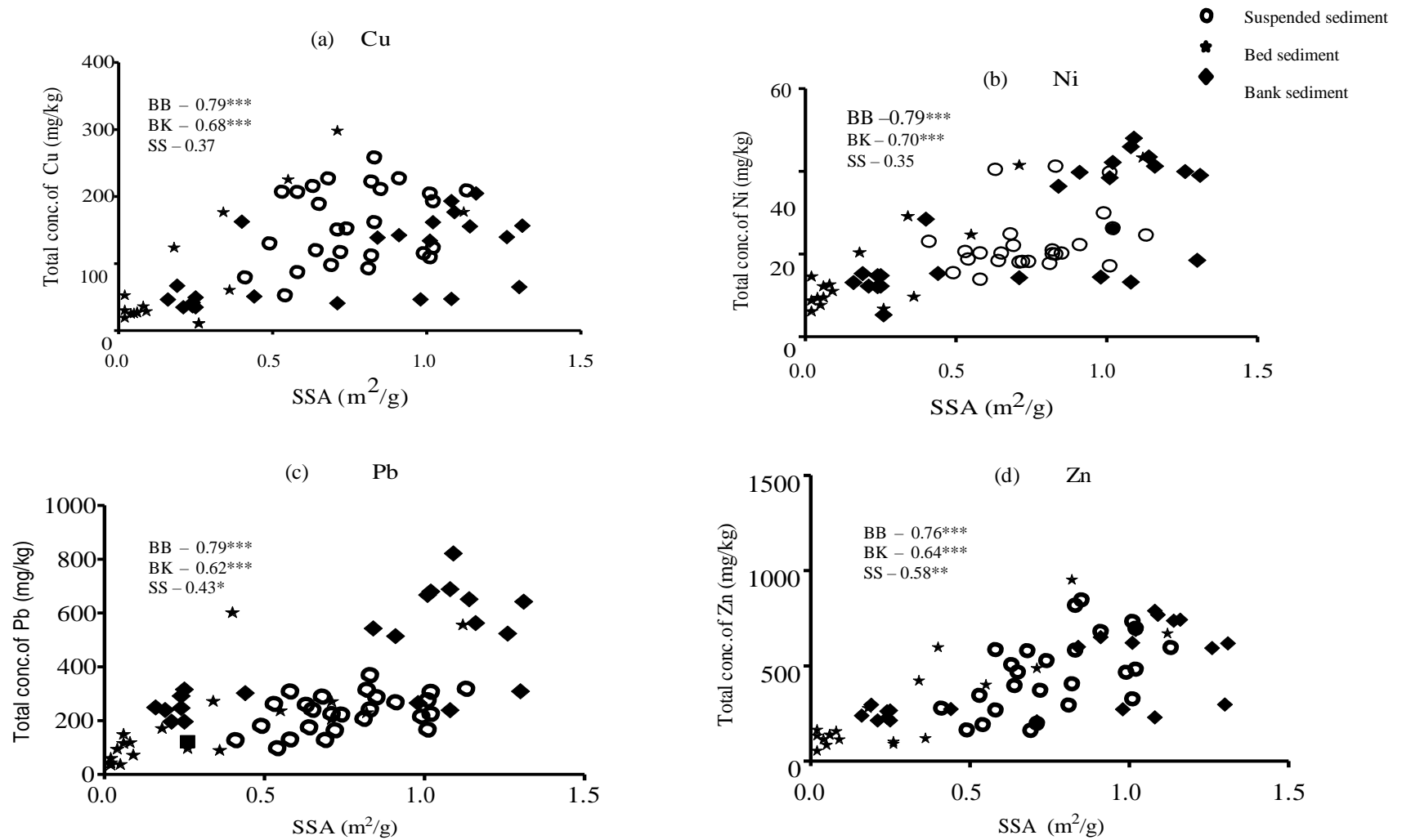
