Title: The Effectiveness and Feasibility of using Ochre as a Soil Amendment to Sequester Dissolved Reactive Phosphorus in Runoff

Article Type: Full research paper

Corresponding Author: Owen Fenton, PhD

Corresponding Author's Institution: Teagasc

First Author: Owen Fenton, PhD

Order of Authors: Owen Fenton, PhD;Laura Kirwan, PhD;Daire Ó hUallacháin, PhD;Mark Gerard Healy, PhD

Abstract: Incidental losses of dissolved reactive phosphorus (DRP) to a surface waterbody originate from direct losses during land application of fertilizer, or where a rainfall event occurs immediately thereafter. Another source is the soil. One way of immobilising DRP in runoff before discharge to a surface waterbody, is to amend soil within the edge of field area with a high phosphorus (P) sequestration material. One such amendment is iron ochre, a by-product of acid mine drainage. Batch experiments utilising two grassland soils at two depths (topsoil and sub-soil), six ochre amendment rates (0, 0.15, 1.5, 7.5, 15 and 30 g kg-1 mass per dry weight (dwt) of soil) and five P concentrations (0, 5, 10, 20 and 40 mg L-1) were carried out. A proportional equation, which incorporated P sources and losses, was developed and used to form a statistical model. Back calculation identified optimal rates of ochre amendment to soil to ameliorate a specific DRP concentration in runoff. Ochre amendment of soils (with no further P inputs) was effective at decreasing DRP concentrations to acceptable levels. A rate of 30 g ochre kg-1 soil was needed to decrease DRP concentrations to acceptable levels for P inputs of ≤ 10 mg L-1, which represents the vast majority of cases in grassland runoff experiments. However, although very quick and sustained metal release above environmental limits occurred, which makes it unfeasible for use as a soil amendment to control P release to a waterbody, the methodology developed within this paper may be used to test the effectiveness and feasibility of other amendments.

1 **The Effectiveness and Feasibility of using Ochre as a Soil**

2 **Amendment to Sequester Dissolved Reactive Phosphorus in**

3 **Runoff**

4

5 Owen Fenton[a*], Laura Kirwan[b], Daire Ó hUallacháin[a], MarkGerard Healy[c]

6 [a] Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

7 [b] Waterford Institute of Technology, Co.Waterford, Ireland

8 [c] Civil Engineering, National University of Ireland Galway, Co. Galway, Ireland.

9

10 *Corresponding author*: Teagasc, Environmental Research Centre, Johnstown Castle,

11 Wexford, Ireland. Tel: +353 53 9171271 Email: owen.fenton@teagasc.ie

12

13 **Abstract**

14 Incidental losses of dissolved reactive phosphorus (DRP) to a surface waterbody
15 originate from direct losses during land application of fertilizer, or where a rainfall
16 event occurs immediately thereafter. Another source is the soil. One way of
17 immobilising DRP in runoff before discharge to a surface waterbody, is to amend soil
18 within the edge of field area with a high phosphorus (P) sequestration material. One
19 such amendment is iron ochre, a by-product of acid mine drainage. Batch experiments
20 utilising two grassland soils at two depths (topsoil and sub-soil), six ochre amendment
21 rates (0, 0.15, 1.5, 7.5, 15 and 30 g kg^{-1} mass per dry weight (dwt) of soil) and five P
22 concentrations (0, 5, 10, 20 and 40 mg L^{-1}) were carried out. A proportional equation,
23 which incorporated P sources and losses, was developed and used to form a statistical
24 model. Back calculation identified optimal rates of ochre amendment to soil to
25 ameliorate a specific DRP concentration in runoff. Ochre amendment of soils (with no
26 further P inputs) was effective at decreasing DRP concentrations to acceptable levels.
27 A rate of 30 g ochre kg^{-1} soil was needed to decrease DRP concentrations to
28 acceptable levels for P inputs of ≤ 10 mg L^{-1}, which represents the vast majority of
29 cases in grassland runoff experiments. However, although very quick and sustained
30 metal release above environmental limits occurred, which makes it unfeasible for use
31 as a soil amendment to control P release to a waterbody, the methodology developed
32 within this paper may be used to test the effectiveness and feasibility of other
33 amendments.
34

35 **Keywords:** phosphorus, adsorption, ochre, water quality

36

37

1 Introduction

Incidental losses of dissolved reactive phosphorus (DRP) in runoff on dairy farms following a rainfall event originate from two sources: organic and inorganic fertilizer inputs to grow grass and P from the soil (Preedy et al. 2001). One way of immobilising this P before discharge to a surface waterbody, is to amend soil in a riparian zone with a material that has a high P sequestration capacity. Iron-rich materials have been used to sequester P from wastewater (Gallimore et al. 1999; Elliot et al. 2002; Rhoton and Bigham, 2005; Johansson-Westholm, 2006; Brennan et al. 2011; Fenton et al. 2011). The capacity of ochre to sequester P from agricultural and municipal wastewater has previously been investigated for ochre from coal mining areas of the U.K. (Bozika, 2001; Heal et al. 2005; Dobbie et al. 2009), the U.S (Sibrell et al. 2009) and metal mining areas of south east Ireland (Fenton et al. 2007). In saturation experiments using low concentrations of inorganic P, Fenton et al. (2007) found that the maximum P retention capacity was approximately 19 g P kg^{-1}, for metal mining ochre sourced from an abandoned copper sulphur mine in the Avoca–Avonmore catchment. In addition, kinetic experiments showed that P removal by Avoca ochre to be very rapid. For example, the supernatant ortho-P (PO$_4$-P) concentration decreased by 97% (Fenton et al. 2009a) within 5 minutes of shaking an ochre/P-enriched mixture. However, the maximum P retention capacity for coal mining iron ochre is site-specific: 26 g P kg^{-1} in Polkemmet, Central Scotland, and 30.5 g P kg^{-1}, in Minto, Central Scotland (Heal et al. 2004). A long-term field study utilising coal mining ochre in pellet and granular forms was successful in reducing total phosphorus (TP) concentrations without metal mobilisation (Dobbie et al. 2009).

63   Although the P adsorption capacity of Avoca ochre in the Fenton et al. (2009a) study

64   was comparable with ochre tested in the U.K., its characteristics were site-specific.

65   Fenton et al. (2009a) showed that Avoca ochre was fine-grained and had low particle

66   density (2.3 g mL^{-1}), which facilitated entrainment and transportation in runoff during

67   flooding events. The study found that the high P adsorption capacity was due to high

68   iron (Fe) mineralogy. Iron minerals such as goethite, jarosite, hydronium jarosite,

69   lepidocrocite, and ferrihydrite, were found in the Avoca ochre, and P readily adsorbed

70   to their surfaces (Fenton et al. 2007). As the acid mine drainage (AMD) exited the

71   underground workings, oxidisation occurred, leading to ochre precipitation. This

72   resulted in higher concentrations of calcium (Ca), Cu, potassium (K), magnesium

73   (Mg), sodium (Na) and zinc (Zn) in the ochre than in the tributary water. Some

74   elements in the AMD ochre were as a result of background geology, while others

75   were directly related to the mining on site. Stereomicroscopy of this ochre identified

76   oolites and diatoms, which were indicative of an AMD environment (Fenton et al.

