

1 **Non-domestic phosphorus release in rivers during low-flow:**
2 **mechanisms and implications for sources identification**
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14 **Abstract:**

15 A common assumption in phosphorus (P) load apportionment studies is that P loads in rivers consist
16 of flow independent point source emissions (mainly from domestic and industrial origins) and flow
17 dependent diffuse source emissions (mainly from agricultural origin). Hence, rivers dominated by
18 point sources will exhibit highest P concentration during low-flow, when flow dilution capacity is
19 minimal, whereas rivers dominated by diffuse sources will exhibit highest P concentration during
20 high-flow, when land-to-river hydrological connectivity is maximal. Here, we show that Soluble
21 Reactive P (SRP) concentrations in three forested catchments free of point sources exhibited
22 seasonal maxima during the summer low-flow period, i.e. a pattern expected in point source
23 dominated areas. A load apportionment model (LAM) is used to show how point sources
24 contribution may have been overestimated in previous studies, because of a biogeochemical process
25 mimicking a point source signal. Almost twenty-two years (March 1995 – September 2016) of
26 monthly monitoring data of SRP, dissolved iron (Fe) and nitrate-N (NO₃) were used to investigate the
27 underlying mechanisms: SRP and Fe exhibited similar seasonal patterns and opposite to that of NO₃.
28 We hypothesise that Fe oxyhydroxide reductive dissolution might be the cause of SRP release during
29 the summer period, and that NO₃ might act as a redox buffer, controlling the seasonality of SRP
30 release. We conclude that LAMs may overestimate the contribution of P point sources, especially
31 during the summer low-flow period, when eutrophication risk is maximal.

32 **Keywords:**

33 Soluble reactive phosphorus, iron, redox processes, catchment, point source, load apportionment

34 **1. Introduction**

35 Phosphorus (P) concentration in freshwater bodies is an important controlling factor of
36 eutrophication worldwide (Smith and Schindler, 2009). Hence, national and federal regulations, such
37 as the European Water Framework Directive (Directive 2000/60/EC), attach much importance to the
38 reduction of P emissions to streams and rivers. Cost-effective alleviation of P emissions requires
39 precise estimation of the contribution of different P sources in catchments to prioritise management
40 efforts (Bowes et al., 2014; Jarvie et al., 2013b; Withers et al., 2014b).

41 Point source emissions, mainly from domestic and industrial origins, consist of direct P delivery into
42 the river system. Diffuse source emissions, mainly from agricultural origin, result from the
43 mobilisation of P sources distributed over the landscape and their delivery to rivers (Haygarth et al.,
44 2005). In the case of point source emissions, P delivery from large waste water treatment plants can
45 be monitored directly, but direct assessment of septic tanks leaking in rural areas requires detailed
46 surveys or use of costly fingerprinting techniques (Arnscheidt et al., 2007; Neal et al., 2010; Richards
47 et al., 2016). As an alternative, indirect methods have been developed to determine the relative
48 contribution of point source and diffuse source emissions based on observed concentration-
49 discharge relationships (Bowes et al., 2008, 2014; Greene et al., 2011; Jarvie et al., 2012). These load
50 apportionment models (LAMs) can take different forms, but rely on the same assumptions: point
51 emissions are assumed to be constant in time while diffuse emissions are assumed to increase with
52 discharge, as a result of increasing P mobilisation and delivery during runoff events (Bowes et al.,
53 2015). The point source contribution to P concentration is thus modelled as a linear function of the
54 inverse of discharge (dilution effect) and several equations have been proposed to describe
55 increasing diffuse P concentration during high flow. For example, Bowes et al. (2008) proposed a
56 power function of discharge, and Greene et al. (2011) proposed a linear combination of discharge
57 and the square of discharge. To account for the temporary retention of P during low-flow and its
58 remobilisation during high flow, and not to attribute all the remobilised P to diffuse sources, Jarvie et

59 al. (2012) proposed an improved version of LAMs using chloride as a conservative tracer of
60 wastewater effluents. In summary, LAMs belong to a large family of empirical models used to fit
61 water quality time series (Minaudo et al., 2017; Moatar et al., 2017; Zhang and Ball, 2017) with the
62 characteristic that they make an explicit distinction between flow dependent and flow independent
63 pollution emissions.

64 The estimated contribution of point and diffuse sources to annual P loads vary according to the area
65 (Jarvie et al., 2010), but even in catchments where diffuse emissions dominate annual loads, it is
66 common to observe that point source emissions dominate daily P loads during a majority of the time
67 (Greene et al., 2011; Serrano et al., 2015; Sharpley et al., 2009; Shore et al., 2017). Another
68 consequence is that the summer low-flow season is assumed to be dominated by point emissions
69 where they occur and are coincident to known point source pressures (Jordan et al., 2007, 2012;
70 Withers et al., 2014a). Also, because this season is when light and temperature conditions are
71 favourable to eutrophication, river basin managers might decide to target point sources as a priority
72 to mitigate river eutrophication problems in a cost-effective manner (Jarvie et al., 2006; Shore et al.,
73 2017; Stamm et al., 2014).

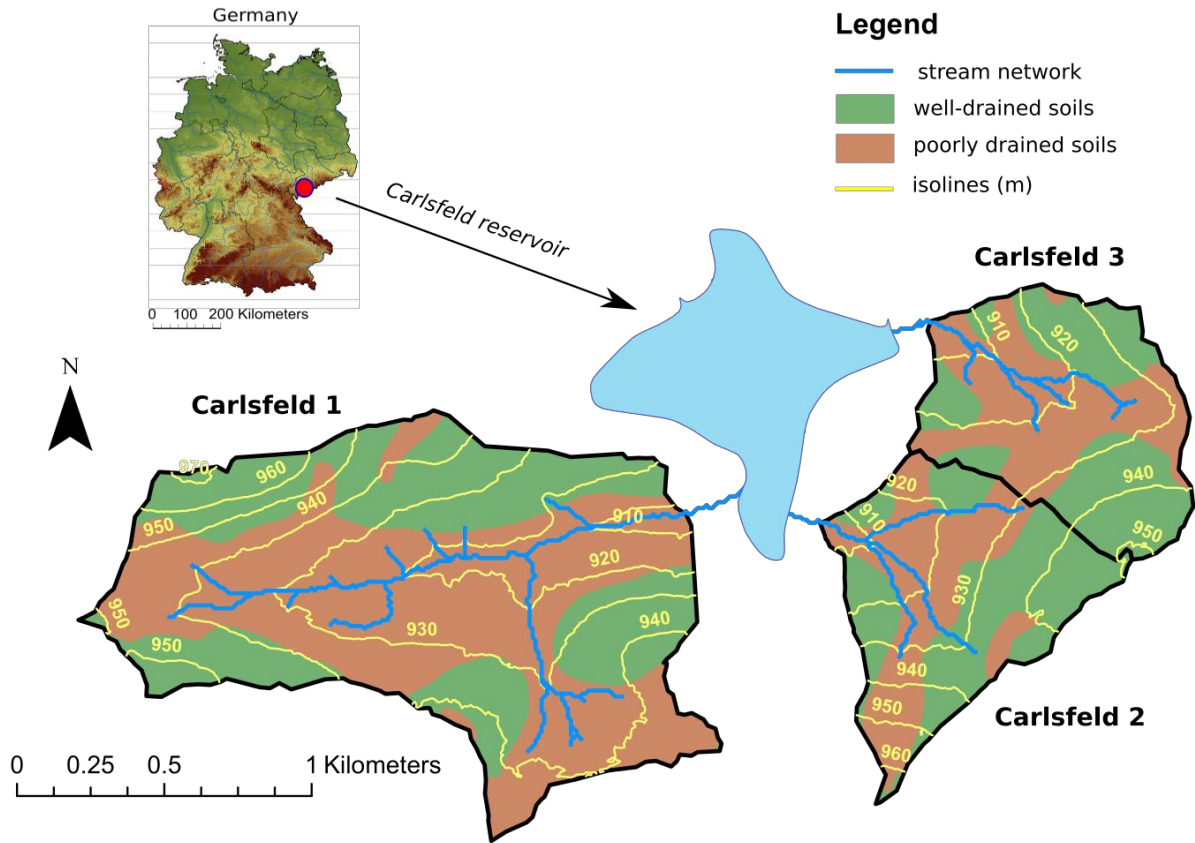
74 However, the low-flow period also corresponds to the warm summer season in catchments of the
75 temperate zone, and it is well known that the biogeochemical processes influencing the P cycle in
76 soils and river sediments are temperature dependent (Withers and Jarvie, 2008). In this paper, we
77 hypothesised that temperature dependent biogeochemical processes could lead to P release to
78 rivers during the summer low-flow period and that this release might be unduly attributed to point
79 source emissions in load apportionment studies. To test this hypothesis, three rivers draining small
80 forested catchments free of any point sources were investigated over a 22-year period to: i) quantify
81 the seasonal variability of Soluble Reactive P (SRP) concentration and other solutes, ii) determine if
82 previous P LAMs can be misrepresented by the seasonal dynamics observed, and iii) identify the
83 controlling factors of this seasonal dynamics in order to improve future LAMs.

