1 A combined geochemical and hydrological approach for understanding
2   macronutrient sources

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4 **Dan J Lapworth [a*], Daren C Gooddy [a], Flo Kent [b], Tim H E Heaton [c], Steven J**
5 **Cole [d], Debbie Allen [a]**

6 [a] British Geological Survey, Maclean Building, Wallingford, Oxfordshire, OX10 8BB,
7 UK

8 [b] Environment Agency, Orchard House, Endeavour Park, Addington, West Malling,
9 Kent, ME19 5SH, UK

10 [c] NERC Isotope Geosciences Laboratory, Keyworth, Nottinghamshire, NG12 5GG,
11 UK

12 [d] Centre for Ecology & Hydrology, Maclean Building, Wallingford, Oxfordshire,
13 OX10 8BB, UK

14 *Corresponding author, email: djla@bgs.ac.uk, Tel: +44(0)1491692327, Fax:
15 +44(0)1491692345

16 **Abstract**

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18 This study employed complementary geochemical techniques and distributed
19 hydrological modelling to investigate multiple sources of catchment macronutrients
20 and characterise their changes in contrasting storm and baseflow conditions. This
21 approach was demonstrated for the Beult catchment in the county of Kent (England),
22 a designated Site of Special Scientific Interest (SSSI) indentified as failing to meet
23 water quality standards for key nutrients under the Water Framework Directive.
24 Significant changes in nutrient stoichiometry and bioavailability are observed for
25 surface waters under contrasting flow regimes. Soluble reactive phosphorus (SRP)
26 concentrations are approximately twice as high during baseflow compared to high
27 flow, while the inverse is true for particulate, colloidal and dissolved hydrolysable
28 phosphorus, dissolved organic carbon and nitrate. N:P ratios are lower during
29 baseflow for most surface waters impacted by diffuse sources of pollution.
30 Fluorescence indices of dissolved organic matter (DOM) show that waste water inputs
31 may be locally important sources of more complex low molecular weight DOM,
32 particularly during baseflow. Nitrate N and O isotope signatures, combined with other
33 dissolved chemical tracer's, confirm the dominance of wastewater N inputs at sites
34 downsteam of sewerage treatment works during baseflow, with a shift towards the
35 soil N pool in surface waters across the catchment during high flow. Distributed
36 hydrological modelling using the Grid-to-Grid model reveal areas with the greatest
37 runoff also export higher N and P concentrations, and hence deliver a greater flux of
38 macronutrients, while forested areas with low nutrient concentrations reduce runoff
39 and nutrient fluxes. During periods of high runoff, nested sampling indicates that
40 nutrient fluxes scale with catchment area. This combined approach enables a more
41 thorough assessment of the macronutrient sources and dynamics, better informing
42 management options in nutrient impacted catchments.

43 **Keywords**: Macronutrients; Beult Catchment; Source identification, Organic Matter
44 Fluorescence Wastewater, Land Use, Grid-to-Grid Modelling

45 **1   Introduction**

46   Carbon (C), nitrogen (N) and phosphorus (P), often referred to as macronutrients, are

47   essential components of a healthy aquatic ecosystem (Whitehead et al., 2012).

48   However, in recent decades anthropogenic inputs of macronutrients have caused

49   perturbations to key macronutrient cycles, and led to widespread N and P pollution of

50   aquatic systems (Heathwaite et al., 1996; Edwards and Withers, 2008; Neal et al.,

51   2010). This is a global problem with implications for food production and security,

52   water quality, as well as potential climate impacts (Meyer et al., 1999; Galloway et

53   al., 2004).

54   In catchments with agricultural land use, diffuse sources usually dominate nutrient

55   inputs to streams and groundwater, while in non-agricultural areas point sources such

56   sewage/waste water treatment works (WWTWs) are important inputs (Johnes et al.,

57   1996; Howarth et al., 1996; Jordan et al., 1997; Palmer-Felgate et al., 2010). The

58   European Water Framework Directive (WFD 2000) requires that water bodies achieve

59   good ecological and water quality status by 2015. Therefore, there is a pressing need

60   to understand nutrient sources, transport processes and attenuation mechanisms at the

61   catchment scale.

62   Phosphorus (P) is an important nutrient in the environment: too little can inhibit plant

63   growth whilst too much can lead to an excess which is subsequently stored in the soil.

64   This excess P can then be released into water bodies and may contribute to

65   eutrophication and associated loss of ecological status (Jarvie et al., 2006, Holman et

66   al., 2008, Withers and Jarvie, 2008). In a catchment, there are several different

67   potential sources of dissolved P that can enter the river or groundwater body.

68   Livestock farming has been shown to be an important source of nutrients from

69   fertilisers, manure and feed concentrates (P and N) in streams (Haygarth et al., 1998,

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70   Withers and Lord, 2002). Other major sources of nutrients are from point sources

71   such as slurry tanks (Gooddy et al., 2002), leaking septic tanks or drains (Palmer-

72   Felgate 2010) and particularly WWTWs which are a key source of PO_4 and the

73   soluble polyphosphates used in detergents (Neal et al., 2010).

74   The bioavailability of nutrients is a key issue when considering the potential

75   ecological status of freshwater bodies. Autotrophs, which can lead to eutrophication

76   in over-enriched waters, can only use PO_4 directly, but are also able to use organic

77   forms of P through indirect extracellular processes (Schindler, 1974). Hence, soluble

78   reactive P (SRP) is often used as a measure of the bioavailable portion of P in

79   environmental studies. However, P is a highly dynamic element, with the species and

80   bioavailability dependent on changes in biological, physical and chemical factors. For

81   example: particulate P (PP) may release surface bound PO_4 and organic forms of P;

82   changes in redox and pH may lead to PO_4 release or binding to mineral-organic

83   complexes; and inputs from runoff and stormflow may dramatically alter the source

84   and form of P over a short time period (Froelich 1988; Hur and Schlautman., 2004).

85   Another important factor is the relative ratio of different nutrients, e.g. the N:P

86   stoichiometry, which is important in limiting autotrophic growth (Schelske et al.,

87   1974). P limited systems have been shown to have an increased turnover of P to

88   compensate for the low availability.

89   Colloids are operationally defined as particles with diameters less than 10^{-5} m (10 m)

90   (Stumm, 1977). An important process that has received some attention in recent years

91   has been colloid bound P transport (e.g. Haygarth et al., 1997; Lapworth et al., 2011).

92   This is the transport of P bound to inorganic and organic particles which cover a large

93   range of sizes from large clay-humic-metal complexes to nanometre scale humic-like

94   compounds and carbonate, iron or silicate fractions.

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95   Increased anthropogenic inputs of N to the UK land surface, largely from fertiliser as

96   well as some depositional sources, have resulted in widespread N pollution and the

97   subsequent deterioration in the quality of both surface water and groundwater (e.g.

98   Foster et al., 1986; MAFF 1993; Wang et al., 2012; Worrall et al., 2012). Nitrogen

99   pollution in UK freshwaters is predominantly in the form of nitrate (NO_3) rather than

100 nitrite (NO_2) or ammonium (NH_4) due to the predominantly oxidising conditions.

101 Nitrate concentrations in rivers often show a distinct seasonal variation, with peak

102 concentrations in winter months and low concentrations in summer months (Johnes

103 and Burt, 1993).

104 Dissolved organic matter (DOM) includes compounds such as carbohydrates and

105 proteins, as well as humic substances including fulvic and humic acids (Thurman,

106 1985). Natural organic matter is derived from the decay of organic material from both

107 plant and animal sources and almost half of all NOM fluoresces (Senesi, 1993).

108 Recent studies suggest that humic substances are a complex mixture of both microbial

109 and plant biopolymers, with their various breakdown products, and cannot be classed

110 as a distinct chemical structure (Kelleher and Simpson, 2006). In the natural

111 environment DOM is often a complex mixture of many compounds, and as such is

112 difficult and costly to characterise (Leenheer and Croue, 2003).

113 Much work has been undertaken in the last decades to quantify C, N and P

114 concentrations and fluxes, and the nature of nutrient transformations at the catchment

115 and continental scale (Gruber and Galloway, 2008). However, there is still a major

116 gap in current understanding of how nutrients are retained within complex landscapes

117 and released to surface and groundwater bodies via surface and subsurface flow

118 pathways. Most published studies to date have tended to focus only on one or two

119 macronutrients; studies that combine all three nutrients are rare but are required to

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120   fully understand nutrient flux and processes within aquatic ecosystems (Whitehead et

121   al., 2012).

122   In this paper nutrient (C, N and P) concentrations, species, fluxes and associations

123   with colloidal and particulate matter are investigated within the Beult catchment of

124   southeast England, UK. The River Beult was chosen for this study as it has

125   'unfavourable status' as a result of failure to meet water quality targets, as well as

126   having other chemical and biological status concerns (Environment Agency, 2005). A

127   spatial survey of water quality across the catchment, for both groundwater and surface

128   water, was carried out during high flow (below a return period of 10 years for the

129   gauged site at Stile Bridge) and baseflow conditions within areas of contrasting land

130   use, giving a snapshot of the nutrient status and mobility across the catchment.

131   This study uses a range of complimentary techniques to investigate nutrient processes

132   within the catchment: (i) tangential flow fractionation (TFF) is used to investigate the

133   association of P and C to particulate, colloidal and dissolved phases (<10 KDa), (ii)

134   dissolved organic matter (DOM) is characterised using excitation-emission matrix

135   (EEM) fluorescence spectroscopy to investigate the nature of both labile and

136   recalcitrant DOM, (iii) N and O isotope techniques are used to investigate different

137   sources of NO_3 within the catchment, (iv) coupled Grid-to-Grid distributed

138   hydrological modelling (Bell et al., 2009; Moore et al., 2006, 2007) and nutrient

139   chemistry data are used to explore spatial relationships between runoff and nutrient

140   flux. This type of novel multi-technique approach enables a more thorough

141   assessment of macronutrient sources and dynamics across the catchment, and so better

142   informs choices of management options in nutrient impacted catchments.

143 **2   Study area**

144 *2.1   Location, hydrology and geology*

145 Figure 1 shows the location of the Beult catchment, simplified geology, and key

146 population centres. The River Beult rises near Ashford, Kent, and then flows North-

147 west through Headcorn, forming the largest tributary of the River Medway. The Beult

148 catchment is predominantly rural with scattered settlements: total urban coverage is

149 <1% of the total catchment area. Over 60% of the land-use is classified as agricultural

150 (CLC, 2000). During the 1930s, the lower section of the river between Smarden and

151 Yalding was straightened, widened and deepened to increase flow and drainage.

152 Today, water abstraction is largely for agricultural use, and therefore temporally

153 variable; surface water flow is increased in some reaches by effluent returns from

154 sewage treatment works.

155 Temporary weirs and sluices are used upstream of Stilebridge in the summer months

156 to maintain river stage and manage flow. Daily mean river flow for the Beult at Stile

157 Bridge, with a catchment area of 277 km^2 (51°12′08.6584″N, 000°30′54.4021″E), is

158 shown in Figure 2a. The Weald Clay formation covers the vast majority of the

159 catchment area (approx. 80%, see Figure 1) and very little natural storage exists

160 causing a flashy runoff regime. There are only minor groundwater inputs (baseflow)

161 from the Lower Greensand Group, resulting in a baseflow index of 0.2 at Stile Bridge

162 (NRFA, 2012).

163 The catchment is underlain by the Weald Clay formation, a thick (110–270m) clay

164 and silty-clay within which are found outcrops of limestone and sand. The Lower

165 Greensand Group, comprising the Folkstone, Sandgate, Hythe and Atherfield Clay

166 formations, crop out along the northern margin of the catchment. The underlying

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167 Wealden Group, the Tunbridge Wells Sand formation, and Wadhurst Clay formation,

168 are located on the southern margin of the catchment (Figure 1). There are substantial

169 superficial deposits of alluvium, silty and sand gravel river terrace deposits adjacent

170 to the River Beult and its tributaries. For a detailed account of the geology of the

171 Maidstone area see Worssam (1963). Some spring flow issues from the Lower

172 Greensand Group, which is exposed along the northern margin of the catchments, and

173 also from the Tunbridge Wells Sand in the south.

174 *2.2   Water quality status of the Beult catchment*

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178 resulted in the River Beult being designated as having 'unfavourable status' and

179 indentified as failing to meet quality standards under the WFD. High phosphate (PO_4)

180 concentrations are the primary reason for the water quality failures, although nitrate

181 (NO_3) concentrations are also high. The water quality at four sites, two downstream of

182 WWTWs and two impacted by other sources, have been monitored by the

183 Environment Agency (EA) between 2002 and 2008 for temporal trends in P and N

184 species. Average ammonium concentrations were low for all of the monitoring sites

185 (<0.5 mg/L), with highest concentrations during low flow periods at all sites. Long-

186 term results for NO_3 and SRP from this water quality monitoring are included in this

187 paper, and provide a context for the detailed follow-up work carried out during high

188 flow and baseflow conditions.