77   2009b).

78

79   Best management practices (BMPs) 'at source' (e.g. on the farmyard) aim to reduce

80   the amount of P lost in runoff and drainage waters. A common BMP is a riparian

81   buffer, or vegetative buffer strip, which limits P movement pathways from the field to

82   a waterbody (Sharpley et al. 2006). These vegetative buffer, or filter, strips are

83   effective in particulate phosphorus (PP) removal and have removal rates of between

84   45% (by concentration) (Schmitt et al. 1999) and 90% (by concentration) (Abu-Zreig

85   et al. 2003), but have limited removal capacity in relation to dissolved reactive

86   phosphorus (DRP) (Sharpley et al. 2006; Dorioz et al. 2006).

87

88   Application of P-immobilizing materials (alum, water treatment residuals (WTR), fly

89   ash, gypsum) to such vegetative buffer (or filter strips) through amendment of edge-

90   of-stream soils, is one possible means of reducing soluble P losses to aquatic systems

91   (Penn et al. 2007; Wagner et al. 2008; Brennan et al. 2011; Fenton et al. 2011). In

92   Ireland, soils receiving inorganic fertilizers as part of the Nitrates Directive (SI 610 of

93   2010) must maintain vegetative buffer zones at a minimum of 1.5 m in width from

94   river bank edge. For organic manures, this width is generally 5 m, but for narrow,

95   small parcels (< 1 ha) of land, it is 3 m. For steep slopes > 10%, it is 5 m, and for

96   Karst areas or water abstraction points, larger buffer distances of 250 m must be

97   maintained. In the current Agri-Environmental Options Scheme, a 1.5 m fenced buffer

98   must be established to prevent bovine access to the water course. Other agri-

99   environment schemes across Europe have similar stipulations (EC 2005).

100

101   The present study examines P sequestration and metal losses from ochre amended

102   soils. The ochre was derived from AMD along a ditch running from the Deep Adit

103   site northeast of Whitebridge to the River Avoca (60 m downstream) (Fig 1).

104   Specifically, the objectives of this paper are:

105   1) to determine the optimal rate of ochre, or similar P sorbing amendments to soil,

106   to produce a given DRP concentration in runoff, to minimise losses to a surface

107   water body.

108   2) to determine if Avoca ochre, when mixed with soil, may be used as a safe soil

109   amendment to sequester P.

110

111   **2 Materials and Methods**

112

4

113   2.1 Ochre and soil collection and analysis

114

115   Ochre from Whitebridge, Avoca, Co. Wicklow, south east Ireland (latitude 52º 48'N,

116   longitude 6º 12'W, mean precipitation 1200 mm and temperature 9.6 ºC) was

117   collected, oven dried, sieved to < 2mm, and physically characterised in a previous

118   study (Fenton et al. 2009a).

119

120   The P adsorption study was conducted using two permanent grassland soils taken

121   from Johnstown Castle Research Centre (latitude 52º 12' N, longitude 6º 30'W, mean

122   annual precipitation 1002 mm and temperature 9.6 ºC). Each soil was sampled at two

123   depths:

124   • Soil A (classified as a humic cambisol after the World Reference Base

125   (WRB); Depth 1, top-soil (0 - 10 cm – standard Irish agronomic sampling

126   depth); Depth 2, sub-soil (11 - 30 cm)

127   • Soil B (WRB classification- gleyic cambisol); Depth 1, top-soil (0 - 10 cm);

128   Depth 2, sub-soil (11 - 30 cm)

129

130   Incorporation of ochre at depth may be important where a perched watertable interacts

131   with buffer zones and contributes to runoff, or where DRP in runoff is leached to

132   groundwater.

133

134   2.2 Physical characterisation of the soil and ochre

135

136   Samples from both sites and depths were air dried, then sieved to < 2mm, wet sieved

137   into coarse sand (0.5 -2 mm), fine sand (0.053 - 0.5 mm), and silt/clay (<0.053 mm)

138 fractions, and then oven dried and weighed. Particle size distribution (PSD) of the silt

139 clay fraction was carried out using the pipette method (BSI 1989; BS 1796).

140

141 2.3 pH, lime requirement, C/N ratio and background nutrient and metal status of soil

142 and ochre

143

144 Soil from both sites and depths, ochre samples, and ochre-amended soils from both

145 sites and depths used in batch experiments, were first analysed for pH in water using

146 an automated Gilson 215 liquid handler dip system (Middleton, Wisconsin, USA)

147 (n=4). The soil-to-distilled water ratio was 1:2, and samples were allowed to settle for

148 no more than 5 minutes before analysis. For quality control, a laboratory soil of

149 known pH and nutrient status was used. The control had the following characteristics

150 and no significant difference was found when analysed with the samples from the

151 present study: pH - 5.89; Mg - 205 mg kg^{-1}; K - 72 mg kg^{-1}; and P - 5.3 mg kg^{-1}.

152

153 The lime requirement (LR) of all soils (i.e. the lime required to adjust soil to a pH of

154 6.3) was determined after Pratt and Blair (1963). In this procedure, 10 ml of soil per

155 volume was added to 20 ml of Shoemacher-McLean-Pratt (SMP) buffer (pH 7.5),

156 shaken for 30 min on a G10 gyratory shaker (New Brunswick Scientific, Edison, New

157 Jersey, USA), and poured through a No. 2 Whatman filter (0.2 μm) before analysis on

158 a flow-Gilson 215 liquid handler. Total organic carbon (TOC) and nitrogen (N) of the

159 soils was determined by placing 0.25 g of soil and standard samples in a porcelain

160 combustion boat on a CN2000 analyser (Leco Corporation, U.S.A).

161

162   In Ireland, the soil test phosphorus (STP) is classified using Morgan's extraction

163   solution. An index varying from 1 to 4 is applied, depending on the STP of a soil.