84 2. Materials and methods

85 2.1. Study area

86 The Carlsfeld reservoir is located in eastern Germany, in the federal state of Saxony (Figure 1). Its
87 catchment area is 5 km² and spans both sides of the German – Czech border. Climate is temperate
88 continental, with mean \pm standard deviations of annual precipitation and temperature of 1237.0 \pm
89 273.0 mm and 5.7 \pm 1.0 °C, respectively (1995 – 2015). Mean monthly temperature varies from -3.0 \pm
90 4.4 °C in January to 14.4 \pm 3.8 °C in July (1995 – 2015). The catchment is located in a low-mountain
91 range, the Ore Mountains, with elevations ranging from 904 to 971 m. The geology is dominated by
92 granite capped by podsols (classified as “well drained”) in the upslope domain and organic gleysols
93 (classified as “poorly drained”) in valley-bottoms. Both dominant soil types were classified as “very
94 acidic” (pH < 5), according to the German soil classification (DBK Sachsen, 1:50.000).

95 Three independent sub-catchments were selected for this study: Carlsfeld 1, 1.8 km²; Carlsfeld 2, 0.6
96 km² and Carlsfeld 3, 0.6 km² (Figure 1). Their topography is gentle with an average slope of 3° in each
97 of the sub-catchments. The percentage of organic gleysols was 58.2% in Carlsfeld 1, 44.4% in
98 Carlsfeld 2 and 50.2% in Carlsfeld 3. Land use was 100% forest (spruce) without any agriculture or
99 human dwellings. Hence, the three study sub-catchments are free of any point source emissions to
100 the streams and any fertiliser application on the land surface.



101

102 **Figure 1: Localisation of the Carlsfeld reservoir and soil types in the three study catchments**

103 **2.2. Hydro chemical monitoring**

104 The total discharge into the Carlsfeld reservoir was estimated daily from a mass balance calculation
 105 involving 15 min record of the reservoir water level (aggregated on a daily basis) and daily record of
 106 outflowing discharge. It was assumed that all three sub-catchments had the same specific discharge
 107 (in mm d^{-1}), equal to the specific discharge estimated for the whole catchment area of the reservoir.
 108 This assumption was considered acceptable because the total catchment area was small, with similar
 109 topography and the same land use over the sub-catchments. Discharge data were available for the
 110 whole study period (March 1995 to September 2016) except from June 1997 to November 1999
 111 (Figure 2).

112 Grab samples were collected monthly from March 1995 to September 2016, at the outlet of the
 113 three sub-catchments, between 8:00 am and 12:00 pm local time, and analysed for Soluble Reactive
 114 Phosphorus (SRP), nitrate-N (NO_3) and dissolved Fe after $0.45 \mu\text{m}$ filtration (Figure 2). Chemical

115 analyses of water samples were performed using standard protocols (Wasserchemische Gesellschaft,
116 2014). SRP was determined colorimetrically by reaction with ammonium molybdate (UV-VIS Specord
117 200); NO₃ was determined as N by ionic chromatography (ICS-1100 Dionex); Fe was determined by
118 atomic absorption spectrometry (AAS Solaar M5, Thermo).

119 The three studied catchments have been previously included in two multi-site biogeochemical
120 studies (Musolff et al., 2016; Sucker et al., 2011). A shorter time series of Carlsfeld 1 has also been
121 selected for a showcase analysis of long-term Dissolved Organic Carbon (DOC) and SRP trends in
122 Musolff et al., (2016), and in a DOC load uncertainty evaluation study (Buettner and Tittel, 2013). In
123 contrast to the previously published biogeochemical studies, the present paper focuses on seasonal
124 SRP variations and their implications for LAM.

125 **2.3.Data analysis**

126 The data analysis was threefold.

- 127 • The seasonal component of concentration and discharge time series was extracted from a
128 long term trend component using Generalised Additive Models (GAM). GAM are generalized
129 linear models in which the linear form is replaced by a sum of smooth functions (Hastie and
130 Tibshirani, 1987). Technically, the year (1995-2016) and the month (1-12) for each data point
131 were used as predictor variables to estimate the long term non-linear trend and a seasonal
132 component, respectively. The R package *mgcv* (Wood, 2006) was used for this purpose, with
133 cyclic cubic spline to avoid discontinuities at the end points of the spline (in other words, no
134 discontinuity between December and January) and a correction for autocorrelation
135 (autoregressive-moving-average model).
- 136 • The significance of trends was quantified by the slope of a linear regression model of annual
137 mean concentration and discharge values as a function of the year. Although the GAM long
138 term trend was not perfectly linear (see results), analysis of residuals showed that a linear
139 model was acceptable to quantify a mean percentage increase or decrease during the study

140 period and whether this increase or decrease was significant ($p < 0.05$). Only fully monitored
141 years were considered here, i.e. from 1996 to 2015 for concentration data, and 1996 and
142 from 2000 to 2015 for discharge. Percentage exceedance of an indicative SRP eutrophication
143 threshold of $0.02 \text{ mg SRP l}^{-1}$ (EC, 2002) was estimated for the first ten full years of study
144 (1996-2005) and the last ten full years of study (2006-2015).

145 • Concentration-discharge (C-Q) plots and concentration-concentration (C-C) plots between
146 each pair of solutes were drawn. A LAM was fitted to the SRP-Q plots, to test whether the
147 observed SRP-Q relationships in catchments without point source emissions could mimic a
148 point source signal. Here the simplest version of the LAM was selected:

$$SRP = \frac{a}{Q} + b * Q^c$$

149 where $\frac{a}{Q}$ is the “virtual” contribution of point sources and $b * Q^c$ is the contribution of diffuse
150 sources. The a and b parameters were constrained to be >0 and the c parameter was
151 constrained to be ≥ 1 . A nonlinear least-squares estimate of the parameters was
152 determined with the nls() function in the R software (R Development Core Team, 2008). The
153 “virtual” contribution of point sources on annual SRP load and the percentage of the time
154 when “virtual” point sources dominated were estimated separately for the first ten full years
155 of study (1996-2005) and the last ten full years of study (2006-2015). Also for the first ten
156 years and the last ten years of study, alternative empirical (linear) models based on identified
157 SRP controlling factors (see result section 3.2.) were tested and compared. For this
158 comparison the LAM was used without a power law function to allow comparison with other
159 linear models including two parameters.

160 **3. Results**

161 **3.1. Long term and seasonal variability of SRP, dissolved Fe and nitrate** 162 **concentrations**

