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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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

1 Introduction

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

River bed, bank and suspended sediment can all be potentially used to monitor sediment environmental quality. The question however is does it matter which sediment compartment (bed, bank and suspended sediment) is monitored for sediment quality monitoring, and are there significant differences in the physical and chemical characteristics of the bed, bank and suspended sediment sampled from the same river? Many studies have focused on metal concentrations in the bed sediment (Jain et al. 2005; Fok et al. 2012; Islam et al. 2015; Hurley et al. 2017), and / or in bed and suspended sediment (e.g. Jelodar et al. 2012; Kuusisto-Hjort and Hjort 2013; Nazeer et al. 2014), and / or the bed and bank sediment (Grosbois et al. 2012). In fact, the bed sediment is commonly used as a basis for monitoring trace metal concentrations in sediment and has been used in setting sediment quality guidelines (SQG)/ sediment quality standards (SQS) in countries such as Canada, Australia, Italy and the Netherlands (Burton 2002). The draft UK sediment quality guidelines are likely to be based on bed sediment (Hudson-Edwards et al. 2008). However, the Fraunhofer Institute (2002) suggested that suspended sediment should be measured and compared with environmental quality standards rather than bed or bank sediment because suspended sediment retains and transports new contaminants whilst the residence time of sediment in the river bed remains largely unknown. The Sediments in the Ravensbourne River are likely to retain historical contaminants from long-lasting English industrial activities and persistent secondary contamination 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 µm) (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; Schaider 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; Schaider 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 63µm - 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 km^2. 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 ºC 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 ºC 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 HNO_3 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 ℃ for 10 minutes, 80 ℃ for 10 minutes, 100 ℃ for 10 minutes and

217   160 ℃ 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 Matersize 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^{-}

232   ^{3}, 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 d50

238   (the median particle size distribution), and $m^2 g^{-1}$ 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 t h e percentage loss after

243   ignition (Donkin 1991; Heiri et al. 2001; Schumacher 2002). Porcelain crucibles were heated in a Griffin furnace

244   at 550 ℃ for 20 minutes to completely remove moisture. The crucibles were allowed to cool in desiccators.

245   Approximately 1.5 g of sediment was t h e n placed i n t o 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 ℃

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 ℃ for 12 hours, allowed to cool and weighed (B). The loss on ignition (LOI %)

249   was calculated using the equation:

250

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

252

253   A = weight of crucible + sample after 105 ℃ for 12 hours
254   B = weight of crucible + sample after 450 ℃ 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 behanate (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 m^2 g^{-1} compared to the bed (1.12 m^2 g^{-1}) and

312 suspended sediment (1.02 m^2 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 µm for sediment monitoring would favour the use of bank sediments because collecting sufficient

315 <63 µm 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 µm - 2 mm fraction for sediment

317 monitoring will tend to omit the significant contribution of heavy metals from the <63 µm 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 µm fraction (Rodrigues

320 and Formoso 2006; Simpson et al. 2011) and the <2 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 µm 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 µm and 63 µm – 2 mm sediment fraction, respectively. Generally, the <63 µm particle

329 fraction mirrored higher organic matter content compared to the 63 µm – 2 mm fraction. Organic matter content

330 ranged from 0.6% (63 µm - 2 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 (Schaider 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%), Mucovite (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. Clinochlore (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   Frančišković-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 $m^2\ g^{-1}$

366   compared to the bed (1.12 $m^2\,g^{-1}$) and suspended sediment (1.02 m^2 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 μm 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 μm. 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 μm fraction) and the

401   suspended sediment samples (Table 3). This however differs significantly with the 63 μm – 2 mm bed sediment

402   fractions. It may be useful when designing a sampling programme for sediment monitoring using the <2 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 μm

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

3.5 Variations in metal concentrations in the integrated tube samplers

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

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

Storms affect sediment characteristics for quality monitoring. Storm events reportedly increase the transportation of sediment and remobilization of trace metals in an urban river system (Smith et al. 2003; Palanques et al. 2006; Horowitz et al. 2008; Barałkiewicz et al. 2014; Ramos et al. 2015; Ciszewski and Grygar 2016). In historically polluted rivers, storms may enhance pollutant fluxes; however, in rivers polluted rather recently the storms may have the opposite impact. The effects of a storm on the concentration of metals in all sediment compartments varied in this study (Table 4). The results indicated Cd was enriched in both suspended and bank sediment. This might imply 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 µm 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 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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543   **References**

544   Allen TA (1990) Particle size measurement, Chapman and Hall, London

545   Alves RIS, Sampaio CF, Nadal M, Schuhmacher M, Domingo JL, Segura-Muñoz SI (2014) Metal concentrations

546   in surface water and sediments from Pardo River, Brazil: human health risks. Environ Res 133:149-155

547   Atibu EK, Devarajan N, Thevenon F, Mwanamoki PM, Tshibanda JB, Mpiana PT, Prabakar K, Mubedi JI, Wildi

548   W, Poté J (2013) Concentration of metals in surface water and sediment of Luilu and Musonoie Rivers,

549   Kolwezi-Katanga, Democratic Republic of Congo. Appl Geochem 39:26-32

550   Bábek O, Grygar TM, Faměra M, Hron K, Nováková T, Sedláček J (2015) Geochemical background in polluted

551   river sediments: How to separate the effects of sediment provenance and grain size with statistical rigour?

552   Catena 135:240-253

553   Barałkiewicz D, Chudzińska M, Szpakowska B, Świerk D, Gołdyn R, Dondajewska R (2014) Storm water

554   contamination and its effect on the quality of urban surface waters. Environ Monit Assess 186:6789-6803

555   Bartoli G, Papa S, Sagnella E, Fioretto A (2012) Heavy metal content in sediments along the Calore river:

556   relationships with physical–chemical characteristics. J of Environ Manage 95:S9-S14

557   Barton N (1992) The lost rivers of London: a study of their effects upon London and Londoners, and the effects of

558   London and Londoners upon them, Historical Publications Ltd London

559   Bilotta GS, Brazier RE (2008) Understanding the Influence of suspended solids on water quality and aquatic biota.

560   Water Res 42:2849-2861

561   Blott SJ, Pye K (2006) Particle size distribution analysis of sand-sized particles by laser diffraction: an experimental

562   investigation of instrument sensitivity and the effects of particle shape. Sedimentology 53:671-685

563   Bonnail E, Sarmiento AM, DelValls TÁ (2016) The use of a weight-of-evidence approach to address sediment

564   quality in the Odiel River basin (SW, Spain). Ecotoxicol and Environ Saf 133:243-251

565   Burton Jr GA (2002) Sediment quality criteria in use around the world. Limnology 3:65-76

566   Charriau A, Lesven L, Gao Y, Leermakers M, Baeyens W, Ouddane B, Billon G (2011) Trace metal behaviour in

567   riverine sediments: role of organic matter and sulfides. Appl Geochem 26:80-90

568   Chen EH (1971) The power of the Shapiro-Wilk W test for normality in samples from contaminated normal

569   distributions. J Am Stat Assoc 66:760-762

570   Chen Y-M, Gao J-b, Yuan Y-Q, Ma J, Yu S (2016) Relationship between heavy metal contents and clay mineral

571   properties in surface sediments: implications for metal pollution assessment. Cont Shelf Res 124:125 -