164   STP Index 1 represents a mineral soil with a P range of 0 to 3 mg L^{-1}, whereas a STP

165   Index 2 represents a P range of 3 to 5 mg L^{-1}. Index 3 represents a range of 3 to 8 mg

166   L^{-1} and Index 4 is >8 mg L^{-1}. Soil A (Depth 1) had a STP of 5.5 mg L^{-1} and Depth 2

167   had a STP of 2.6 mg L^{-1}. Soil B (Depth 1) had a STP of 2.8 mg L^{-1} and Depth 2 had a

168   STP of 2.7 mg L^{-1} (Table 1). This low STP minimised native P desorption during the

169   experiments. Optimum growing conditions for grassland is STP Index 3 with a soil P

170   range of 3 to 8 mg L^{-1} for mineral soils. Soil test phosphorus was measured as

171   Morgan's phosphorus (P_m; mg L^{-1}) and converted to Mehlich 3 phosphorus (M3P; mg

172   kg^{-1}) for indicative purposes, using the following equation (Tunney et al. 1998):

173

174     $M3P = 8.52 * P_m^{0.85}$ [1]

175

176   Oven dried soil samples, with a grain size < 2mm (6 replicates for each soil type),

177   were analysed for STP, Mg and K as follows: 3 mL of soil by volume was added to 15

178   mL of Morgan's extracting solution in a round-bottomed flask and shaken on a G10

179   gyratory shaker for 30 min. The suspension was then filtered through a No. 2

180   Whatman filter into disposable test tubes and analysed colorimetrically using the

181   chemical reaction between P and ammonium molybdate.

182

183   To investigate metal mobilisation and the suitability of metal mining ochre to

184   sequester P from runoff, the supernatant water from all batch experiments was

185   analysed for trace metals (cadmium (Cd), chromium (Cr), Cu, iron (Fe), manganese

186 (Mn), nickel (Ni), lead (Pb) and Zn) using an ICP-MS. Metal release from ochre-

187 amended soil over time was carried out in a kinetic test at 1, 5, 10, 15, 30, 60 min.

188

189 2.4 Batch experiment with soil and ochre amendment

190

191 To achieve a homogenous < 2 mm mix, the soils were saturated with distilled water,

192 manually mixed into a slurry, and left to air dry for 60 d. After this time, ochre was

193 mixed to soil aliquots in the following proportions: 0 (the study control), 0.15, 1.5,

194 7.5, 15 and 30 g ochre kg^{-1} mass per dry weight (dwt) of soil. Such amendment rates

195 were also used for ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) amendments to soils for P

196 sequestration (Rhoton and Bigham 2005).

197

198 The ochre amendment was applied during continuous mixing of the soil with a spray

199 of distilled water to allow greater incorporation of the ochre into the soil. Next, the

200 soil and ochre mix was air dried, and the bulk dry samples were crushed, rolled and

201 sieved to < 2 mm. All batch experiment protocols were carried out after Cucarella and

202 Renman (2009). For each soil and depth, in each 100-ml- capacity container, 2.5 g of

203 oven dried-ochre-and-soil mixture (mixed in the ratios described above) and air dried

204 soil-only was overlain with 50 ml of synthetic P solution (potassium phosphate

205 (KH_2PO_4) with concentrations of 0, 5, 10, 20, or 40 mg P L^{-1} (n=2). Although end-

206 over-end shakers do not simulate overland flow, for consistency with other studies,

207 the samples were sealed and then mixed in an end-over-end shaker for 24 hr, after

208 which the samples were vortexed for 2 min, centrifuged at 100 rpm for 10 min,

209 filtered and analysed for DRP in a nutrient analyser (Konelab, Ontario, USA).

210

211   2.5 Data analysis

212

213   A proportional equation, which incorporated P sources (P inputs) and losses (DRP

214   losses in runoff and STP), was developed. Back calculation identified optimal rates of

215   ochre amendment to soil to ameliorate a particular DRP concentration in runoff.

216

217   In the batch experiment, ochre with negligible background P content was added to a

218   soil of known STP. This content was based on historic records of inorganic and

219   organic fertilizer application. P_{Lost} (%) was calculated as:

220

221    $$P_{Lost}(\%) = \frac{P_{Runoff}}{P_{Input} + STP} * 100 \qquad [2]$$

222

223   The proportion of P not adsorbed by the amendment after P equilibrium (P_{Lost}; %)

224   depends on the P in runoff (P_{Runoff}; mg L^{-1}) that has not been adsorbed to the ochre;

225   the Morgan's STP of the soil before any ochre amendment (STP; mg L^{-1}); and the P

226   added in the batch experiments or as a fertilizer (P_{Input} ; mg L^{-1}). A high P_{Lost} (%)

227   signifies a greater amount of P in solution available to be lost to a waterbody and a

228   low P_{Lost} signifies more P has been adsorbed by the ochre. Statistical analysis was

229   conducted in SAS v 9.1, using a generalised linear mixed model (GLMM) with a logit

230   link and a normal distribution:

231

232    $$x\beta = \ln\left(\frac{P_{Lost}}{1 - P_{Lost}}\right) \qquad [3]$$

233

234   where 1-P$_{Lost}$ is P adsorbed onto ochre. The effects of ochre additions, P$_{Input}$, soil type,

235   and soil depth (topsoil or subsoil), and their interactions were tested in the model

236   using Type III tests of fixed effects. The background pH of the soils before

237   amendments was variable. To compare results, pH needed to be accounted for in the

238   statistical analysis. The soil variation was accounted for by including pH, determined

239   in a SMP buffer, as a random effect.

240

241   After initial analysis was complete, back-calculation within the model made it

242   possible to predict P$_{Runoff}$. This then allowed calculation of the amount of ochre

243   amendment needed per kg of soil to reduce P$_{Runoff}$ to acceptable levels.

244

245   **3. Results & Discussion**

246

247   3.1 Physical characterisation of soil

248

249   The PSD of both soils are presented in Table 1. Soil A (Depth 1) contained a higher

250   sand fraction and lower silt and clay fractions than Depth 2. There was a slight

251   textural change with depth, but it remained within the sandy-loam textural class. Soil

252   B (Depth 1 and 2) had similar coarse and fine sand fractions, but differed with respect

253   to their silt and clay fractions. Both soil depths also had a sandy-loam textural class.

254   Both soils were well-drained in the field and it was easy to amend the soils with

255   ochre.

256

257   Physical characterisation of the ochre used in this study was carried out by Fenton et

258   al. (2009a). The ochre was fine-grained with the following constituency: coarse sand,

259   21.6% by mass; fine sand, 19.5% by mass; silt, 22.3% by mass; and clay, 30.9% by

260   mass.

261

262   3.2 STP, pH and C/N ratio

263

264   The study sites had similar topography and low to very low STP (Table 1). Such STP

265   concentrations are deemed environmentally sound and thereby minimised native P

266   desorption during the experiments. The average pH of all soils and soil depths was

267   6.5±0.6, which is the optimal pH for grass growth. With little ochre amendment, pH

268   remained at, or above, this optimal pH. At higher amendment rates (7.5 − 15 g ochre

269   kg^{-1} mass per dwt of soil), Depth 1-soils become acidic and would need lime

270   correction to maintain grass growth. Leonard et al. (2006) found that the mean C/N

271   ratio was 12.0±1.8, compared with 8.8 and 12.5 for Soils A and B, respectively (Table

272   1). Such results match the soil P status of the soils used in the current study i.e., low

273   fertilizer inputs and risk of P loss to surface water.

