Factors Influencing Dissolved Copper Concentrations in Oregon Highway Stormwater Runoff

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Abstract: Highway stormwater runoff represents a significant source of dissolved copper to surface waters. It is well established that even low concentrations of dissolved copper can be toxic to many aquatic organisms. In the Pacific Northwest of the United States, recent research has focused on the effects of low-level copper exposure to salmonids listed as threatened or endangered under the Endangered Species Act (ESA). In light of these recent studies, increasingly stringent guidelines for the discharge of highway stormwater runoff have been imposed as part of ESA assessments of transportation projects. Assessing factors that may impact dissolved copper concentrations in stormwater provides a practical framework for predicting when and where copper toxicity could be problematic. A stormwater sampling effort was performed to examine the influence of site locale, traffic density, storm hydrology, the "first-flush" effect, and water quality parameters on measured dissolved copper concentrations in highway stormwater runoff. In general, runoff from urban/high traffic sites and "first-flush" samples exhibited higher copper concentrations than other samples. Increased dissolved copper concentrations were highly correlated with both dissolved organic carbon (DOC) and alkalinity. However, multiple linear regression modeling suggests that only the correlation

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18 with DOC has the potential to be causative. These findings will help inform State and Federal

19 transportation and environmental protection agencies regarding the conditions under which elevated

20 copper concentrations (and potential copper toxicity) are most likely to occur.

21 CE Database subject headings: Runoff; Stormwater management; Heavy metals; Copper

Introduction

23 Stormwater runoff can be a significant source of metals (*e.g.*, Cu, Zn, Cd, Pb, Ni) to surface waters

24 (Dean*, et al.*, 2005, Kayhanian*, et al.*, 2003, Kayhanian*, et al.*, 2007b, USEPA, 1983). Of these metals,

25 copper is of particular concern due to its effects on salmonid species at very low concentrations. Recent

26 research has shown that concentrations of dissolved copper as low as 0.18 to 2.1 µg/L above background

27 levels (≤3 µg/L) can adversely affect salmonid species (Hecht*, et al.*, 2007, McIntyre*, et al.*, 2008,

28 Sandahl*, et al.*, 2007). Large stormwater studies have shown that untreated highway runoff often

29 contains dissolved copper concentrations above these levels (Bannerman*, et al.*, 1996, Driscoll*, et al.*,

30 1990, Kayhanian*, et al.*, 2003) and dissolved copper has been shown to contribute to aquatic toxicity

31 (Kayhanian*, et al.*, 2007a). Because salmonids and other threatened or endangered species inhabit

32 surface waters that receive stormwater inputs, increased scrutiny has been placed on the discharge of

33 highway stormwater runoff to those receiving bodies. Often, the impacts of highway stormwater runoff

34 on these water bodies are evaluated based on end-of-pipe concentrations. As such, it is important to

35 understand the variables controlling dissolved copper concentrations in highway stormwater runoff as a

36 means of identifying characteristics of the most problematic sites and designing appropriate treatment

37 strategies. The objectives of this work were to: 1) identify the effects of site location, storm hydrology,

38 and water quality parameters on the concentration of dissolved copper in Oregon highway runoff; and 2)

39 develop a qualitative understanding of conditions under which elevated dissolved copper concentrations

40 in highway stormwater runoff have the greatest potential to impact receiving waters.

41 The sources of copper in highway stormwater runoff include engine oil, combustion of lubricating

42 oils, roof/gutter runoff, building siding corrosion, fertilizers, pesticides, industrial releases, and wet and

43   dry deposition (Davis, *et al.*, 2001, Kim and Fergusson, 1994, Makepeace, *et al.*, 1995, Rosselot,

44   2006b). However, the biggest single source of copper to highway stormwater runoff is brake pad wear

45   (Legret and Pagotto, 1999, Rosselot, 2006a). The total concentration of copper in stormwater, $[Cu]_T$,

46   consists of particulate copper, $[Cu]_p$, and dissolved copper, $[Cu]_d$, where $[Cu]_d$ is operationally defined

47   as the fraction of $[Cu]_T$ passing a 0.45 µm filter. Copper can partition between these phases via

48   dissolution/precipitation, adsorption, and redox processes in rainwater and stormwater runoff.

49   Dissolved copper endangers salmonids at low concentrations by inhibiting their olfactory system,

50   thereby decreasing their predator avoidance behavior (Sandahl, *et al.*, 2007). A number of factors may

51   influence the concentration of copper in stormwater. The "first flush effect" (Barrett, *et al.*, 1998, Flint

52   and Davis, 2007, Kayhanian, *et al.*, 2007b), increased traffic density (Driscoll, *et al.*, 1990, Kayhanian,

53   *et al.*, 2003), and lengthy antecedent dry periods (ADPs) (Driscoll, *et al.*, 1990, Kayhanian, *et al.*, 2003,

54   Prestes, *et al.*, 2006, Soller, *et al.*, 2005), have been linked to increased copper concentrations in

55   stormwater. Total rainfall volume, rainfall duration, and rainfall intensity have been correlated to

56   decreased copper levels, likely due to dilution (Driscoll, *et al.*, 1990, Kayhanian, *et al.*, 2003). Other

57   factors, such as ecoregion classification may also affect copper in highway runoff. For the purposes of

58   regulating copper in highway stormwater runoff and planning transportation projects, it is important to

59   know what conditions/locations may be most problematic.

60   Although the concentration of dissolved copper is a key factor in determining toxicity, it is important

61   to recognize that only a fraction of dissolved copper (consisting of free ionic and weakly complexed

62   species) is bioavailable in natural waters (Brooks, *et al.*, 2007, Luider, *et al.*, 2004, Sigg and Behra,

63   2005, USEPA, 2007). A number of water quality (WQ) parameters may influence copper toxicity. Both

64   organic and inorganic anionic species form aqueous complexes with copper. pH affects the solubility of

65   dissolved copper while hydronium ions also compete with free ionic copper (Cu^{2+}) for adsorption sites

66   on ligands and biota. Additionally, hardness cations (primarily Ca^{+2} and Mg^{+2}) compete with Cu^{2+} for

67   adsorption sites on ligands and can also be an indicator of inorganic anions (Luider, *et al.*, 2004,

68   USEPA, 2007). The presence of hardness cations can decrease the solubility of Cu through competition

with Cu for natural organic matter ligands (e.g., EDTA, NTA, humic and fulvic substances) and also through competition with Cu^{+2} for adsorption sites on aquatic organisms. Despite these effects, toxicity guidelines have historically been based on dissolved copper concentrations with a correction for water hardness. Only recently has the Environmental Protection Agency (EPA) adopted a biotic ligand model to establish copper toxicity criteria in freshwater (USEPA, 2007) that considers aqueous copper speciation, including complexation by organic matter and competition of cations for organic and biotic ligand sites.

The work reported here focuses on the factors controlling the presence and concentration of copper in highway stormwater runoff. A stormwater sampling program was executed to examine the correlations between copper concentrations and a number of variables. The resulting storm and chemical concentration data was then statistically analyzed to determine which variables may influence or correlate with copper concentrations in highway stormwater runoff. The work was completed as part of a larger study focused on the speciation of copper in highway stormwater runoff; results of the speciation analysis are reported elsewhere (Sprick, 2009).

Materials and methods

Sites

Stormwater samples for this study were collected between March 2008 and October 2009 from four sites (Bend, Corvallis, Portland, and Wemme) in the State of Oregon. The characteristics of each site are detailed in Table 1. The sites used in this study were selected based on their varied traffic levels, measured as annual average daily traffic (AADT), and differing ecoregions. A map of Oregon Highways can be found at http://www.oregon.gov/ODOT/TD/TDATA/gis/docs/statemaps/hwy_sys.pdf and a map and description of ecoregions can be found at ftp://ftp.epa.gov/wed/ecoregions/or/or_eco_lg.pdf. The Portland site is located in an urban area and receives a much higher traffic volume than the other sites. Being on the eastern slope of the Cascade Mountains, the Bend site receives less average annual rainfall than the other sites. Also of note, the

94   Corvallis site has a much smaller drainage area than the other locations. This site was selected because

95   it exclusively drains the surrounding highway and is located close to our analytical lab.

96   *Sample Collection*

97   All storms sampled in this study were characterized by $\geq$ 0.15" of rainfall over a 24-hour period

98   preceded by a dry period receiving < 0.04" of precipitation over six hours. A minimum storm duration

99   of one hour was specified and the end of a storm was defined as a six-hour period receiving < 0.04" of

100 precipitation (Washington State Department of Ecology, 2008).

101 Samples at all sites were collected with automated samplers triggered by flow measurements in the

102 collection system using bubbler flow meters. Flow-weighted composite samples were collected at the

103 Portland, Bend and Wemme sites and grab, first flush and discrete flow-weighted samples were

104 collected at the Corvallis site. Rainfall data was collected on-site in Corvallis using a tipping-bucket

105 rain gauge. Local weather stations were used at the other three sites. At each of the sites, field

106 personnel verified the proper function of the autosampler, installed a clean polyethylene sampling

107 bottles, and surrounded them with crushed ice prior to sampling. Further details of the sample collection

108 procedures and equipment, along with schematics of the systems are provided in the supporting

109 information.

110 *Sample Handling*

111 At the Portland, Bend, and Wemme sites, bulk composite samples were delivered to a contract lab

112 (Test America) within 24 hours of initial collection. At the lab, composite samples were separated into

113 subsamples where one was immediately analyzed for cations and anions and the other mailed overnight

114 to Corvallis in coolers packed with ice. Composite samples from the Corvallis site were formed by

115 combining aliquots from discrete samples. The volume of the aliquots was based on the number of

116 discrete samples collected. Individual flow-weighted samples were thoroughly mixed and a large bore

117 volumetric pipette was used to collect an aliquot of the sample and put it in a new, clean container. This

118 process was completed within one hour of sample pickup from the site.