572   133

573   Ciszewski D, Grygar TM (2016) A review of flood-related storage and remobilization of heavy metal pollutants in

574   river systems. Water Air Soil Pollut 227:1-19

575   Copas R (1997) The river landscapes of London and the Thames catchment: their status and future. Landsc Res

576   22:115-131

577   Counihan TD, Waite IR, Nilsen EB, Hardiman JM, Elias E, Gelfenbaum G and Zaugg SD (2014) A survey of

578   benthic sediment contaminants in reaches of the Columbia River Estuary based on channel sedimentation

579   characteristics. Sci Total Environ 484:331-343

580   Couture R, Hindarc A, Rognerudd S (2018) Emerging investigator series: geochemistry of trace elements associated

581   with Fe and Mn nodules in the sediment of limed boreal lakes. Environ Sci: Processes Impacts 20:406-414

582   Crane M (2003) Proposed development of sediment quality guidelines under the European Water Framework

583   Directive: a critique. Toxicol Lett 142:195-206

584   Davide V, Pardos M, Diserens J, Ugazio G, Thomas R, Dominik J (2003) Characterisation of bed sediments and

585   suspension of the river Po (Italy) during normal and high flow conditions. Water Res 37:2847-2864

586   Dawson E, Macklin M (1998) Speciation of heavy metals on suspended sediment under high flow conditions in the

587   River Aire, West Yorkshire, UK. Hydrol Process 12:1483-1494

588   Dean WE (1974) Determination of carbonate and organic Matter in calcareous sediments and sedimentary rocks by

589   loss on ignition; comparison with other methods. J Sediment Petrol 44:242-248

590   Di Stefano C, Ferro V, Mirabile S (2010) Comparison between grain-size analyses using laser diffraction and

591   sedimentation methods. Biosyst Eng 106:205-215

592   Donkin MJ (1991) Loss on Ignition as an estimator of soil organic carbon in a Horizon Forestry soils. Commun Soil

593   Sci Plant Anal 22:233-241

594   Environment Agency (2006) The determination of metals in solid environmental samples: methods for the

595   examination of waters and associated materials, in National Laboratory Service p 100, Standing

596   Committee of Analysts, Leicestershire

597   Environment Agency (2016) M18 - Monitoring of discharges to water and sewer. Technical guidance note

598   Field A (2001) Discovering statistics using SPSS for Windows, The Cromwell Press Ltd, Great Britain

599   Fok L, Peart MR, Chen J (2012) The influence of geology and land use on the geochemical baselines of the East

600   River basin, China. Catena 101:212-225

601   Frančišković-Bilinski S, Cukrov N (2014) A critical evaluation of using bulk sediment instead of fine fraction in

602   environmental marine studies, investigated on example of Rijeka harbor, Croatia. Environ Earth Sci

603   71:341-356

604   Fraunhofer Institute (2002) Towards the derivation of quality standards for priority substances in the context of the

605   Water Framework Directive:final report of the study: identification of quality standards for priority

606   substances in the field of water policy. EAF(3)-06/06/FHI. Fraunhofer-Institute environmental chemistry

607   and ecotoxicology, Germany

608   Gasperi J, Garnaud S, Rocher V, Moilleron R (2009) Priority pollutants in surface waters and settleable particles

609   within a densely urbanised area: case study of Paris (France). Sci Total Environ 407:2900-2908

610   Gellis A, Noe G (2013) Sediment source analysis in the Linganore Creek watershed, Maryland, USA, using the

611   sediment fingerprinting approach: 2008 to 2010. J Soils Sediments 13:1735-1753

612   Gilbert B, Ono RK, Ching KA, Kim CS (2009) The effects of nanoparticle aggregation processes on aggregate

613   structure and metal uptake. J Colloid Interface Sci 339:285-295

614   Gray AB, Pasternack GB, Watson EB (2010) Hydrogen peroxide treatment effects on the particle size distribution

615   of alluvial and marsh sediments. Holocene 20: 293–301

616   Grosbois C, Meybeck M, Lestel L, Lefèvre I, Moatar F (2012) Severe and contrasted polymetallic contamination

617   patterns (1900–2009) in the Loire River sediments (France). Sci Total Environ 435–436:290-305

618   Han C, Qin Y, Zheng B, Ma Y, Zhang L, Cao W (2014) Sediment quality assessment for heavy metal pollution in

619   the Xiangjiang River (China) with the equilibrium partitioning approach. Environ Earth Sci 72:5007-5018

620   He C, Bartholdy J, Christiansen C (2012) Clay mineralogy, grain size distribution and their correlations with trace

621   metals in the salt marsh sediments of the Skallingen barrier spit, Danish Wadden Sea. Environ Earth Sci

622   67:759-769

623   Hedrick LB, Anderson JT, Welsh SA, Lin L-S (2013) Sedimentation in mountain streams: a review of methods of

624   measurement. Nat Resour J 4: 92-104

625   Heiri O, Lotter A, Lemcke G (2001) Loss on ignition as a method for estimating organic and carbonate content in

626   sediments: reproducibility and comparability of results. J Paleolimnol 25:101-110

627   Helios Rybicka E, Calmano W, Breeger A (1995) Heavy metals sorption/desorption on competing clay minerals; an

628   experimental study. Appl Clay Sci 9:369-381

629   Ho HH, Swennen R, Cappuyns V, Vassilieva E, Van Gerven T, Van Tran T (2012) Potential release of selected

630   trace elements (As, Cd, Cu, Mn, Pb and Zn) from sediments in Cam River-mouth (Vietnam) under

631   influence of pH and oxidation. Sci Total Environ 435:487-498

632   Holcombe G (2009) Certificate of measurement - river sediment certified reference material LGC 6187. Middlesex,

633   UK

634   Horowitz AJ (1991) A primer on sediment-trace element chemistry, CRC Press; 2 edition (April 23, 1991), USA

635   Horowitz AJ (1995) The use of suspended sediment and associated trace elements in water quality studies,

636   International Association of Hydrological Sciences, Oxfordshire, UK

637   Horowitz AJ (2003) An evaluation of sediment rating curves for estimating suspended sediment concentrations for

638   subsequent flux calculations. Hydrol Process 17:3387-3409

639 Horowitz AJ, Elrick KA, Smith JJ (2008) Monitoring urban impacts on suspended sediment, trace element, and
640   nutrient fluxes within the City of Atlanta, Georgia, USA: program design, methodological considerations,
641   and initial results. Hydrol Process 22:1473-1496

642 Hudson-Edwards KA, Macklin MG, Brewer PA, Dennis IA (2008) Assessment of metal mining-contaminated river
643   sediments in England and Wales (science report: SC030136/SR4). Environment Agency, Bristol

644 Hurley RR, Rothwell JJ, Woodward JC (2017) Metal contamination of bed sediments in the Irwell and Upper
645   Mersey catchments, northwest England: exploring the legacy of industry and urban growth. J Soils
646   Sediments 17: 2648–2665