274

275   3.3 P_{Lost} and P_{Runoff}

276

277   All factors tested (Soil, ochre, P, ochre*P, ochre*Soil, Soil*P, and ochre*Soil*P) had

278   a significant influence on P_{Lost}, so no terms were removed from the predictive

279   statistical model (Table 2). For Soil (A, B) Depth (1, 2), the regressions of P_{Lost}

280   against ochre amendment are displayed in Figures 2 and 3. The slopes and intercepts

281   of the predicted lines using the P_{Lost} equation differed depending on the amount of

282   P_{Input}. Statistically, differences in background soil pH before any ochre amendment

283   explains variation in P_{Lost} between soils. Predicted lines occurred at an average pH for

284   that soil and ochre interaction. Actual and predicted results showed good agreement,

285   which allowed prediction of DRP in solution for given P inputs and ochre amounts on

286   these soils.

287

288   The P index of the soils ranged from 1 to 3. Soils in Index 1 and 2 are P deficient,

289   while in Index 3 are at target index, with a low risk of loss to water. This indicates P

290   concentrations from these soils in runoff will not affect maximum admissible

291   concentrations i.e. 0.035 mg DRP L^{-1} due to dilution in the surface water body.

292   Phosphorus losses from Index 2-3 soils can still be quite high; for example, Kurz et al.

293   (2005) found DRP in runoff ranged from <0.005 to 0.19 mg L^{-1} before fertilization

294   and 1.38 mg L^{-1} after fertilization on grassland soils. For soils with no ochre or P

295   amendment, the P_{Runoff} concentrations were within this range (Table 3). Any P

296   addition increased P_{Runoff}, but ochre amendment (≥ 1.5 g ochre kg^{-1} soil) was

297   successful in decreasing DRP losses. There was no significant difference between 0

298   and 0.15 g ochre kg^{-1} soil results. Ochre amendment to soil without any P inputs

299   substantially decreased DRP losses. A rate of 30 g ochre kg^{-1} soil was needed to

300   decrease DRP concentrations to acceptable levels for P inputs of ≤ 10 mg L^{-1}, which

301   represents the vast majority of cases in grassland runoff experiments.

302

303   3.4 Metal mobilisation during batch experiments

304

305   The ochre had the following metal content: Al, 4.8 ± 0.0 g kg^{-1}; Cu 0.3 ± 0.0 g kg^{-1},

306   Fe, 246 ± 0.0 g kg^{-1}; Mg, 0.5 ± 0.0 g kg^{-1}; arsenic (As), 162 ± 18.3 mg kg^{-1}; Cd, 3.2 ± 0.3

307   mg kg^{-1}; Cr, 3.1 ± 1.8 mg kg^{-1}; Pb, 2087 ± 75.3 mg kg^{-1}; nickel (Ni), 1.7 ± 0.9 mg kg^{-1};

308   and Zn, 250 ± 19.8 mg kg^{-1}. In the present study, the ratio of ochre to solution was

309 1:20. Average mobilisation of metals into solution after 24 h for distilled water

310 amended with ochre was: Cu, 14,044±290 µg L^{-1}; Fe, 1892±109 µg L^{-1}; K, 123±1.6

311 mg L^{-1}; Mg, 1.78±0.2 mg L^{-1}; Mn, 323±30.4 µg L^{-1}; Na, 2.9±0.2 mg L^{-1}; and Zn,

312 18034±795 µg L^{-1}. The pH of ochre in distilled water was 3, thereby allowing for

313 greater metal release. The soil and ochre combinations reduced much of the metal

314 mobilisation, but not enough in some cases to prevent recommended limits (Table 4a

315 and 4b). The control soils without ochre amendment had, in some cases, metal

316 concentrations above allowable limits. Soil A had high Cd, Cr, Fe, Ni and Pb

317 concentrations and Soil B had high Cd, Pb and Zn concentrations.

318

319 Kinetic tests indicated that most of the metal mobilization occurred within 1 min of

320 mixing P solutions with the ochre (Table 5). For all metals, high concentrations were

321 released in the first minute, decreased, and rose again after 1 hr. For P adsorption to

322 ochre, the opposite occurred, which involved rapid ligand exchange with surface

323 hydroxide groups at reactive sites and the formation of binuclear bridging complex

324 between a phosphate group and two Fe surface atoms, followed by a weaker ligand

325 exchange.

326

327 There has been some documentation of hazardous release of metals from coal mining

328 ochre in 5 out of 49 mine-water treatment facilities in the U.K. (Hancock 2005). The

329 ochre used in this study released toxic concentrations of metals in runoff. Inductively

330 coupled plasma mass spectrometry and bulk energy dispersive spectroscopy showed

331 potentially toxic concentrations of Fe, Zn, Pb, As and Cu (Fenton et al. 2009b).

332 Remobilisation of heavy metals might occur due to any reduction of iron oxides in the

333 soil and ochre, for example, by rising groundwater depths in a perched watertable

334 scenario e.g. glaciated tills or by incorporation into the buffer. International studies by

335 Winner et al (1980), Clements et al (1992) and Beltman et al (1999), have all shown

336 that discharge from AMD has negative effects on aquatic communities. These effects

337 include a reduction in species diversity and abundance, and a change in the

338 community structure from sensitive species such as Stonefly Larva to more tolerant

339 groups such as Tubificid worms. A study by Curran (2001) on the Avoca catchment,

340 found that there was a major decrease in aquatic invertebrate diversity and abundance

341 downstream from the Deep Adit discharge site (Figure 1). It was concluded that the

342 inflow adit ditch stream was uninhabitable for macro fauna because of its elevated

343 conductivity, acidic pH and high levels of metals and sulphates. Although these

344 concentrations will, to some extent, also be diluted by the main surface waterbody,

345 any release of toxic metal makes Avoca ochre unsuitable for use in buffer strips.

346

347 However, the methodology developed within this paper may be used to test the

348 effectiveness and feasibility of other amendments.

349

350 **4 Conclusions**

351 The findings of this grassland study are:

352 1. A proportional equation, which incorporated P sources and losses, was developed.

353 Back calculation identified optimal rates of ochre amendment to soil to ameliorate a

354 particular DRP concentration in runoff. A rate of 30 g ochre kg^{-1} soil was needed to

355 decrease DRP concentrations to acceptable levels for P inputs of ≤ 10 mg L^{-1}.

356 2. Very quick and sustained metal release from the ochre tested during P sequestration

357 makes it unsuitable for use as a soil amendment to control P release to a waterbody.

358 However, the methodology developed in this study allows the optimal rate of addition

359   of any P sorbing amendment, when mixed with soil, to reduce the DRP below a

360   certain threshold value, to be determined.