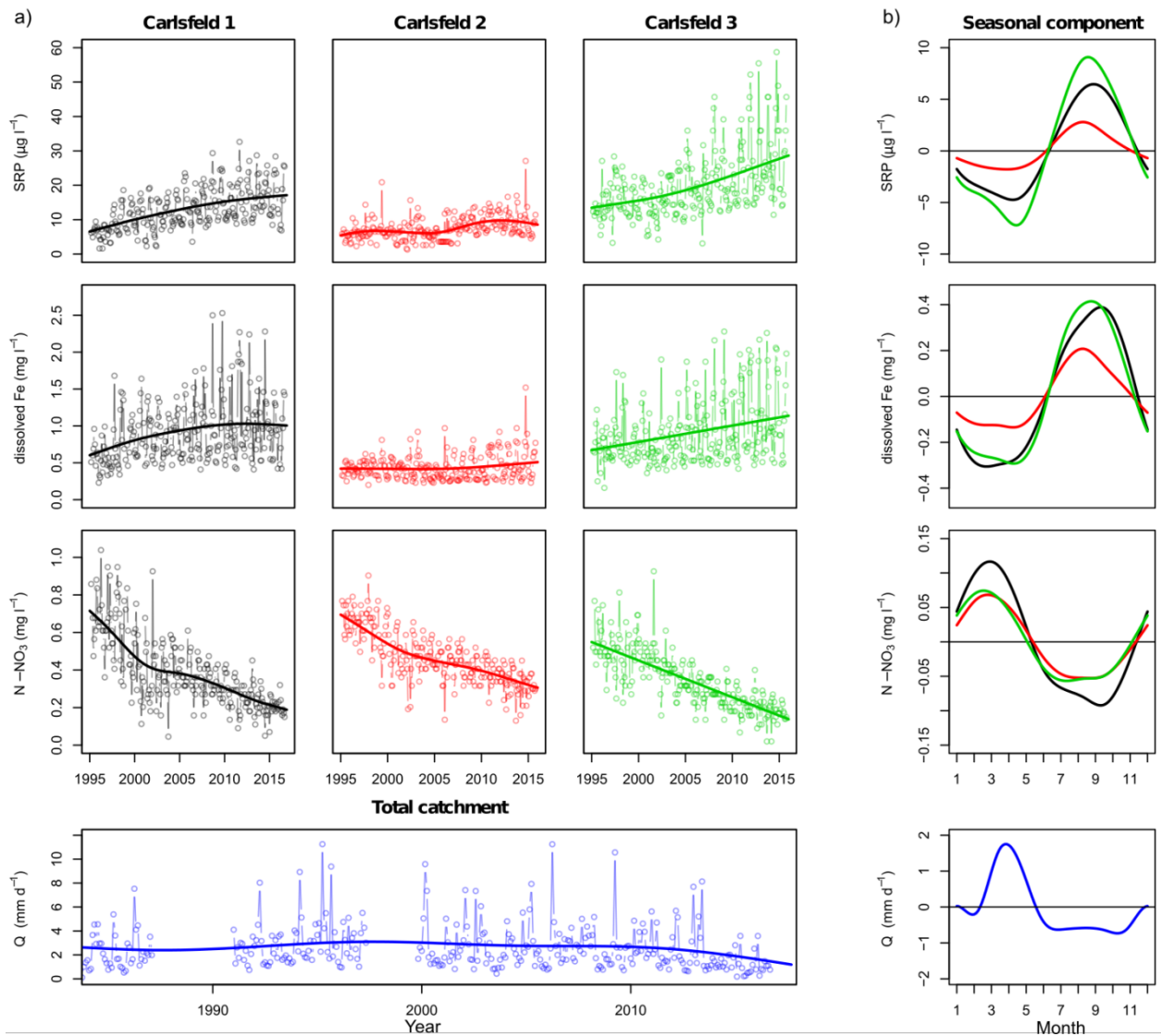
163 Mean (\pm standard deviation) annual SRP and dissolved Fe concentrations in Carlsfeld 1 ($13.1 \pm 3.5 \mu\text{g}$
164 P l^{-1} ; $0.92 \pm 0.16 \text{ mg Fe l}^{-1}$) and Carlsfeld 3 ($19.9 \pm 5.3 \mu\text{g P l}^{-1}$; $0.91 \pm 0.17 \text{ mg Fe l}^{-1}$) were significantly
165 higher than in Carlsfeld 2 ($7.6 \pm 1.8 \mu\text{g P l}^{-1}$; $0.44 \pm 0.07 \text{ mg Fe l}^{-1}$) (paired Wilcoxon test, $p < 0.05$,
166 $n=20$). Conversely, mean annual NO_3 concentration in Carlsfeld 1 ($0.38 \pm 0.14 \text{ mg N l}^{-1}$) and Carlsfeld
167 3 ($0.34 \pm 0.12 \text{ mg N l}^{-1}$) was significantly lower than in Carlsfeld 2 ($0.46 \pm 0.11 \text{ mg N l}^{-1}$). Differences
168 between Carlsfeld 1 and Carlsfeld 3 were also significant for SRP and NO_3 but not for Fe, and the
169 differences between Carlsfeld 1 and Carlsfeld 3 were generally smaller than between Carlsfeld 1 or 3
170 and Carlsfeld 2 ($6.8 \mu\text{g P l}^{-1}$ versus 5.5 and $12.3 \mu\text{g P l}^{-1}$, $0.01 \text{ mg Fe l}^{-1}$ versus 0.48 and $0.47 \text{ mg Fe l}^{-1}$,
171 0.04 mg N l^{-1} versus 0.08 and 0.12 mg N l^{-1} , respectively).

172 From 1996 to 2015, mean annual SRP concentration increased significantly (linear model, $p < 0.05$,
173 $n=20$) in the three catchments ($+121\%$ in Carlsfeld 1, $+72\%$ in Carlsfeld 2 and $+106\%$ in Carlsfeld 3).
174 In Carlsfeld 1 and Carlsfeld 3, significant increases in the mean annual concentration of dissolved Fe
175 ($+47\%$ and $+62\%$, respectively) were also observed, but not in Carlsfeld 2 ($p > 0.05$). Conversely,
176 mean annual NO_3 concentration decreased significantly in the three catchments (-66% in Carlsfeld 1,
177 -48% in Carlsfeld 2 and -67% in Carlsfeld 3). No trend in mean annual discharge, precipitation or
178 temperature could be detected from 1996 to 2015 (Figure S1), although the discharge long term
179 trend appeared to decrease between 2012 and 2016 (Figure 2a).

180 Similar to the long-term trend, the seasonal dynamics of SRP and dissolved Fe mirrored that of NO_3
181 (and discharge) in the three catchments: SRP and dissolved Fe reached their seasonal maximum in
182 the late summer (August to October) which corresponded to the period with the lowest NO_3
183 concentration and the lowest discharge (Figure 2b). Conversely, NO_3 reached its seasonal maximum
184 during the high flow period (March to May). The SRP and dissolved Fe seasonal dynamics and trends
185 also seemed to be dependent on NO_3 values and NO_3 decreasing trends: in Carlsfeld 2, where NO_3
186 concentrations were the highest and NO_3 decreasing trend was the lowest, the seasonal amplitude

187 of the dissolved Fe and SRP signal was weaker than in Carlsfeld 1 and 3, where NO₃ concentrations
188 were lower and NO₃ decreasing trends were stronger (Figure 2).

189 The number of months for which SRP concentration exceeded the indicative eutrophication
190 threshold of 0.02 mg l⁻¹ increased for two of the three study catchments, between the first ten full
191 years of record (1996-2005) and the last ten full years of record (2006-2015). In Carlsfeld 1, this
192 threshold was exceeded 3% of the time during the first period and 24% of the time during the second
193 period. In Carlsfeld 3, the threshold was exceeded 26% of the time during the first period and 53% of
194 the time during the second period. In Carlsfeld 2, exceedance represented less than 0.1% of the time
195 during both periods. The season at which this exceedance was observed in Carlsfeld 1 and 3 was
196 mainly the late summer period (Figure 2), i.e., a period where light and temperature conditions are
197 favourable for eutrophication.



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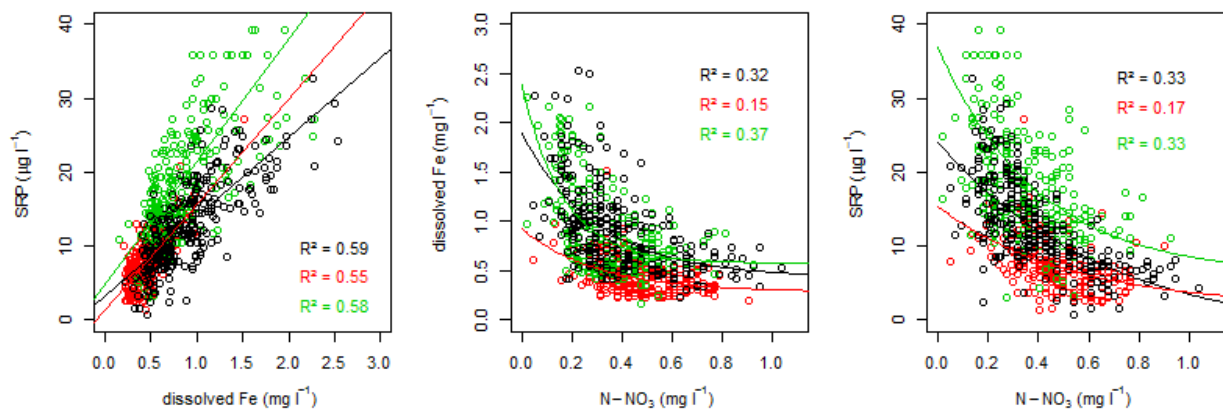
199 **Figure 2: Monthly concentration and discharge data and long term components of GAM model (a) and seasonal**
 200 **component of GAM model (b). Open circles represent the original monthly time series and bold lines represent long term**
 201 **(a) and seasonal (b) GAM components.**

202 3.2.C-Q and C-C relationships

203 None of the three solutes studied exhibited a clear and univocal relationship with discharge for the
 204 entire study period (1995-2016). Nitrate concentration was not significantly correlated with
 205 discharge ($p > 0.1$) and SRP and dissolved Fe exhibited high concentrations both for the lowest and
 206 the highest discharge values (Figure S2). This lack of a clear relationship between concentrations and
 207 discharge is in apparent contradiction with the seasonal GAM component (Figure 2b), which shows
 208 that NO₃ dynamics were in phase with discharge while SRP and dissolved Fe had opposite seasonal

209 dynamics to discharge. However, the solutes were affected by large long term trends, and this was
210 not the case for discharge; consequently, the C-Q relationships changed from year to year and these
211 relationships taken for the entire study period could not exhibit clear patterns.