119 *Analytical Methods*

120   Upon arrival, raw samples were immediately analyzed for total suspended solids (TSS) in accordance

121   with Standard Method 2540D (APHA 2005) and a 60 mL aliquot was extracted to measure total cations.

122   In this work, "total" cations refers to the concentration of acid-extractable cations released after >1 hour

123   equilibration in 1% (v/v) ultrapure HNO_3 (Aristar Ultra), dropping the pH to below 2. This procedure is

124   a modification of Standard Method 3030C (APHA, *et al.*, 2005) and was meant to represent the bio-

125   available fraction of metals lightly adsorbed to particulates in the sample (Li, *et al.*, 2009). For thirteen

126   samples also analyzed by traditional digestion techniques (EPA Method 200.8), the acid-extractable

127   fraction of the total metal concentration (as measured by EPA Method 200.8) was not significantly

128   different than 1 ($\alpha = 0.05$). Following extraction, samples were vacuum-filtered through 0.45 µm filters

129   (Pall Supor 450). Dissolved samples were fractionated by vacuum-filtering raw, undigested samples

130   through 0.45 µm filters. Filters were stored in 1% ultrapure HNO_3 for at least one day and were rinsed

131   with 250 mL of DDI water prior to use.

132   After the bulk dissolved sample was obtained, aliquots for various measurements were separated out

133   into appropriate containers and stored in the dark at 4 °C until analysis. Aliquots for dissolved cation

134   determinations were acidified (1% ultrapure HNO_3 addition). Clean labware was used to contain

135   samples for all tests except trace metal determinations, where unused 15-mL BD Falcon polypropylene

136   test tubes were utilized. Alkalinity determinations were typically done in duplicate while all other

137   measurements were done in triplicate.

138   pH and conductivity were measured using a VWR symphony probe and Accumet AR50 control panel

139   within 1 hour of sample receipt. Alkalinity was measured within 8 hours of sample receipt using the

140   Gran Titration method with 0.02 N H_2SO_4. Dissolved organic carbon (DOC) was measured within a

141   week of sample collection on a Shimadzu TOC-V$_{CSH}$ total organic carbon analyzer (EPA Method

142   415.1). Major cations (Ca, Fe, K, Mg, Na) were measured using Inductively Coupled Plasma (ICP)

143   Atomic Emission Spectrometry (Varian Liberty 150). Trace metals (Cd, Cu, Ni, Pb, Zn) were measured

144   using either ICP- Optical Emission Spectrometry (Teledyne Leeman Prodigy) or ICP-Mass

145   Spectrometry (Thermo PQ ExCell). Further details of QA/QC procedures for trace metals analysis are

146 provided in the supporting information. Anions (NO_3^-, NO_2^-, SO_4^{-2}, PO_4^{-3}, and Cl^-) were measured on

147 a Dionex DX500 Ion Chromatograph. Measurements for major cations, trace metals, and anions were

148 performed within 6 months of sample collection.

149 *Statistical Analysis*

150 S-Plus® 8.0 statistical software was used for all statistical analyses. A 95% confidence level was used

151 in this study. Fisher's Least Significant Difference (LSD) procedure (Ramsey & Schafer 2002) was used

152 to quantify differences in constituent concentrations in composite samples collected at each of the four

153 sites. Samples were grouped based on their location and those groups were then compared. These

154 comparisons were planned, so individual confidence levels are acceptable. Simple linear regression and

155 multiple linear regression (MLR) procedures were used for a number of analyses. Where applicable,

156 binary indicator variables were used in regression analysis to indicate a sample's presence in a certain

157 group – as in the case of first flush samples or samples taken from different sites. Model variable

158 selection was done using backwards stepwise regression, in which a full model including all possible

159 explanatory variables is reduced to a final model including only the explanatory variables that are found

160 to be statistically significant (Ramsey & Schafer 2002).

161 **Results and Discussion**

162 As outlined above, factors likely to influence the presence of copper in runoff samples include AADT,

163 urban site classification, ADP, the "first flush effect", total rainfall, and rainfall intensity. All of these

164 factors were considered in this study; roadway and site characteristics are shown in Table 1 and a

165 summary of the storm-specific hydrologic data is summarized in Table 2. The sampled events were

166 characterized by a wide variety of ADP (10 h – 2 weeks), total rainfall (0.09 – 2.11 in), and event

167 duration (6 – 48.2 h).

168 Several water quality parameters were examined for correlations with both total and dissolved copper.

169 Aggregate WQ data, including total and dissolved trace metal concentrations from the composite

170 samples collected at all sites are shown in Table 3. Important among these parameters are TSS and

171 DOC. TSS is both a potential source (via dissolution of Cu-containing solids) and sink (via adsorption)

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172 for dissolved copper, and DOC is known to form strong aqueous complexes with dissolved copper

173 (Allen and Hansen, 1996, Buck and Bruland, 2005, Gerringa, *et al.*, 1998, Lee, *et al.*, 2005, Stead-

174 Dexter and Ward, 2004). Due to the ability of natural organic matter (NOM) to strongly complex

175 copper, both dissolved copper and DOC (a surrogate measure for NOM) were examined. Possible

176 correlations with other water quality parameters were introduced above.

177   Copper was detected in every composite sample. $[Cu]_T$ ranged from 2.09 – 60.9 µg/L while $[Cu]_d$

178 ranged from 1.9 – 22.7 µg/L; the median value of the % dissolved copper was 39.3%. This distribution

179 of copper is in agreement with recent research focused on the distribution of metals in urban stormwater

180 (Sansalone, *et al.*, 2010). Although the discussion here focuses on copper, of the five metals examined,

181 zinc had the highest concentrations with $[Zn]_T$ ranging from 26.1 – 219 µg/L and $[Zn]_d$ ranging from

182 10.6 – 193 µg/L. In general, stormwater samples collected at the Portland site showed consistently

183 higher concentrations of all constituents (including copper and other heavy metals). Also significant is

184 the fact that the Wemme samples from 1/6, 3/11, 3/16 and 3/24/2009 had unusually high conductivity

185 stemming from abnormally high concentrations of magnesium and chloride (>10X those in other

186 samples). These outliers are attributed to the addition of magnesium chloride to the roadway surface as

187 an anti-icing chemical. Only two samples were collected at the Bend site, which limits the inferences

188 that can be made for that location. For the purposes of data analysis, the concentrations of most

189 constituents and hydrologic variables have been log-transformed. Concentrations of constituents in

190 stormwater are typically log-normally distributed (Burton Jr and Pitt 2002), an observation that was

191 found to be true in this study.

192 ***Site Comparisons***

193   In comparing data across the four sites, the concentrations of total copper, dissolved copper, and DOC

194 are of particular interest and are displayed in Fig. 1. The most apparent difference between the sites is

195 that the concentrations of all these constituents are higher at the Portland site than at the other sites. The

196 statistically significant (at $p < 0.05$) multiplicative differences between all of these sites are compiled in

197 Table 4.   Because these parameters have been log-transformed, the differences displayed are

198   multiplicative and based on medians. For example, the median $[Cu]_d$ at the Portland site was 3.78 times

199   higher than the median concentration at the Corvallis site, with a 95% confidence interval (CI) of 2.18 to

200   6.58 times higher. The comparisons of Corvallis site with the Bend and Wemme sites did not result in

201   any statistically significant differences.

202   The influence of roadway characteristics (AADT and urban site association) on total and dissolved

203   copper concentrations were investigated using multiple linear regression modeling. Using the roadway

204   classification of Kayhanian *et al.* (2003) based on AADT levels, only the Portland site is classified as

205   urban (specifically, medium-high urban), with an AADT of 130,000. All other sites are classified as

206   non-urban, with AADT levels below 30,000. MLR modeling of $[Cu]_d$ as a function of both the Portland

207   site indicator and AADT showed that only one of these variables is necessary in the model; the two

208   variables are not simultaneously significant. In an attempt to isolate the effect of AADT from urban

209   association, the composite samples from only the non-urban sites (Bend, Corvallis and Wemme) were

210   examined. The linear regression of AADT vs. $\log[Cu]_d$ for the non-urban sites did not result in a slope

211   statistically different than zero ($p > 0.05$, two sided t-test). Regression data are shown in Figs. S3 and

212   S4 of the supporting information. With the data collected here, it is only possible to establish that the

213   Portland site shows higher copper concentrations. The individual effects of AADT and urban site

214   association cannot be conclusively determined.

215   The lack of a good correlation between traffic and $[Cu]_d$ is not surprising considering the differing

216   conclusions reached by others. Previous research involving larger datasets has suggested only weak

217   correlations between copper concentrations and AADT (Kayhanian 2003, Driscoll 1990). Significant

218   differences in pollutant concentrations have been demonstrated between sites deemed urban and non-

219   urban, based on AADT; yet, there has been little research to suggest any continuous relationship

220   between pollutant concentrations and traffic density. In summary, these results confirm the findings of

221   others who have suggested that urban site association is the single biggest factor influencing copper

222   concentration.

223   ***The First Flush Effect***

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224   Fig. 2 illustrates a clear first flush effect for $[Cu]_T$, $[Cu]_d$ and DOC at the Corvallis site. All three

225   constituents showed significantly higher concentrations in first flush samples than in composite samples

226   ($p \ll 0.05$, two sided t-test). On average, first flush samples showed 3.06 times more $[Cu]_T$ (1.68-5.60,

227   95% CI) and 4.01 times more $[Cu]_d$ than composite samples (2.20-7.32, 95% CI). In terms of DOC,

228   first flush samples showed an average of 4.75 times the concentration found in composite samples

229   (2.83-7.96, 95% CI). These findings are in line with previous work (Flint and Davis, 2007, Han, *et al.*,

230   2006, Kayhanian, *et al.*, 2007a, Sansalone and Buchberger, 1997) and suggest that runoff from early in a

231   storm may be most important with respect to copper toxicity. As such, potential treatment strategies

232   must be designed with the first flush effect in mind. One example might include diverting runoff from

233   early portions of the storm to an appropriate BMP.