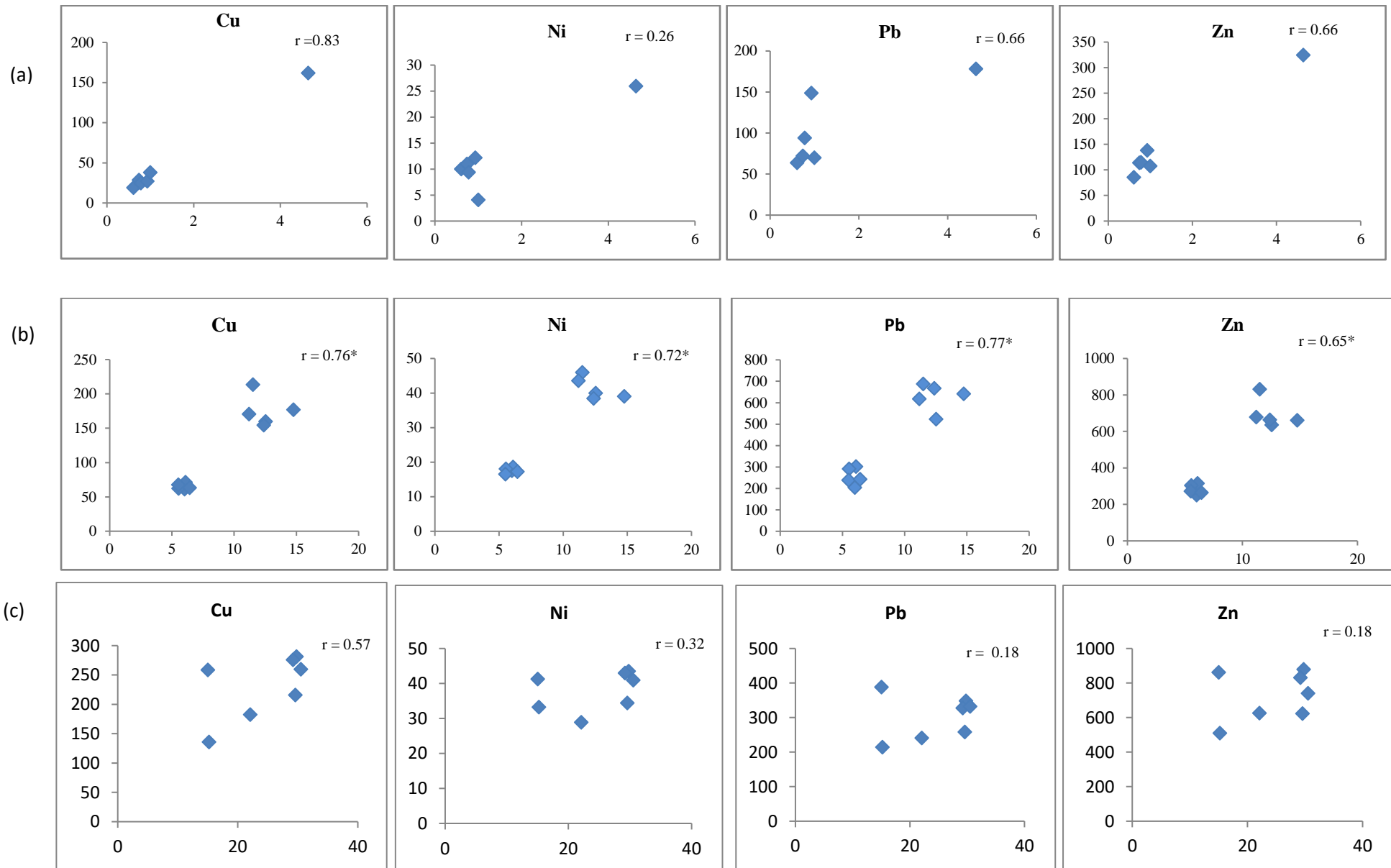