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189 **3 Methods**

190 *3.1 Sites and sampling*

191 Figure 1 shows the location of sites that are investigated as part of this study. A total

192 of 20 sites from across the Beult catchment were sampled on two occasions, once

193 during a period of high flow following intense rainfall in November 2008 and then

194 during baseflow conditions in July 2009. The four EA monitoring sites that feature in

195 this study are also shown. Table S1, supplementary information, shows details on site

196 location, water type, and potential sources of nutrients.

197 Sites with potentially contrasting nutrient input sources were selected across the

198 catchment based on land-use data and information on licensed discharges to the Beult.

199 Two surface water sites that were impacted by local WWTW discharges, Sutton

200 Valence and Biddenden, were included in this study. Twelve sites were impacted by

201 diffuse pollution from agricultural land-use, and two sites were selected where

202 forest/woodland was the predominant land-use. Groundwater samples were collected

203 at three locations from springs that issue at the contact between the Lower Greensand

204 and the Weald Clay formations to the north of the catchment.

205 Groundwater sites were located to the north of the catchment. The sewage impacted

206 sites were sampled downstream of discharges from the Sutton Valence WWTW, to

207 the northwest of the catchment and downstream of Biddenden WWTW in its southern

208 part. Samples upstream of the Sutton Valence WWTW were also collected for

209 comparison. Agriculturally impacted sites, including field drains, were sampled from

210 the River Sherway, a tributary of the River Beult. Two sites with predominantly

211 forested land-use were located in the southern part of the catchment (see Figure 1),

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212   and represent nutrient water quality for parts of the catchment that have been

213   unaffected by either agricultural or wastewater inputs.

214   River samples were collected using a bucket; samples were taken from the centre of

215   the flowing watercourse. Care was taken to ensure that the inlet did not disturb river

216   bed sediment during sampling. Groundwater samples were collected from springs

217   taking care to obtain samples from close to the inlet of collection tanks. On-site water

218   quality variables - dissolved oxygen (DO), pH, redox potential temperature and

219   specific electrical conductance (SEC) - were measured and allowed to stabilise prior

220   to sampling where appropriate. DO, pH and redox potential were measured in a flow-

221   through cell to obtain a representative field value. Alkalinity, referred to as HCO_3 in

222   this paper, was determined in the field using 50 mL of sample by titration against

223   1.6N sulphuric acid. The average values from two repeat titrations obtained in the

224   field were reported.

225   Samples for inorganic analysis were filtered in the field using 0.45 m cellulose nitrate

226   filters (Whatman™). Samples for DOC were filtered through a 0.45 μm silver filters

227   (Millipore™) into sterile acid-washed glass containers and stored refrigerated in the

228   dark at 4º C. A 2 litre unfiltered sample was collected and stored in dark plastic

229   bottles for analysis of the $^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotope ratios of

230   nitrate.

231   *3.2   Tangential Flow Fractionation*

232   The use of Tangential-Flow Fractionation (TFF) has been investigated as an improved

233   method for fractionation of colloidal material (Guéguen et al., 2002; Morrison and

234   Benoit, 2004), as the tangential arrangement minimises the clogging at the membrane

235   surface. Although this is better than the classical method of filtration it does not avoid

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236   coagulation altogether. Previous work by Lapworth et al. (2009a and 2011) has

237   successfully used this method to investigate P and DOM association with different

238   size fractions in surface and groundwaters. The mass balance recovery of P was

239   calculated for all samples and was found to vary between 89 and 102% for P, and was

240   slightly lower for DOC (72 to 86%) presumably due to adsorption effects on the filter

241   membrane.

242   A Pellicon 2 Millipore™ system was used for TFF with a range of large surface area

243   composite regenerated cellulose filters (nominal cut-off 10 kDa). A thorough protocol

244   for cleaning membranes is required (Gu*é*guen et al., 2002), and was followed for this

245   work. All samples were pre-filtered prior to the TFF treatment to remove the larger

246   particulate matter using Whatman ® glass fibre filters (nominal cut-off 2.7 m). An

247   unfiltered sample was collected and stored in acid-washed glass bottles for analysis of

248   the whole sample. The full suite of filters were used in the initial round sampled under

249   high flow conditions to investigate the association of P with different sample

250   fractions. TFF using the nominal 10 KDa filter, representing the truly dissolved phase,

251   was carried out for a subset of seven sites of contrasting land-use during both high

252   and low flow conditions.

253   *3.3   Chemical analysis*

254   *3.3.1   Inorganic Chemistry*

255   Soluble reactive P (SRP) is a measure of the inorganic monomeric and easily-

256   hydrolysable phosphorus in the sample that has been filtered through a 0.45 m filter.

257   The SRP was determined colorimetrically using the method of Murphy and Riley

258   (1962) as modified by Neal et al. (2000). Total phosphorus (TP) is the combination of

259   total dissolved P and particulate P; this was measured by the method of Eisenreich et

260   al. (1975). Total dissolved P (TDP) was determined using the method of Eisenreich et

261   al. (1975) after filtration through a 0.45 m cellulose filter. The dissolved poorly-

262   hydrolysable P (DHP) was calculated by difference. DP, the 'truly' dissolved P was

263   isolated by TFF (10 KDa) and P determined using the Eisenreich et al. (1975) method.

264   Colloidal P (CP) is operationally defined as <0.45 mm and >10 KDa and was

265   calculated by difference. Major anions (NO_3-N, SO_4 and Cl) were analysed by Dionex

266   ™ liquid chromatography on filtered (0.45 m) samples. HCO_3, pH and specific

267   electrical conductance (SEC), and DO were determined in the field. P analysis was

268   carried out within a week of sampling. A breakdown of P analysis used in this study is

269   shown in the electronic supplementary information (Table S2). Limits of detection

270   (LOD) for the P species were 7 g/L, LODs for the other analytes were as follows:

271   DOC (0.5 mg/L), NO_3-N SO_4 and Cl (0.1 mg/L), HCO_3 (5 mg/L).

272   *3.3.2 ^{15}N and ^{18}O NO₃ analysis*

273   Nitrate was separated on anion resins and prepared as silver nitrate for analysis of

274    $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios by oxidative combustion and high-temperature pyrolysis,

275   respectively, in Thermo Finnigan (Bremen, Germany) Flash 1112 and TC elemental

276   analysers linked to a Delta+ XL mass spectrometer (Silva et al., 2000; Heaton et al.,

277   2004). Isotope ratios were calculated as ^{15}N values versus atmospheric N_2 and ^{18}O

278   values versus SMOW by comparison with IAEA standards N-1, N-2, and NO-3.

279   Analytical precision (1 SD) was typically <0.3‰ for ^{15}N and <0.6‰ for ^{18}O.

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281   *3.3.3 Organic matter characterisation*

282   Dissolved organic carbon (DOC) was measured using a Thermalox™ C analyser after

283   acidification and sparging, for both sampling rounds. In addition, organic matter

284 fluorescence analysis was carried out to investigate the changes in dissolved organic

285 matter characteristics for selected sites in both sampling rounds following TFF (<10

286 KDa).

287 Fluorescence spectroscopy has been used in many studies to characterise and

288 understand the sources of DOM in wastewater, surface water, groundwater and

289 terrestrial ecosystems (Baker, 2001, 2002; Lapworth et al., 2008, 2009a). Florescence

290 indices of DOM structure can provide information on key characteristics of DOM,

291 including the degree of humification, differentiating microbial and terrestrial sources

292 and the degree of structural conjugation and aromaticity (Zolsay et al., 1999;

293 McKnight et al., 2001).

294 All organic matter fluorescence analysis was carried out within a week of sampling.

295 Samples were stored in glass vials in the dark at 4°C, and allowed to equilibrate to

296 20°C prior to analysis. A Varian™ Cary Eclipse fluorescence spectrometer was used

297 for the fluorescence analysis. Excitation (Ex) wavelengths were set between 200 and

298 400 nm with a 5 nm bandwidth and emission (Em) wavelength were set between 250

299 and 500 nm with a 2 nm bandwidth. The PMT voltage was set to 700 V, and all

300 analysis was carried out in quartz vials with a path length of 1 cm. All fluorescence

301 results are reported as an average of three repeat analyses, following blank

302 subtraction, and are presented in Raman units (R.U), normalised to the area under the

303 water Raman peak of Ultrapure water blanks at Ex350nm–Em397nm. Ultraviolet

304 absorbance measurements (A254nm) were carried out using a Varian (UV/visible)

305 spectrophotometer with a cell path of 1cm. Due to the high DOC (>5 mg/L) in several

306 samples, dilution was required prior to fluorescence analysis to minimise absorbance

307 effects. Ultrapure water (ASTM type I reagent grade water, including a UV cracker)

308 was used for blank samples and to clean the quartz cell between samples.

309   Three fluorescence organic matter (FOM) peaks within the EEM were used in this

310   study to compare intensities between sites, and sampling rounds: the fulvic-like (FA)

311   maxima (Ex330–340 nm, Em410–460 nm), the tryptophan-like (TRP) maxima

312   (Ex270nm–290nm, Em320–360nm) and the tyrosine-like (TY) maximum (Ex280nm–

313   270nm, Em294-302nm).

314   DOM characteristics were investigated through the use of three indices which have

315   been shown to relate to DOM structure: (i) the fluorescence index (FI) which is

316   commonly used to differentiate between terrestrial and microbial DOM sources

317   (McKnight et al., 2001), (ii) the humification index (HI), an indication of humicity,

318   and the condensing of fluorescing molecules (Zsolnay et al., 2001), (iii) the ratio of

319   two fluorescing components( ), representing recent labile OM, and representing

320   recalcitrant OM (Wilson and Xenopoulos., 2009; Parlanti et al., 2000). Data was

321   processed and indices calculated using R software (Lapworth and Kinniburgh, 2009).

322   *3.3.4   Mineralogy of suspended material*

323   X-ray diffraction (XRD) analysis was carried out on the fine fraction (<2 m) of

324   suspended material from five river samples, to characterise the mineralogy of this

325   material during the high flow survey. Analytical details and a summary table of

326   results are presented in the electronic supplementary information (Table S4).

327   *3.4   Modelling runoff contributions across the catchment*

328   The hydrological model used in this study was the Grid-to-Grid (G2G) Model (Bell et

329   al., 2009; Moore et al., 2006, 2007) which is a distributed grid-based rainfall-runoff

330   and routing model. It was developed as a means of modelling "everywhere" through

331   use of an area-wide approach that provides a natural way of addressing the ungauged

332   hydrological forecasting problem (i.e. locations where observed flows are not

333 available). The distributed form of G2G means that modelled flows are sensitive to

334 both the storm pattern and landscape shaping (through use of supporting spatial

335 datasets on terrain, soil/geology and land-cover), allowing unusual and extreme floods

336 to be better simulated through capturing the spatio-temporal evolution of river flows

337 across the model domain (Cole and Moore, 2009; Moore et al., 2006).

338 G2G is used operationally by the Flood Forecasting Centre (FFC) over England &

339 Wales (Price et al., 2012) and the Scottish Flood Forecasting Service over Scotland

340 (Cranston et al., 2012) to support national Flood Guidance Statements. The FFC

341 countrywide configuration of the G2G Model, which runs on a 1km grid with a 15

342 minute time-step, is used in this study. Gridded rainfall inputs to the model are formed

343 from the national network of EA tipping-bucket raingauges using multiquadric

344 surface fitting techniques (Moore et al., 2004; Cole and Moore, 2008) with automated

345 quality-control applied to the raingauge records (Howard et al., 2012).

346 In this study, the G2G Model has been used for the high flow monitoring survey.

347 Modelled flows have been extracted for grid-cells that correspond to the sample

348 locations and aggregated runoff volumes mapped across the domain to understand the

349 contribution to runoff and river flow from different parts of the Beult catchment.

350 **4 Results**

351 *4.1 Historical changes in PO_4 and NO_3 between 2002 and 2008*

352 Figure 2b, 2c and 2d show the temporal variations for NO_3-N, SRP-P and molar N:P

353 at the four long-term monitoring sites within the Beult catchment. Two sites,

354 Biddenden and Sutton Valence-ds, are situated downstream of sewage treatment

355 inputs, and the other two sites, Romden Castle and Franks Bridge, do not have

356 significant upstream inputs from WWTW.

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357   Overall, the sites with WWTW inputs show higher mean SRP and NO_3 concentrations

358   compared to sites without sewage inputs (see Figure 2b and 2c). Mean concentrations

359   of SRP g/L) and NO_3-N (mg/L) are 194 and 4.1 (Romden Castle), 227 and 7.4

360   (Franks Bridge), 639 and 12 (Biddenden-ds), 2034 and 19.7 (Sutton Valence-ds).

361   Mean concentrations for SRP and NO_3-N at Sutton Valence-ds> Biddenden-ds >

362   Franks Bridge> Romden Castle, and sites downstream of WWTW discharges also

363   show the greatest variations (Figure 2b-d).

364   The temporal trends for NO_3 at the four long-term sites show less similarity based on

365   the historical time-series data between 2003 and 2008 (Figure 2b). At the Sutton

366   Valence site there is an overall increase in concentration, and the highest

367   concentrations are found in periods of low flow. At Franks Bridge and Biddenden,

368   while higher concentrations are also generally found during periods of low flow, and

369   when temperatures are higher, there is no obvious long-term change in mean annual

370   concentrations. At Romden Castle the temporal trend is less distinct, although there is

371   still considerable variation. At Romden Castle NO_3-N concentrations are usually

372   below the EU drinking water limit of 11.3 mg/L, while concentrations are consistently

373   above this water quality limit at the other sites.