234   ***Relationships with Hydrologic Parameters***

235   To examine the effect of hydrologic variables on $[Cu]_d$ in composite samples, a backwards stepwise

236   regression procedure was used. The reduced model contained only the site indicator variables, having

237   already established their significance, while the full model contained all site indicator variables and

238   variables accounting for ADP, total rainfall, and rainfall intensity (Table 2). Rainfall duration was

239   dropped from the analysis due to its co-variation with total rainfall. The MLR analysis revealed the lack

240   of any significant relationship between $[Cu]_d$ and any of these hydrologic parameters after accounting

241   for the effect of different sites. However, ADP might be expected to affect first flush concentrations

242   more than composite copper concentrations. This relationship was examined with the Corvallis first-

243   flush samples modeling $[Cu]_d$ only as a function of ADP. No significant association between $[Cu]_d$ and

244   ADP was found in first flush samples ($p > 0.05$, two sided t-test). Scatter plots of $[Cu]_d$ as a function of

245   individual hydrologic variables are shown in Fig. S5 of the supporting information.

246   Previous studies with larger datasets have found that the relationship between either total rainfall or

247   rainfall intensity with pollutant event mean concentrations (EMCs) is often weakly negative (Driscoll, *et*

248   *al.*, 1990, Kayhanian, *et al.*, 2003, USEPA, 1983). Other studies have also shown longer ADPs to be

249   correlated to increased pollutant concentrations (Kayhanian 2003, Prestes 2006). The smaller sample

250   size in this study may have contributed to the lack of significant correlations of $[Cu]_d$ with hydrologic

251   variables or ADP. Additionally, the samples gathered in this study were primarily from storms in the

252   fall, winter, and spring, and were marked by relatively low ADPs. The sampling of summer storms

253   would likely have provided data over a much greater range of ADPs. However, the unpredictability (and

254   infrequency) of these storms prevented their collection within the time constraints of this study.

255   *Correlating Copper Concentrations with other Water Quality Parameters*

256   Measuring dissolved copper directly requires highly sensitive instruments and may be expensive,

257   limiting the ability of local, state, and federal highway departments to routinely monitor for copper.

258   Using MLR modeling can help determine other more easily measured variables that correlate with

259   dissolved copper. Knowing these predictor variables may give regulators an idea of when dissolved

260   copper levels are likely to be elevated.

261   Backwards stepwise regression was again employed to examine the effect of water quality parameters

262   on $[Cu]_d$ in stormwater samples. Here, measured concentrations of constituents in the samples were

263   used to predict the concentration of copper. Because the present MLR analysis did not involve

264   comparing different sites or sample types, but rather the presence of constituents in any water sample, all

265   fully quantified samples were examined. In all, 41 samples of various types (grab, first flush, flow-

266   weighted, and composite) and from all four sites were available for this analysis. However, four

267   composite samples from the Wemme site (1/6/2009, 3/11/2009, 3/16/2009 and 3/24/2009) were

268   removed from the analysis as they contained artificially elevated levels of hardness stemming from road

269   salt ($MgCl_2$) application (Fig. S6 in supporting information). The predictor variables that were

270   examined in the full model were pH, alkalinity, hardness, conductivity, DOC, and TSS. Omitting the

271   four Wemme samples, the final predictive model for $[Cu]_d$ reached in the analysis identified only

272   alkalinity, DOC and pH as significant predictors of $[Cu]_d$. Table 5 summarizes the results of this

273   analysis. This preliminary analysis identifies the variables important for predicting $[Cu]_d$, but regression

274   coefficients should be verified through additional sampling prior to using regression models for

275   prediction of $[Cu]_d$ (Ramsey and Schafer, 2002).

276   The most significant variables in predicting $[Cu]_d$ were DOC and alkalinity. The weak negative

277   association with pH is reasonable as acidic runoff would dissolve more particulate copper. The

278   relatively low p-value may be indicative of the fact that the pH of stormwater samples collected in this

279   study were approximately neutral and did not vary greatly. As a result, other effects are more

280   pronounced. Hardness and alkalinity were highly correlated (Fig. S6 in supporting information); this

281   relationship is likely due to the dissolution of carbonate minerals such as $CaCO_3$ from the road surface

282   and drainage system. The strong co-variation of hardness and alkalinity explains why only one of these

283   variables (alkalinity) was retained in the MLR model.

284   Correlations of $[Cu]_d$ with DOC and alkalinity are shown in Fig. 3. Although the correlation of $[Cu]_d$

285   with DOC and alkalinity may only demonstrate the presence of many pollutants (including copper) in

286   the runoff, the simultaneous significance of these two parameters in predicting $[Cu]_d$ indicates they are

287   accounting for distinct effects. Based on these preliminary results, measurement of alkalinity and DOC

288   could be used as a screening tool prior to more detailed sampling and analysis for trace metals.

289   The strong positive relationship between DOC and copper has been observed in other systems

290   (Martinez and McBride, 1999, Romkens and Dolfing, 1998) and highlights the ability of NOM to

291   increase $[Cu]_d$ through complexation. In this study, the similar increases in DOC and $[Cu]_d$ in first

292   flush samples as compared to composite samples (Fig. 2) also supports the association between $[Cu]_d$

293   and DOC. Examining Fig. 3a, an order of magnitude increase in $[Cu]_d$ at the μg/L level is correlated

294   with an order of magnitude increase in DOC at the mg/L level. This suggests that although there are

295   many binding sites on a NOM macromolecule, relatively few may actually bind copper. Hoffman *et al.*

296   (2007) suggested that copper is bound to uncommon binding sites or sites with special conformation

297   within the macromolecule. Although these copper-binding moieties may be relatively uncommon,

298   NOM is often present in great excess compared to $[Cu]_d$. The fact that NOM complexes dissolved

299   copper makes the overall correlation between DOC and toxicity complicated. NOM draws copper into

300   the aqueous phase, increasing $[Cu]_d$. However, the strong binding of copper and great excess of NOM

301   may be indicative of low concentrations of Cu^{2+}.

302   Because $[Cu]_d$ predictably correlates with $[Cu]_T$ (Fig. S7 in supporting information), another MLR

303   model was constructed to see if DOC or alkalinity had any effect on $[Cu]_d$ after $[Cu]_T$ was accounted

304   for. This model revealed that, after accounting for the effect of $[Cu]_T$, DOC was still a significant

305   predictor of $[Cu]_d$ ($p < 0.0001$, F-test). Alkalinity showed an insignificant association with $[Cu]_d$ after

306     $[Cu]_T$ had been accounted for in the model ($p = 0.19$, F-test). These findings suggest that while both

307   alkalinity and DOC are associated with $[Cu]_d$, only the relationship with DOC could potentially be

308   causative. The inclusion of alkalinity in the $[Cu]_d$ model may only be indicative of the presence of total

309   copper, possibly because both stem from the dissolution of solid phases (e.g., roadway surfaces and

310   particles from brake pad wear). This is a reasonable conclusion; NOM has a strong affinity for copper

311   and is likely to cause particulate copper (part of the total copper measurement) to partition into the

312   dissolved phase.

313   ***Intra-Storm Variations in Copper Concentration***

314   Flow-weighted samples collected throughout 9 different storms were examined at the Corvallis site.

315   These flow-weighted samples were analyzed for dissolved trace metals and DOC. An example of the

316   data collected is shown in Fig. 4 for the 10/13-10/14/09 storm at the Corvallis site. Clearly, higher

317   concentrations of $[Cu]_d$ and DOC are present in samples collected early in the storm. Furthermore, the

318   drop in concentrations of both $[Cu]_d$ and DOC after the first flush is precipitous at first, and more

319   gradual as the storm continues. These trends were consistent in other storms as well. Interestingly, the

320   concentrations of $[Cu]_d$ and DOC increased (from the 2nd to the 3rd samples) following a 4-hour break in

321   the storm. This short dry period may have allowed a small amount of pollutant accumulation on the

322   roadway or led to dissolution of particulate matter in the collection system. In either case, the result was

323   a jump in $[Cu]_d$ and DOC concentrations in the 3rd sample. In all cases, a relative increase or decrease

324   in the concentration of DOC between samples showed a corresponding increase or decrease in $[Cu]_d$,

325   which also agrees with the strong correlation of $[Cu]_d$ and DOC discussed previously.

326   The intra-storm data was also analyzed with simple linear regression, modeling the normalized

327   concentrations of $[Cu]_d$ or DOC (*i.e.*, C_i/C_0 where C_0 represents the concentration in the first flush) as a

328 function of V_i/V_{tot}, or 'normalized cumulative volume' (Figs. S8 and S9 in supporting information).

329 V_i/V_{tot} is a ratio which represents the cumulative volume of runoff when sample i was taken divided by

330 the total runoff volume produced by the storm. This measure can be applied to all storms and is used

331 here to show the overall progress of a storm, though it does not account for the storm magnitude.

332 Normalized $[Cu]_d$ and DOC concentrations were found to decrease with increasing V_i/V_{tot} ($p < 0.05$,

333 two sided t-tests).

Conclusions

335 Results of the study confirm earlier findings that urban (high traffic) highways show the most

336 potential for producing runoff that would expose aquatic species to elevated levels of $[Cu]_d$, increasing

337 the possibility of copper toxicity. Additionally, first-flush samples displayed consistently higher $[Cu]_d$

338 than samples collected at later times during a storm. Therefore, best management practices (BMPs)

339 aiming to ameliorate the effect of copper should focus on high traffic, urban areas, the first flush of

340 storms, and discharges to receiving waters inhabited by salmonid species. Specific conclusions include:

341   1. Dissolved copper concentrations in highway runoff from an urban site were significantly

342   higher than those from three non-urban sites when characterized on the basis of AADT.

343   However, there were no significant differences in dissolved copper EMCs in runoff measured

344   at the three non-urban sites, which varied in terms of eco-region and AADT.