361

364

365   **References**

366   Abu-Zreig, M., Rudra, R.P., Whiteley, H.R., Lalonde, M.N., & Kaushik, N.K. (2003).

367   Phosphorus removal in vegetated filter strips. *Journal of Environmental Quality*, 32,

368   613-619.

369

370   Beltman, D.J., Clements, W.H., Lipton, J., & Cacela, D. (1999) Benthic invertebrate

371   metals exposure, accumulation, and community-level effects downstream from a

372   hard-rock mine site. *Environmental Toxicology and Chemistry*, 18, 2999-307.

373

374   Brennan, R. B., O. Fenton, Rodgers, M., & Healy, M. 2011. Evaluation of chemical

375   amendments to control phosphorus losses from dairy slurry. *Soil Use and*

376   *Management*,27(2), 238-246.

377

378   BSI..(1989). BS 1796: *Method of test for soils for civil*

379   *engineering purposes*. BS 1796. London: British Standards Institution.

380

381   Bozika, E. (2001). Phosphorus removal from wastewater using sludge from mine

382   drainage treatment settling ponds. University of Edinburgh. Unpublished MSc thesis**.**

383

384   Clements, W. H., Cherry, D.S., & Van Hassel, J.H. (1992) Assessment of the impact

385   of heavy metals on benthic communities at the Clinch River (Virginia): Evaluation of

386   an index of community sensitivity. *Canadian Journal of Fisheries and Aquatic*

387   *Science*, 49, 1686-1694.

388

389   Council of the European Union. (2009). European Communities environmental

390   objective (surface waters) regulations. S.I. No. 272 of 2009.

391

392   Cucarella, V. & Renman,G. (2009). Phosphorus sorption capacity of filter materials

393   used for on-site wastewater treatment determined in batch experiments-a comparative

394   study. *Journal of Environmental Quality*, 38, 381-92.

395

396   Curran, F. (2001) Ecological and ecotoxicological investigation of ongoing discharge

397   of acid mine drainage (AMD) from the abandoned Avoca copper mines, Co.

398   Wicklow. PhD Thesis, University College Dublin.

399

400   Dobbie, K.E., Heal, K.V., Aumonier, J., Smith, K.A., Johnston, A., & Younger, P.L.

401   (2009). Evaluation of iron ochre from mine drainage treatment for removal of

402   phosphorus from wastewater. *Chemospher*e**, 75, 795-800.

403

404   Dorioz, J.M., Wang, D., Poulenard, J., & Trévisan, D. (2006). The effect of grass

405   buffer strips on phosphorus dynamics - a critical review and synthesis as a basis for

406   application in agricultural landscapes in France. *Agriculture Ecosystems Environment*,

407   117, 4-21.

408

409 European Community. 2005. "Agri-environment Measures." European

410 Commission/Directorate General for Agriculture and Rural Development.

411

412 Elliott, H. A., O'Connor, G.A., Lu, P., & Brinton, S. 2002. Influence of Water

413 Treatment Residuals on Phosphorus Solubility and Leaching. *Journal of*

414 *Environmental Quality,* 31, 1362-1369.

415

416 Fenton, O., Healy, M.G., & Rodgers, M. (2007). Assessing the performance of

417 phosphorus retention using an Avoca – Avonmore catchment, ochre, Ireland in: IAH

418 (Ed.) Securing Groundwater Quality in Urban and Industrial Environments (Proc. 6th

419 International Groundwater Quality Conference). IAH, Fremantle, Western Australia.

420

421 Fenton, O., Healy, M.G., & Rodgers, M. (2009a). Use of ochre from an abandoned

422 metal mine in the South East of Ireland for phosphorus sequestration from dairy dirty

423 water. *Journal of Environmental Quality,* 38, 1120-5.

424

425 Fenton, O., Healy, M.G., Rodgers, M., & ÓhUallacháin, D. (2009b). Site-specific P

426 absorbency of ochre from acid mine drainage near an abandoned Cu-S mine in the

427 Avoca-Avonmore catchment, Ireland. *Clay Minerals*, 44, 113-123.

428

429 Fenton, O., Serrenho, A., & Healy, M.G. (2011). Evaluation of Amendments to

430 Control Phosphorus Losses in Runoff from Dairy-Soiled Water. *Water, Air, & Soil*

431 *Pollution*: 1-10. DOI 10.1007/s11270-011-0815-8

432

433   Gallimore, L.E., Basta, N.T., Storm, D.E., Payton, M.E., Huhnke, R.H., & Smolen,

434   M.D. 1999. Water treatment residual to reduce nutrients in surface runoff from

435   agricultural land. *Journal of Environmental Quality*, 28, 1474-1478.

436

437   Hancock, S. (2005). Quantifying ochre arisings: Output from the U.K. Coal

438   Authority's Mine Water Treatment sites. 9th International Mine Water Conference.

439

440   Heal, K.V., Younger, P.L., Smith, K.A., McHaffie, H., Batty, L.C. (2004). Removing

441   P From Sewage Effluent and Agricultural Runoff Using Ochre Recovered From Mine

442   Water Treatment. In: Valsami-Jones, E. (Ed.), Phosphorus in Environmental

443   Technology: removal, recovery and applications. IWA Publishing, London, pp. 320-

444   334.

445

446   Heal, K.V., Dobbie, K.E., Bozika, E., McHaffie, H., Simpson, A.E., & Smith, K.A.

447   (2005). Enhancing phosphorus removal in constructed wetlands with ochre from mine

448   drainage treatment. *Water Science Technology*, 51, 275-82.

449

450   Johansson-Westholm, L. (2006). Substrates for phosphorus removal-potential benefits

451   for on-site wastewater treatment? *Water Resources*, 40, 23-36.

452

453   Kurz, I., Tunney, H., & Coxon, C.E. (2005). The impact of agricultural management

454   practices on nutrient losses to water: data on the effects of soil drainage

455   characteristics. *Water Science Technology*, 51, 73-81.

456

457 Leonard, C., Mullen, G.J., Culleton, N., & Breen, J. (2006). Soil Properties and their

458 Influence on Grassland Production under Low Input and Organic Farming Conditions.

459 End of Project Report 4478, www.teagasc.ie

460

461 Moore, P.A., Jr., & Miller, D.M. (1994). Decreasing phosphorus solubility in poultry

462 litter with aluminium, calcium, and iron amendments. *Journal of Environmental*

463 *Quality*, 23, 325-330.

464

465 Penn, C., Bryant, R.B., Kleinman, P.J.A., & Allen, A.L. (2007). Removing Dissolved

466 Phosphorus From Drainage Ditch Water With Oxyhydroxides. 17th National Meeting

467 of the American Society for Surface Mining and Reclamation, Tampa, Florida.