212 Contrary to the C-Q plots, the C-C plot showed clear relationships between pairs of solutes (Figure 3),
213 for the entire study period (1995-2016). Soluble reactive P was significantly ($p < 0.05$) correlated with
214 Fe ($r = 0.74 - 77$), and both SRP and Fe exhibited a similar non-linear decreasing relationship with
215 NO₃, fitted with an exponential function in Figure 3.

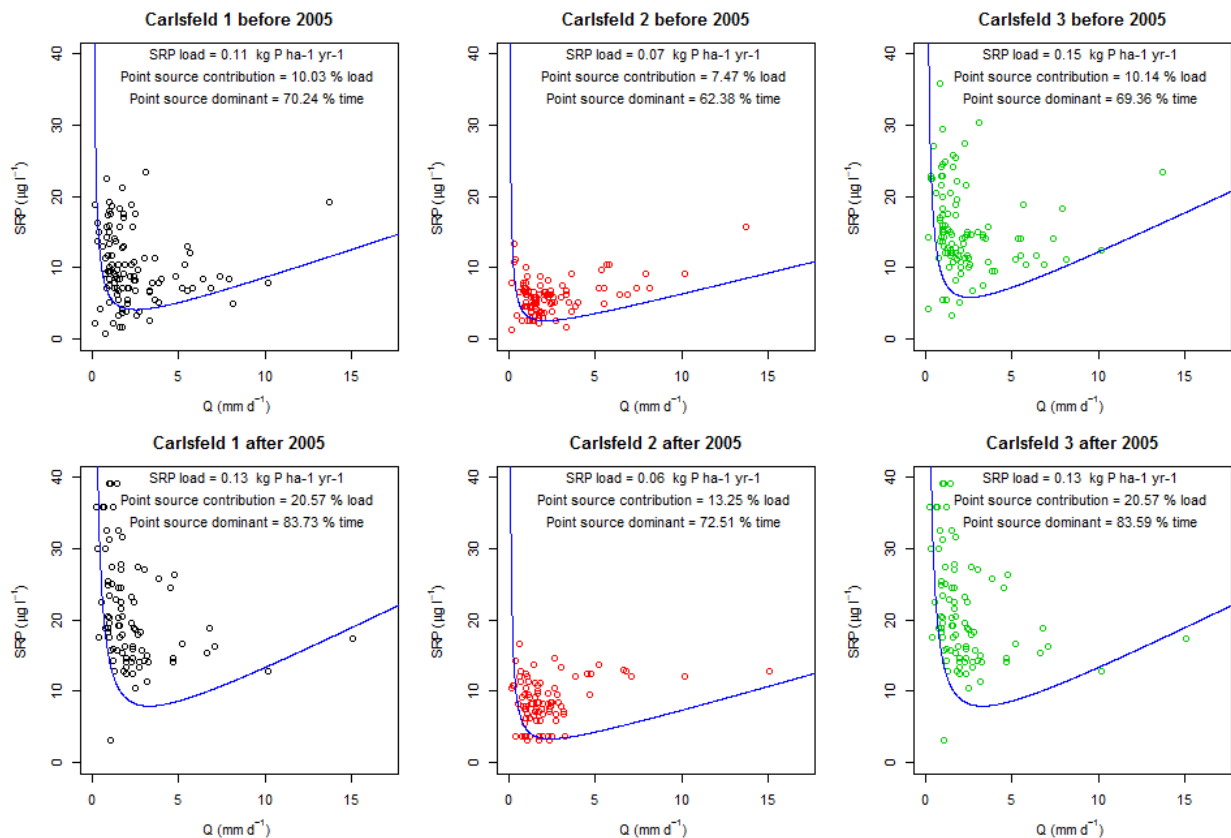


216

217 **Figure 3: Concentration-concentration relationships between pairs of solutes. The relationship between SRP and**
218 **dissolved iron was fitted with a linear model $y = a + b \cdot x$, and the relationship between NO₃ and dissolved Fe and between**
219 **NO₃ and SRP was fitted with an exponential model $y = a + b \cdot \exp(-c \cdot x)$. Carlsfeld 1 in black, Carlsfeld 2 in red, Carlsfeld 3**
220 **in green.**

221 According to the SRP-Q LAM (Figure 4), annual loads varied from 0.06 to 0.15 kg SRP ha⁻¹ yr⁻¹ for all
222 three catchments and for the two periods considered: prior to 2005 and after 2005. The differences
223 between catchments reflected their different SRP concentrations visible in Figure 2, as specific
224 discharge was assumed to be the same. Estimated loads were similar before and after 2005, but this
225 result must be considered with care as the load estimation method is very sensitive (by construction)
226 to the high flow data points, and the number of these may differ between the two periods.
227 Therefore, it would not be reasonable to split the 22 years into more than two periods to apply the
228 LAM, as these models are very sensitive to the monitoring frequency and/or duration (Crockford et

229 al., 2017). More interestingly, the estimated virtual contribution of point sources increased in the
 230 three sub-catchments. In Carlsfeld 1, the virtual contribution of point sources increased from 10% to
 231 21% between the first ten years of study (1996-2005) and the last ten years (2006-2015), and this
 232 virtual point sources contribution dominated daily loads during 70% and 84% of the time during the
 233 two periods, respectively. In Carlsfeld 2, the virtual contribution of point sources increased from 7%
 234 to 13%, and this virtual point sources contribution dominated daily loads during 62% and 73% of the
 235 time during the two periods, respectively. In Carlsfeld 3, the virtual contribution of point sources
 236 increased from 10% to 21%, and this virtual point source contribution dominated daily loads during
 237 70% and 84% of the time during the two periods, respectively. By construction, the model predicted
 238 point sources to dominate during the low-flow period, i.e., the late summer period (Figure 2), which
 239 is also the period at highest eutrophication risk due to optimal light and temperature conditions.



240

241 **Figure 4: Result of the concentration-discharge load apportionment model (blue line) in the three study catchments and**

242 **for two periods (before and after 2005).**

243 Five alternative empirical models were compared for their capacity to fit the SRP data. Simple linear
 244 regressions including discharge or the inverse of discharge all performed poorly, with R^2 close to 0
 245 (Table 1). The LAM performed fairly well with two variables ($R^2 = 0.57 - 0.79$) but the performance of
 246 the “biogeochemical model” (Table 1) was almost as high with only dissolved Fe as a predictor
 247 variable ($R^2 = 0.37 - 0.64$). The fitted parameters with this equation were:

$$\text{Carlsfeld1 (before 2005): } SRP = 1.4 * 10^{-3} + 1.1 * 10^{-2} * Fe$$

$$\text{Carlsfeld1 (after 2005): } SRP = 6.1 * 10^{-3} + 9.1 * 10^{-3} * Fe$$

$$\text{Carlsfeld2 (before 2005): } SRP = 1.1 * 10^{-3} + 1.2 * 10^{-2} * Fe$$

$$\text{Carlsfeld2 (after 2005): } SRP = 3.0 * 10^{-3} + 1.3 * 10^{-2} * Fe$$

$$\text{Carlsfeld3 (before 2005): } SRP = 5.6 * 10^{-3} + 1.3 * 10^{-2} * Fe$$

$$\text{Carlsfeld3 (after 2005): } SRP = 7.4 * 10^{-3} + 1.5 * 10^{-2} * Fe$$

248 With SRP and Fe in mg.l^{-1} and Q in mm.d^{-1} .

249 The best model with two variables was the “biogeochemical model” + discharge ($R^2 = 0.92 - 0.93$), in
 250 which the part of the equation corresponding to the dilution of a constant source in the LAM is
 251 replaced by a linear function of dissolved Fe.