345   2. There were no significant effects of ADP, total rainfall, rainfall duration, or average rainfall

346   intensity on $[Cu]_d$ in composite samples. There was also no significant effect of ADP on

347        $[Cu]_d$ in first flush samples from the Corvallis site. In sum, amongst these varied sites in

348   Oregon, storm hydrology was not a significant factor controlling dissolved copper

349   concentrations.

350   3. In a MLR model, the water quality parameters that demonstrated the greatest ability to predict

351        $[Cu]_d$ were DOC and alkalinity, both having positive associations with $[Cu]_d$. The model also

352   included a term for pH, which was negatively correlated with $[Cu]_d$. Of these parameters,

353   DOC represents an independent driving force for copper dissolution. These findings are

14

354 important in that these models will guide the design of future sampling efforts and provide

355   screening tools for preliminary sampling and evaluation of dissolved copper. Having

356   identified the important variables, coefficients in the model can be determined that may allow

357   the empirical prediction of dissolved copper concentrations on the basis of simple measures of

358   water quality.

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Table 1. Characteristics of the stormwater sampling sites in Bend, Corvallis, Portland, and Wemme, OR

Site	Ecoregion	Catchment Area	AADT	No. of sampled storms
	(-)	(m^2)	(vehicles/day)	(-)
Bend (Hwy 20)	Eastern Cascades Slopes & Foothills	5,670	24,000	2
Corvallis (Hwy 20/34)	Willamette Valley	450	8,000	8
Portland (I-5)	Willamette Valley	93,480	130,000	5
Wemme (Hwy 26)	Cascades	87,010	12,000	7

Table 2. Summary of hydrologic indices for storms sampled at the four sites

Site	Date	ADP	Total Rainfall	Duration	Average Intensity	Maximum Discharge
		hrs	cm	hrs	cm/hr	L/s
Bend	12/29/08	12.5	1.09	11.8	0.093	NR
	3/16/09	<24	0.23	9	0.025	18.6
Portland	3/17/08	14	1.14	11	0.104	148.5
	10/6/08	12	0.43	11	0.039	23.8
	11/2/08	12	0.74	25	0.030	23.5
	11/3/08	14	2.34	26	0.090	22.3
	11/20/08	175	1.22	11	0.111	19.2
Wemme	11/20/08	NR	NR	NR	NR	NR
	12/1/08	31	2.59	8.7	0.298	13.2
	1/6/09	74	5.36	37	0.145	9.9
	3/11/09	20	0.86	6	0.144	4.7
	3/16/09	97	5.36	48.2	0.111	10.2
	3/24/09	10	1.27	24.3	0.052	4.0
	5/5/09	15	3.00	23	0.130	13.6
Corvallis	11/20/08	172	0.76	9	0.085	0.4
	12/1/08	245	0.41	8	0.051	0.3
	2/6/09	188	0.69	13.5	0.051	0.2
	2/23/09	109	1.78	23	0.077	0.4
	3/14/09	109	1.96	24	0.082	0.3
	4/12/09	235	0.56	6	0.093	0.2
	5/13/09	141	0.43	5.5	0.079	0.3
	10/13/09	340	0.99	14.5	0.068	1.0

Note: NR = not recorded

6 Table 3. Summary of water quality data from composite samples collected at the Bend, Corvallis,

7 Portland and Wemme Sites

Site	Portland		Corvallis		Wemme		Bend	
Number of Samples	5		8		7		2	
Parameter (Units)	Range	Median	Range	Median	Range	Median	Range	Median
General Water Quality								
pH	6.24 – 7.15	6.92	6.26 – 7.31	6.63	6.41 – 7.04	6.80	6.66 – 6.86	6.76
Conductivity (μS/cm)	55.2 – 141	83.9	16.3 – 48.2	23.5	18.2 – 1065	206.5	77.4 – 152	115
Alkalinity (mg/L as $CaCO_3$)	13.8 – 29.9	18.41	4.19 – 10.0	6.29	3.62 – 14.1	8.84	9.68 – 10.1	9.89
Hardness (mg/L as $CaCO_3$)	22.7 – 43.4	30.9	5.24 – 12.2	8.25	9.61 – 477	95.9	27.3 – 72.8	50.1
TSS (mg/L)	23.1 – 118	89.9	14.5 – 162	26.1	26.6 – 117	61.8	85.8 – 241	163
DOC (mg/L)	5.88 – 9.97	7.00	1.81 – 10.8	4.51	1.54 – 5.97	2.50	5.16 – 5.8	5.48
Major Cations (dissolved)								
Calcium (mg/L)	5.96 – 11.6	9.14	1.62 – 3.51	2.46	1.64 – 21	10.9	2.72 – 4.27	3.50
Magnesium (mg/L)	1.14 – 3.51	1.78	0.29 – 0.83	0.45	0.62 – 103	16.5	4.98 – 15.1	10.0
Sodium (mg/L)	1.61 – 5.14	2.38	0.83 – 2.50	1.17	0.56 – 9.62	1.68	1.17 – 1.6	1.39
Potassium (mg/L)	0.56 – 2.53	1.49	0.33 – 0.85	0.62	brl[1] – 0.52	0.35	0.48 – 0.74	0.61
Iron (mg/L)	brl[2]	brl[2]	brl[2] – 0.059	0.031	brl[2] – 0.009	brl[2]	brl[2] – 0.24	NA
Anions								
Chloride (mg/L)	2.13 – 16.7	3.52	0.77 – 3.27	1.14	2.42 – 489	40.3	17.5 – 55.8	36.6
Nitrate (mg/L)	1.95 – 5.85	3.86	0.58 – 2.51	1.25	0.37 – 1.28	0.47	0.77 – 1.96	1.36
Nitrite (mg/L)	0.1 – 0.3	0.2	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]
Phosphate (mg/L)	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]	brl[1]
Sulfate (mg/L)	3.33 – 6.86	6.19	0.32 – 1.28	0.75	0.43 – 12.9	2.18	1.42 – 2.47	1.94
Trace Metals (Total)								
Copper (μg/L)	36.8 – 60.9	40.9	4.74 – 26.2	9.91	2.09 – 21.9	9.08	21.8 – 25.8	23.8
Cadmium (μg/L)	0.37 – 0.74	0.68	brl[3] – 1.75	brl[3]	brl[3] – 0.16	brl[3]	brl[3] – 0.12	NA
Nickel (μg/L)	1.91 – 3.92	2.84	brl[3] – 10.7	2.10	0.51 – 7.30	1.30	8.40 – 8.50	8.45
Lead (μg/L)	11.0 – 31.3	15.8	brl[3] – 101	6.86	2.01 – 25.5	10.4	8.52 – 27.6	18.0
Zinc (μg/L)	106 - 219	162	26.1 – 189	62.7	31.2 – 138	58.6	148 – 150	149
Trace Metals (dissolved)								
Copper (μg/L)	12.8 – 22.7	17.3	1.78 – 13.2	4.12	1.90 – 5.20	3.19	5.21 – 8.95	7.08
Cadmium (μg/L)	0.06 – 0.25	0.19	brl[3] – 1.52	brl[3]	brl[3] – 0.14	brl[3]	brl[3] – 0.08	NA
Nickel (μg/L)	0.76 – 1.46	1.35	brl[3] – 9.58	0.95	0.12 – 4.32	1.10	1.15 – 4.95	3.05
Lead (μg/L)	0.10 – 0.64	0.30	brl[3] – 84.3	brl[3]	brl[3] – 1.8	0.22	brl[3] – 0.42	NA
Zinc (μg/L)	43.8 – 193	60	10.6 – 45.4	31.7	12.0 – 70.7	23.9	28.7 – 63.5	46.1

8 **Note:** brl = below reporting limit; [1] 0.050 mg/L; [2] 0.001 mg/L; [3] 0.01 μg/L (see supporting information for methods of determination)
9

10   Table 4. Results of statistically significant site-wise comparisons for composite samples collected at the

11   Bend, Corvallis, Portland and Wemme sites.

Comparison	Parameter	Multiplicative Difference	95% CI
Portland > Corvallis	$[Cu]_d$	3.78	2.18 – 6.58
	$[Cu]_T$	4.62	2.26 – 9.46
	DOC	1.99	1.15 – 3.44
Portland > Wemme	$[Cu]_d$	5.33	3.03 – 9.38
	$[Cu]_T$	5.36	2.57 – 11.2
	DOC	2.92	1.67 – 5.13
Portland > Bend	$[Cu]_d$	2.40	1.07 – 5.40
Bend > Wemme	$[Cu]_d$	2.20	1.02 – 4.82
	$[Cu]_T$	2.82	1.03 – 7.71

12

13   Table 5. Multiple linear regression modeling of dissolved copper concentrations in all stormwater

14   samples collected at the Bend, Corvallis, Portland and Wemme sites.

$$\log[Cu]_d = 0.59 \log[DOC] + 0.69 \log[Alk] - 0.17\ pH + 0.94$$

multiple $R^2 = 0.87$; $p < 0.0001$ (F test)

$[Cu]_d$ in µg/L, [DOC] in mg/L, [Alk] in mg/L as $CaCO_3$

Coefficient	p-value (two-sided t test)
intercept	0.0542
pH	0.0246
log[Alk]	<0.0001
log[DOC]	<0.0001

15

1   **Figure Captions**

2   Fig. 1. Comparisons of the concentrations of total copper (a), dissolved copper (b) and dissolved organic

3   carbon (c) in composite samples collected at the Bend, Corvallis, Portland and Wemme sites. Shaded

4   boxes represent the upper and lower quartiles with the horizontal line representing the median; bars