Figure 5 Relationship between SSA and total metal concentration (a) Cu, (b) Ni, (c) Pb, (d) Zn for the bed (n=16), bank (n=24) and suspended sediment (n=27) samples (<63 μm and 63 μm – 2 mm (n=10) (***) $p < 0.001$, ** $p < 0.01$, * $p < 0.05$). BB - bed sediment, BK - bank sediment, SS – suspended sediment



* $p < 0.05$

Figure 6 Spearman correlation coefficient for LOI (%) of (a) bed (n=6), (b) bank (n = 10), and (c) suspended sediment (n = 7) with trace metals

Electronic Supplementary Materials

Table ESM_1 Particle size analysis of the bed and bank sediment

Table ESM_2 Particle size analysis of the suspended sediment

Table ESM_3 Organic matter content determined by loss on ignition

Figure ESM_4 Concentration of cadmium, copper, nickel, lead and zinc in selected topsoil in the

Ravensbourne River catchment

Figure ESM_5 Temporal variation of metals in the bed, bank and suspended sediment

Trace metals distribution in the bed, bank and suspended sediment of the Ravensbourne River and its implication for sediment monitoring in an urban river

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Table ESM_1 Particle size analysis of the bed and bank sediment (n = 3)

Sample	Bed <63 µm		Bed 63 µm - 2 mm		Bank <63 µm		Bank 63 µm - 2 mm	
	SSA	D50 (µm)	SSA	D50 (µm)	SSA	D50 (µm)	SSA	D50 (µm)
Jan-11	a	a	a	a	1.26	10	0.71	100
Feb-11	a	a	a	a	0.91	16	0.21	191
Apr-11	0.34	37	0.09	466	1.31	9	0.25	174
May-11	1.12	11	0.08	333	1.16	10	0.44	133
Jun-11	0.18	221	0.02	483	0.84	19	0.19	177
Jul-11	0.55	127	0.04	438	1.01	14	0.24	168
Aug-11	0.71	22	0.26	190	1.02	18	0.24	145
Sep-11	a	a	0.06	505	1.09	14	0.25	185
Oct-11	a	a	0.06	266	1.08	11	1.08	130
Nov-11	a	a	0.05	403	1.14	12	0.98	131
Dec-11	a	a	0.02	570	0.40	53	0.16	178
May-12	0.36	60	0.02	635	1.30	10	0.26	157

a indicates where there was insufficient sample for analysis. SSA-specific surface area, D50- median particle size distribution. **Results in bold are storm samples**

Table ESM_2 Particle size analysis of the suspended sediment (n=3)

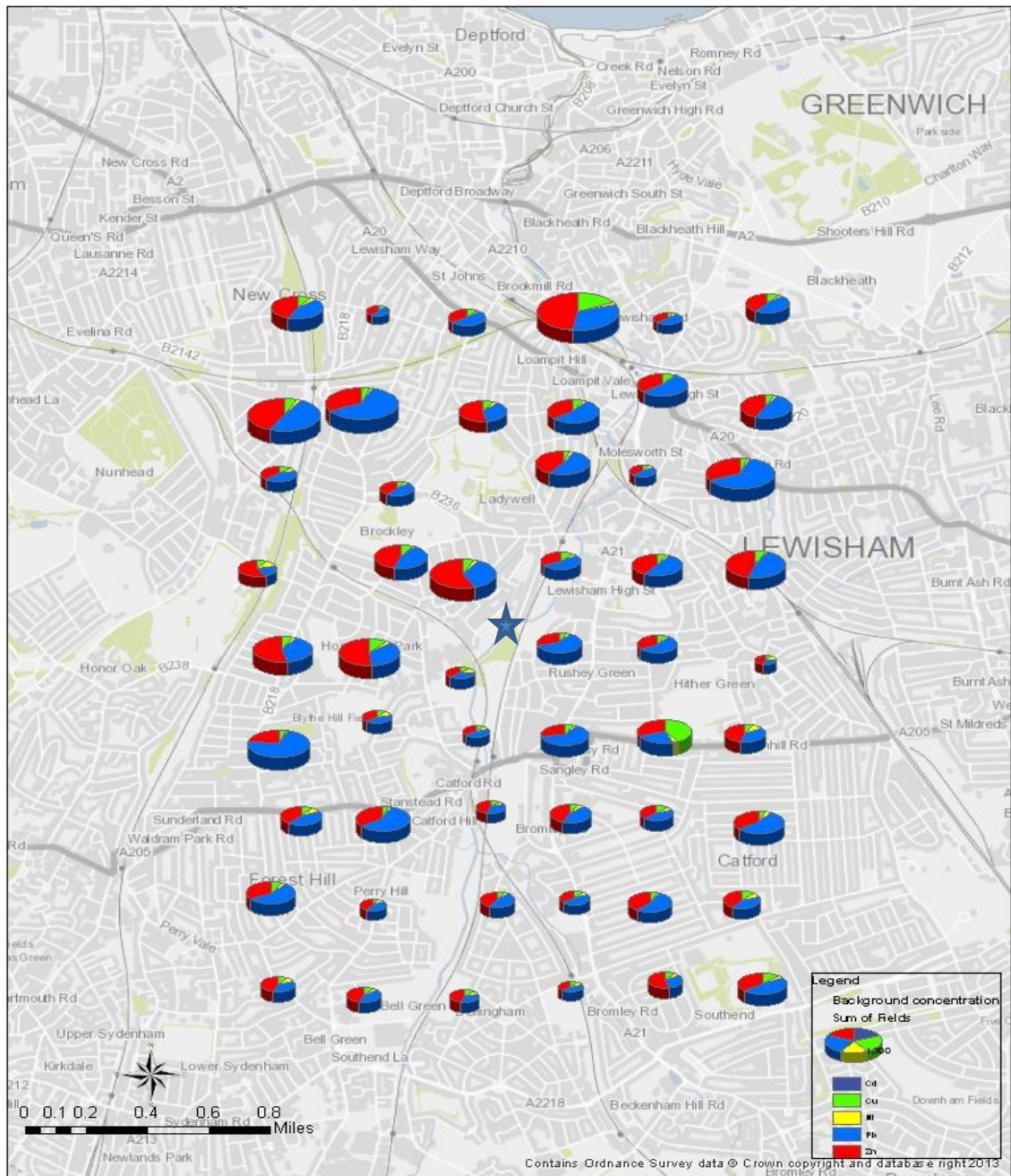
	LM1		LM2		RM1		RM2	
	SSA	D50 (µm)	SSA	D50 (µm)	SSA	D50 (µm)	SSA	D50 (µm)
Jan-11	0.83	17	a	a	0.74	22	0.65	27
Apr-11	0.99	16	0.41	77	0.54	38	a	a
May-11	1.01	12	a	a	a	a	0.63	31
Jun-11	a	a	a	a	0.53	36	0.68	27
Jul-11	0.83	17	1.13	11	0.69	23	a	a
May-12	0.58	33	0.64	27	0.72	25	1.01	14