252 **Table 1: Comparison of the coefficient of determination R^2 for five linear models fitted to the first ten years of study**
 253 **(1996 - 2005) and the last ten years (2006-2015) of study in the Carsfeld sub-catchments.**

		R^2 Carlsfeld 1		R^2 Carlsfeld 2		R^2 Carlsfeld 3	
model	model equation	before	after	before	after	before	after
description		2005	2005	2005	2005	2005	2005
Dilution of a constant source	$SRP \sim 1/Q + \text{intercept}$	0.02	0.05	0.00	0.01	0.01	0.22

Increasing export with discharge	SRP ~ Q + intercept	0.01	0.01	0.14	0.04	0.01	0.03
Load apportionment model	SRP ~ 1/Q + Q	0.64	0.57	0.79	0.58	0.66	0.62
"Biogeochemical model"	SRP ~ Fe + intercept	0.59	0.64	0.37	0.57	0.47	0.56
"Biogeochemical model" + increasing export with discharge	SRP ~ Fe + Q	0.92	0.93	0.93	0.93	0.93	0.92

254 **4. Discussion**

255 A recent study of SRP and DOC trends in 110 German catchments draining into drinking water
256 reservoirs (including the 3 Carlsfeld sub-catchments) has documented a long term increase in SRP
257 and DOC, associated with an increase in dissolved Fe and a decrease in NO₃ in catchments with acidic
258 soils (Musolff et al., 2016). The authors concluded that Fe oxyhydroxide reduction was the dominant
259 mechanism explaining increased SRP and DOC release into streams and that NO₃, being a stronger
260 electron acceptor than Fe, acted as a redox buffer. According to this hypothesis, decreasing
261 atmospheric N deposition could lead to a decrease in NO₃ redox buffering capacity and this decrease
262 is the main cause of the observed increasing SRP and DOC trends in these catchments. Our trend
263 observations are compatible with the redox hypothesis, hence long term trends in the Carlsfeld sub-
264 catchment will not be discussed further in this paper. Rather, in section 4.1. we discuss whether the
265 redox hypothesis and NO₃ redox buffering could also explain the seasonal variability in SRP observed

266 in the Carlsfeld sub-catchments. Also, in section 4.2., we discuss the implications of the observed SRP
267 seasonal dynamics in terms of water quality assessment and management.

268 **4.1. Interplay of hydrological and biogeochemical processes**

269 Previous studies have demonstrated that variability in dominant flow pathways or in the contribution
270 of several conceptual compartments with different chemical signatures exert a large control on SRP
271 and NO₃ concentrations in rivers (Mellander et al., 2012; Dupas et al., 2017a), and that this variability
272 is influenced by changing hydroclimatic conditions on a seasonal or inter annual basis (Ockenden et
273 al., 2016). In catchments with similar shallow groundwater systems and presence of riparian
274 wetlands, the seasonal variability of SRP and NO₃ has previously been explained by the high
275 contribution of a riparian compartment (rich in SRP due to the shallow groundwater interacting with
276 the organic soils and poor in NO₃ due to denitrifying conditions) during the dry season, and by the
277 high contribution of an upslope compartment (poor in SRP due to the deeper groundwater and richer
278 in NO₃ because of limited denitrification in well-drained soils) during the wet season (Dupas et al.,
279 2016, 2017a; Exner-Kittridge et al., 2016; Martin et al., 2004; Woodward et al., 2013). Here, the fact
280 that the two sub-catchments with substantially higher SRP concentrations, and lower NO₃
281 concentration (Carlsfeld 1 and 3), are also those with the highest percentage of organic riparian soils
282 (see section 2.1), supports previous assertions that organic riparian soils are internal sources of SRP
283 (Dupas et al., 2017b; Gu et al., 2017; Records et al., 2016), and a buffer zone for NO₃ (Anderson et
284 al., 2014; Oehler et al., 2009). Other factors such as P speciation in soils may also play a role (Gu et
285 al., 2017). However, a conceptual model relying only on the hydrological connectivity of two
286 conceptual compartments with different chemical signatures is questionable, as all water flows pass
287 through the riparian wetland and/or hyporheic zone and should, according to this conceptual model,
288 lose NO₃ through denitrification and gain SRP through interactions with organic soils regardless of
289 the season. In this respect, the question of water residence time and temperature is crucial, in
290 conjunction with an interpretation based on the mixing of conceptual compartments (Hrachowitz et
291 al., 2016; Pinay et al., 2015). In the Carlsfeld sub-catchments, residence times in the riparian

292 compartment were arguably too short during the wet period, when groundwater hydraulic gradients
293 are maximal and flow velocity at their highest, and temperatures too low, for denitrification and SRP
294 solubilisation to take place. The central role played by biogeochemical processes in SRP release
295 mechanisms is illustrated by the C-C relationships (Figure 3) which, contrarily to the C-Q plots (Figure
296 S2), appeared to be stable in the long term. The strong correlation between SRP and dissolved Fe,
297 and the negative relationships between SRP or dissolved Fe with NO₃ support the hypothesis of a
298 dominant redox control on seasonal SRP release during the summer period (Li et al., 2012; Musolff et
299 al., 2016; Smolders et al., 2017). Furthermore, sulphate concentrations and pH do not exhibit
300 seasonal cycles in these catchments (Figure S3). Simultaneous release of ferrous Fe and SRP have
301 been measured in-situ in riparian soils (Dupas et al., 2015; Gu et al., 2017; Surridge et al., 2007; van
302 der Grift et al., 2014), and the same authors observed that NO₃ could play the role of a redox buffer
303 that determines the timing of Fe oxyhydroxides reductive dissolution and subsequent SRP release.
304 Hence, the seasonal variability of NO₃ inputs to the riparian wetland, with high inputs from the
305 upslope nitrate rich compartment during the wet period and lower inputs combined with higher
306 denitrification during the warmer summer period (Dupas et al., 2016; Exner-Kittridge et al., 2016;
307 Woodward et al., 2013), could govern SRP seasonal dynamics via reductive desorption of SRP
308 previously bound to Fe oxyhydroxides. Hydrology is both a proximate and ultimate control (e.g.
309 Thomas et al., 2016) of the seasonal variability in SRP and NO₃ in the streams of the Carlsfeld
310 catchment.

311 The hypothesis of a dominant redox control on SRP and dissolved Fe dynamics is apparently
312 contradicted by field observation in intensively farmed regions of Belgium and the Netherlands that
313 phosphate and Fe oxyhydroxides usually co-precipitate during exfiltration of anoxic groundwater to
314 oxic stream waters, and thus phosphate is retained within soils and sediments (Baken et al., 2015;
315 van der Grift et al., 2014). However, Baken et al. (2016) have shown in the same region that in-
316 stream water with a P:Fe molar ratio below 0.1, co-precipitation of phosphate and Fe oxyhydroxides
317 was not leading to retention but instead could form mobile Fe-rich colloids which can be transferred

318 to the streams. The mean and maximum P:Fe molar ratio in the three Carlsfeld sub-catchments
319 ranged from 0.03 to 0.04 and 0.06 to 0.12 respectively, i.e. below or close to the threshold proposed
320 by Baken et al. (2016). This means that with the relatively low SRP concentrations observed in the
321 Carlsfeld sub-catchments, it is likely that Fe-rich colloids are the vector of P, and that these Fe-P
322 colloids can still be measured as SRP (Gu et al., 2017; Sinaj et al., 1998; Van Moorlegghem et al.,
323 2011).

324 To conclude, a biogeochemical process releasing SRP during the summer period was identified: both
325 a temperature control and a hydrological control, via residence times and NO₃ influx to the riparian
326 reactive zone, and are likely to explain the seasonal dynamics observed.