647 International Atomic Energy Agency (IAEA) (2003) Collection and preparation of bottom sediment samples for
648   analysis of radionuclides and trace elements (IAEA-TECDOC-1360), IAEA, Vienna, Austria

649 Islam MS, Ahmed MK, Raknuzzaman M, Habibullah -Al- Mamun M, Islam MK (2015) Heavy metal pollution in
650   surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecol Indic
651   48:282-291

652 Jain CK, Singhal DC, Sharma MK (2005) Metal pollution assessment of sediment and water in the River Hindon,
653   India. Environ Monit Assess 105:193-207

654 Jelodar AH, Rad HA, Navaiynia B, Zazouli M (2012) Heavy metal ions adsorption by suspended particle and
655   sediment of the Chalus River, Iran. Afr J Biotechnol 11:628-634

656 Juracek K, Ziegler A (2009) Estimation of sediment sources using selected chemical tracers in the Perry Lake
657   Basin, Kansas, USA. Int. J. Sediment Res. 24:108-125

658 Karlsson K, Viklander M, Scholes L, Revitt M (2010) Heavy metal concentrations and toxicity in water and
659   sediment from stormwater ponds and sedimentation tanks. J Hazard Mater 178:612-618

660 Kellagher R (2012) Flood and coastal defence R&D programme, in preliminary rainfall runoff management for
661   developments R&D technical report W5-074/A/TR/1 Revision D, Environment Agency, Bristol, London

662 Kim Y, Kim K, Kang H-D, Kim W, Doh S-H, Kim D-S, Kim B-K (2007) The accumulation of radiocesium in
663   coarse marine sediment: Effects of mineralogy and organic matter. Mar Pollut Bull 54:1341-1350

664 Knight C (1842) The journey-book of England- Kent with fifty-eight engravings on wood, and an illuminated map
665   of the county, William Clowes and sons, London

666 Konert M, Vandenberghe JEF (1997) Comparison of laser grain size analysis with pipette and sieve analysis: a
667   solution for the underestimation of the clay fraction. Sedimentology 44:523-535

668 Kuusisto-Hjort P, Hjort J (2013) Land use impacts on trace metal concentrations of suburban stream sediments in
669   the Helsinki region, Finland. Sci Total Environ 456–457:222-230

670 Lee S, Moon J-W, Moon H-S (2003) Heavy metals in the bed and suspended sediments of Anyang River, Korea:
671   implications for water quality. Environ Geochem Health 25:433-452

672   Lewisham Council and Environment Agency (2010) Ravensbourne River corridor improvement plan, London

673   Li Y, Wang XL, Huang GH, Zhang BY, Guo SH (2009) Adsorption of Cu and Zn onto Mn/Fe oxides and organic

674   materials in the extractable fractions of river surficial sediments. Soil Sediment Contam 18:87–101

675   Lin JG, Chen SY, Su CR (2003) Assessment of sediment toxicity by metal speciation in different particle-size

676   fractions of river sediment. Water Sci Technol 47:233-241

677   Liu B, Hu K, Jiang Z, Yang J, Luo X, Liu A (2011) Distribution and enrichment of heavy metals in a sediment core

678   from the Pearl River Estuary. Environ Earth Sci 62:265-275

679   Liu C, Xu J, Liu C, Zhang P, Dai M (2009) Heavy metals in the surface sediments in Lanzhou Reach of Yellow

680   River, China. Bull Environ Contam Toxicol 82:26-30

681   Luoma S, Rainbow P (2008) Metal contamination in aquatic environment. science and lateral management,

682   Cambridge University Press, United Kingdom

683   Maity S, Sahu S, Pandit G (2016) Determination of heavy metals and their distribution in different size fractionated

684   sediment samples using different analytical techniques. Soil Sediment Contam 25:332-345

685   Matys Grygar T, Nováková T, Bábek O, Elznicová J, Vadinová N (2013) Robust assessment of moderate heavy

686   metal contamination levels in floodplain sediments: A case study on the Jizera River, Czech Republic. Sci

687   Total Environ 452-453:233-245

688   Matys Grygar T, Popelka J (2016) Revisiting geochemical methods of distinguishing natural concentrations and

689   pollution by risk elements in fluvial sediments. J Geochem Explor 170:39-57

690   McCartney S, West J (1998) The Lewisham silk mills and the history of an ancient site, Lewisham Local History

691   Society, in association with Greater London Industrial Archaeology Society, London

692   McDonald DM, Lamoureux SF, Warburton J (2010) Assessment of a time-Integrated fluvial suspended sediment

693   sampler in a high arctic setting. Geogr Ann Ser A 92:225-235

694   McKenzie ER, Money JE, Green PG, Young TM (2009) Metals associated with stormwater-relevant brake and tire

695   samples. Sci Total Environ 407:5855

696   Mudroch A, Azcue JM (1995) Manual of aquatic sediment sampling., CRC/Lewis, Boca Raton, Florida

697   Mudroch A, MacKnight SD (1994) Handbook of techniques for aquatic sediment sampling, 2nd edition, CRC

698   Press, Boca Raton, Florida

699   Nazeer S, Hashmi MZ, Malik RN (2014) Heavy metals distribution, risk assessment and water quality

700   characterization by water quality index of the River Soan, Pakistan. Ecol Indic 43:262-270

701   O'Connor TP (2004) The sediment quality guideline, ERL, is not a chemical concentration at the threshold of

702   sediment toxicity. Mar Pollut Bull 49:383-385

703   Palanques A, de Madron XD, Puig P, Fabres J, Guillén J, Calafat A, Canals M, Heussner S, Bonnin J (2006)

704   Suspended sediment fluxes and transport processes in the Gulf of Lions submarine canyons. The role of

705   storms and dense water cascading. Mar Geol 234:43-61

706   Palleiro L, Patinha C, Rodríguez-Blanco ML, Taboada-Castro MM, Taboada-Castro MT (2016) Metal fractionation

707   in topsoils and bed sediments in the Mero River rural basin: bioavailability and relationship with soil and

708   sediment properties. Catena 144:34-44

709   Palma P, Ledo L, Alvarenga P (2015) Assessment of trace element pollution and its environmental risk to

710   freshwater sediments influenced by anthropogenic contributions: The case study of Alqueva reservoir

711   (Guadiana Basin). Catena 128:174-184

712   Palmer M (1984) Manual for bottom sediment sample collection, in Surveillance and Research, U.S Environmental

713   Protection Agency, Chicago, Illinois

714   Perks M, Warburton J, Bracken L, Reaney S, Emery S, Hirst S (2017) Use of spatially distributed time-integrated

715   sediment sampling networks and distributed fine sediment modelling to inform catchment management. J

716   Environ Manage 202: 469-478

717   Phillips JM, Russell MA, Walling DE (2000) Time-integrated sampling of fluvial suspended sediment: a simple

718   methodology for small catchments. Hydrol Process 14:2589-2602

719   Plathe K (2010) Nanoparticle - Heavy metal associations in river sediments, in Geosciences p 116, Virginia

720   Polytechnic Institute and State University, Blacksburg, VA

721   Polakowski C, Sochan A, Bieganowski A, Ryzak M, Földényi R, Tóth J (2014) Influence of the sand particle shape

722   on particle size distribution measured by laser diffraction method. Int Agrophys 28:195-200

723   Quek U, Förster J (1993) Trace metals in roof run-off. Water Air Soil Pollut 68:373-389

724   Quevauviller P (1998) Operationally defined extraction procedures for soil and sediment analysis I. standardization.