468

469 Pratt, P.F., & Blair, F.L. (1963). Buffer method for estimating lime and sulphur

470 applications for pH control of soils. *Soil Science*, 93, 329-331.

471

472 Preedy, N., McTiernan, K., Matthews, R., Heathwaite, L., & Haygarth, P. (2001).

473 Rapid incidental phosphorus transfers from grassland. *Journal of Environmental*

474 *Quality*, 30, 2105-2112.

475

476 Rhoton, F.E., & Bigham, J.M. (2005). Phosphate adsorption by ferrihydrite-amended

477 soils. *Journal of Environmental Quality*, 34, 890-896.

478

479 Schmitt, T.J., Dosskey, M.G., & Hoagland, K.D. (1999). Filter strip performance and

480 processes for different vegetation, widths, and contaminants. *Journal of*

481 *Environmental Quality*, 28, 1479-1489.

482

483 Sharpley, A.N., Daniel, T., Gibson, G., Bundy, L., Cabera, M., Sims, T., Stevens, R.,

484 Lemunyon, J., Kleinman, P., & Perry, R. (2006). Best Management Practices To

485 Minimise Agricultural Phosphorus Impacts On Water Quality. USDA-ARS,

486 Washington, DC.

487

488 Sibrell, P.L., Montgomery, G.A., Ritenour, K.L., & Tucker, T.W. (2009). Removal of

489 phosphorus from agricultural wastewaters using adsorption media prepared from acid

490 mine drainage sludge. *Water Research*, 43, 2240-2250.

491

492 Tunney, H., Sims, T., Foy, R.H., Luka, N., & Byrne, J.E. (1998). Comparison of five

493 extractants for available phosphorus in 100 Irish soils. (Abstract) *Irish Journal of*

494 *Agricultural & Food Research*, 37 (1), 110

495

496 Wagner, D.J., Elliott, H.A., Brandt, R.C., & Jaiswal, D. (2008). Managing Biosolids

497 Runoff phosphorus using buffer strips enhanced with drinking water treatment

498 residuals. *Journal of Environmental Quality*, 37, 1567-1574.

499

500 Winner, R.W., Boesel, M.W., & Farrell, M.P. (1980). Insect community structure as

501 an index of heavy metal pollution in lotic ecosystems. *Canadian Journal of Fisheries*

502 *and Aquatic Sciences*, 37, 647-655.

503

504 **Captions for Figures**

505 **Fig 1** Schematic of Avoca Avonmore catchment and sampling location.

506 **Fig 2** P_{Lost} (%) results and model predictions for both soils, soil depths for all ochre

507 amendments, and P concentrations (A-D). A high P_{Lost} (%) signifies a greater amount

508 of P in solution available to be lost to a waterbody and a low P_{Lost} (%) signifies more

509 P has been adsorbed by the ochre

510

511 **Fig 3** P_{Runoff} results and predictions for both soils, soil depths for all ochre

512 amendments, and P concentrations (A-D).

513

514

515

516

Table 1 Soil particle size distribution and organic fraction analysis for Soil A and B, Depth 1 and 2.

Soil (Depth)	Soil P Index	Coarse Sand	Fine Sand	Silt	Clay	C	N	C/N	Pm*	M3P**	Mg	K
			%			mg kg^{-1}				mg kg^{-1}		
Soil A (Depth 1)	3 (3.0-8.0 P$_m$-mg L^{-1})	43	25	30	2	2.1	0.2	8.8	5.5	36.2	206.2	102.8
Soil B (Depth 1)	1 (0.0-3.0 P$_m$-mg L^{-1})	26	14	45	15	0.2	-	-	2.6	19.1	202.7	122.1
Soil A (Depth 2)	1 (0.0-3.0 P$_m$-mg L^{-1})	40	30	17	13	1.5	1.2	12.5	2.8	20.4	256.9	199.8
Soil B (Depth 2)	1 (0.0-3.0 P$_m$-mg L^{-1})	48	28	6	18	0.7	-	-	2.7	19.8	212.1	132.0

517   *P$_m$- Morgan's P, **M3P - Mehlich 3 P

518

519

520

521

522

523

524

Table 2 Type 3 Tests of Fixed Effects

	Num - DF	Den - DF	F value	Pr > F
Soil	3	207	46.89	<.0001
Ochre	1	207	166.56	<.0001
P	3	207	474.90	<.0001
Ochre*P	3	207	25.36	<.0001
Ochre*Soil	3	207	17.47	<.0001
Soil*P	9	207	7.36	<.0001
Ochre*Soil*P	9	207	3.44	0.0006

525
526
527
528
529
530
531
532
533
534
535

536 **Table 3** Predicted P_{Lost} (%) and P_{Runoff} (mg L^{-1}) with different P and ochre

537 amendments.

Ochre amendment	P amendment					P amendment				
g ochre kg^{-1} soil	mg P L^{-1}									
	0	5	10	20	40	0	5	10	20	40
	P_{Lost} (%)					P_{Runoff} (mg L^{-1})				
0	3	15	39	50	62	0.109	2.5	5.2	11.7	26.9
0.15	3.2	16	38	56	75	0.113	2.6	5.1	13.1	32.3
1.5	2.3	12	33	51	70	0.076	2.1	4.5	12.0	30.5
7.5	0.9	3	22	32	56	0.027	1.5	3.0	7.5	24.5
15	0.6	2	10	23	46	0.018	0.8	1.4	5.5	19.8
30	0	0	3	11	36	<DL	<DL	0.301	2.3	14.5

A high P_{Lost} (%) signifies a greater amount of P in solution available to be lost to a waterbody and a low P_{Lost} (%) signifies more P has been adsorbed by the ochre. Average P_{Runoff} after equilibrium with different P and ochre amendments. Both soils and soil depths included and all samples used (n=8).
DL = detection limit

538

539

540

Table 4 a. Average mobilisation of metals (n=2) ± (standard deviation) into solution after 24 h. Soil A (Depth 1), all P concentrations and ochre