374   The highest SRP concentrations (Figure 2c) are found during the periods of low flow

375   for all four sites. SRP-P concentrations at both WWTW impacted sites are regularly

376   >1000 g/L throughout the monitoring period. Figure 2c shows that there is a marked

377   decrease in SRP concentrations during spring 2004 at the Sutton Valence site, and

378   concentrations are now comparable with the Biddenden site, also downstream of a

379   WWTW. This sudden decrease in SRP concentration, and increase in N:P (Figure 2),

380   at Sutton Valance coincides with the use of reed-beds at this site as part of a water

381   treatment upgrade for P stripping.

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382   *4.2   Inorganic and nutrient chemistry*

383   Table 1 shows results for key nutrient species (DOC, NO_3, TDP, SRP, DHP, TP, PP

384   and ratios of NO_3:SRP, SRP:DHP, NO_3:Cl TDP:Cl and SRP:Cl), for twenty sites

385   across the Beult catchment. Results for both high flow (R1) and baseflow (R2)

386   conditions are presented. All nitrate concentrations are expressed as N (mg/L). Table

387   S3, electronic supplementary information, shows results for selected chemical

388   parameters: pH, SEC, HCO_3, SO_4, Cl. Figure 3 shows a ternary plot of key nutrients:

389   DOC, SRP and NO_3 for the different land-use types during both sampling rounds.

390   Analysis of variance (ANOVA) was used to explore the differences in variable

391   concentrations (pH, SEC, HCO_3, SO_4, Cl, DOC, NO_3, TDP, SRP and DHP) both

392   between different types of water and between the two sampling rounds. Values were

393    $\log_{(10)}$ transformed prior to ANOVA and results are shown in Table 2. Significant

394   differences ($p<0.05$) in all variables are found between the different sources (i.e.

395   springs, field drains etc) as well as between the two sampling rounds with the

396   exception of SO_4 and DHP.

397   Groundwater from springs were found to have low concentrations of all P species, and

398   high SEC and concentrations of NO_3, compared to most surface waters and all waste

399   water impacted sites. River samples from the two sites with dominantly forested land-

400   use had the lowest average SEC, NO_3 and dissolved P concentrations of any group,

401   including the springs. These two sites had contrasting PP concentrations, which

402   accounts for a significant proportion (>50%) of TP at both sites. Sites impacted by

403   WWTW have NO_3 concentrations <10 mg/L, and higher mean SRP and TDP

404   concentrations compared to those sites where agricultural land-use dominated.

405   The SRP:DHP ratio was either greater for the baseflow survey or showed no change

406   for the majority of sites, with the exception of Sutton Valance WWTW, Snapmill and

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407   Little Ommerden, two agriculturally impacted sites. In many cases the %DHP was

408   twice as high during the high flow conditions compared to baseflow.

409   Considerably higher concentrations of HCO_3, Cl, and dissolved P species were found

410   during the baseflow survey for most surface waters. In contrast, NO_3, PP, SO_4 and

411   DOC concentrations were lower at many sites during the baseflow survey. The

412   chemistry of the springs did not vary significantly during the study, with perhaps the

413   exception of moderately higher dissolved P, NO_3 and DOC during the high flow

414   survey at Pope Hall Spring (Table 1). The field drains had lower mean baseflow TDP,

415   SRP and DHP, similar DOC and higher NO_3 concentrations, compared to the

416   agriculturally impacted rivers. However, PP concentrations were greater in the

417   agriculturally impacted rivers compared to the field drains during both surveys. Mean

418   NO_3 data were similar for both groups if values from Little Southernden were

419   excluded from the analysis, which was not unreasonable as this site was clearly an

420   outlier having the highest concentrations across the whole survey (51 mg/L-N) which

421   did not vary between the two surveys (Table 1).

422   Molar NO_3:SRP ratios showed considerable variation between sites and between

423   survey (Table 1). In the high flow survey NO_3:SRP ratios were found to be greatest

424   for springs>field drains>forested>Agriculturally impacted>WWTW impacted, while

425   in the baseflow survey WWTW>Agriculturally impacted sites. NO_3:SRP ratios for

426   springs and sites that were impacted by WWTW showed the least change between the

427   two surveys, while agriculturally impacted sites, field drains and forested sites

428   showed the greatest changes with significantly lower ratios ($p<0.001$) during the

429   baseflow survey. This is due to a combination of both lower NO_3 and higher SRP

430   concentrations during baseflow. The results from the two surveys suggest that the

431   long-term trends of lower NO_3:SRP ratios during periods of low flow compared to

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432   high flow (see Figure 2) represent processes that are occurring more widely across the

433   catchment.

434   The results from the two surveys are summarised in Figure 3 using a ternary plot of

435   DOC, NO_3 and SRP. This illustrates several key results: (i) the change in nutrient

436   stoichiometry in surface waters due to inputs from diffuse agricultural land use and

437   WWTW point sources, (ii) the changes in nutrient stoichiometry in WWTW and

438   agriculturally impacted surface waters during contrasting flow conditions, (iii) the

439   relative stability of end members from groundwater, and particularly forested sub-

440   catchments.

441   *4.3   Colloidal and particulate P*

442   Figure 4 summarises the changes in P composition (PP, CP and DP) for six sites

443   between sampling rounds. Overall, the spring sample (Knowle Game Farm) showed

444   no significant changes in DP between the two surveys. The proportion and

445   concentration of PP and CP was greater for most of the river sites (Sherway Bridge,

446   Franks Bridge and the Sutton Valance sites) during the high flow conditions (Figure

447   4a). DP concentrations and proportions were significantly higher during the baseflow

448   survey (Figure 4b), accounting for more than 50% TP at all sites.

449   Colloidal P was found to be an important proportion of TP at the Field Drain site and

450   the site upstream of the WWTW, which showed the highest concentration of TP as

451   well as DP of any site, even during baseflow. There were dramatic changes in P

452   composition at the Sutton Valence site, downstream of WWTW inputs, during

453   baseflow. At this location, there appears to be a significant source of P upstream of

454   the WWTW, which the treated effluent was actually diluting during both surveys. The

455   concentration of WWTW SRP-P inputs was significantly lower during the high flow

18

456   conditions (260 g/L compared to 928 g/L), presumably due to dilution from rainfall

457   (Table 1). The downstream composition at Sutton Valence is clearly dominated by the

458   WWTW inputs during baseflow conditions (Figure 4b), due to very low natural river

459   flow. The similarities in inorganic chemistry are noticeable during the baseflow

460   survey (see Table 1).

461   XRD analysis indicates that the suspended sediment samples have similar

462   mineralogies with major amounts of quartz, minor illite/smectite, 'kaolin' (one of the

463   kaolin group minerals including halloysite, kaolinite etc.) and 'mica' (undifferentiated

464   mica species possibly including muscovite, biotite, illite) and trace amounts of K-

465   feldspar and calcite (Table S4). There was no evidence of calcite in the field drain

466   sample.

467   *4.4   Fluorescence DOM characteristics*

468   Table 3 shows the results for selected dissolved organic matter indices (TFF<10

469   KDa), for six sites sampled during both surveys. The spring site showed no significant

470   changes in DOM character for the two surveys, indicative of a stable structural

471   composition of DOM, even during extreme rainfall events. The other sites showed

472   marked decreases in FA-like, TRP-like, TY-like fluorescence and HI during the

473   baseflow survey. This shows the relatively high concentrations of both bioavailable

474   (TRP and TY-like) and more recalcitrant (FA-like) DOM from the rapid overland

475   inputs from the soil zone during high flow conditions.

476   For the river samples, the marked difference in HI between the two surveys suggests

477   contrasting sources of DOM, with lower structural complexity during baseflow

478   conditions compared to high flow conditions, suggesting more recalcitrant sources of

479   DOM. The average FI of 1.56 is strongly indicative of terrestrially derived fulvic-like

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480   DOM (McKnight et al., 2001), while the consistently higher FI's during the baseflow

481   survey does perhaps suggest a larger proportion of microbial DOM during this period.

482   In addition, the higher   at the spring site, and upstream and downstream of the

483   WWTW during the baseflow survey, also suggests a shift in DOM character to be

484   more autochthonous, from in-situ microbially derived sources (Table 3). The shift in

485   FI downstream of the WWTW, and consistent signature in this reach irrespective of

486   flow conditions, perhaps indicates a consistent input of microbial derived DOM from

487   the WWTW.

488   *4.5 ^{15}N and ^{18}O isotopes of NO_3*

489   Figure 5a shows a cross plot of ^{15}N and ^{18}O for NO_3 in a spring, four agriculturally

490   impacted sites, two sites impacted by WWTW as well as the two WWTW discharge

491   waters. The WWTW discharge was only sampled during baseflow conditions. A cross

492   plot for ^{15}N and NO_3 for the same samples is shown in Figure 5b. Open symbols are

493   results from the baseflow survey, filled symbols results from the high flow survey.

494   The isotopic composition of nitrate at the spring site (Knowle Game Farm) showed

495   little change between the high flow and baseflow surveys. The average ^{15}N value of

496   about +4.9‰ is typical for UK groundwater (Heaton et al., 2005); and the average

497   ^{18}O value of +2.9‰ exactly matches the value which would be expected for

498   bacterially-produced nitrate if one third of its oxygen is derived from water oxygen

499   (Knowle Game Farm spring water ^{18}O = -7‰), and two thirds is from atmospheric

500   O_2 (+24 ‰; Kendall et al., 2007). The nitrate in the spring water is ultimately derived

501   from soils in the recharge area, and we would expect soil-derived nitrate in the

502   catchment to have broadly similar values.

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503   In contrast, samples of discharge from the two WWTW (which were only sampled

504   during the baseflow survey) have both higher ^{15}N (+12.0 and +17.6‰) and slightly

505   higher ^{18}O values (+6.1 and +7.7‰). These values conform to data published for

506   discharge from other sewage treatment works (Anisfeld et al., 2007; Vane et al.,

507   2007), where preferential removal of the lighter ^{14}N and ^{16}O molecules during

508   ammonia volatilisation or denitrification result in elevated ^{15}N and ^{18}O values in

509   residual nitrate in the discharge. Elevated ^{18}O values may also be found in fertilizer

510   nitrate and in rainfall (though the latter can be excluded from consideration here by its

511   low concentration), but these sources tend to have low ^{15}N values (Curtis et al., 2012;

512   Heaton et al., 2012)

513

514   ^{15}N and ^{18}O values for nitrate in most of the river waters fall within the range

515   encompassed by groundwater or soil-derived nitrate and WWTW nitrate sources

516   (Figure 5a). For the agriculturally impacted river sites it is evident that whilst there

517   were large differences between their nitrate concentrations in high flow and baseflow

518   periods, there was little difference in their isotope compositions. Differences were

519   found, however, for the WWTW impacted sites. During baseflow the nitrate isotope

520   compositions and concentrations of the sites downstream of the WWTWs are similar

521   to those of the WWTW discharge, confirming the dominance of this source during

522   baseflow. This association is absent during high flow, however, where lower ^{15}N and

523   ^{18}O values for sites downstream of the WWTWs suggest a greater proportion of soil-

524   derived nitrate.

21

525   *4.6   Mapping runoff and nutrient flux in the Buelt during the high flow survey*

526   Hydrographs of the G2G modelled flow during the high flow survey period are

527   presented in Figure 6 for selected sample sites. Gauged river flows for the Beult at

528   Romden Castle are also provided for comparison. Since these observations were not

529   used in the G2G model configuration they provide an independent assessment of the

530   ungauged performance of G2G. The good agreement at Romden Castle during this

531   period gives confidence that G2G may provide meaningful flow estimates at other

532   ungauged sample locations, particularly in terms of timing of flow peaks.

533   To aid understanding of the rainfall dynamics and resulting model response,

534   catchment average rainfall and modelled soil moisture deficit (SMD) are also shown

535   for the Romden Castle catchment (top plots, Figure 6). This identifies two distinct

536   rainfall periods which correspond to the two observed flow peaks at Romden Castle

537   and are marked in Figure 6. The first period is a single storm with estimated

538   catchment average rainfall of 6.8mm in 4 hours (average 1.7mm/hr). The second

539   period is longer and consists of three individual rainfall storms crossing the catchment

540   which are generally less intense than the first period and give an estimated catchment

541   average rainfall of 20.2mm in 18 hours (average 1.1mm/hr).