a indicates where there was insufficient sample for analysis. LM - Left monthly suspended sampler RM - Right monthly suspended sampler, SSA-specific surface area, D50 - median particle size distribution. Results in bold are storm samples

Table ESM_3 Organic matter content determined by loss on ignition (±SD, n=2)

Season	Sample	Average LOI %
Winter (January)	Left monthly 1	22.1 ± 0.1
	63 µm - 2 mm bed	0.6 ± 0.0
	<63 µm bank	12.5 ± 0.2
	63 µm - 2 mm bank	6.0 ± 0.1
Spring (April)	Left monthly 1	15.2 ± 0.3
	63 µm - 2 mm bed	0.7 ± 0.0
	<63 µm April bank	14.8 ± 0.1
	63 µm-2 mm April bank	6.1 ± 0.2
Summer (July)	Left monthly 1	15.0 ± 0.1
	Bed 63 µm - 2 mm	0.8 ± 0.0
	Bank <63 µm	12.4 ± 0.2
	Bank 63 µm - 2 mm	5.5 ± 0.0
Autumn (October)	Bed 63 µm - 2 mm	0.9 ± 0.0
	Bank <63 µm	11.5 ± 0.2
	Bank 63 µm - 2 mm	5.5 ± 0.3
Storm (May 2012)	Left after storm 1 May 2012	29.6 ± 0.3
	Left after storm 2 May 2012	29.8 ± 0.2
	Right after storm 1 May 2012	29.2 ± 0.6
	Right after storm 2 May 2012	30.5 ± 0.2
	Bed <63 µm	4.6 ± 0.0
	Bed 63 µm - 2 mm May 2012	1.0 ± 0.1
	Bank <63 µm May 2012	11.2 ± 0.2
	Bank 63 µm - 2 mm May 2012	6.4 ± 0.2

Note: There was insufficient mass of the <63µm in most bed sediment samples and in the Left monthly 1 (LM1) October samples for organic matter analysis



(Data was obtained from British Geological Survey by personal communication 12/12/2012)