amendments

Ochre	P	pH	Ca	±**	Cd	±	Cr	±	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Ni	±	Pb	±	Zn	±
g kg⁻¹	mg L⁻¹		mg L⁻¹														µg L⁻¹									
0	0	7.3	4.3	0.2	0.0	0.1	3.3	1.4	47.9	2.7	1500.1	478.0	4.1	0.3	1.5	0.1	2447.2	396.9	1.3	0.1	8.5	1.8	23.5	3.8	13.7	1.5
0	10	7.3	4.4	0.2	0.0	0.0	1.3	1.2	52.5	3.7	1055.4	703.2	10.5	0.2	1.5	0.1	2749.5	157.9	1.3	0.0	11.4	0.9	23.6	8.0	12.6	2.8
0	20	7.3	4.9	0.3	0.0	0.0	0.1	0.3	52.2	6.1	739.9	439.1	18.4	0.2	1.6	0.1	2972.2	209.9	1.3	0.1	10.1	2.2	25.8	5.6	12.6	4.7
0	40	7.3	5.2	0.5	0.0	0.0	1.7	3.3	46.5	15.2	486.5	508.9	36.4	1.1	1.6	0.2	2992.2	392.8	1.3	0.0	11.3	4.3	25.7	4.1	11.0	3.2
0.15	0	6.2	4.7	0.2	0.0	0.0	1.7	1.6	163.8	97.5	1495.0	1173.6	4.2	0.3	1.6	0.3	2900.0	458.0	1.3	0.0	10.1	1.5	36.6	7.9	17.6	4.1
0.15	10	6.2	4.6	0.2	0.0	0.0	0.0	0.2	79.7	3.4	594.9	465.8	10.8	0.0	1.5	0.0	2901.2	237.9	1.3	0.1	9.3	3.1	26.9	14.4	16.8	1.3
0.15	20	6.2	4.9	0.2	0.0	0.0	0.8	1.4	74.1	6.2	307.6	102.9	19.6	0.5	1.5	0.1	3126.8	200.7	1.3	0.1	6.4	4.0	32.9	10.8	13.3	1.2
0.15	40	6.2	6.0	0.4	0.0	0.0	0.5	0.1	81.8	12.6	405.6	101.9	37.1	0.5	1.9	0.1	3736.2	219.5	1.4	0.0	8.8	0.8	31.4	14.3	13.7	1.5
1.5	0	6.1	4.7	1.5	2.0	3.5	6.9	6.2	66.0	22.5	1966.2	2859.0	4.3	1.2	1.8	0.7	2828.9	898.9	1.3	0.4	15.1	8.6	18.3	18.1	21.1	13.2
1.5	20	6.1	5.9	0.5	1.0	1.4	7.1	4.6	85.7	9.4	1150.7	1497.5	11.7	0.6	1.9	0.3	3536.4	277.5	1.5	0.2	7.5	3.6	1.5	2.7	21.0	6.1
1.5	10	6.1	6.2	0.6	0.0	0.0	10.4	3.0	82.7	14.1	3010.4	1001.0	20.1	1.5	2.2	0.8	3770.1	394.6	1.4	0.1	12.5	7.2	5.1	5.0	24.7	15.7
1.5	40	6.1	6.7	0.7	0.0	0.0	4.8	1.4	71.1	12.5	277.5	19.0	37.7	1.5	2.0	0.2	3777.4	430.5	1.5	0.1	5.4	1.7	0.0	0.0	15.3	1.9
7.5	0	5.9	11.8	2.5	0.0	0.2	4.6	1.6	61.4	6.9	340.1	85.7	5.2	0.7	3.2	0.7	6713.2	1360.7	1.4	0.3	11.1	5.0	3.7	6.4	24.2	5.2
7.5	10	5.9	11.6	0.8	0.0	0.2	4.2	2.4	63.5	4.9	368.4	261.1	13.2	0.3	3.1	0.3	6545.3	463.8	1.4	0.1	8.8	5.7	0.0	0.0	27.6	1.0
7.5	20	5.9	11.6	0.6	0.1	0.2	9.1	6.8	76.3	14.6	2050.7	2989.2	22.2	1.1	3.3	0.5	6409.3	105.3	1.4	0.1	13.5	4.0	2.4	2.4	32.1	8.6
7.5	40	5.9	11.2	0.7	0.0	0.1	7.7	5.4	76.4	12.4	2301.0	3175.7	40.8	0.5	3.2	0.5	6201.6	399.6	1.3	0.1	14.9	5.7	4.8	8.3	31.7	9.8
15	0	5.7	17.0	1.1	0.0	0.0	3.6	1.3	76.5	13.2	739.2	356.0	5.8	0.1	4.2	0.2	10366.7	701.8	1.5	0.0	7.4	2.9	0.4	0.6	69.1	13.3
15	10	5.7	15.7	0.2	-0.1	0.1	6.0	1.8	97.9	4.8	655.5	284.0	13.6	1.2	3.9	0.0	9280.6	172.3	1.4	0.1	13.0	8.7	6.0	8.5	66.0	6.8
15	20	5.7	16.1	1.3	4.5	3.4	8.4	3.6	85.3	11.2	400.2	44.8	23.5	0.4	4.0	0.3	9604.4	726.7	1.5	0.2	13.0	5.6	11.9	10.5	72.8	5.2
15	40	5.7	16.0	0.5	0.7	0.3	5.2	5.5	95.0	41.2	1507.3	2105.7	50.8	6.7	4.0	0.5	9546.0	391.8	1.4	0.2	13.2	0.9	4.6	5.0	76.2	8.7
Limit*					0.2		0.6		5													20		7.2		40	

*Annual average environmental quality standards for surface waters (other than inland surface waters) (Council of the European Union, 2009) **± standard deviation

546   **Table 4 b.** Metal concentrations in solution after batch experiments (n=2) ± (standard deviation) with Soil B (Depth 1), all P concentrations and
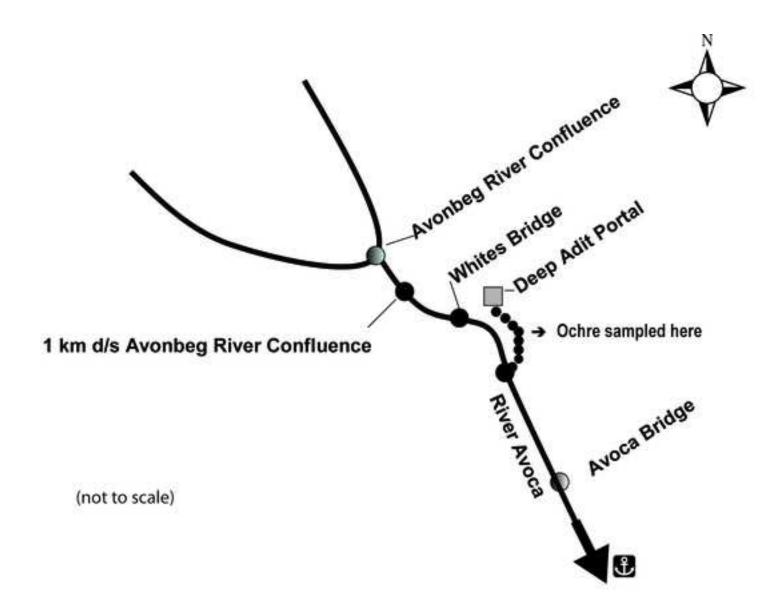
547   ochre amendments