542   Maps of the time-averaged runoff ratio (runoff divided by rainfall) for each grid

543   square derived from G2G modelling over the two storm events are shown in Figure 7

544   along with flux results for DOC, SRP and NO_3. The spatial heterogeneity in G2G

545   runoff ratio provides an insight into the runoff generation across the catchment and is

546   a reflection of the following model processes and datasets that support the G2G

547   formulation: (i) geology – moderate permeability of the sand formations in the

548   southwest increases recharge and lowers runoff relative to the impermeable clay that

549   dominates elsewhere (see Figure 1); (ii) soil HOST (Hydrology of Soil Type) class

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550   (Boorman et al., 1995) – mainly HOST class 25 overlies the impermeable clays which

551   enhances runoff, a small area of class 18 to the southwest with lower runoff, and class

552   9 in lower reaches where groundwater frequently rises to within 40cm of the surface;

553   (iii) Slope – increased runoff from steep slopes, particularly the steep scarp slope to

554   the northeast (see Figure 1); and (iv) capturing the antecedent soil moisture conditions

555   through the continual water accounting of the model. The relationship between

556   modelled flux and catchment area for DOC, NO_3-N, SRP and DHP are shown in

557   Figure 8.

558   **5   Discussion**

559   *5.1   Macronutrient sources and concentrations*

560   Streams draining forested parts of the catchment, while only representing a low

561   proportion of total land-use (<10%), provide the lowest concentrations of P and N

562   inputs to the Beult. These sites did not exceed NO_3-N or SRP-P water quality criteria

563   (11.3 mg/L and 100 g/L) for samples collected as part of this study. All the other

564   surface water sites in this study exceeded the SRP quality limit on at least one

565   occasion.

566   Groundwater sources were shown to provide a stable and low input of P and C within

567   the Beult catchment, but have consistently high NO_3 concentrations. Groundwater

568   DOM fluorescence characteristics are consistent with other UK groundwater areas

569   with agricultural land-use (Lapworth et al., 2008; 2009). These are due to a

570   combination of factors: the relatively conservative transport of NO_3 in groundwater,

571   the attenuation of PO_4 in the soil and aquifer, and the microbial breakdown of DOM

572   in the soil and unsaturated zone and their long groundwater residence times compared

573   to other waters. While the groundwater contribution to river flow in the Beult is low

574 (BFI = 0.2), the high concentrations of NO_3-N (ca. 15 mg/L) and high bioavailability

575 of groundwater P (largely SRP) suggests that groundwater inputs may be ecologically

576 significant, particularly during baseflow (Holman et al., 2008; Lapworth et al., 2011).

577 The nutrient composition of field drains is comparable with that of agriculturally

578 impacted rivers, into which they drain. These can be characterised as having, on

579 average, high concentrations of DOC (>15 mg/L), NO_3-N (>8 mg/L) and TP (>400

580 g/L) during high flow, and much lower DOC (ca.10mg/L) and NO_3-N (<1 mg/L)

581 during baseflow (excluding the anomalously high result from site 7). The shift in HI

582 in the surface waters shows that there is an important change in DOM character as

583 well as the abundance during contrasting flow conditions (Conran et al., 1999; Hood

584 et al., 2006). Under high flow, the surface waters of the Beult catchment are enriched

585 with a DOM of higher complexity as well as more abundant sources of bioavailable

586 C, in the form of proteins, due to C export from the dominantly agricultural land-use

587 (Conran et al., 1999). The   values (ca. 0.6) are consistent with other studies for

588 catchments with a high proportion of agricultural land-use (Wilson and Xenopoulos

589 2009).

590 SRP concentrations were noticeably less for the majority of field drain sites during the

591 baseflow survey (see Table 1), while they were greater for the agriculturally impacted

592 rivers. This suggests either (i) greater potential for P attenuation or a greater

593 proportion of shallow groundwater in field drain sources during baseflow, or (ii)

594 perhaps other important sources of SRP within the agriculturally dominated

595 catchment such as septic tanks (Palmer-Felgate et al., 2010). In-stream and hyporheic

596 zone uptake during baseflow conditions has been widely reported as an important

597 mechanism for P attenuation in surface waters (Mulholland et al., 1997; Jarvie et al.,

598 2006). River CP and PP concentrations and proportions were found to be greater

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599 during high flow periods compared to low flow periods, presumably due to the

600 mobilisation of decomposing mineral and organic P sources in leaf litter and river bed

601 sediment as a result of the increase in hydrological energy (Haygarth et al., 2005).

602 The site upstream of the WWTW had the highest SRP concentrations during both

603 high and baseflow conditions: 430 and 1252 g/L respectively (Table 1). This is

604 downstream of a dairy farm, which can contain important sources of TDP, in part due

605 to rapid runoff to surface water from areas of hard standing (Hively et al., 2005).

606 WWTW impacted sites have lower DOM concentrations compared to those from

607 agriculturally impacted sources, but NO_3 and SRP concentrations are significantly

608 higher compared to other groups during baseflow conditions (Figure 3). Average

609 NO3-N concentrations were 8.8 and 29 mg/L for WWTW impacted sites during the

610 high and low flow survey respectively. At the Sutton Valance site, although WWTW

611 inputs actually improved the water quality with respect to P, SRP-P concentrations are

612 still very high (349-912 g/L), and the inorganic chemistry suggests that the stream is

613 composed of a significant proportion (perhaps as high as 80%) of treated water during

614 baseflow conditions.

615 The shift in FOM indices (and HI) downstream of the WWTW indicates a more

616 microbial source of DOM (see Table 3). The higher   and lower HI found at the site

617 downstream of the WWTWs, compared to the agriculturally impacted sites, also

618 means that WW inputs may be locally important sources of more complex DOM,

619 particularly during baseflow (Imai et al., 2002).

620 Nitrate N and O isotopes signatures, combined with other chemical tracers (e.g. NO_3,

621 SRP, Cl), confirm the dominance of WWTW N inputs at sites down-steam of

622 WWTW during baseflow (Curt et al., 2004). During high flow the nitrate isotope

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623   signature is shifted towards the soil N pool for all surface water sites, suggesting that

624   this, i.e. diffuse agricultural sources, is the dominant source N across the catchment

625   during these conditions (Neal et al., 2008).

626   Sites that were impacted by diffuse pollution from agriculture showed no net change

627   in ^{15}N during contrasting flow conditions, with the exception of one site upstream of

628   Sutton Valence which is shifted to higher values (in excess of 17) during baseflow.

629   This illustrates two processes: (i) a relatively stable N source from agricultural

630   catchments, probably derived from the soil N pool, and (ii) the importance of point

631   sources of N, in this case perhaps indicative of a manure source of N (Wassenaar,

632   1995; Choi et al., 2007). This could be from a dairy farm upstream and in close

633   proximity to the site. The combined uses of geochemistry and isotopes have helped

634   identify the different N pools, and the complex temporal dynamics and relative

635   dominance of these pools originating from different sources within the catchment.

636   *5.2   Spatial variations in runoff and nutrient fluxes*

637   Modelled runoff ratio across the catchment shows a large degree of spatial

638   heterogeneity for the high flow survey periods (Figure 7). The southwest of the

639   catchment shows a lower runoff ratio as well as significantly lower nutrient

640   concentrations and fluxes. This is a result of the soil, geological and topographical

641   controls on modelled runoff as well as the wooded land-use. These contrast with the

642   higher runoff and nutrient concentrations and fluxes in the centre and north of the

643   catchment, which are hotspots for nutrient export to the Beult. There is a consistent

644   relationship between DOC, NO_3-N and SRP fluxes at six selected sample sites during

645   the first event (see Figures 7a, c and e), and it is clear from Figure 8 (filled circles)

646   that these fluxes scale linearly with catchment size. Linear regression using data from

647   the first event give coefficient of determination values between 0.995-0.985 for the

648   six flux/catchment area relationships shown in Figure 8. The strong relationships

649   found between all chemical fluxes and catchment size is a surprising result given the

650   potential errors associated with the modelling, sampling and analysis, but perhaps

651   provides a measure of confidence in the point flow estimates generated from the G2G

652   hydrological model. The relationship is poorer, as would be expected, for smaller

653   catchments and lower fluxes, due to larger uncertainties in the modelling. Given the

654   high flow/runoff conditions, this suggests that at the selected sample sites the nutrient

655   fluxes from this event are dominated by diffuse surface runoff sources, which are

656   evenly distributed across these sub-catchments and mask out any point source inputs.

657   The response to the second larger event (see Figure 6) is different, both in terms of

658   spatial flux patterns (see Figure 7) and the slope of flux-catchment size relationships

659   for all the nutrients based on three sample sites (Figure 8, hollow squares). An

660   exception is the conservative tracer Cl (Figure 8f) where the flux-catchment

661   relationship holds over both events as might be expected since catchment inputs are

662   dominated by rainfall sources (Figure 8f). These results could be explained in terms of

663   spatial differences in runoff ratio, with proportionally higher catchment runoff ratio

664   values as well as the magnitude of the second event. The higher magnitude event

665   mobilised greater DOC, TDP, SRP and particularly DHP (see Figure 8e) from the soil

666   for a given catchment area. In contrast, the more conservative (unbound) pollutant

667   NO_3 shows a reduction in flux during the higher magnitude runoff event: this is most

668   likely due to the proportionally higher runoff ratio for this event and subcatchment

669   (see Figure 7b). This is also corroborated by the lower NO_3 concentrations at these

670   sites and lower molar N:P ratios compared to the sites sampled during the first event

671   (see Table 1). The apparent loss of P flux downstream of site 9 (Figure 7f) may reflect

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672   the sample timing at site 9 and the fact that this site was sampled a day later on the

673   falling rather than rising hydrograph limb of the event as was the case for the two

674   downstream sites (see Figure 6). This is consistent with a "clockwise" solute

675   hysteresis effect during storm events where higher concentrations are observed during

676   the hydrograph rising limb of an event compared with those measured on the falling

677   limb (House and Warwick, 1998). This combined approach using a distributed

678   hydrological model and hydrochemical sampling shows good potential for evaluating

679   how different nutrient fluxes and pools respond temporally and spatially depending on

680   antecedent conditions and changes in catchment runoff characteristics. Such an

681   approach could help inform catchment-based water quality management plans for

682   reducing and understanding diffuse and point source pollution for the River Beult and

683   elsewhere, particularly as the G2G Model is already configured for England, Wales

684   and Scotland.

685   *5.3   Macronutrient bioavailability under contrasting flow conditions*

686   Within the Beult catchment there are significant changes in nutrient bioavailability

687   and stoichiometry for surface waters during baseflow and high flow conditions

688   following intense rainfall. SRP concentrations are approximately twice as high during

689   baseflow compared to high flow, while the inverse is true for PP, CP and DHP and

690   DOC and NO_3.

691   Overall, N:P ratios are lower during baseflow for most surface waters that are

692   impacted by diffuse sources pollution (Table 1 and Figure 2). If N and P values are

693   normalised using Cl, a conservative tracer with respect to the potential evaporation

694   and rainfall inputs to the hydrological model, there are no net changes in TDP and

695   SRP between contrasting flow conditions at sites impacted by diffuse sources of

696   pollution. However, sites impacted by WWTW are relatively enriched with respect to

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697   TDP and SRP during baseflow (Table 1), and all surface water sites show relative

698   depletion in NO_3, so other wastewater sources upstream of these sites such as septic

699   tanks or dairy waste cannot be ruled out (Palmer-Felgate et al., 2010; Hively et al.,

700   2005). At some sites (Field Drain, Sutton Valence-us, Franks Bridge, Snoadhill Farm)

701   there are increases in SRP:Cl ratios during baseflow, possibly due to release of

702   surface bound P from sediments under higher pH and temperatures.

703   TFF results also show that there is a shift in the association of P from PP towards

704   'truly' dissolved forms and colloidal particles during low flow conditions. These are

705   more bioavailable forms of P, and could also be in greater abundance due to the in-

706   stream breakdown of PP and CP, as well as other physical and chemical factors

707   (Bostrom 1988; Furumai et al., 1989). The higher pH and temperatures during

708   baseflow could facilitate the release of PO_4 from sediments, both bed sediments and

709   suspended particulate and colloidal matter, due to increased completion for binding

710   sites on ferric complexes between hydroxyl and PO_4 ions (Kim et al., 2003; Abrams

711   and Jarrell, 1995).

712   The low flow rates could also result in changes in bioavailable P within the water

713   column, shifting the N:P ratio and potential for eutrophication. Cyclical periods of

714   high flow will be important in replenishing nutrient sources within river networks,

715   sustaining the cycle of bioavailable P release and inputs to the catchment. They will

716   also be important in transferring nutrients from zones of excess to zones of relative

717   depletion. Autotrophic growth, and the potential deterioration in ecological status, is

718   likely to be limited by N availability during baseflow, which could partly account for

719   the relative enrichment in SRP and TDP in surface waters in this period.

720   There is a complex interaction between river sediments, which are largely composed

721   of illite/smectite, kaolin and mica (Table S4, electronic supplementary information),

29

722   and DOM. This is controlled by pH and major ion chemistry (Gu et al., 1994). At

723   lower pH there is greater adsorption to clay surfaces by fulvic and humic acids,

724   particularly of higher molecular weight (MW) fractions, and PO_4 has been shown to

725   inhibit the adsorption of low MW DOM fractions due to competition with surface

726   ligand exchange and electrostatic interactions (Hur and Schlautman, 2004).