725   Trends Analyt Chem 17:289-298

726   Ramos TB, Gonçalves MC, Branco MA, Brito D, Rodrigues S, Sánchez-Pérez J-M, Sauvage S, Prazeres Â, Martins

727   JC, Fernandes ML, Pires FP (2015) Sediment and nutrient dynamics during storm events in the Enxoé

728   temporary river, southern Portugal. Catena 127:177-190

729   Rasmussen C, Dalsgaard K (2017) Documentation of tests on particle size methodologies for laser diffraction

730   compared to traditional sieving and sedimentation analysis. Department of Geoscience, Aarhus University.

731   Aarhus Universitetsforlag, Denmark

732   Rodrigues M, Formoso M (2006) Geochemical distribution of selected heavy metals in stream sediments affected

733   by tannery activities. Water Air Soil Pollut 169:167-184

734   Roig N, Sierra J, Moreno-Garrido I, Nieto E, Gallego EP, Schuhmacher M, Blasco J (2016) Metal bioavailability in
735   freshwater sediment samples and their influence on ecological status of river basins. Sci Total Environ
736   540:287-296

737   Rotman R, Naylor L, McDonnell R, MacNiocaill C (2008) Sediment transport on the Freiston Shore managed
738   realignment site: an investigation using environmental magnetism. Geomorphology 100:241-255

739   Russell MA, Walling DE, Hodgkinson RA (2000) Apprisal of a simple sampling device for collecting time-
740   integrated fluvial suspended sediment samples, in The role of erosion and sediment transport in nutrient
741   and contaminant transfer (proceedings of a symposium) IAHS Publ no 263, 2000 (Stone M ed) pp 119-
742   127, IAHS Press, Wallingford, UK

743   Santisteban J, Mediavilla R, López-Pamo E, Dabrio C, Zapata MB, García MJ, Castaño S, Martínez-Alfaro P
744   (2004) Loss on ignition: a qualitative or quantitative method for organic matter and carbonate mineral
745   content in sediments? J Paleolimnol 32:287-299

746   Schaider LA, Senn DB, Estes ER, Brabander DJ, Shine JP (2014) Sources and fates of heavy metals in a mining-
747   impacted stream: temporal variability and the role of iron oxides. Sci Total Environ 490:456-466

748   Schumacher B (2002) Methods for the determination of total organic carbon (TOC) in soils and sediments, pp 1-
749   25, Ecological Risk Assesment Division, Office of Research and Development. U.S Enviromental
750   Protection Agency, Las Vegas

751   Sekabira K, Origa HO, Basamba T, Mutumba G, Kakudidi E (2010) Assessment of heavy metal pollution in the
752   urban stream sediments and its tributaries. Int J Environ Sci Technol (Tehran) 7:435-446

753   Simpson SL, Batley GE, Chariton AA, Stauber JL, King CK, Chapman JC, Hyne RV, Gale SA, Roach AC, Maher
754   WA (2005) Handbook for sediment quality assessment, Centre for Environment Contaminants Research,
755   CSIRO Energy Technology, Lucas Heights, Sydney

756   Simpson SL, Batley GE, Hamilton IL, Spadaro DA (2011) Guidelines for copper in sediments with varying
757   properties. Chemosphere 85:1487-1495

758   Smith BPG, Naden PS, Leeks GJL, Wass PD (2003) The influence of storm events on fine sediment transport,
759   erosion and deposition within a reach of the River Swale, Yorkshire, UK. Sci Total Environ 314–316:451-
760   474

761   Sperazza M, Moore JN, Hendrix MS (2004) High-resolution particle size analysis of naturally occurring very fine-
762   grained sediment through laser diffractometry. J Sediment Res 74:736-743

763   Swapp S (2013) Geochemical instrumentation and analysis: scanning electron microscopy (SEM), Univesity of
764   Wyoming

765   Talling P (2011) London's lesser known rivers - Ravensbourne, in London's lost rivers, Random House Books,
766   London

767   Taylor K, Owens P (2009) Sediments in urban river basins: a review of sediment–contaminant dynamics in an
768   environmental system conditioned by human activities. J Soils Sediments 9:281-303

769   Tessier A, Campbell PGC, Bisson M (1979) Sequentail extraction procedure for the speciation of particulate trace
770   metals. Anal Chem 51:844-850

771   Theuring P, Rode M, Behrens S, Kirchner G, Jha A (2013) Identification of fluvial sediment sources in the Kharaa
772   River catchment, Northern Mongolia. Hydrol Process 27:845-856

773   Tiquio MGJ, Hurel C, Marmier N, Taneez M, Andral B, Jordan N, Francour P (2017) Sediment-bound trace metals
774   in Golfe-Juan Bay, northwestern Mediterranean: Distribution, availability and toxicity. Mar Pollut Bull
775   118:427-436

776   United Nations Environment Programme (2006) Methods for sediment sampling and analysis (Mediterranean
777   action plan), in Review Meeting of MED POL - Phase III Monitoring Activities, Palermo (Sicily) Italy

778   United States Environmental Protection Agency (USEPA) (2001) Methods for collection, storage and manipulation
779   of sediments for chemical and toxicological analyses: technical manual EPA 823-B-01-002, U.S.
780   Environmental Protection Agency, Office of Water, Washington, DC

781   Vega FA, Covelo EF, Andrade ML, Marcet P (2004) Relationships between heavy metals content and soil
782   properties in minesoils. Anal Chim Acta 524:141-150

783   Wang X, Li Y (2011) Measurement of Cu and Zn adsorption onto surficial sediment components: New evidence for
784   less importance of clay minerals. J Hazard Mater 189:719-723

785   Weaver C (1956) A discussion on the origin of clay minerals in sedimentary rocks. Clays Clay Miner 5:159-173

786   Yao Q, Wang X, Jian H, Chen H, Yu Z (2015) Characterization of the particle size fraction associated with heavy
787   metals in suspended sediments of the Yellow River. Int J Environ Res Public Health 12:6725

788   Yutong Z, Qing X, Shenggao L (2016) Distribution, bioavailability, and leachability of heavy metals in soil particle
789   size fractions of urban soils (northeastern China). Environ Sci Pollut Res Int 23:14600-14607

790   Zafra C, Temprano J, Tejero I (2011) Distribution of the concentration of heavy metals associated with the
791   sediment particles accumulated on road surfaces. Environ Technol 23:997-1008

792   Zhang G, Yang X, Liu Y, Jia Y, Yu G, Ouyang S (2004) Copper(II) adsorption on Ca-rectorite, and effect of static
793   magnetic field on the adsorption. J Colloid Interface Sci 278:265-269