★ - Sampling location

Fig. ESM_4 Concentration of cadmium, copper, nickel, lead and zinc in selected top soil surrounding the Ravensbourne River

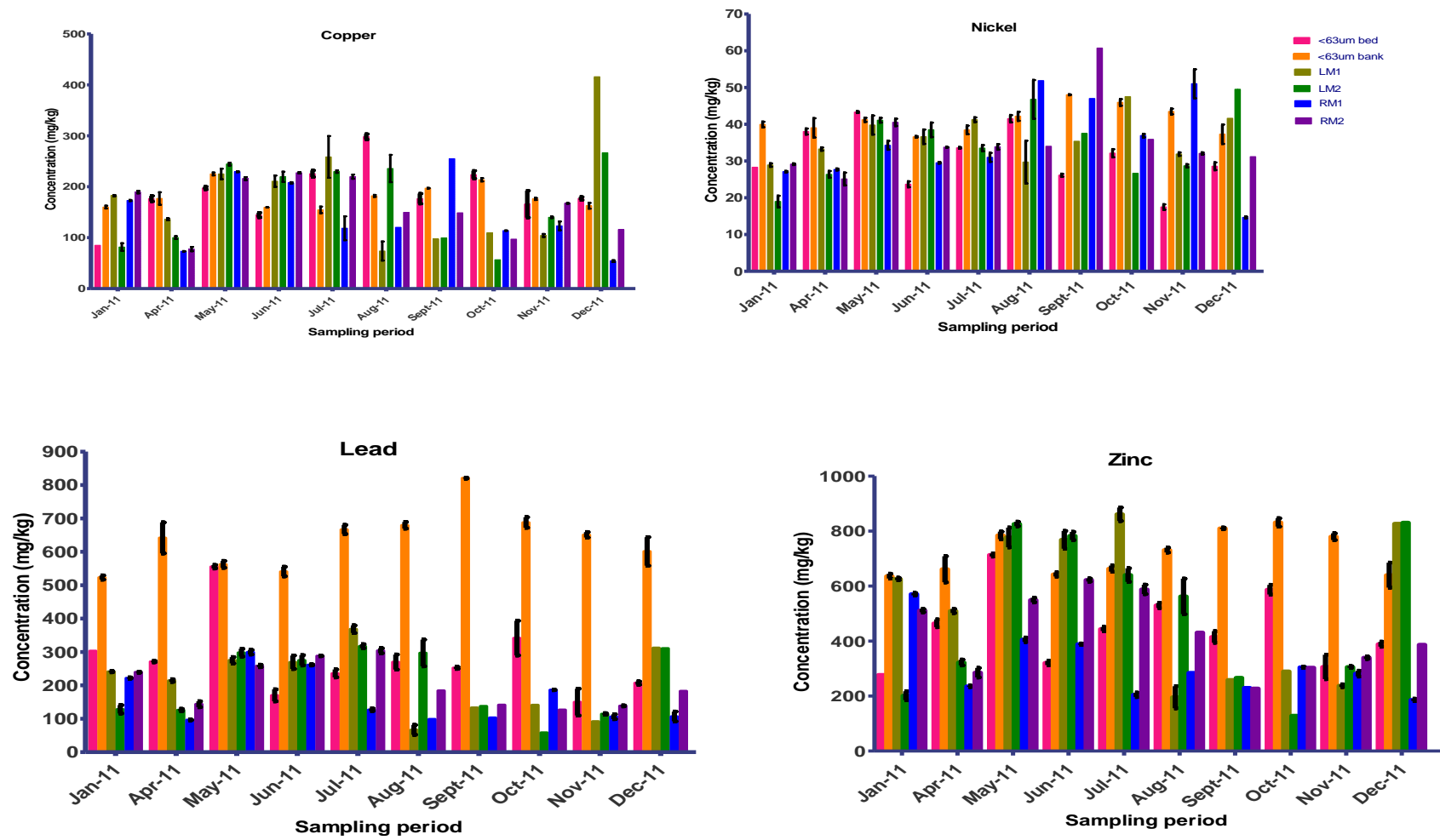


Fig. ESM_5 Temporal variation of metals in the bed, bank and suspended sediment