Ochre g kg^{-1}	P mg L^{-1}	pH	Ca mg L^{-1}	±**	Cd	±	Cr	±	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Ni	±	Pb	±	Zn	±
															µg L^{-1}											
0	0	7.0	3.9	0.8	0.3	0.4	6.3	1.8	54.2	9.0	1518.7	707.6	3.4	0.5	1.8	0.4	573.3	181.9	1.4	0.0	4.0	1.1	12.0	6.9	28.8	8.9
0	10	7.0	2.2	0.6	0.1	0.1	5.7	1.0	58.2	5.6	965.0	90.7	9.7	0.4	1.5	0.2	527.6	81.4	1.4	0.2	2.4	1.6	0.0	0.2	32.5	4.9
0	20	7.0	2.8	0.2	0.0	0.2	7.5	1.0	61.4	2.8	1247.9	234.2	18.2	0.2	1.8	0.1	626.8	36.6	1.5	0.1	10.5	3.4	1.3	2.3	39.8	2.8
0	40	7.0	3.1	0.3	0.0	0.1	8.0	1.2	64.1	2.7	1201.7	245.1	41.3	1.1	1.8	0.0	621.8	48.0	1.7	0.3	7.4	2.2	2.6	3.9	39.5	4.3
0.15	0	5.9	3.6	0.7	0.4	0.7	4.9	1.8	37.6	7.5	1391.7	329.3	3.6	0.3	2.2	0.3	749.9	116.1	1.8	0.3	10.7	7.0	8.4	3.9	31.7	5.9
0.15	10	5.9	3.2	0.5	0.2	0.3	6.4	1.6	38.4	2.3	1352.8	147.1	11.1	0.4	2.0	0.1	722.0	74.9	1.7	0.1	8.6	1.9	9.1	15.8	35.1	1.7
0.15	20	5.9	3.7	1.1	0.0	0.1	14.2	2.5	52.5	10.5	2995.6	1450.3	20.6	0.6	2.5	0.5	797.9	194.4	1.9	0.2	12.3	6.5	13.0	9.9	46.4	12.7
0.15	40	5.9	4.5	0.6	3.5	6.0	9.6	4.2	53.8	15.4	1412.1	103.9	43.0	3.4	2.4	0.0	748.6	134.3	1.9	0.1	16.3	4.7	16.3	16.4	45.9	8.4
1.5	0	6.0	5.2	1.4	0.7	1.1	8.8	4.9	47.8	17.4	2098.5	1570.9	3.6	0.4	2.2	0.6	681.9	205.5	1.6	0.0	11.7	2.8	8.9	11.0	36.9	8.6
1.5	10	6.0	4.4	0.1	0.0	0.2	5.9	1.2	47.9	4.3	1481.6	105.7	9.9	0.1	1.7	0.0	596.1	12.0	1.6	0.1	9.9	4.1	17.4	16.6	39.1	2.8
1.5	20	6.0	4.5	0.2	0.0	0.2	3.7	0.4	53.5	2.5	1276.9	486.7	17.6	0.4	1.7	0.1	595.3	26.2	1.5	0.0	10.3	4.1	11.8	14.8	41.2	3.3
1.5	40	6.0	5.1	0.8	0.1	0.1	2.8	2.3	43.1	10.7	1017.3	269.9	39.0	1.9	1.9	0.2	632.7	92.6	1.8	0.3	4.8	5.2	7.9	6.1	39.5	5.4
7.5	0	5.7	9.3	1.0	0.0	0.1	1.3	1.0	61.4	6.4	1165.2	223.4	3.9	0.4	3.3	0.3	1187.2	91.1	1.6	0.1	8.3	1.7	6.5	11.3	53.8	8.6
7.5	10	5.7	7.7	2.2	0.0	0.2	1.4	1.0	63.4	11.4	1049.4	262.0	11.5	0.6	2.8	0.6	943.7	313.2	1.8	0.3	9.4	3.6	17.7	4.5	57.0	14.0
7.5	20	5.7	10.1	3.6	0.2	0.3	4.3	0.9	102.3	14.3	1234.5	66.8	20.3	0.9	3.5	1.2	1236.1	369.8	2.0	0.7	5.6	3.1	22.5	14.7	73.9	5.9
7.5	40	5.7	7.5	0.3	0.2	0.4	2.6	0.4	83.9	5.0	1055.1	256.2	40.8	0.3	2.7	0.1	935.8	33.1	1.6	0.0	9.0	6.0	8.7	11.4	64.9	2.8
15	0	5.6	23.6	2.5	0.0	0.3	8.3	12.5	9.8	9.8	5262.2	5987.8	2.7	1.9	1.6	1.4	128.5	95.8	0.5	0.1	7.6	9.3	7.6	13.2	20.4	14.3
15	10	5.6	27.0	1.7	3.5	3.9	16.0	7.1	22.9	7.1	6366.1	1747.4	12.4	1.0	2.1	0.5	80.0	33.3	0.6	0.1	3.8	4.4	24.8	19.5	23.0	9.8
15	20	5.6	30.7	0.5	0.6	0.2	4.3	1.5	9.7	3.4	1541.1	1320.5	22.7	1.1	1.0	0.3	23.3	12.2	0.5	0.0	2.2	3.8	20.4	7.0	5.4	2.4
15	40	5.6	35.7	0.4	0.3	0.5	1.8	1.7	4.2	1.4	1181.4	52.9	47.1	1.0	1.0	0.1	15.7	1.1	0.5	0.0	0.9	1.1	21.4	7.3	4.5	0.9
Limit*					0.2		0.6		5												20		7.2		40	

548   *Annual average environmental quality standards for surface waters (other than inland surface waters) (Council of the European Union, 2009) **± standard deviation

549 **Table 5** Kinetic experiment. Metal concentration release over time ± (standard deviation).

Minutes	Ca	±*	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Zn	±
	mg L^{-1}								µg L^{-1}							
1	8.4	0.0	8699	2761	1369	238	134.8	2.4	1.6	0.1	280.2	18.3	2.6	0.0	13045	1163
5	8.1	0.2	12570	121	1358	168	135.8	0.8	1.3	0.0	231.8	8.1	2.2	0.0	15905	308.
10	5.9	2.9	6570	8573	667	441	137.1	3.9	0.6	0.8	187.4	52.9	1.8	0.5	8218	10905
15	4.2	1.9	6180	2491	732	86.0	69.3	27.2	0.6	0.2	118.8	43.4	1.2	0.6	7421	2840
30	3.2	0.0	9014	345	817	28.6	62.5	3.2	0.5	0.0	105.7	8.6	0.8	0.0	10318	842
60	6.1	1.4	14918	4294	973	192.0	109.2	19.5	0.9	0.2	165.6	34.1	1.5	0.3	16564	4295

550 *± standard deviation

551

N

Avonbeg River Confluence

Whites Bridge

Deep Adit Portal

1 km d/s Avonbeg River Confluence

→ Ochre sampled here

River Avoca

Avoca Bridge

(not to scale)

line figure
Click here to download high resolution image