794   Zhao H, Li X, Wang X, Tian D (2010) Grain size distribution of road-deposited sediment and its contribution to
795   heavy metal pollution in urban runoff in Beijing, China. J Hazard Mater 183:203-210

796   Zhou X, Li A, Jiang F, Lu J (2015) Effects of grain size distribution on mineralogical and chemical compositions: a
797   case study from size-fractional sediments of the Huanghe (Yellow River) and Changjiang (Yangtze River).
798   Geol J 50:414-433

799 **Tables**

800 **Table 1 The average (± 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 µm	2.0 ± 1.3	187.0 ± 55.9	31.3 ± 8.1	275.0 ± 114.0	444.0 ± 136.0
	63 µm - 2 mm	0.8 ± 0.2	30.3 ± 1.9	10.6 ± 1.9	85.0 ± 55.0	127.0 ± 33.4
Bank	<63 µm	4.6 ± 1.3	180.7 ± 24.2	41.2 ± 3.8	637.0 ± 87.0	718.0 ± 77.8
	63 µm - 2 mm	2.1 ± 0.7	67.0 ± 8.5	17.2 ± 1.2	259.0 ± 33.9	293.6 ± 26.7
Suspended	LM1	2.7 ± 1.8	181.0 ± 103.0	36.6 ± 5.9	211.0 ± 99.7	535.0 ± 269.0
	LM2	2.9 ± 1.9	167.0 ± 79.3	34.8 ± 9.7	206.0 ± 101.0	487.0 ± 272.0
	RM1	2.3 ± 1.4	147.0 ± 66.8	35.1 ± 11.9	161.0 ± 76.1	309.0 ± 117.0
	RM2	2.6 ± 1.7	160.0 ± 52.9	35.6 ± 9.7	201.0 ± 66.5	424.0 ± 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 ± 0.2	80.8 ± 11.4	32.3 ± 3.7	771.0 ± 5.3	428.4 ± 52.4
Certified recovery (%)		91.5	96.6	93.2	91.9	97.6

802 (Source for sediment quality guidelines: Hudson-Edwards *et al*., 2008)
803 **a** TEL: Threshold effect level; draft freshwater sediment quality guidelines, **b** PEL: Probable effects level ; draft freshwater sediment quality
804 **c** Source from the British Geological Survey (Personal Communication)
805
806 **Table 2 The percentage phase proportion of minerals in July 2011 and May 2012 (storm) samples (n=2)**
807

July 2011	Quartz, %	Illite-Smectite, %	Muscovite, %	Clinochlore, %	Calcite, %	Kaolinite, %	Dolomite, %	Goethite, %
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 µm	48.1	39.2	4.8	1.4	4.5	1.4	0.4	0.2
Bed 63 µm- 2 mm	82.4	9.4	4.4	1.3	1.1	1.3	0.0	0.2
Bank <63 µm	34.5	51.2	5.1	1.5	3.6	2.9	0.9	0.2
Bank 63 µm- 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 µm	41.1	36.6	13.3	2.8	2.2	2.7	0.9	0.4
Bed 63 µm- 2 mm	62.1	23.4	1.8	0.3	1.6	2.5	8.0	0.4
Bank <63 µm	39.3	44.7	6.1	3.0	3.0	2.9	0.6	0.5
Bank 63 µm- 2 mm	68.4	20.2	1.8	2.6	1.3	2.5	3.2	0.0

808 (See figure 2 for tube sampler deployment).

Table 3 The Kruskal-Wallis test (two-way ANOVA using the Bonferroni method) for metal concentration

811   **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).

Table 4 The mean (± 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 µm bed	<	161.9 ± 7.9	26.0 ± 1.4	178.4 ± 6.9	324.7 ± 6.7
63 µm - 2 mm bed	<	38.1 ± 14.5	12.3 ± 0.0	70.0 ± 14.3	108.0 ± 12.0
<63 µm bank	33.8 ± 0.8	170.8 ± 2.7	43.6 ± 1.0	617.3 ± 6.9	679.4 ± 5.8
63 µm - 2 mm bank	13.8 ± 0.5	63.3 ± 2.1	17.2 ± 1.3	243.0 ± 4.5	265.3 ± 1.7
LM1	15.2 ± 1.6	215.9 ± 19.6	34.5 ± 3.5	257.9 ± 25.2	623.7 ± 56.8
LM2	20.1 ± 0.6	281.4 ± 4.3	43.5 ± 0.5	348.2 ± 3.1	879.0 ± 8.6
RM1	20.8 ± 0.6	275.9 ± 6.3	43.0 ± 1.1	327.4 ± 6.0	830.7 ± 7.7
RM2	19.2 ± 2.1	260.0 ± 3.4	40.9 ± 0.8	332.1 ± 2.3	740.3 ± 7.4

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

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
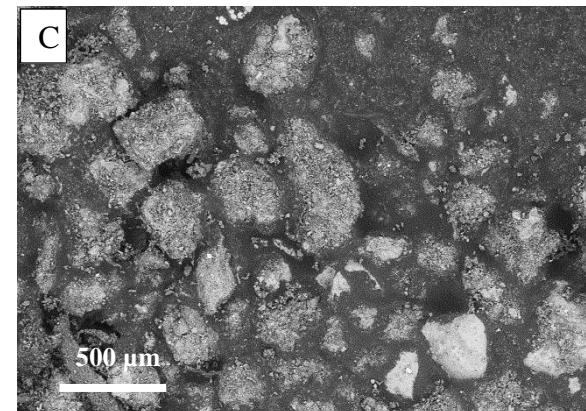
Figure 2 Layout of the time integrated suspended sediment tube samplers placed on opposite sides of the Ravensbourne River
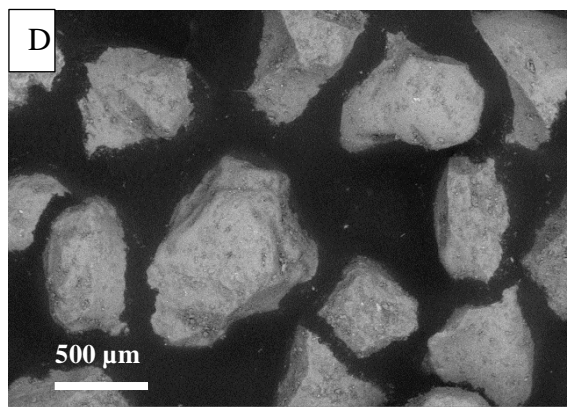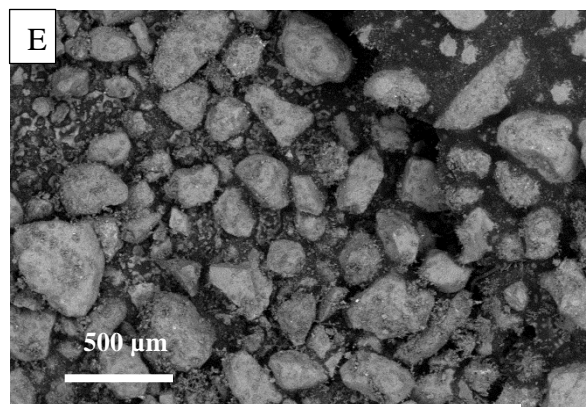
Bed 63 µm - 2 mm January 2011
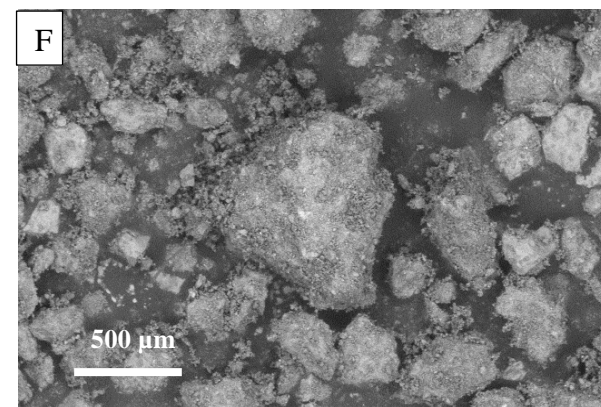
Bank 63 µm - 2 mm January 2011