327 **4.2. Implications for water quality assessment and management**

328 The observed SRP dynamics has implications for water quality assessment. LAMs based on C-Q
329 relationships might overestimate point source contributions in some contexts where there is a
330 presence of point sources (i.e. the contexts where load apportionment models can usually be used),
331 because a biogeochemical process releasing SRP during summer low-flow can augment the point
332 source signal. This summer SRP release, exceeding 0.05 mg l⁻¹ in one of the study catchments, is likely
333 to have a significant impact on LAMs in many contexts where small point sources occur: for example
334 in the TERENO Harz/Central German Lowland Observatory, a 3300 km² area encompassing large
335 gradients of land use and elevation in Central Germany and including small point sources, summer
336 SRP concentrations range from < 0.01 mg l⁻¹ to 0.12 mg l⁻¹ (Kamjunke et al., 2013). Therefore, we
337 recommend combining these C-Q LAMs with markers of effluent discharge and survey of point
338 emissions, at least to test the method in catchments where point emissions are well identified and
339 quantified (Arnscheidt et al., 2007; Neal et al., 2010; Richards et al., 2016). Error in source
340 identification will have an impact on the cost-effectiveness of measures to remediate P in rivers
341 because managers might choose to target point sources as a priority, whereas diffuse source
342 contribution during the summer growing season might be larger than previously estimated (Jarvie et

343 al., 2006, 2013b; Withers et al., 2014a, 2014b). In addition, evaluation of water quality remediation
344 programmes targeting reduction of P inputs on agricultural land might be misled by the long term
345 SRP trend, controlled by processes independent from inputs, which could mask the effect of
346 improved management practices within catchments.

347 Although the seasonal SRP dynamics can mimic a point source signal, as highlighted by the relatively
348 good fit of the LAM, a better fit to the data was obtained with an empirical model including dissolved
349 Fe as a predictor variable. However, the latter cannot be transferred to catchments where both the
350 summer SRP release from riparian wetlands and point source emissions take place, because the
351 dissolved Fe – SRP relationship established for the Carlsfeld sub-catchment will probably not be valid
352 in other areas. It would, therefore, be necessary for further research to determine the controlling
353 factor(s) of this dissolved Fe – SRP relationship (e.g. soil Fe and P content and speciation, hydrology,
354 land use), as it could provide a basis for a new generation of LAMs that disentangle summer SRP
355 release from riparian wetlands and point source emissions.

356 The observed SRP dynamics has implications for water quality management, because management
357 options generally do not take into account the interactions between nitrogen and phosphorus. If the
358 hypothesis of NO₃ buffering SRP release is confirmed in catchments with higher anthropogenic
359 pressures, remediation programmes targeting N as a priority might result in increasing SRP
360 concentrations in streams and rivers. Even when both N and P are targeted by remediation
361 programmes, the long term legacy of P in soils (Jarvie et al., 2013a) might lead to a slow depletion of
362 the P accumulated in the catchment as compared to N, thus increased SRP release from riparian
363 wetlands (in summer) is possible.

364 Further research is needed to determine if the hypothesis of NO₃ buffering SRP release, followed by
365 SRP delivery to streams, can take place also in agricultural catchments, where N inputs are much
366 higher than in the study case presented here. The comparison of the three Carlsfeld sub-catchments
367 suggests that redox mediated SRP release needs extremely low NO₃ concentration to take place: in

368 Carlsfeld 2, where SRP release seemed to be almost inhibited compared to Carlsfeld 1 and 3, the
369 mean annual NO₃ concentration was only $0.46 \pm 0.11 \text{ mg N l}^{-1}$, a concentration far below what is
370 commonly measured in agricultural areas. However, redox mediated SRP release has been
371 documented in some of the regions with the highest agricultural pressures in Europe such as
372 Western France (Dupas et al., 2015; Gu et al., 2017), Belgium (Baken et al., 2016) and the
373 Netherlands (van der Grift et al., 2014). Hence stream nitrate NO₃ may not in isolation be a good
374 indicator of redox mediated SRP release, as this process can take place in local organic rich hotspots
375 where NO₃ is absent, whereas in agricultural areas NO₃ can still be high in deeper flow paths.

376 **5. Conclusions**

377 In this study, with direct implications for catchment management and monitoring programmes
378 where eutrophication is an issue, we showed that:

- 379 • a biogeochemical process releasing SRP during summer low-flow can mimic a point source
380 signal and may lead to overestimation of point source contributions in P load apportionment
381 studies;
- 382 • a long term increasing SRP trend could possibly mask the effect of reduced P inputs in some
383 areas;
- 384 • seasonal reductive dissolution of Fe oxyhydroxides is a probable mechanism for the summer
385 SRP release from riparian wetland soils, under the control of temperature, residence times
386 and NO₃ influx.

387 Further methodological developments are necessary to include summer SRP release from riparian
388 wetlands into LAMs, especially in rural areas where domestic P emissions are difficult to evaluate due
389 to their scattered distribution throughout catchments.

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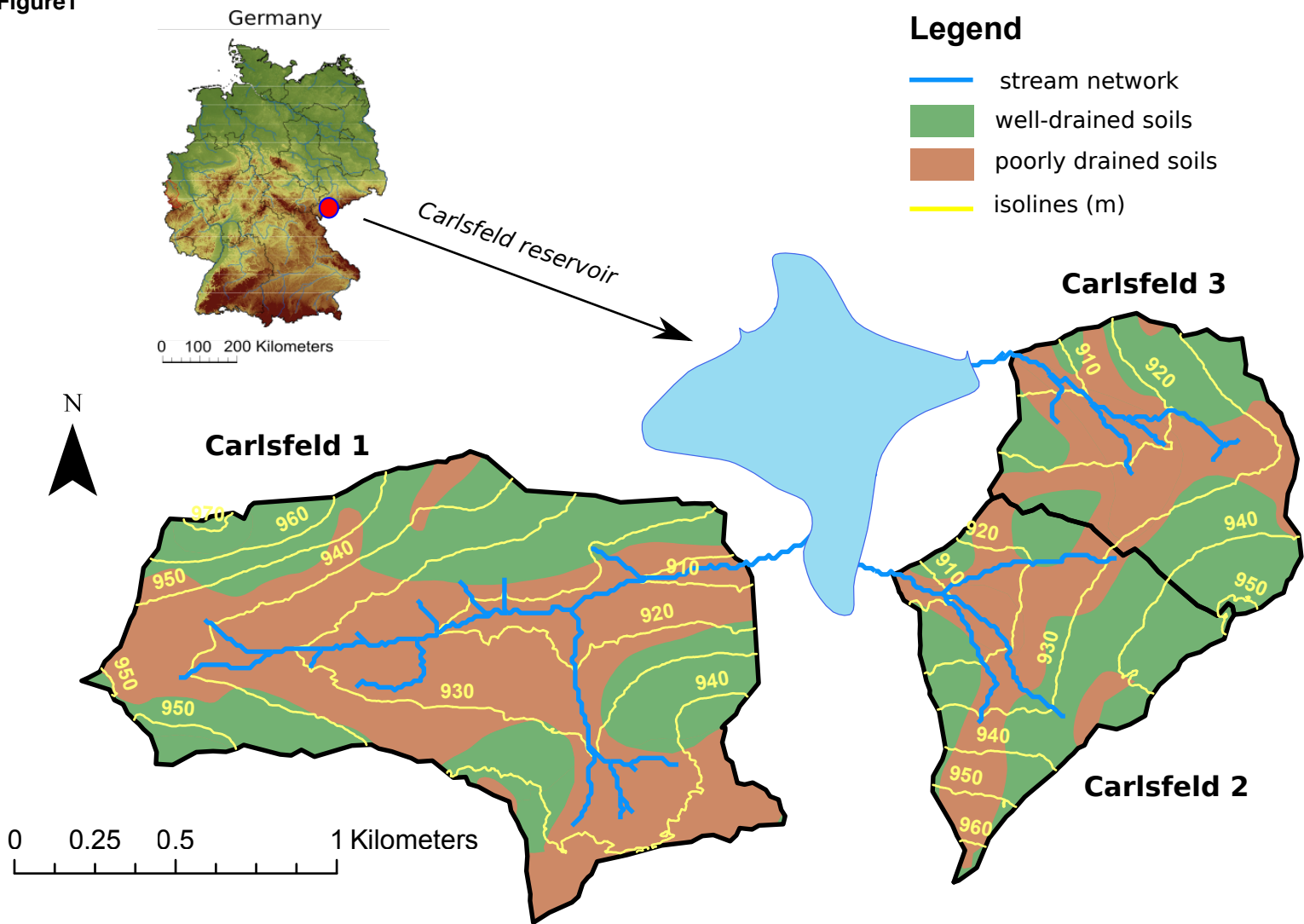
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Figure1