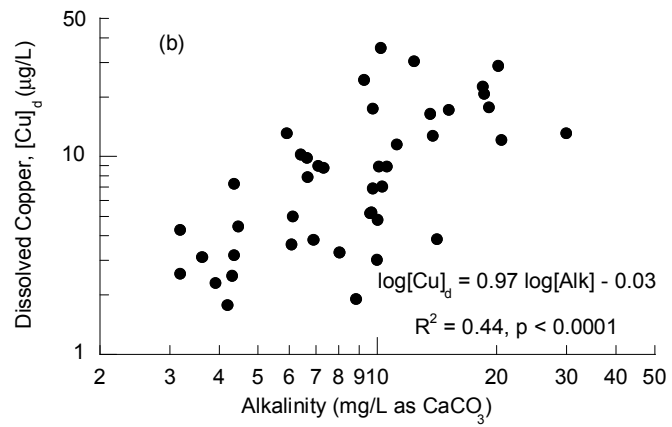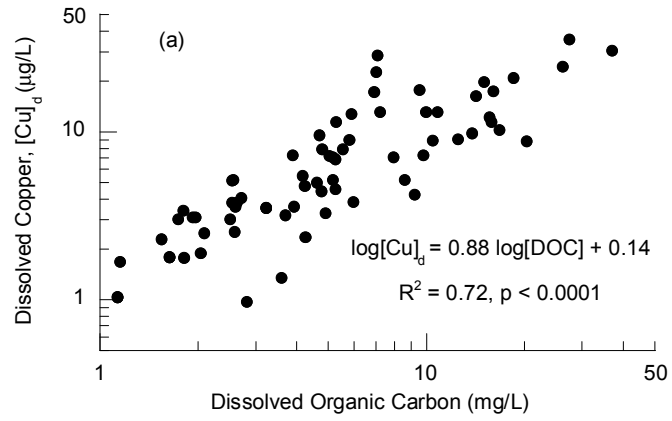5   extending from the box represent the minimum and maximum values and the hollow circles are outliers.

6   Fig. 2. Comparison of the concentrations of total copper (a); dissolved copper (b) and dissolved organic

7   carbon (c) in composite and first-flush samples collected at the Corvallis site. Shaded boxes represent

8   the upper and lower quartiles with the horizontal line representing the median; bars extending from the

9   box represent the minimum and maximum values and the hollow circles are outliers.

10   Fig. 3. Correlations of dissolved copper concentrations with dissolved organic carbon (a) and alkalinity

11   (b) in grab, first-flush, flow-weighted and composite samples collected at the Bend, Corvallis, Portland

12   and Wemme sites.

13   Fig. 4. Intra-storm variation in dissolved copper and dissolved organic carbon concentrations during the

14   10/13-10/14/2009 storm at the Corvallis site.
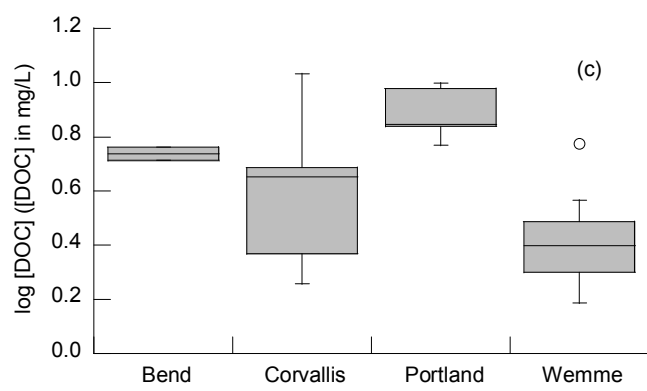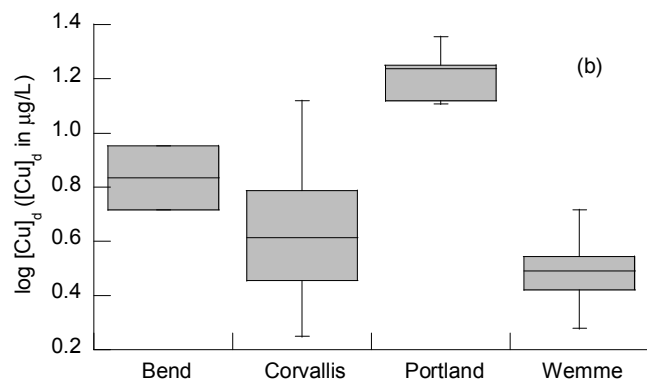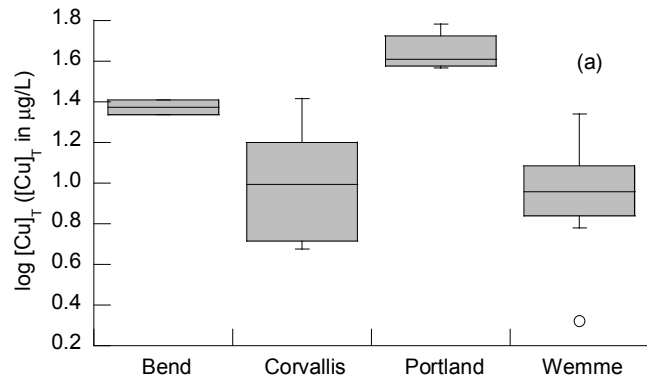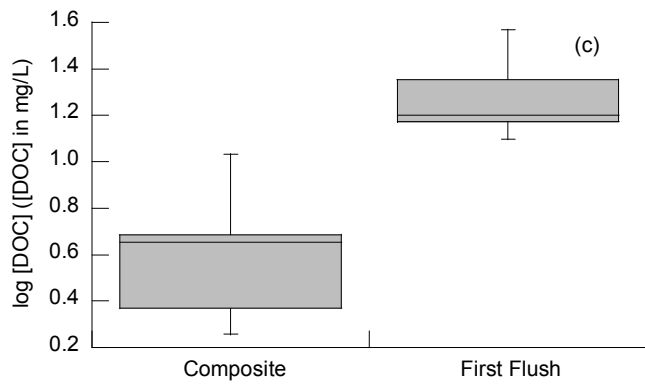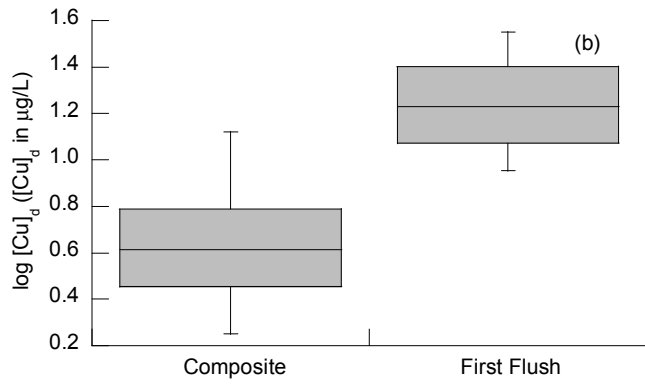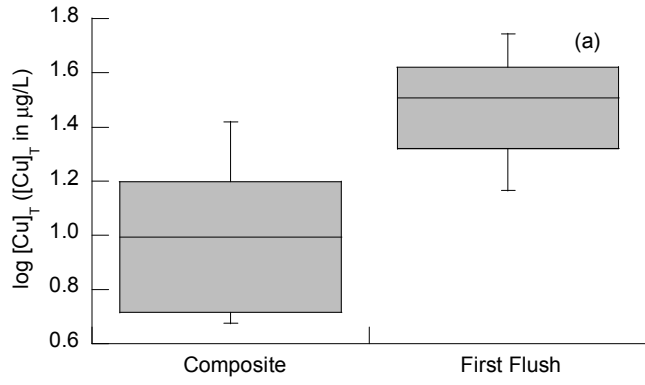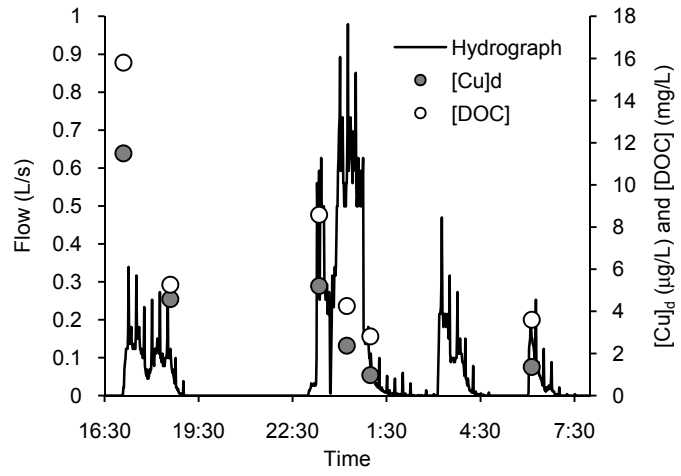
(a)

(b)

(c)

(a)

$\log[Cu]_d = 0.88 \log[DOC] + 0.14$

$R^2 = 0.72$, $p < 0.0001$

Dissolved Copper, $[Cu]_d$ (μg/L)

Dissolved Organic Carbon (mg/L)

(b)

$\log[Cu]_d = 0.97 \log[Alk] - 0.03$

$R^2 = 0.44$, $p < 0.0001$

Dissolved Copper, $[Cu]_d$ (μg/L)

Alkalinity (mg/L as $CaCO_3$)

Factors Influencing Dissolved Copper

Concentrations in Oregon Highway Stormwater

Runoff

Jeffrey A. Nason[1], Don J. Bloomquist[2], and Matthew S. Sprick[3]

13 Pages

2 Tables

9 Figures

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Supporting Information

Stormwater Sampling Equipment

Portland, Bend, and Wemme. Flow-weighted composite samples were collected at the Portland, Bend and Wemme sites by staff of Herrera Environmental Consultants (Portland, OR). At these sites, a bubbler flow meter (Sigma 950) was used to measure water level in a pipe (converted to flow with Manning's Equation) and triggered a portable autosampler (Sigma 800 at Portland and Bend, Sigma SD900 at Wemme) to take 100 ml sub-samples at a preset flow-pacing increment into one composite sample. A 3/8" inner diameter Teflon tube was used for the intake line. Rainfall data was collected from local weather stations. At each of these sites, field personnel verified the proper function of the autosampler, installed a clean 15.2-liter polyethylene carboy, and surrounded it with crushed ice prior to sampling. A schematic of the sampling equipment is shown in Fig. S1.
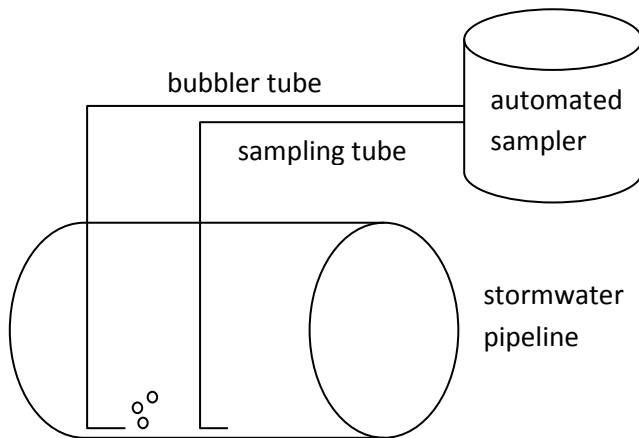
Fig. S1. Schematic of the stormwater collection equipment and setup used at the Bend, Portland and Wemme sites.