727   The change in the DOM character within receiving rivers is partly due to inputs of

728   lower MW hydrophilic acids from WWTW sources (Imai et al., 2002). The interplay

729   between these multiple factors, different sources of C (natural and anthropogenic),

730   and the combined effect of higher pH and higher PO_4, are all likely to contribute to

731   the overall shift in DOM character during contrasting flow conditions within the

732   catchment (Hood et al., 2006). Immediately after periods of high flow, and

733   mobilisation of soil nutrient pools, and during baseflow when WWTW inputs are

734   proportionally greater, autotrophic growth may be stimulated, producing temporal

735   zones of more rapid biological growth (McClain et al., 2002; Merseburger et al.,

736   2005).

737   As groundwater NO_3 concentrations are high compared to surface waters, these results

738   confirm that baseflow groundwater inputs are low for most sites impacted by diffuse

739   nutrient sources, perhaps with the exception of inputs of shallow groundwater sources

740   to field drains. However, this could in part be due to the relatively long residence time

741   within the subsurface and does not rule out the possibility of increased N inputs in the

742   future due to the delayed arrival of increased NO_3 concentrations at the water table

743   where unsaturated zones are deep or downward flow is slow (Wang et al., 2012).

744   As well as the obvious temporal variability in water quality due to changes in flow,

745   longer term trends (Figure 2) show that water sources impacted by WWTW can have

746   dramatic shifts in nutrient quality due to changes in the efficiency of P and N

747   stripping (Neal et al., 2008). While over the same period, sites impacted by

748   predominantly diffuse sources have not shown any long-term changes in nutrient

749   chemistry. However, there is no simple or clear distinction between diffuse and point

750   sources of pollution within the catchment: the reality is more dynamic and complex.

751   For example, reaches with obvious point source inputs have been shown to be equally

752   impacted by diffuse sources during high flow conditions.

753   **6   Summary and Conclusions**

754   The results from this catchment-wide study reflect the fact that the River Beult fails to

755   meet water quality standards under the WFD. All surface waters in this study had

756   SRP-P concentrations >100 g/L on at least one occasion. Average groundwater SRP-P

757   concentrations were 36 g/L, almost three times the concentrations found in surface

758   waters draining wooded areas. Groundwaters, and some field drains, had consistently

759   high NO_3-N concentrations, >11.3 mg/L, as did sites downstream of WWTW during

760   baseflow.

761   Overall, the nutrient chemistry within the Beult catchment is controlled by diffuse

762   exports from arable agricultural land-use, as well as point source pollution from

763   WWTW and dairy farms. Wooded areas provide relatively small areas of low nutrient

764   input to the River Beult.

765   There were significant changes in nutrient bioavailability and stoichiometry for

766   surface waters during baseflow and high flow conditions following intense rainfall.

767   SRP concentrations were approximately twice as high during baseflow conditions

768   compared to high flow conditions, while the inverse is true for PP, CP and DHP and

769   DOC and NO_3. N:P ratios are lower during baseflow for most surface waters that are

770   impacted by diffuse sources of pollution. Cl normalised values suggest that changes in

771   P are largely due to evaporative/dilution effects in catchments impacted by diffuse

772   pollution, while those impacted by WWTW sources showed net enrichments in P

773   during baseflow.

774   The higher FI,   and lower HI found at the site downstream of the WWTWs,

775   compared to the agriculturally impacted sites, also mean that WW inputs may be

776   locally important sources of more complex DOM, particularly during baseflow. This

777   is likely due to inputs of lower MW hydrophilic acids from WW sources.

778   N and O isotopes signatures, combined with other chemical tracers (e.g. NO_3),

779   confirm the dominance of WWTW N inputs at sites downsteam of WWTW during

780   baseflow conditions. During high flow the nitrate isotope signature is shifted towards

781   the soil N pool for all surface water sites, suggesting that diffuse sources of N

782   dominate during these conditions.

783   The combined use of different methods: P speciation, TFF, organic matter florescence

784   and N and O isotope analysis of NO_3 and distributed hydrological modelling using the

785   G2G model has helped to characterise the highly dynamic nature of nutrient sources,

786   pollution and bioavailability in this typical lowland clay catchment. Future

787   applications of ^{18}O-PO4 methods (e.g. Li et al., 2011) may further our understanding

788   of P sources, fate and turnover within catchments. Given the dynamic nature of these

789   and other catchments, long-term high-resolution monitoring of nutrients within such

790   catchments (Neal et al., 2012) coupled with distributed hydrological modelling

791   appears to be a useful approach to understand changes in nutrient fluxes and process

792   within catchments.

793   **Acknowledgements**

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1122
1123 **Table captions**:

1124 **Table 1**. Summary of the nutrient chemistry for the Beult catchment

1125 **Table 2**. Summary ANOVA table for selected chemical variables

1126 **Table 3**. TFF and fluorescence results

1127

1128 **Figure captions**:

1129 **Figure 1**. Location of study area, sampling sites, drainage, geology and main
1130 population centres. a) Geology, drainage network and centres of population within the

39

1131 Beult catchment; b)Location of the Beult catchment (shown in bold) as part of the
1132 Medway catchment, Kent, UK . Site numbers refer to sites in Table 1. * EA water
1133 level and flow monitoring sites. Population centres: a=Cranbrook, b=Smarden,
1134 c=Staplehurst, d=Headcorn, e=Stilebridge. Drainage data courtesy of CEH (NERC).
1135 Sites 4, 5 and 11 are located on a small low order tributary of the River Beult.

1136 **Figure 2**. Long-term flow and nutrient data: a) Daily mean flow between 2003 and
1137 2010 at Stilebridge, the outlet of the Beult catchment, b) NO_3-N, c) SRP-P, d) Molar
1138 N:P ratios. Red stars in Figure 2a show sampling rounds.

1139 **Figure 3**. Ternary plot of DOC, SRP and NO_3. Circles show results during the storm
1140 flow survey, triangles results from the baseflow survey.

1141 **Figure 4**. Phosphorus association with particulate, colloidal and dissolved fractions
1142 by TFF. a) storm flow results, b) baseflow results.

1143 **Figure 5**. Nitrate N and O isotope results. a) Nitrate ^{15}N and ^{18}O cross plot, b) ^{15}N
1144 vs NO_3-N scatter plot. Filled symbols show results during storm flow conditions,
1145 open symbols show results during baseflow conditions. Numbers refer to sites, see
1146 Table 1. WW indicates sites that are impacted by wastewater sources, WWTW,
1147 discharge from wastewater treatment works.

1148 **Figure 6**. G2G modelled flow at selected gauged and ungauged sites across the study
1149 area during the high-flow survey. River flows for the Beult at Romden Castle are
1150 provided for comparison. Catchment average rainfall and modelled soil moisture
1151 deficit are shown for the Romden Castle catchment area (top plots). The two main
1152 rainfall/runoff events during this period are highlighted and used in Figure 7 and 8.

1153 **Figure 7**. Time-averaged G2G gridded runoff ratio and relationship to site nutrient
1154 flux during the storm flow survey a-b) DOC, c-d) NO_3-N, e-f) SRP. Left hand panels
1155 show results for the first storm event (21:00 08/11/08 – 01:00 09/11/08), and right
1156 hand panels for second event (07:00 10/11/08 – 01:00 11/11/08). Site numbers are
1157 shown in Figure 7a (see Table 1 for details).