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
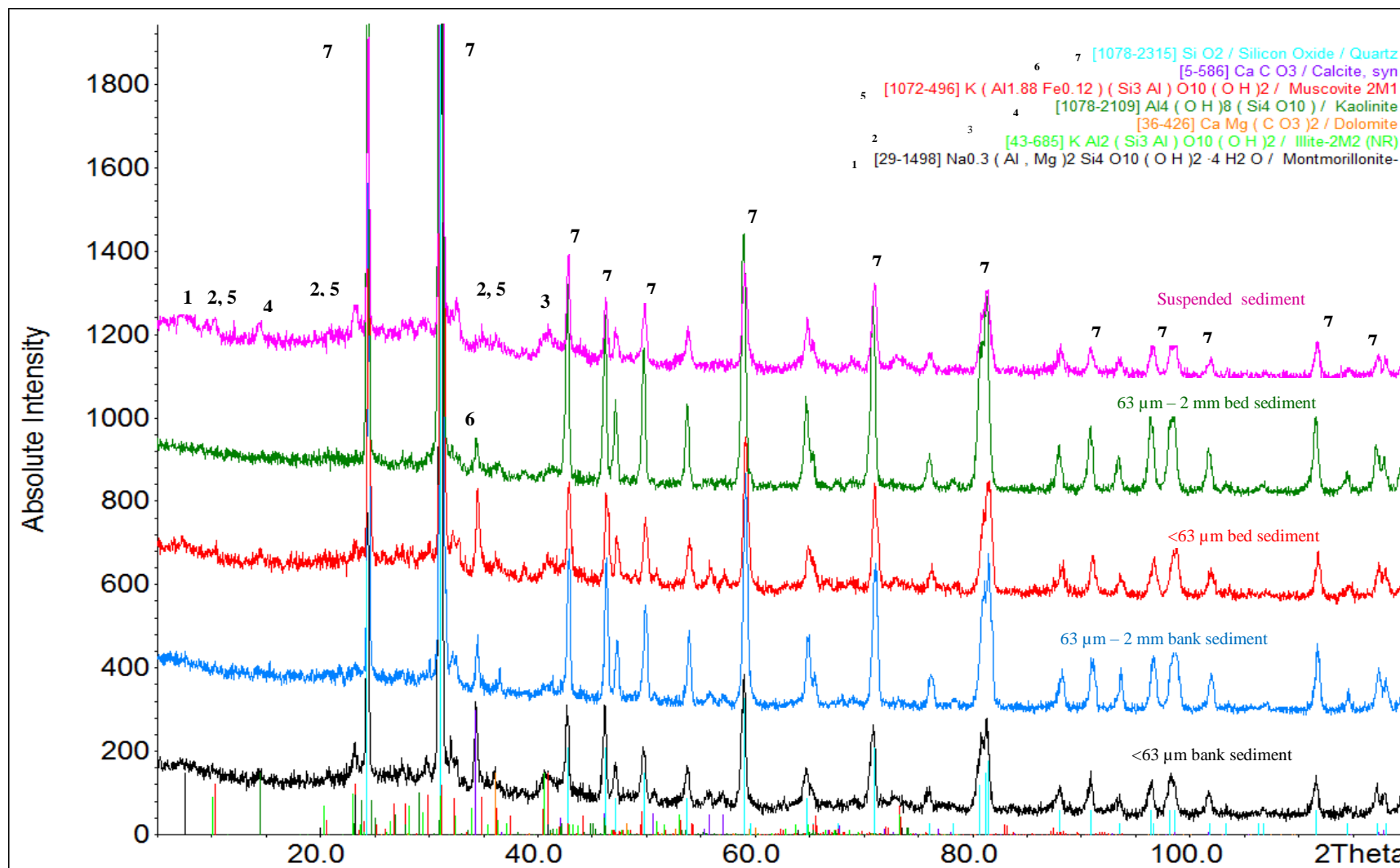
Figure 4 Mineral compositions by X-ray diffraction of the bed, bank and suspended sediment compartments for the month of July 2011
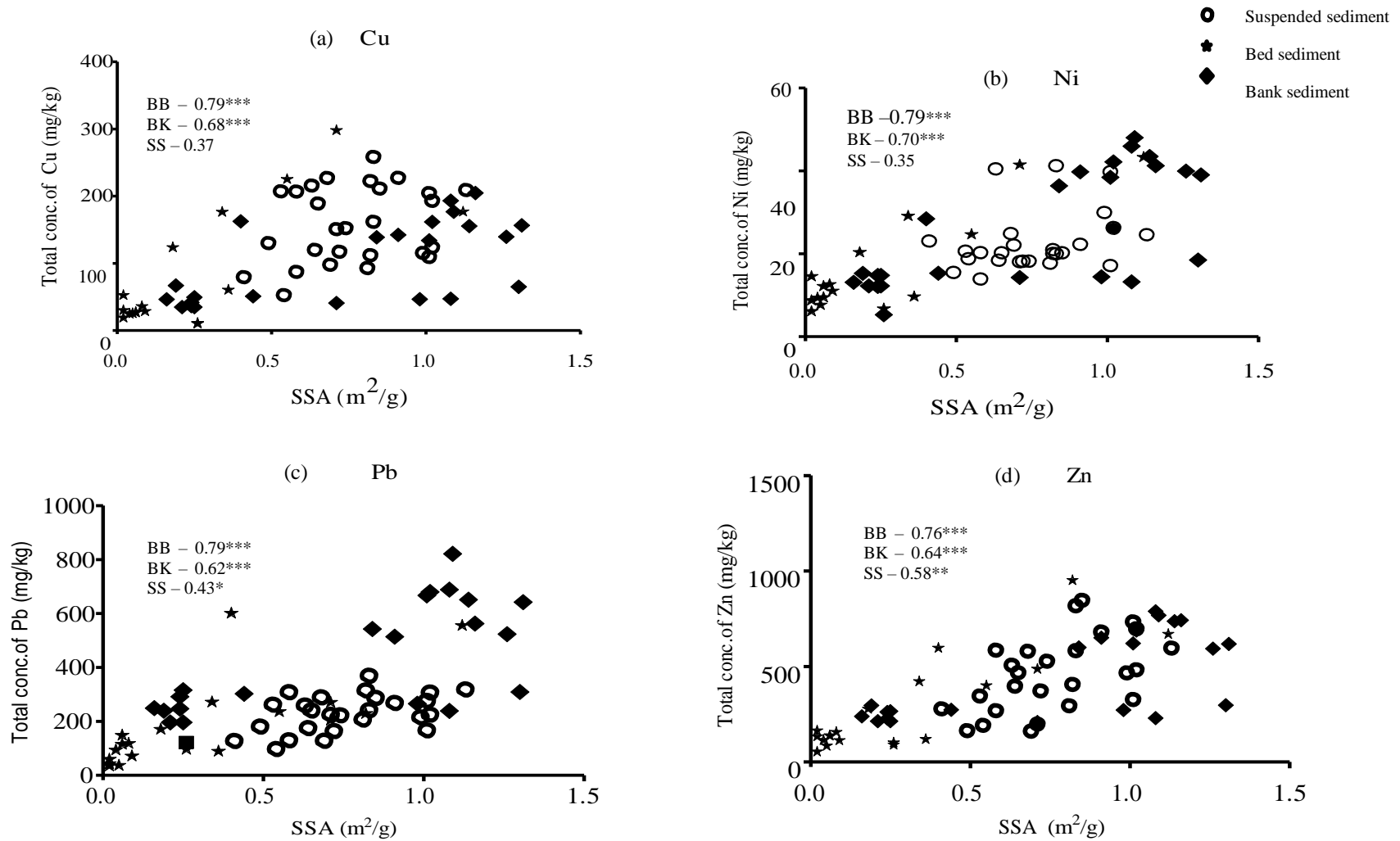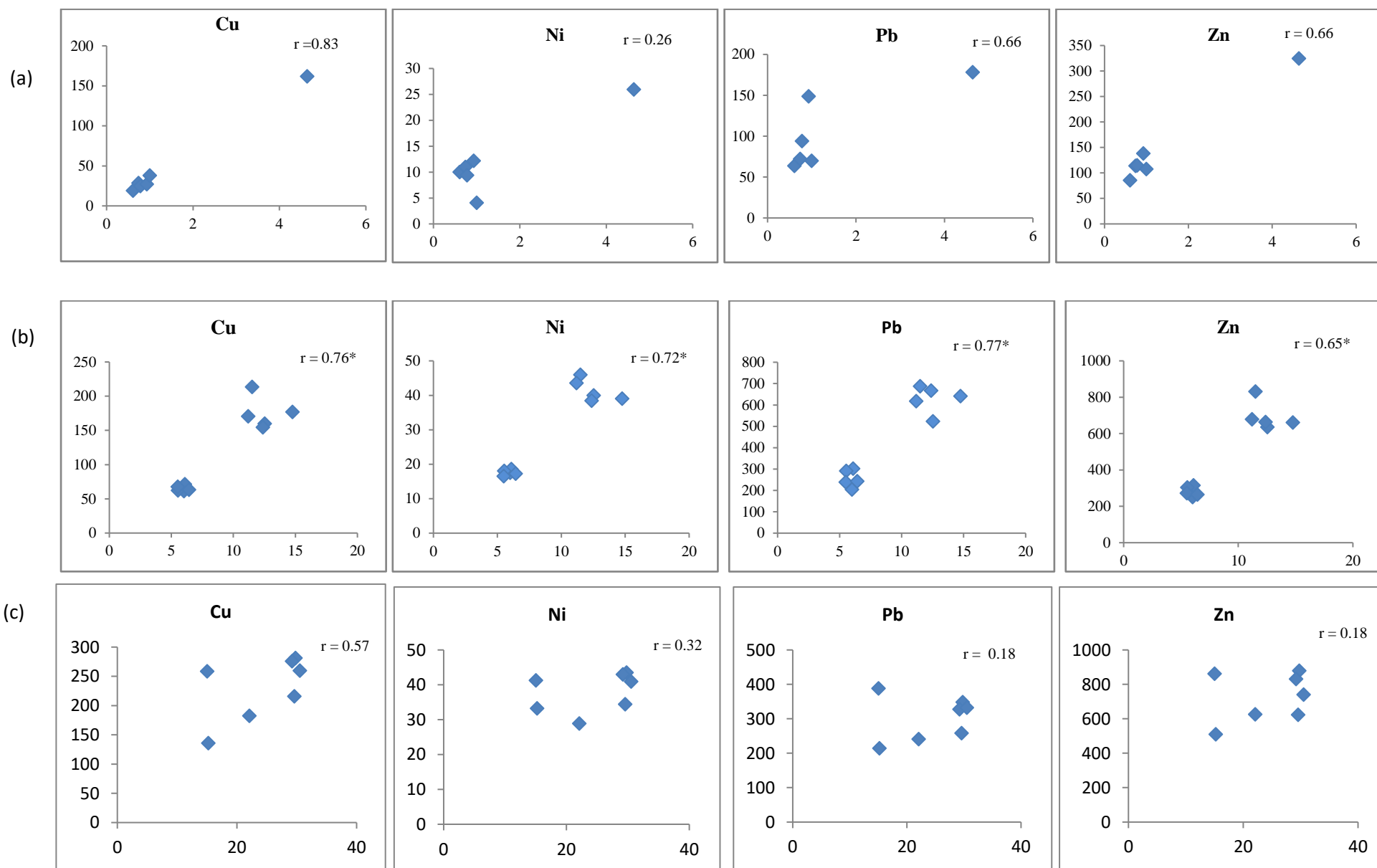
Figure 5 Relationship between SSA and total metal concentration (a) Cu, (b) Ni, (c) Pb, (d) Zn for the bed (n =16), bank (n = 24) and suspended sediment (n = 27) samples (<63 µm and 63 µm – 2 mm (n=10) (*** p<0.001, **p<0.01, *p<0.05). BB - bed sediment, BK - bank sediment, SS – suspended sediment