Corvallis. Grab, first flush, and discrete flow-weighted samples were collected at the Corvallis site by members of our research group and transported immediately to our laboratory on the Oregon State University campus. An autosampler (ISCO 6712) was used to collect discrete

flow-weighted samples into as many as 24 separate bottles. A bubbler flow meter (ISCO 730) and rain gauge (ISCO 674) were both connected to the autosampler. The intake line consisted of a 3/8" inner diameter Teflon tube connected by a small piece of tygon tubing to a Teflon-coated strainer. A 12" V-notch weir (Thel-mar®) was placed at the end of the outfall pipe to create submerged conditions. This setup allowed for more accurate level measurement and created a sufficient stormwater volume from which to collect samples. Measured water levels were converted to flow rates using the V-Notch Weir equation (Walkowiak, 2008). Data for water level, precipitation, and sampling events was typically recorded at 1-minute intervals. A schematic of the sampling equipment is shown in Fig. S2.
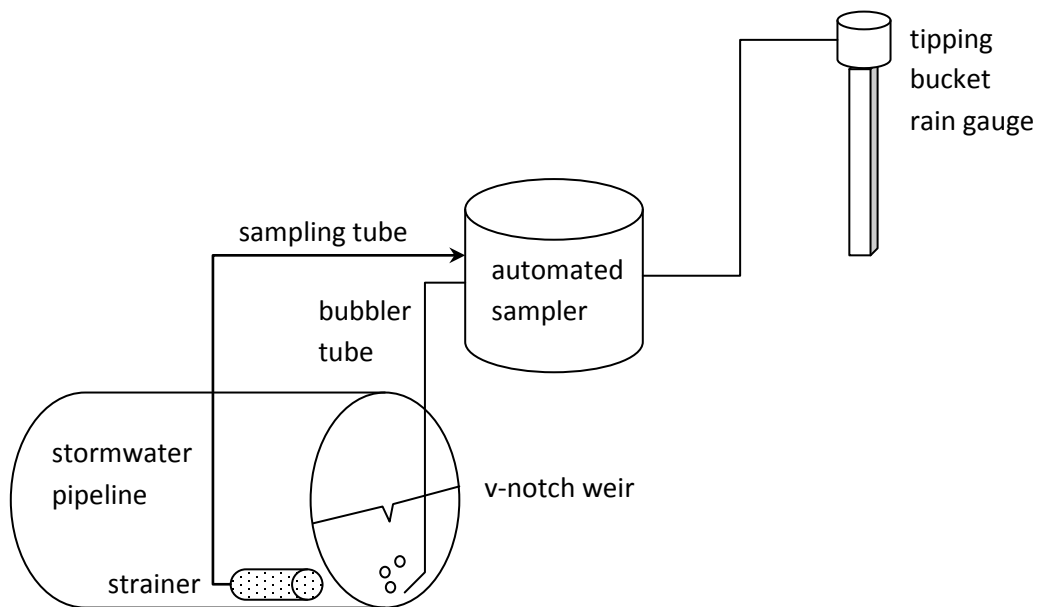
Fig. S2. Schematic of the stormwater collection equipment and setup used at the Corvallis site.

Prior to field deployment, the intake tubing was washed successively with 10% HCl, 10% HNO_3, and distilled deionized (DDI) water (Barnstead NANOpure II). Before each storm event, the intake volume and bubbler level were calibrated in the field with deionized (DI) water and ice was put in the autosampler cavity. The autosampler was programmed to take a first flush

sample at the first sign of runoff (a level of 0.12" above the v-notch weir) and discrete flow-weighted samples (based on projected rainfall) from that point forward. Sampling bottles were acid washed in a 10% (v/v) HCl for 18 hours, followed by 10% (v/v) HNO_3 for an additional 18 hours. Then, bottles were rinsed with deionized water and soaked in a bath of ultrapure water for 30 minutes. Finally, bottles were rinsed 3 times with fresh ultrapure water and capped until use.

QA/QC Procedures for Trace Metals Analysis

Method reporting limits. Method reporting limits were set to be the lowest non-zero calibration standard used in each analytical method. For cations, these concentrations were 50 µg/L for the ICP-AES, 1 µg/L for the ICP-OES, and 0.01 µg/L for the ICP-MS. For anions, the lowest calibration standard was 50 µg/L.

Field Blanks and Method Blanks. Field blanks and method blanks for trace metals were analyzed for several storms at the Corvallis site. The results of those analyses are presented below in Table S1. There was some slight contamination of field blanks, especially by Zn. However, in cases where trace metals were detected in field blanks, they were at concentrations less that 10% of the measured concentrations during the storm. Method blanks revealed that no contamination occurred during processing of the samples in the laboratory.

Method Precision. Table S2 displays the results of spike and recovery experiments where the composite stormwater sample was spiked with Zn, Cu, Cd, Ni, and Pb at roughly double the expected concentrations in the stormwater sample. In every case, errors were less than 2% when comparing the expected values with those measured by ICP-OES.

Supporting Information

Table S1. Results of trace metals analysis in field blanks and methods blanks collected in association with storms at the Corvallis site.

Sample	Cd	Cu	Ni	Pb	Zn
	μg/L	μg/L	μg/L	μg/L	μg/L
12/1/08 Field Blank	brl	1.23	brl	brl	2.31
2/23/09 Field Blank	brl	brl	brl	1.99	14.5
3/14/09 Field Blank	brl	1.43	1.62	brl	13.6
4/12/09 Field Blank	brl	brl	brl	brl	5.57
10/13/09 Field Blank	brl	brl	brl	brl	brl
10/13/09 Method Blank	brl	brl	brl	brl	brl

Note: brl = below reporting limit of 1 µg/L for ICP-OES.

Table S2. Results of matrix spike experiments on the 2/6/09 composite sample collected at the Corvallis site

Analyte	Cd	Cu	Ni	Pb	Zn
% difference in expected vs. measured values	−1.5	−1.6	+2.0	+0.8	−1.8