1158 **Figure 8.** Scatter plots of nutrient flux and catchment area. a) DOC, b) SRP, c) TDP,
1159 d) NO_3-N, e) DHP and f) Cl. Circle symbols are data from the first runoff event,
1160 square symbols are from the second runoff event. The red line shows a robust linear
1161 regression line for data from the first event.
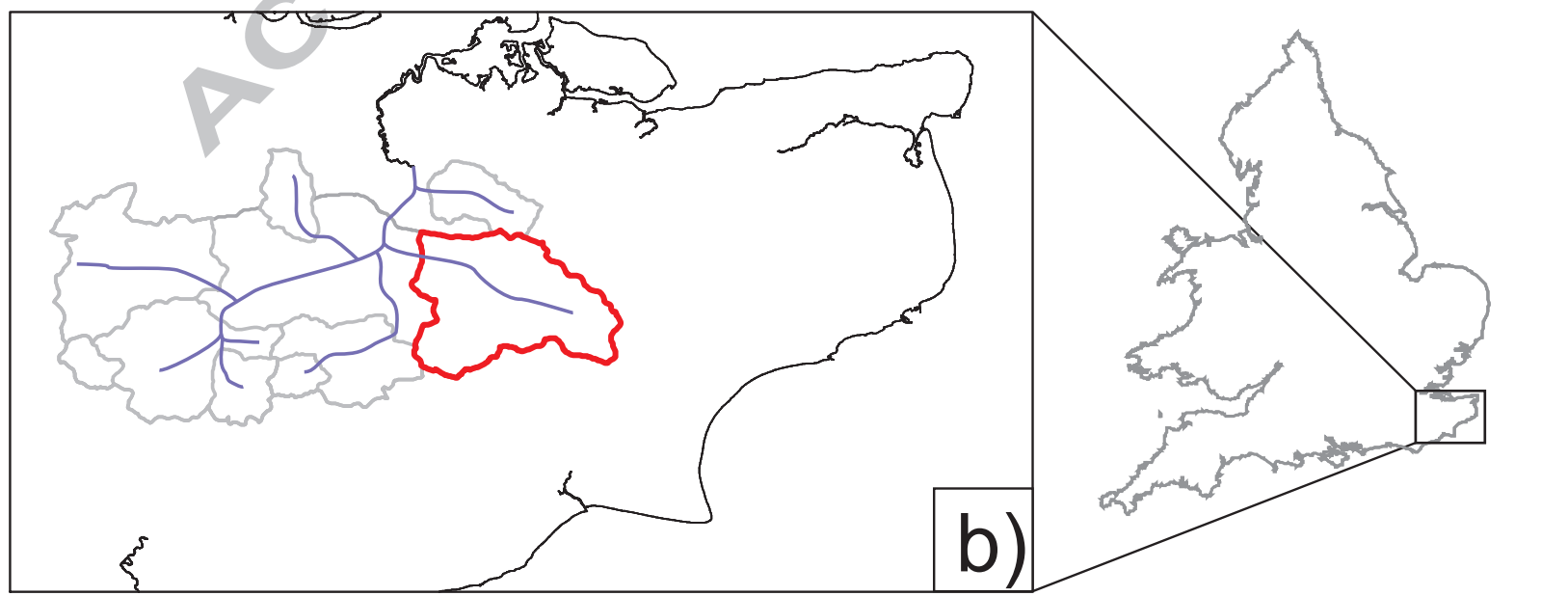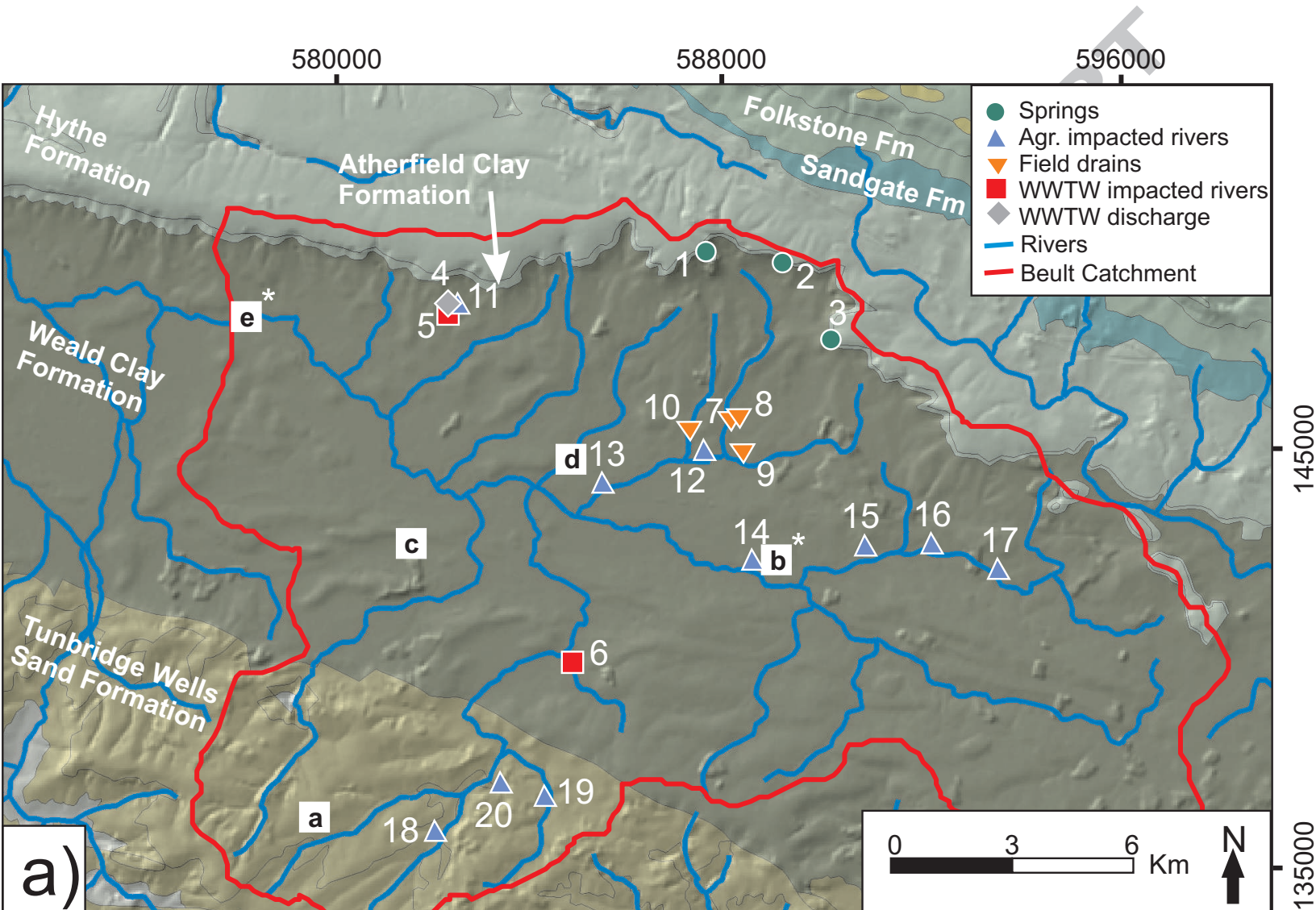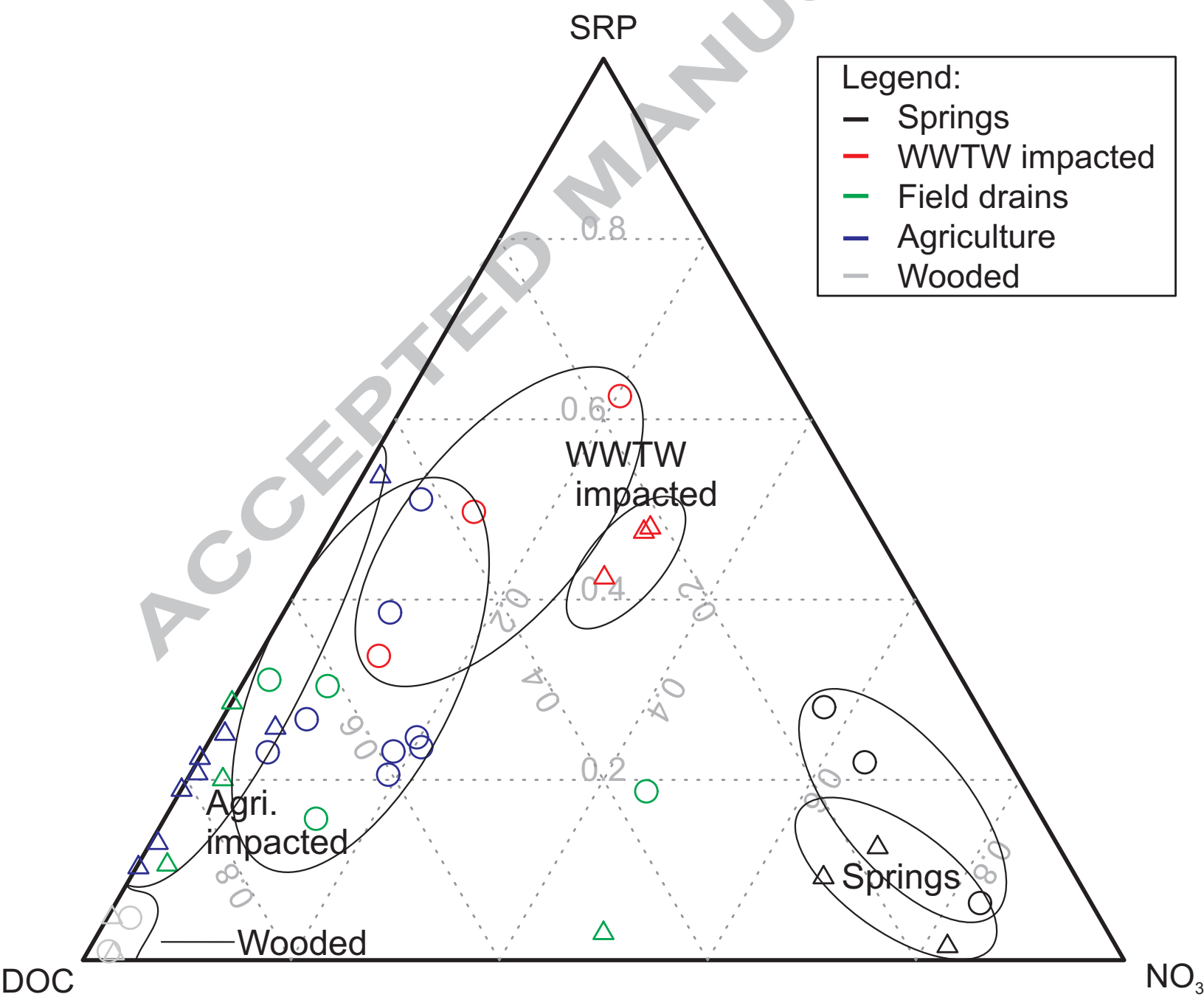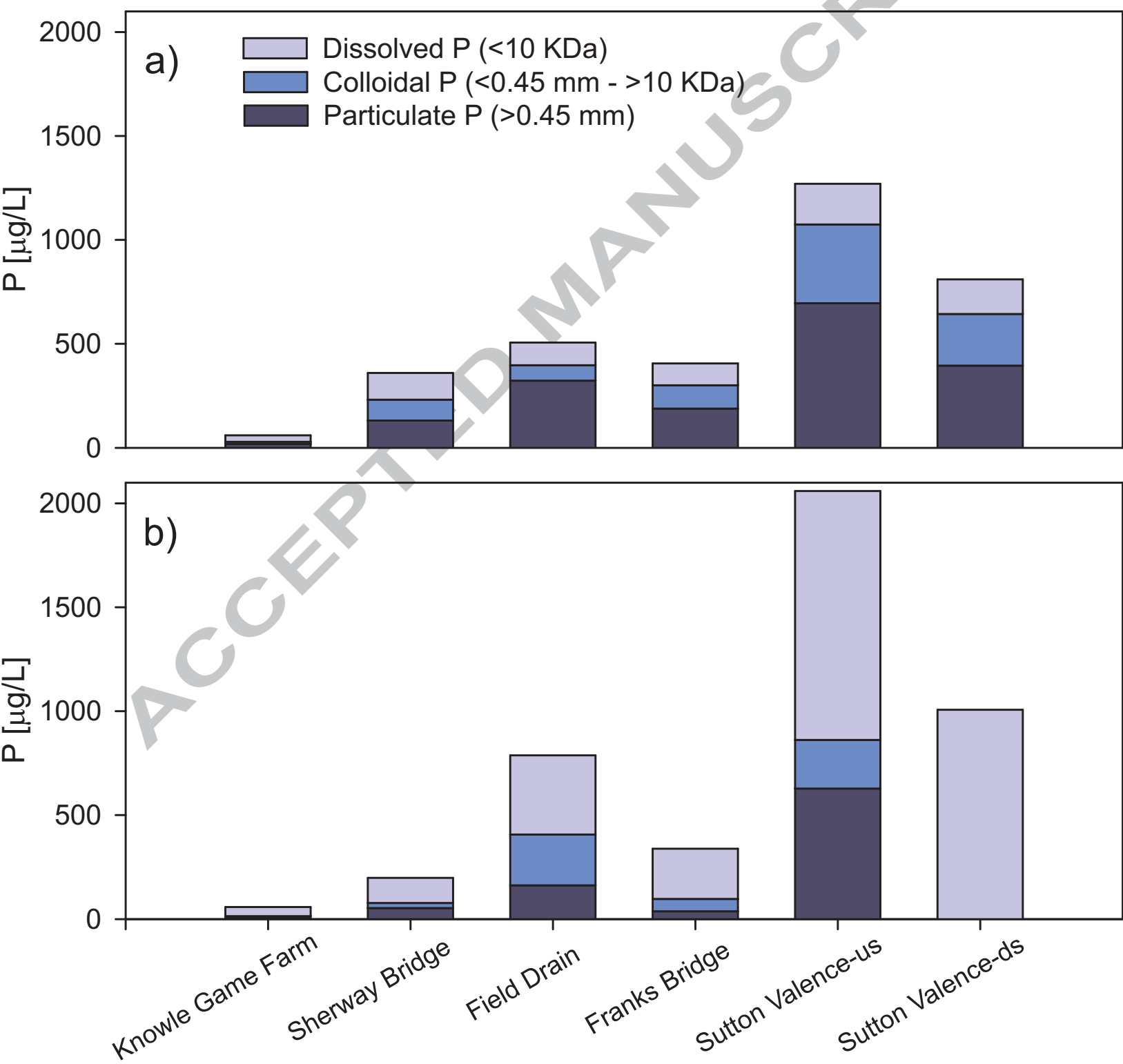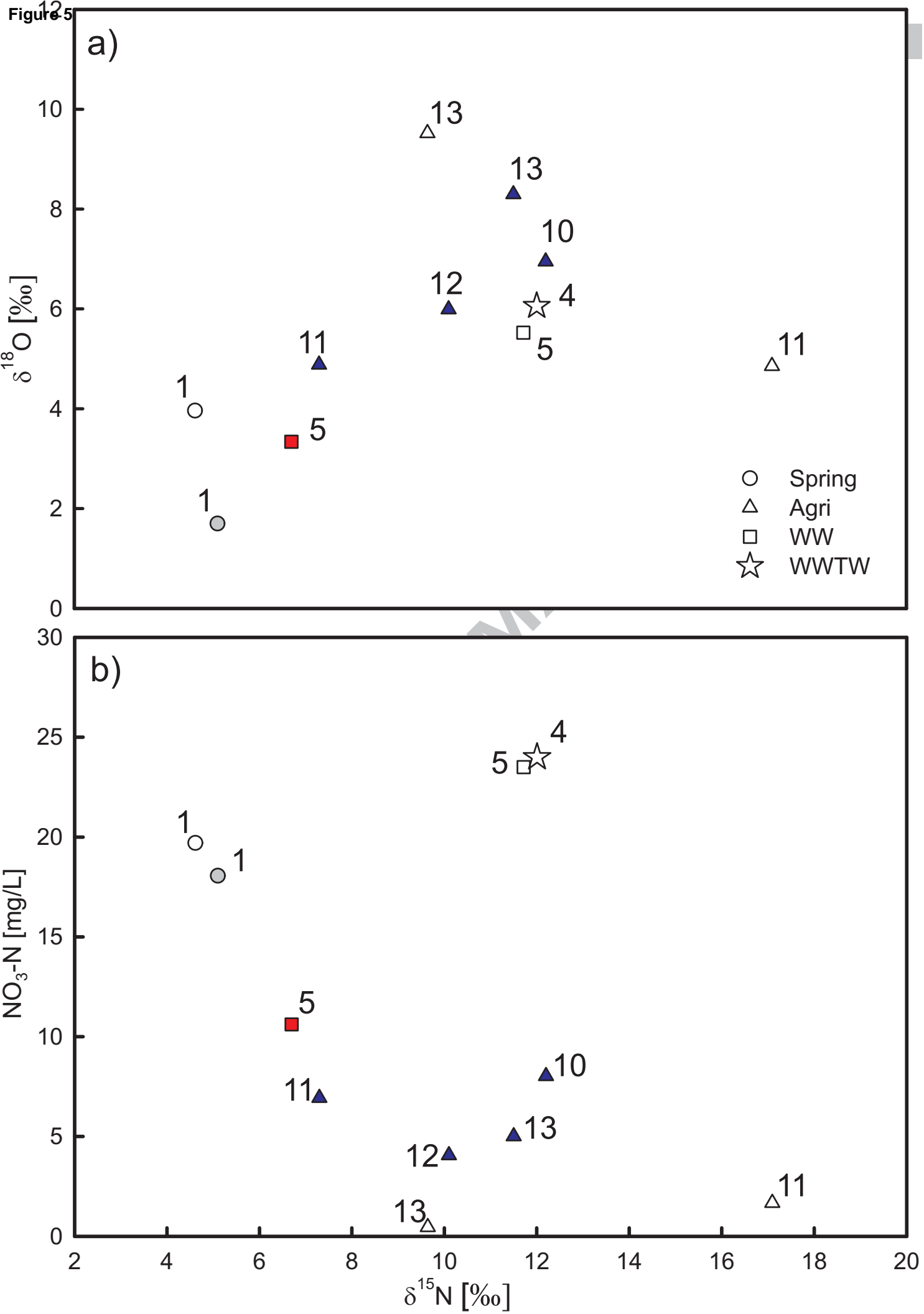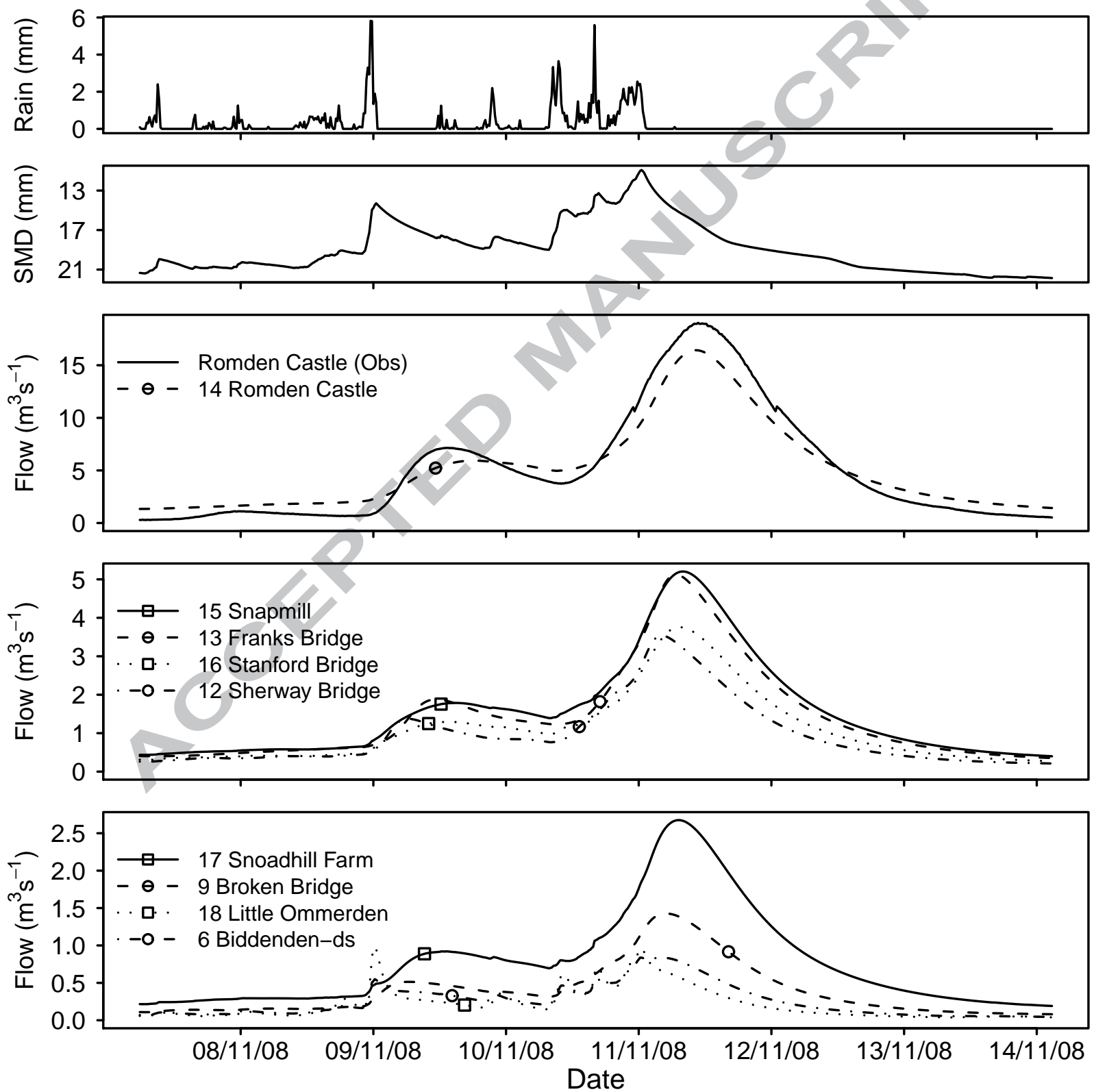
40