(a)

Cu   r =0.83

Ni   r = 0.26

Pb   r = 0.66

Zn   r = 0.66

(b)

Cu   r = 0.76*

Ni   r = 0.72*

Pb   r = 0.77*

Zn   r = 0.65*

(c)

Cu   r = 0.57

Ni   r = 0.32

Pb   r = 0.18

Zn   r = 0.18

*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

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**

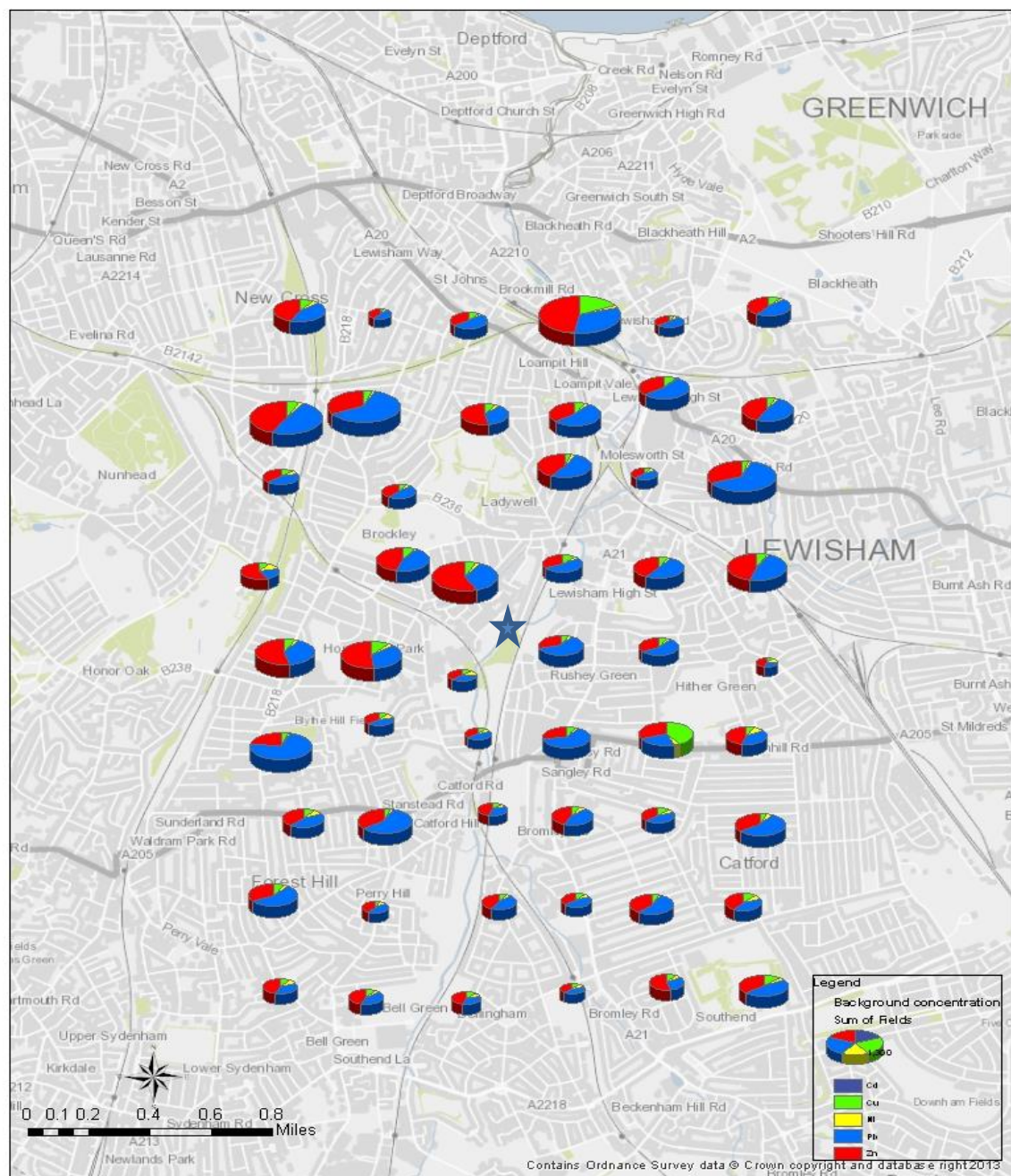**Table ESM_2 Particle size analysis of the suspended sediment (n=3)**

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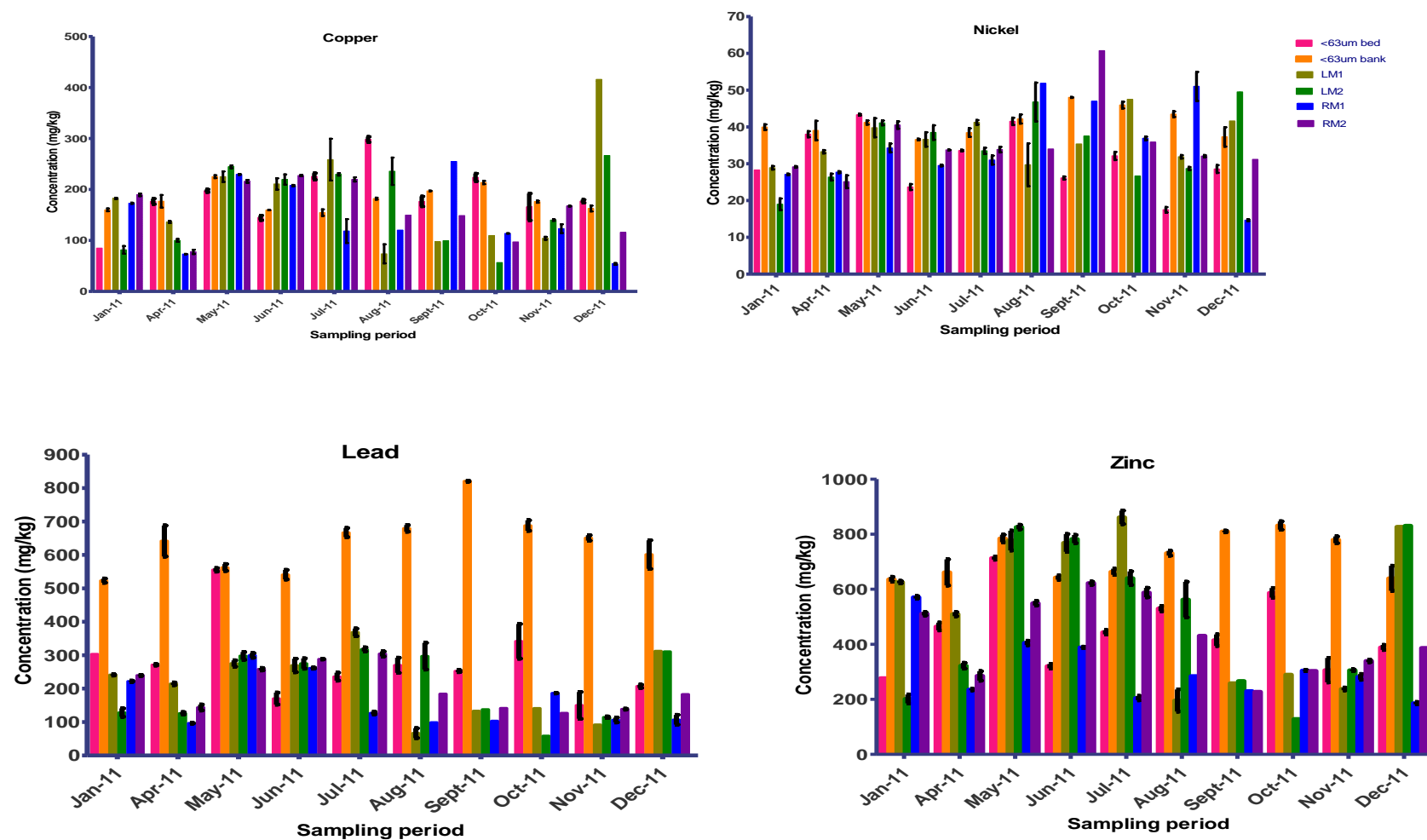
Fig. ESM_5 Temporal variation of metals in the bed, bank and suspended sediment