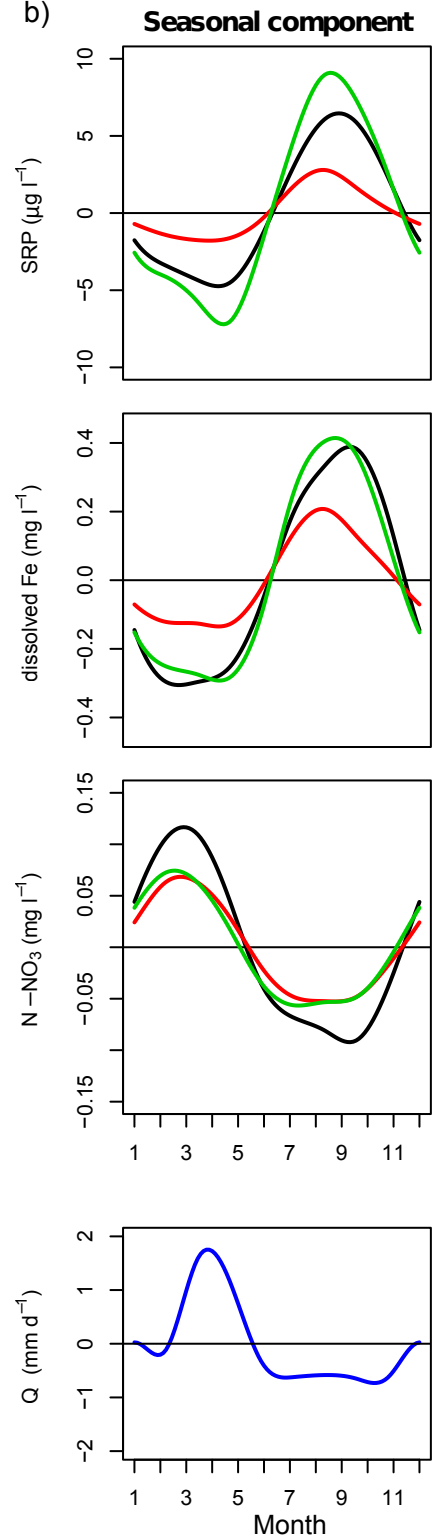
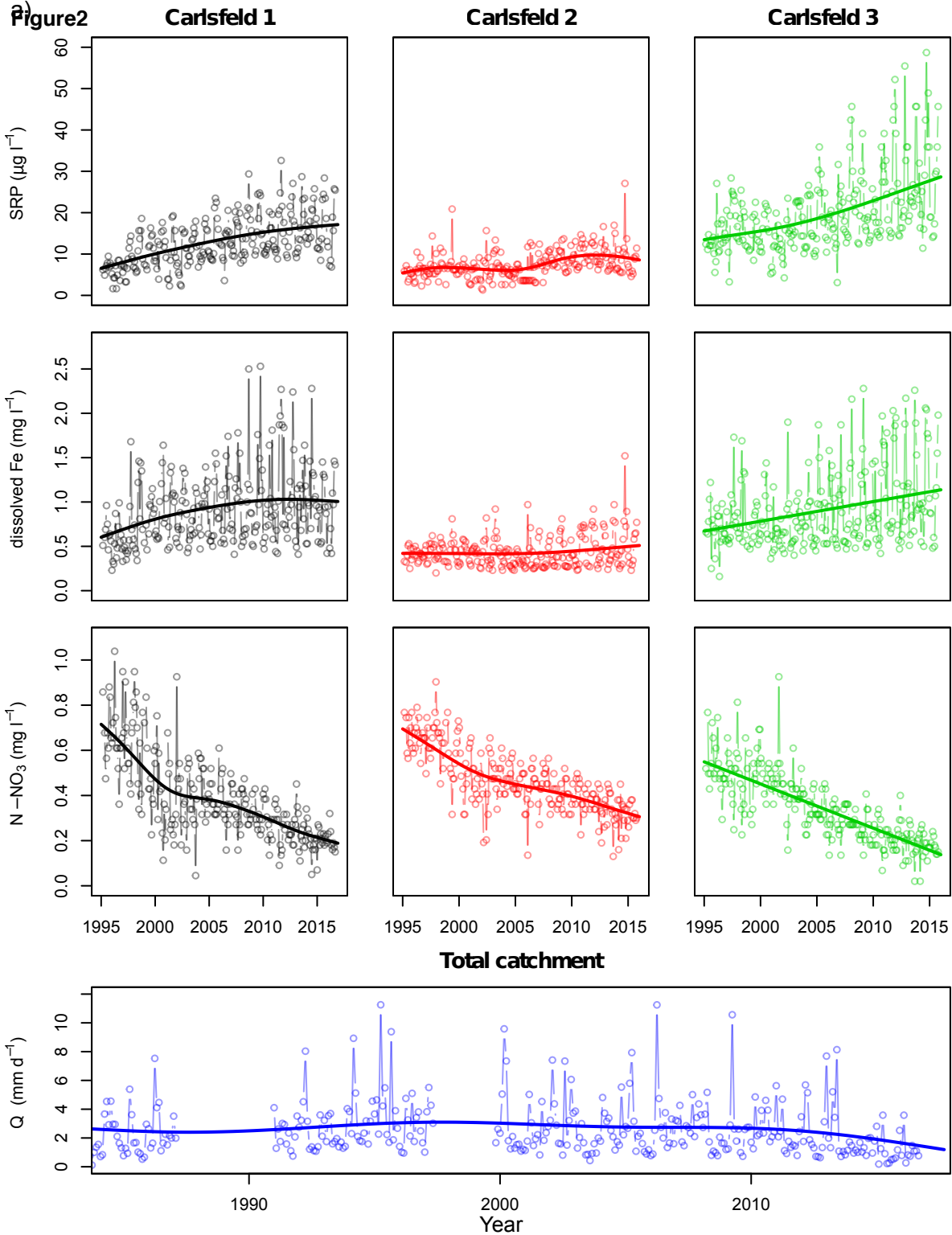