Figure 1

Figure 2

Figure 3

SRP

Legend:
— Springs
— WWTW impacted
— Field drains
— Agriculture
— Wooded

0.8

0.6

WWTW
impacted

0.4

Agri.
impacted

Wooded

Springs

DOC

NO$_3$

Figure 4

a)

Dissolved P (<10 KDa)
Colloidal P (<0.45 mm - >10 KDa)
Particulate P (>0.45 mm)

P [µg/L]

b)

P [µg/L]

Knowle Game Farm Sherway Bridge Field Drain Franks Bridge Sutton Valence-us Sutton Valence-ds

Figure 5

Figure 6

Figure 6

Figure 7

Figure 8
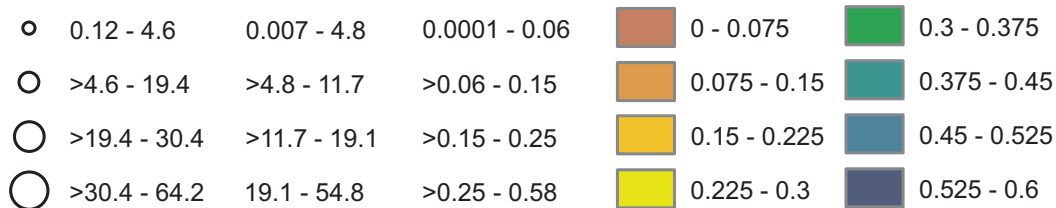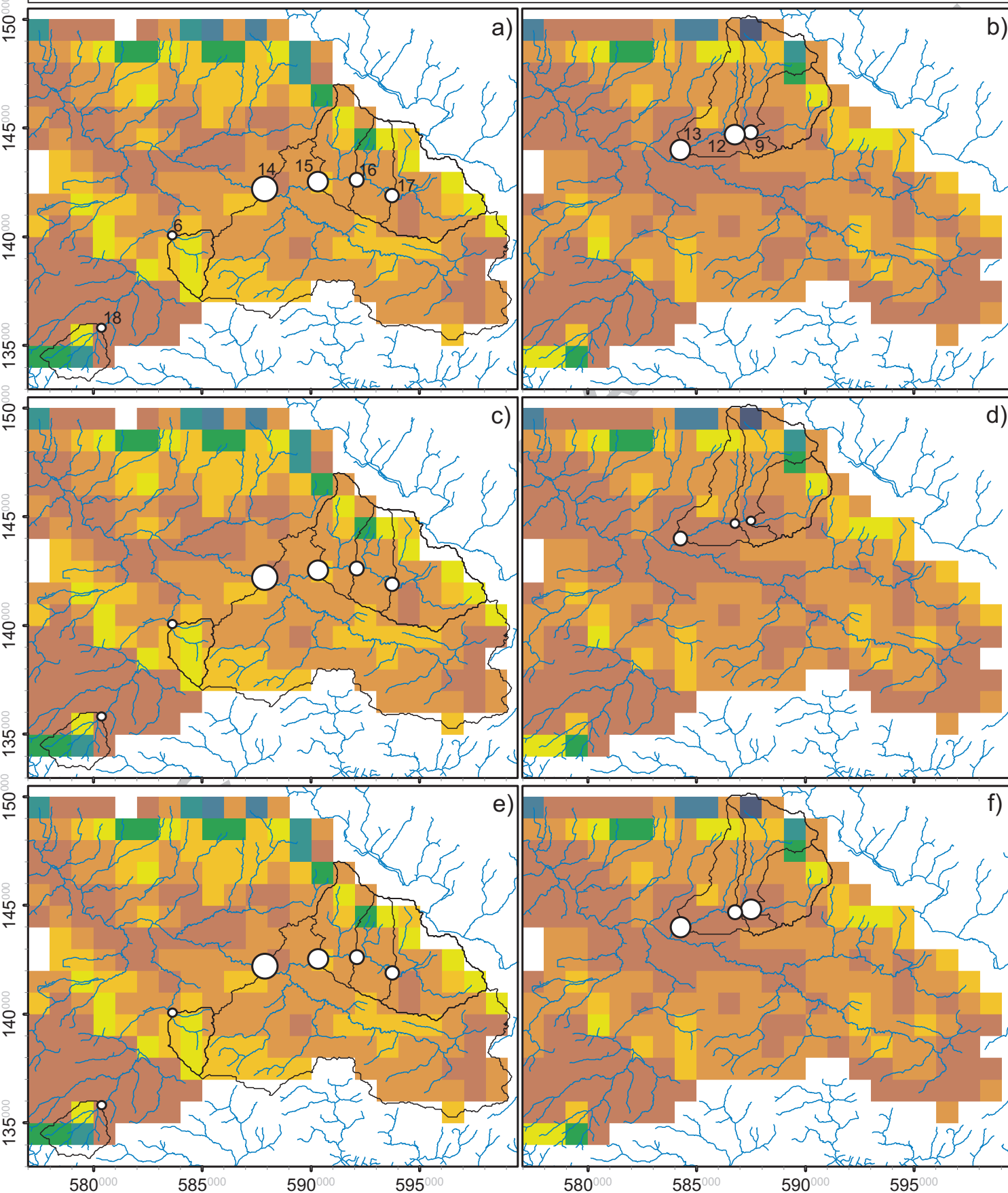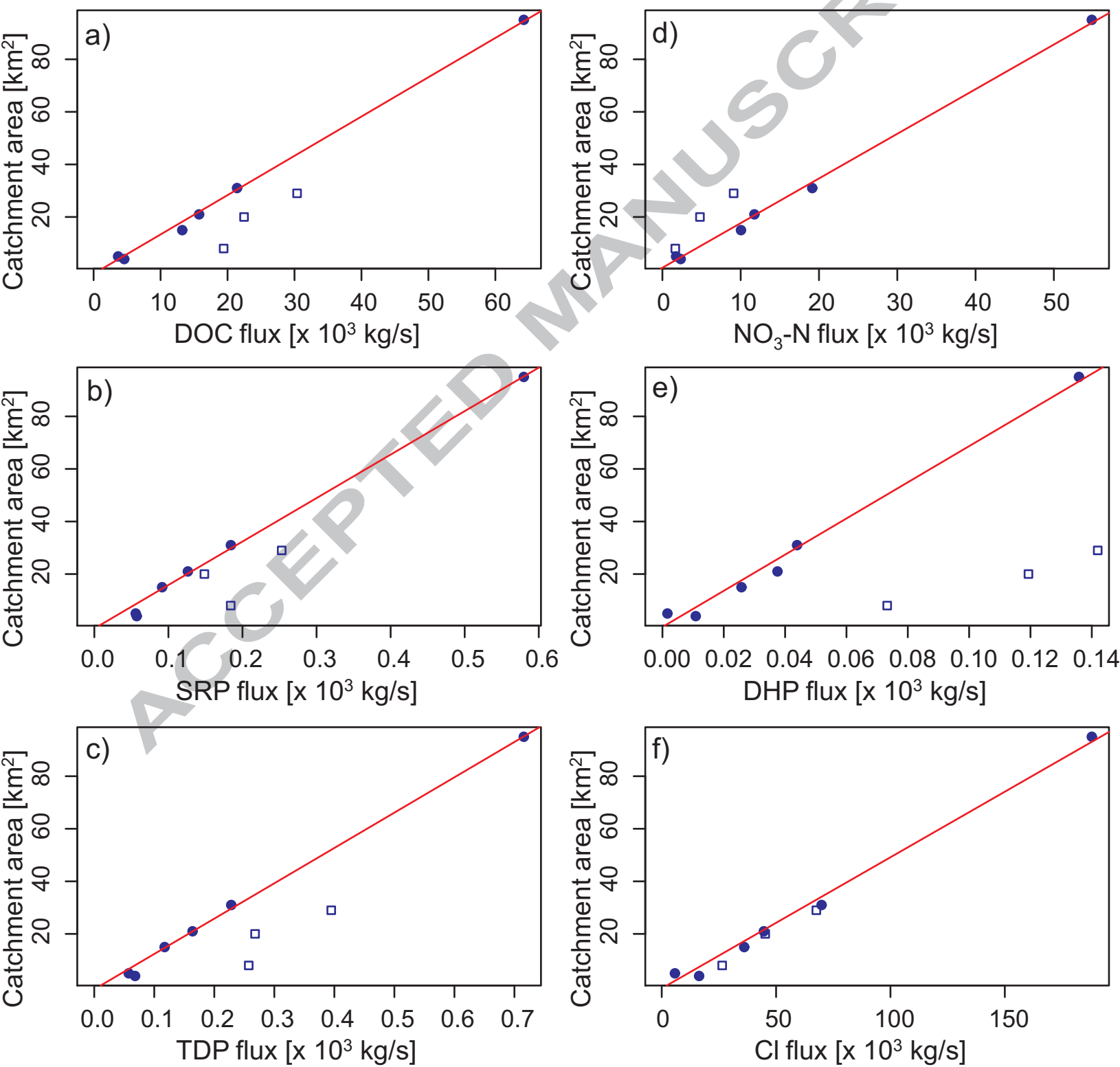
Table1-3

Table 1.