Correlation of $[Cu]_d$ with AADT

As shown in Fig. 2 of the manuscript, $[Cu]_d$ varied with site locale. In particular, $[Cu]_d$ at the Portland site was significantly higher than all other sites. As such, site indicator variables were included in the multiple linear regression (MLR) analysis. Fig. S3 shows the correlation of $\log[Cu]_d$ with average annual daily traffic. $\log[Cu]_d$ is positively correlated with AADT ($R = 0.79$, $p < 0.0001$). However, in the MLR modeling, it was found that only the Portland site indicator or the relationship with AADT was necessary to describe this variability in the model. Fig. S4 shows the correlation between $\log[Cu]d$ and AADT at the Bend, Corvallis, and Wemme sites. Here there is no statistical correlation ($R = 0.23$, $p = 0.37$), leaving the urban/non-urban classification as the only clear influence on $[Cu]_d$.
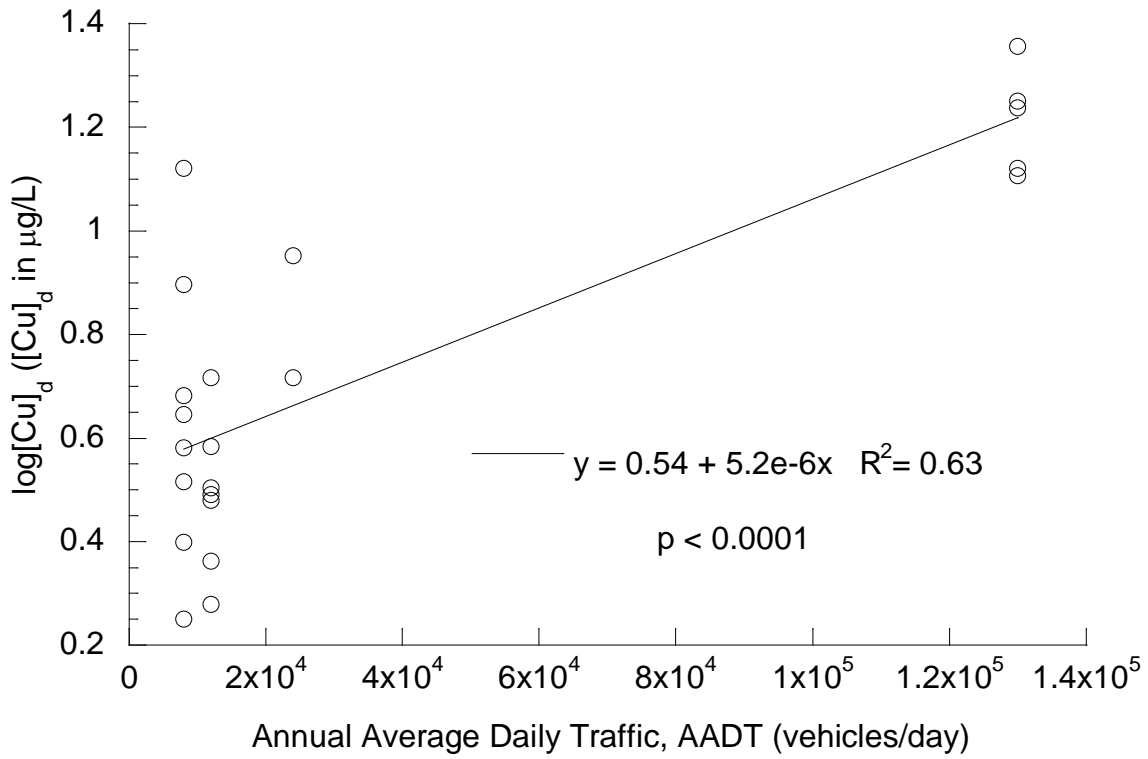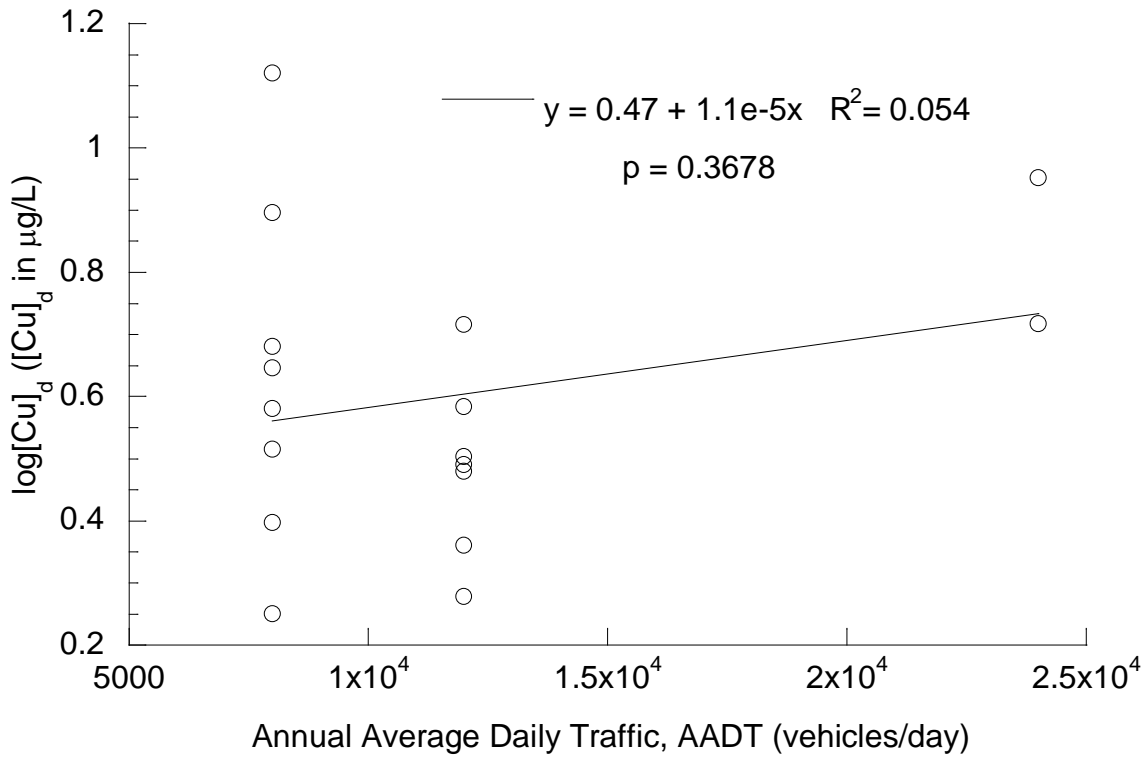
Fig. S3. Correlation of dissolved copper concentrations in composite stormwater samples with annual average daily traffic for all sites.

Fig. S4. Correlation of dissolved copper concentrations in composite stormwater samples with annual average daily traffic for the non-urban sites (Bend, Corvallis, and Wemme).

Correlation of [Cu]$_d$ with Hydrologic Variables

After accounting for site location, there were no statistical correlations between [Cu]$_d$ and hydrologic variables as shown in Fig. S5. The figure also indicates the co-variation of rainfall duration and rainfall intensity with total rainfall. Additionally, [Cu]$_d$ in first flush samples was not correlated with antecedent dry period.
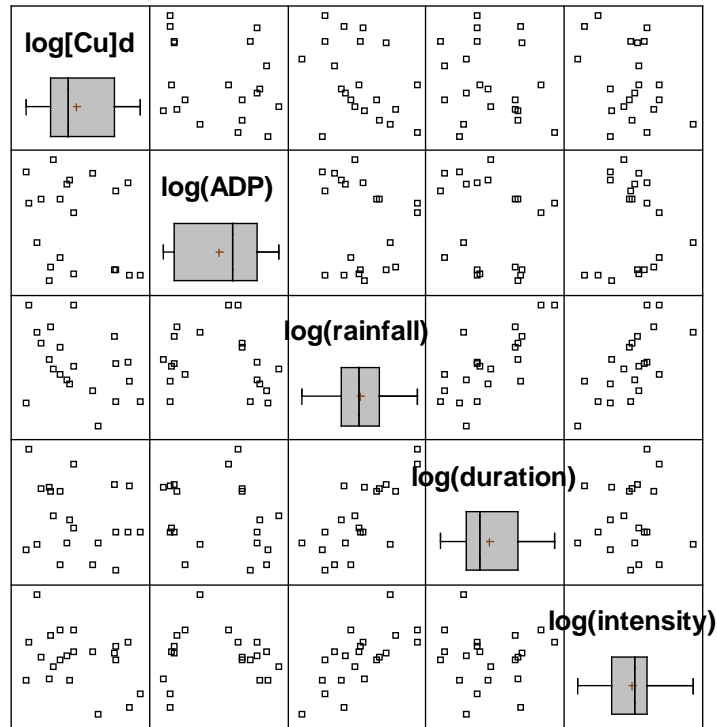
Fig. S5. Matrix plot of [Cu]$_d$ in composite samples from all sites and hydrologic variables including antecedent dry period, ADP (d), total rainfall (in), rainfall duration (hr), and rainfall intensity (in/hr). All variables were log-transformed.

Correlation of Hardness and Alkalinity

Figure S6 shows the correlation between alkalinity and hardness in all of the samples collected at the four sites. The four Wemme samples that were omitted from the MLR modeling lie well-above the expected trend. In these samples, hardness was added (as $MgCl_2$) without an addition of alkalinity, as would have been the case for the dissolution of $CaCO_3$. The four samples exhibit $[Cu]_d$ that are much lower than would be expected, given their alkalinity and DOC concentrations. As a result, the inclusion of those points in the analysis yields a model that also includes a negative correlation with hardness ($p = 0.0321$) and a positive association with TSS ($p = 0.1168$). The inclusion of these variables in the model is likely correcting for the high hardness/low $[Cu]_d$ samples that are not well explained by the alkalinity-$[Cu]_d$ correlation. As a result, the four Wemme samples were omitted from the MLR analysis described in the manuscript.
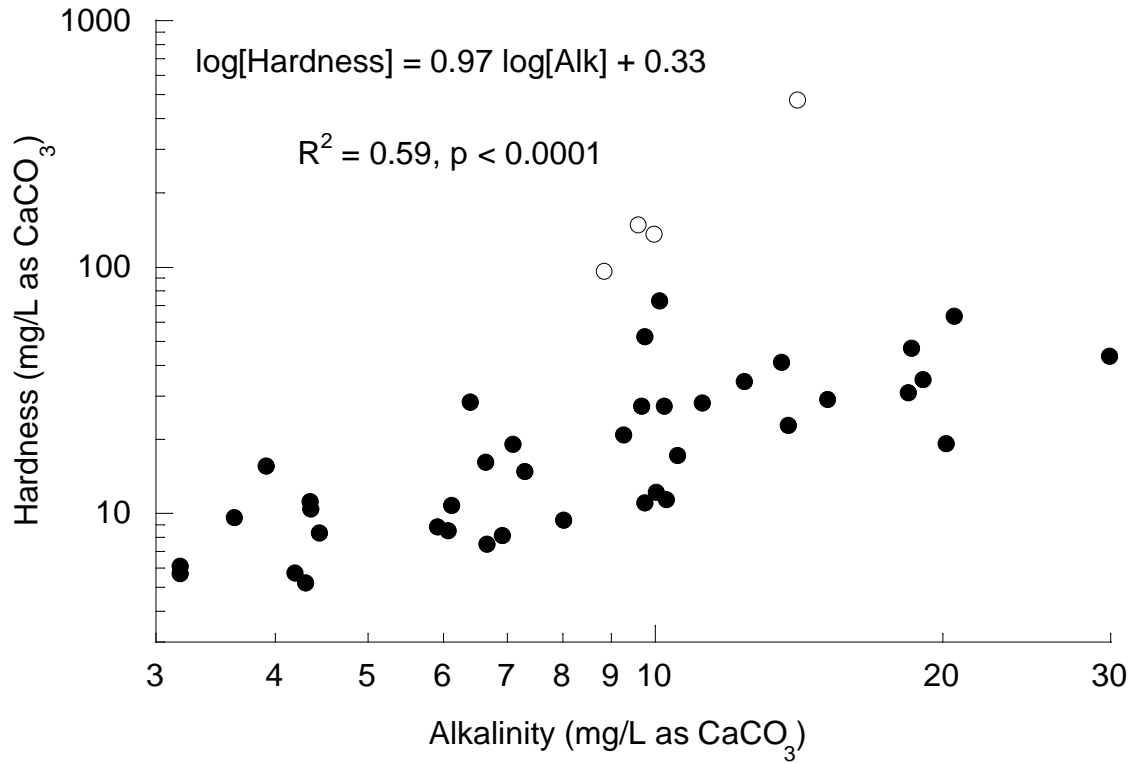
Fig. S6. Co-variation of hardness and alkalinity in grab, first-flush, flow-weighted and composite samples collected at the Bend, Corvallis, Portland and Wemme sites. Hollow data points (○) indicate data from four storms (1/6, 3/11, 3/16 and 3/24/2009) collected at the Wemme site where $MgCl_2$ was being applied as a road deicer.