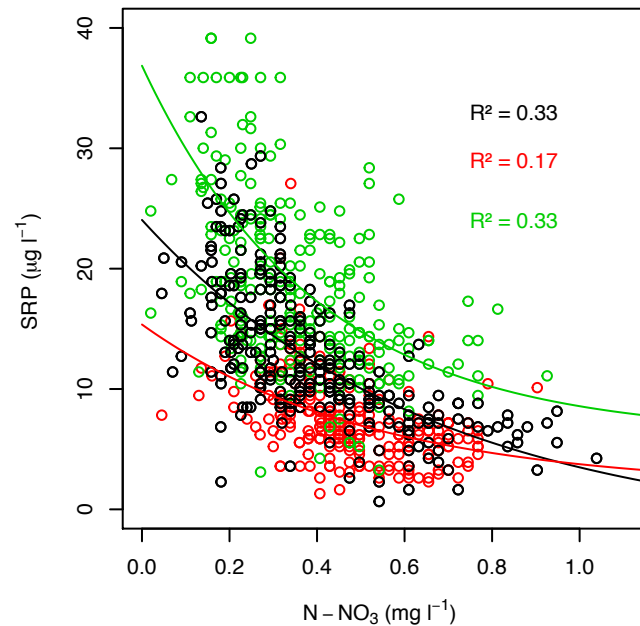
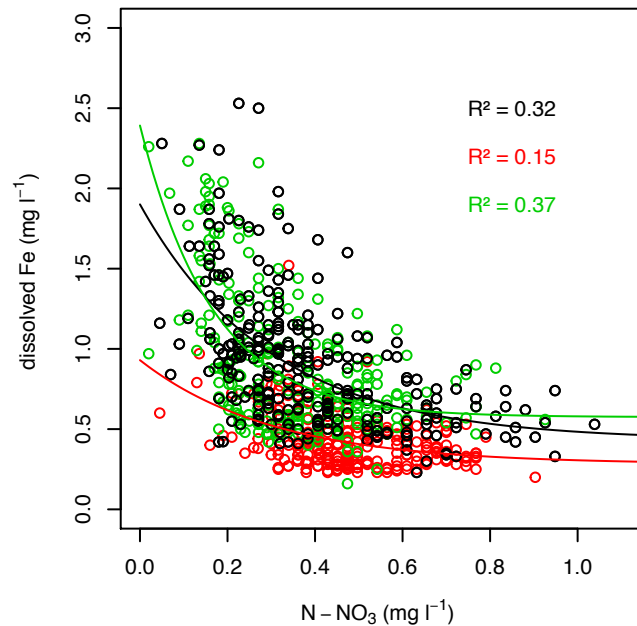
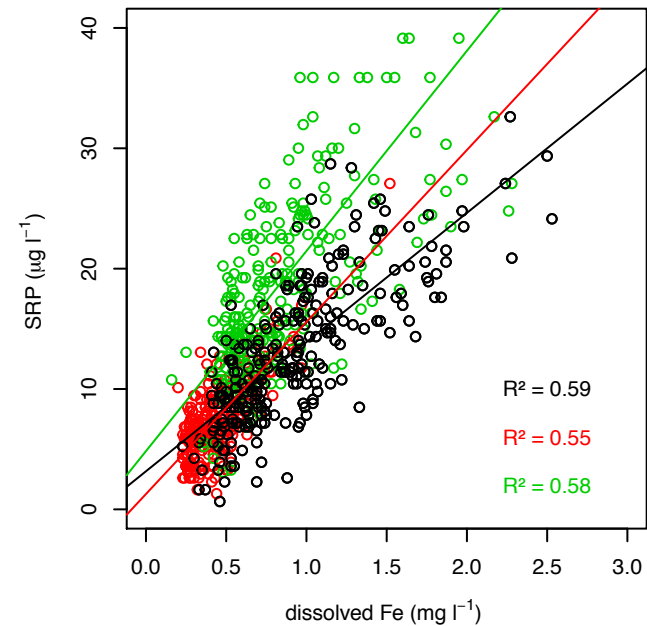
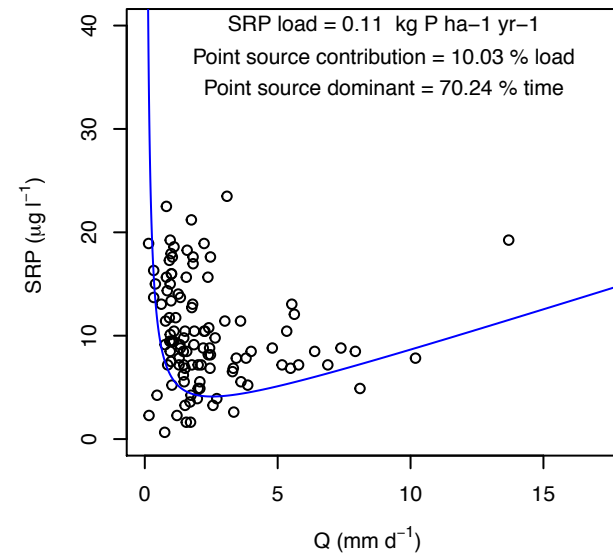
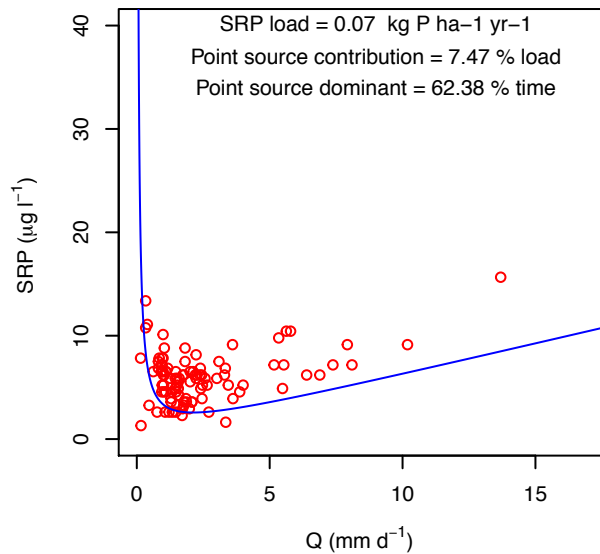
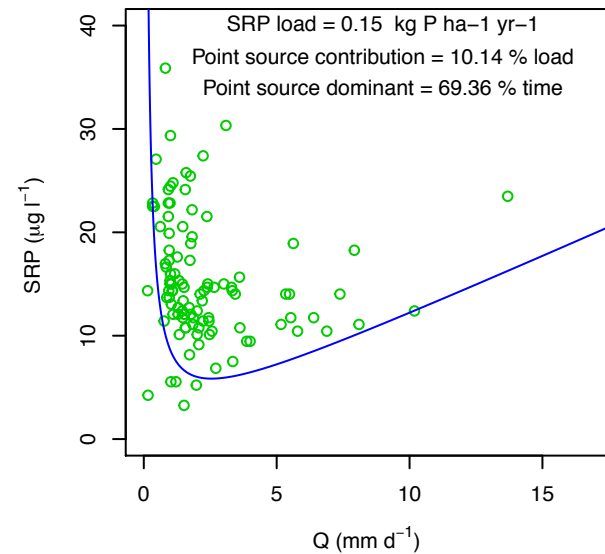
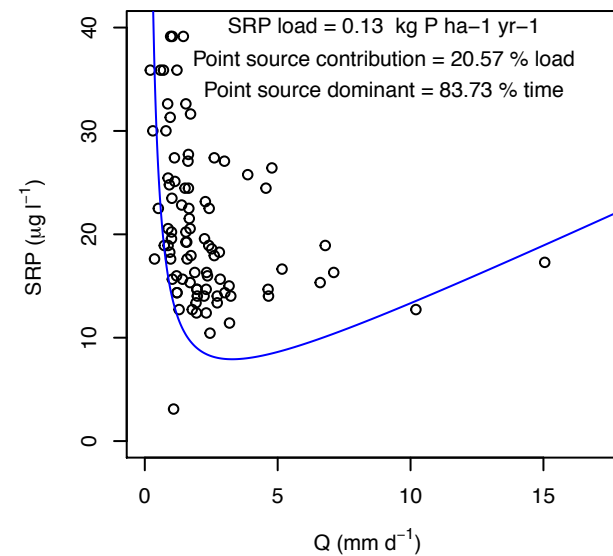
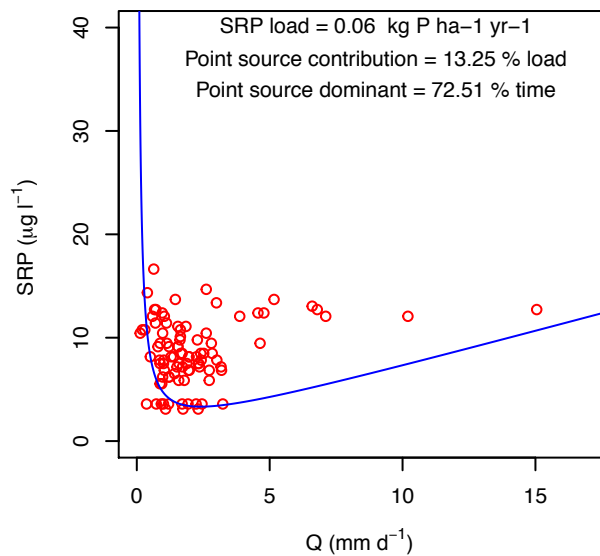
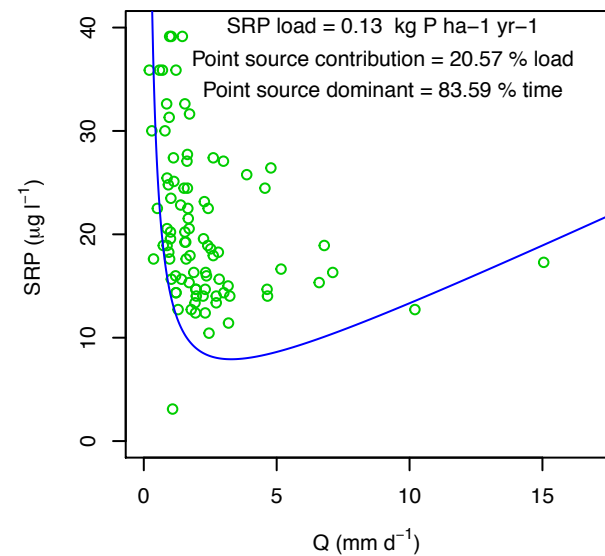
Figure3

Figure4**Carlsfeld 1 before 2005****Carlsfeld 2 before 2005****Carlsfeld 3 before 2005****Carlsfeld 1 after 2005****Carlsfeld 2 after 2005****Carlsfeld 3 after 2005**

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