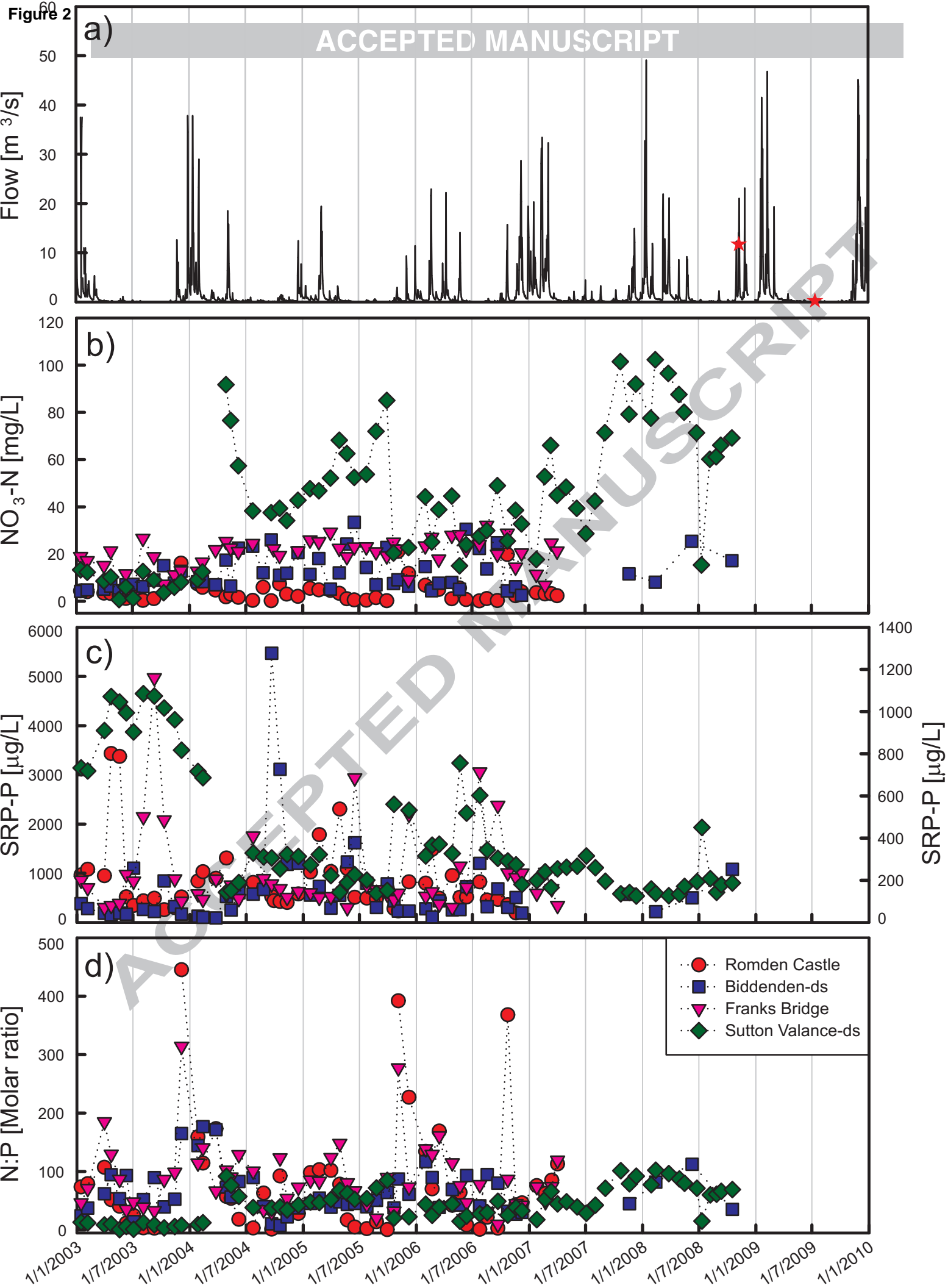| Variable	DOC	DOC	NO$_3$-N	NO$_3$-N	TDP	TDP	SRP	SRP	DHP	DHP	TP	TP	PP	PP	N:P	N:P	SRP:DHP	SRP:DHP	SRP	SRP	DHP	DHP
Unit	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L					%	%	%	%
Sampling round	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
Springs																						
1 Knowle Game Farm	1.1	1.0	20.2	19.7	42	31	13	9	29	22	60	45	18	14	3437	4853	0.4	0.4	31	29	69	71
2 Hollis Farm	1.2	1.3	13.2	13.3	41	48	38	45	<7	3	47	N/A	<7	N/A	766	654	12.7	15.0	93	94	7	6
3 Pope Hall	1.5	0.8	13.8	12.5	84	56	57	55	27	1	85	N/A	<7	N/A	534	505	2.1	55.0	68	98	32	2
Mean	1.3	1.0	15.7	15.2	56	45	36	36	28	8.7	64	45	18	14	1579	2004	1.8	2.8	64	74	36	26
WWTW discharge																						
4 Sutton Valence	3.5	4.4	10.0	24.0	266	1004	260	928	<7	76	276	992	10	<7	85	57	43.3	12.2	98	92	2	8
WWTW impacted rivers																						
5 Sutton Valence-ds	13.0	4.5	10.6	23.5	415	1000	349	912	66	92	810	1006	395	<7	67	57	5.3	10.4	84	91	16	9
6 Biddenden-ds	13.9	9.1	7.1	35.1	207	1344	174	1268	33	76	330	N/A	123	N/A	90	61	5.3	16.7	84	94	16	6
Mean	13.5	6.8	8.8	29.3	311	1172	262	1090	49.5	84	570	1006	259	<7	78	59	5.3	12.8	84	93	16	7
Field drains																						
7 Southernden	16.4	4.7	5.3	0.8	247	144	165	117	82	27	424	N/A	177	N/A	72	15	2.0	4.3	67	81	33	19
8 Little Southernden	17.3	13.4	51.0	51.6	242	101	180	78	62	23	426	170	184	69	627	1463	2.9	3.4	74	77	26	23
9 Broken Bridge	21.2	7.7	1.8	1.0	281	142	201	89	80	53	436	N/A	155	N/A	20	24	2.5	1.7	72	63	28	37
10 Field Drain	16.0	14	8.0	0.03	183	626	73	530	110	96	506	788	323	162	243	0.1	0.7	5.5	40	85	60	15
Mean	17.7	10	16.5	13.4	238	253	155	203.5	83.5	50	448	479	210	116	240	376	1.7	3.2	63	76	37	24
*Agriculturally impacted rivers**																						
11 Sutton Valence-us	17.4	11.0	6.9	1.7	575	1432	430	1252	145	180	1270	2060	695	628	35	3	3.0	7.0	75	87	25	13
12 Sherway Bridge	19.2	7.5	4.1	0.2	229	145	127	106	102	39	360	198	131	53	71	5	1.2	2.7	55	73	45	27
13 Franks Bridge	16.7	8.0	5.0	0.5	217	301	139	256	78	45	406	339	189	38	80	4	1.8	5.7	64	85	36	15
14 Romden Castle	12.3	10.4	10.5	0.3	137	297	111	259	26	38	698	N/A	561	N/A	209	3	4.3	6.8	81	87	19	13
15 Snapmill	12.2	11.6	10.9	0.1	130	320	105	126	25	194	867	N/A	737	N/A	230	2	4.2	0.6	81	39	19	61
16 Stanford Bridge	12.6	12.4	9.4	0.02	131	499	101	339	30	160	570	N/A	439	N/A	207	0.2	3.4	2.1	77	68	23	32
17 Snoadhill Farm	14.9	15.8	11.3	0.04	132	404	103	348	29	56	510	N/A	378	N/A	243	0.2	3.6	6.2	78	86	22	14
18 Little Ommerden	18.0	8.7	8.6	2.8	283	342	275	310	8	32	429	N/A	146	N/A	70	20	34.4	9.7	97	91	3	9
Mean	15.4	10.7	8.3	0.7	229	468	174	375	55	93	639	866	410	240	143	5	3.2	3.4	76	77	24	23
Wooded catchment																						
19 Rogley Hill	11.7	4.9	0.7	0.1	34	32	12	23	22	9	218	N/A	184	N/A	122	8	0.5	2.6	35	72	65	28
20 Chittenden wood	17.0	4.9	0.8	0.5	10	10	<7	3.5	<7	6.5	24	N/A	14	N/A	533	323	0.5	0.5	35	35	65	65
Mean	14.4	4.9	0.8	0.3	22	21	12	13.25	22	7.75	121	N/A	99	N/A	327	165	0.5	1.1	35	53	65	47

R1=High flow conditions, R2=Baseflow conditions, *predominantly agricultural with limited WW inputs, N:P are NO3:SRP (molar ratios).

Table 1 continued

Variable	$NO_3\text{-}N$:Cl	$NO_3\text{-}N$:Cl	TDP:Cl	TDP:Cl	SRP:Cl	SRP:Cl
Sampling round	R1	R2	R1	R2	R1	R2
Springs						
1 Knowle Game Farm	0.834	0.851	0.002	0.001	0.001	0.000
2 Hollis Farm	0.400	0.439	0.001	0.002	0.001	0.001
3 Pope Hall	0.508	0.445	0.003	0.002	0.002	0.002
Mean	0.560	0.558	0.002	0.002	0.001	0.001
WWTW discharge						
4 Sutton Valence	NA	0.270	NA	0.011	NA	0.010
WWTW impacted rivers						
5 Sutton Valence-ds	0.214	0.266	0.008	0.011	0.007	0.010
6 Biddenden-ds	0.142	0.280	0.004	0.011	0.004	0.010
Mean	0.178	0.274	0.006	0.011	0.005	0.010
Field drains						
7 Southernden	0.183	0.024	0.008	0.004	0.006	0.003
8 Little Southernden	1.747	1.088	0.008	0.002	0.006	0.002
9 Broken Bridge	0.062	0.016	0.010	0.002	0.007	0.002
10 Field Drain	0.206	0.001	0.005	0.018	0.002	0.016
Mean	0.524	0.307	0.008	0.006	0.005	0.005
*Agriculturally impacted rivers**						
11 Sutton Valence-us	0.153	0.032	0.013	0.027	0.010	0.024
12 Sherway Bridge	0.105	0.005	0.006	0.003	0.003	0.002
13 Franks Bridge	0.135	0.011	0.006	0.007	0.004	0.006
14 Romden Castle	0.292	0.005	0.004	0.004	0.003	0.004
15 Snapmill	0.274	0.001	0.003	0.005	0.003	0.002
16 Stanford Bridge	0.264	0.000	0.004	0.005	0.003	0.004
17 Snoadhill Farm	0.278	0.001	0.003	0.007	0.003	0.006
18 Little Ommerden	0.304	0.020	0.010	0.002	0.010	0.002
Mean	0.222	0.010	0.006	0.007	0.005	0.005
Wooded catchment						
19 Rogley Hill	0.022	0.002	0.001	0.001	0.000	0.000
20 Chittenden wood	0.022	0.012	0.000	0.000	NA	0.000
Mean	0.022	0.006	0.001	0.000	0.000	0.000

Table 2.

Variable	Source[a]	Round[b]
pH	0.00084 ***	0.01088 *
SEC	1.0e-11 ***	3.7e-09 ***
HCO_3	3.3e-06 ***	1.8e-05 ***
SO_4	9.9e-05 ***	0.52
Cl	2.6e-06 ***	2.0e-05 ***
DOC	3.4e-15 ***	6.4e-05 ***
NO_3	0.0011 **	0.0013 **
TDP	0.00067 ***	0.01225 *
SRP	0.00046 ***	0.00951 **
DHP	0.029 *	0.361
NO3:SRP	0.00056 ***	0.00044 ***

[a]Grouped according to source type (see Table 1).

[b]Grouped by sampling occasions R1 and R2

Significance denoted as follow: 0 *** 0.001 **0.01 * 0.05

Table 3.

Variable	DP	DP	FA	FA	TRP	TRP	TY	TY	FI	FI	β/α	β/α	HI	HI	TRP:FA	TRP:FA
Unit	μg/L	μg/L	R.U	R.U	R.U	R.U	R.U	R.U								
Sampling round	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
1. Knowle Game Farm	31	44	0.1	0.1	0.18	0.20	0.09	0.26	1.59	1.62	0.68	0.71	1.55	1.48	1.77	1.66
5. Sutton Valence-ds	166	1004	12.6	1.7	3.33	0.66	0.99	0.25	1.60	1.60	0.57	0.79	17.62	8.96	0.26	0.38
10. Field Drain	109	381	15.9	3.3	3.31	0.95	0.98	0.31	1.45	1.53	0.56	0.53	21.08	15.67	0.21	0.29
11. Sutton Valence-us	196	1198	10.4	2.7	2.45	0.90	0.80	0.25	1.54	1.61	0.59	0.64	19.16	12.74	0.24	0.34
12. Sherway Bridge	129	121	17.0	1.6	3.54	0.48	0.85	0.25	1.60	1.51	0.57	0.59	20.02	11.46	0.21	0.31
13. Franks Bridge	105	242	15.8	1.7	3.33	0.59	0.82	0.26	1.54	1.70	0.56	0.57	21.21	12.24	0.21	0.34

DP = 'truly' dissolved P (<10 Kda), RU= Raman Unit, fluorescence indices (see section 3.3.3 for full explanations): FA=Fulvic acid, TRP=Tryptophan,

TY=Tyrosine, FI=fluorescence index (McKnight et al., 2001), β/α=labile/recalcitrant OM ratio (Parlanti et al., 200), HI=humification index (Zsolnay et al., 2001).

1220   Multi technique approach to understand C, N and P within catchment
1221   processes
1222   Changes in nutrient stoichiometry/bioavailability under contrasting flow
1223   conditions
1224   N and O isotopes show dominance of waste water (WW) inputs during
1225   baseflow
1226   Fluorescence DOM indices characterise WW inputs to rivers
1227   Grid-to-Grid distributed model used to assess spatial variations in nutrient flux

1228