Correlation of Total and Dissolved Copper

As shown in Fig. S7, dissolved copper concentrations are clearly correlated with total copper concentrations. As stated in the manuscript, 39.3% of the total copper was dissolved (median).
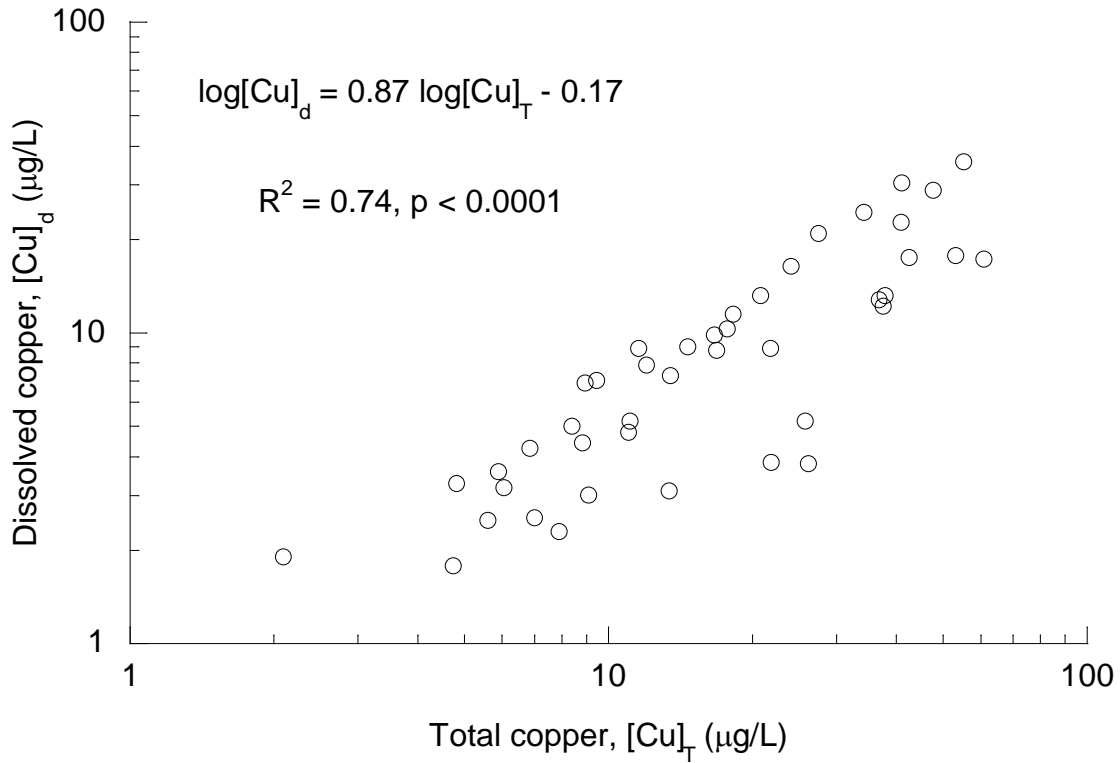

Fig. S7. Correlation of dissolved and total copper in composite and first flush samples collected at all sites.

Intra-storm Variations in $[Cu]_d$ and DOC

As shown in Fig. S8, a negative trend in C/C_0 for $[Cu]_d$ when plotted against normalized cumulative volume (V_i/V_{tot}) for flow-weighted samples collected at the Corvallis site reveals that $[Cu]_d$ generally decreases over the course of the storm (R = −0.819, p < 0.0001). A similar trend can be seen with respect to dissolved organic carbon in Fig. S9 (R = −0.812, p < 0.0001). In both cases, C/C_0 represents the concentration at a given time normalized by the concentration in the first collected sample (*i.e.*, the first flush).
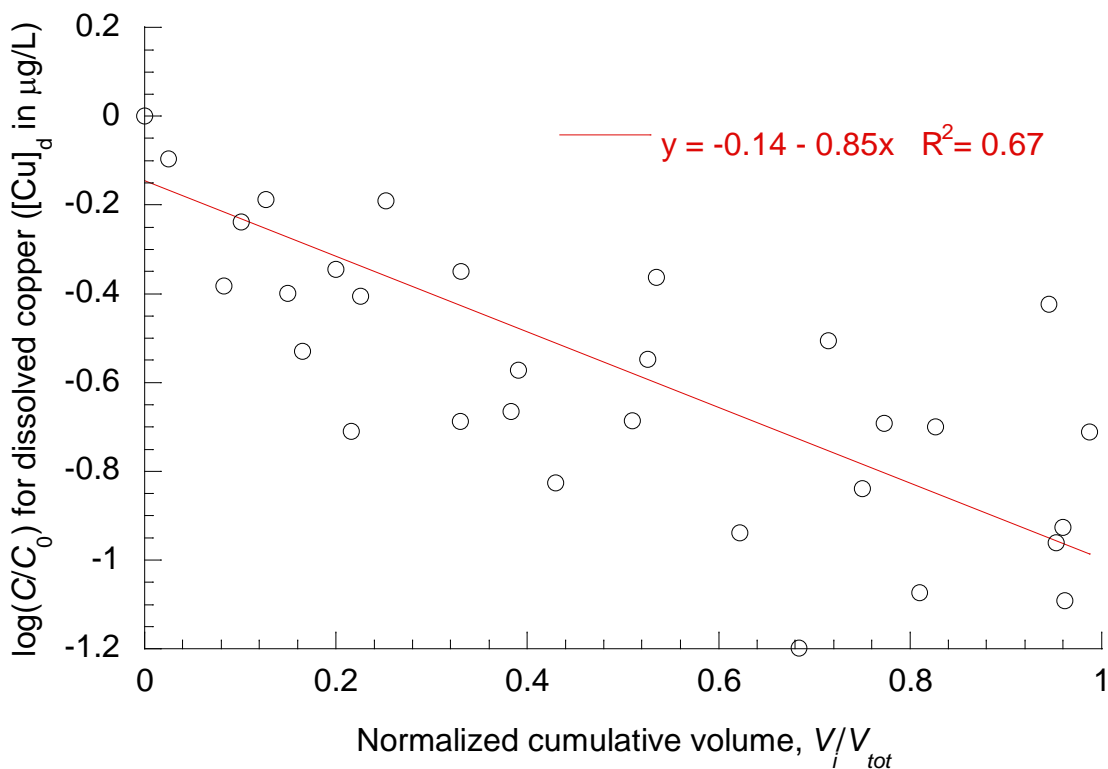
Fig. S8. Correlation of C/C_0 for $[Cu]_d$ with normalized cumulative volume for first-flush and flow-weighted samples collected at the Corvallis site.
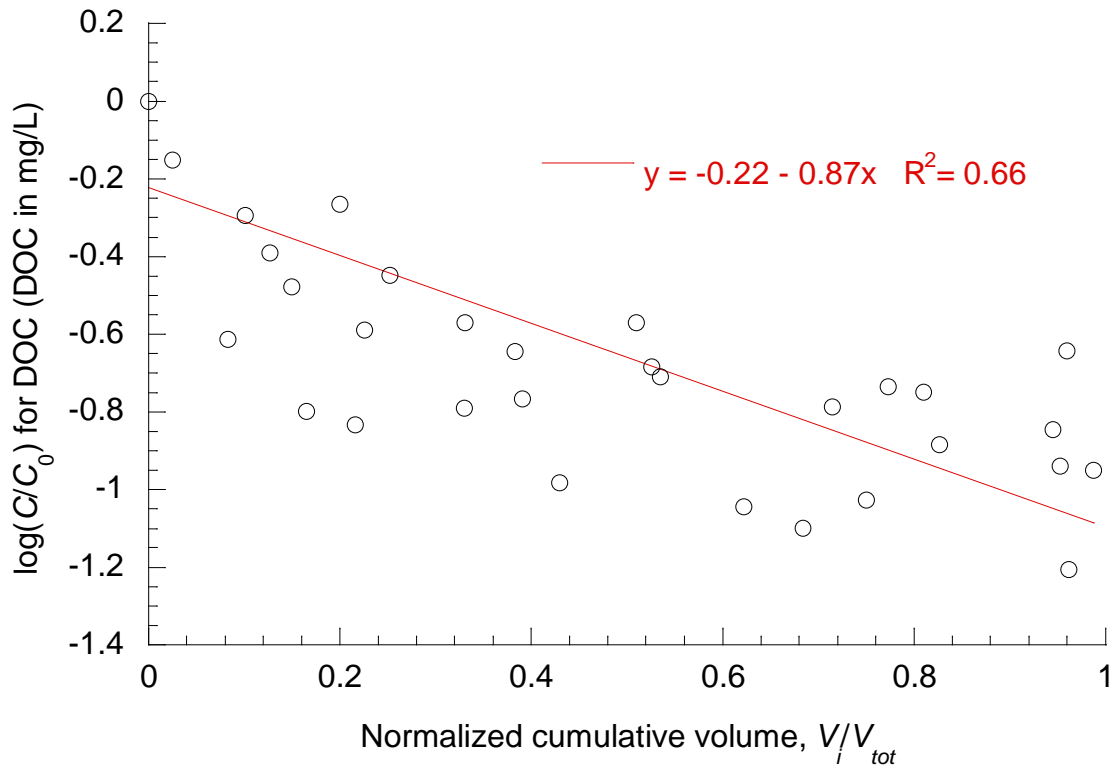
Fig. S9. Correlation of C/C_0 for DOC with normalized cumulative volume for first-flush and flow-weighted samples collected at the Corvallis site.