In-stream oxygenation to mitigate internal loading of phosphorus in lowland streams

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7   **Highlights**

8   • Lowland sediments can act as P source when their P/Fe ratio is large and DO is low.

9   • Oxygenation improves DO and subsequently lowers the P concentration.

10   • Flow velocity is a major parameter controlling the DO and P concentration.

Abstract

Many lowland regions are afflicted with episodic high phosphorus (P) concentrations in streams during low flow periods. It has been hypothesised that these P peaks are due to internal loading after reductive dissolution of ferric iron (Fe(III)) minerals in sediments with a high P/Fe ratio. Here, we experimentally tested that hypothesis by measuring the sediment/water fluxes of P in streams and by testing responses to in-stream oxygenation. A phosphate stock solution with a bromide (Br$^-$) tracer was administered during 3 h in four streams with varying sediment P/Fe ratios during summer (low DO concentration). The experiment was repeated in winter (high DO concentration) in one of the streams. The sediments were either net P sinks (three cases), net unreactive (one case) or a net source (one case), with the net source occurring in the stream with the highest sediment P/Fe and at lowest DO concentration. A direct oxygenation experiment in one stream increased downstream DO concentration with about 1 mg O_2 L^{-1} and decreased the P concentration with, on average, about 0.3 mg P L^{-1} over a two-week period. The efficiency of oxygenation to reduce P concentrations enhanced when flow rates were lower. In conclusion, this experimental study confirmed the hypothesis that internal P loading in streams is largest in high P/Fe sediments at low DO conditions. Lowering P concentrations in lowland streams should combine reduced P emission and strategies avoiding low DO concentration, i.e. reduced biological oxygen demand (BOD) and nutrient emissions.

Introduction

31   Due to increased nutrient loading since the green revolution, eutrophication of freshwater ecosystems

32   has become a worldwide problem (Diaz and Rosenberg, 2008; Mainstone and Parr, 2002). Phosphorus (P)

33   is often a limiting nutrient in freshwater systems (Correll, 1998; Schindler, 2012) and controlling P

34   emissions to the environment is thus crucial in reducing eutrophication. The lowland regions in Europe

35   suffer from extremely high P concentrations, that are disproportionally large compared to their P inputs

36   (Baken and Smolders, 2016).

37   Lowland river systems have seasonal low flow periods that lead to low dissolved oxygen (DO)

38   concentrations in the streams. Recently, it has been found that such seasonally low DO concentrations in

39   lowland streams in Flanders are associated with seasonally high total dissolved P (TDP) concentrations;

40   several lines of evidence suggested that this was related to internal loading of P from sediments (Smolders

41   et al., 2017). Low DO concentrations induce reductive dissolution of ferric iron (Fe(III)) (oxy)hydroxides in

42   sediments (Li et al., 2012; Schwertmann, 1964), which may lead to the release of previously adsorbed P

43   (Carlyle and Hill, 2001; Frossard et al., 1995). This P release only occurs if the P binding capacity in the

44   sediment is small. If not, Fe(III) reduction might take place, but the electron flux from organic matter

45   degradation will not be sufficiently large to reduce all Fe(III) in the sediment and P will remain on the

46   remaining binding sites. As a cut-off value, a molar sediment P/Fe ratio of 0.12 mol mol^{-1} was found

47   experimentally in lab experiments below which no significant P release occurs (Jensen et al. 1992) and

48   field data suggested that this cut-off may be valid (Smolders et al., 2017).

49   The internal loading of P under period of hypoxia is a well-established mechanism in lakes (McQueen et

50   al., 1986; Mortimer, 1941; Palmer-Felgate et al., 2011). However, stream sediments were believed to have

51   an inherent P uptake capacity that depends on a number of different mechanisms, including abiotic

52   processes such as hydrological variation, sedimentation, adsorption and precipitation, and biotic

53   processes such as P assimilation in organisms (Macrae et al., 2003; Meyer, 1979; Mulholland et al., 2009).

54   However, flow rates during warm and dry periods can be sufficiently low for anoxia to occur and for

55   reductive dissolution to become a major component in the P cycle in lowland regions (Smolders et al.,

56   2017).

57   To date, management of P concentrations in surface waters in Europe has mostly consisted of limiting the

58   diffuse P losses from agricultural sources and increasing the degree of wastewater treatment (Schoumans

59   et al., 2014; Sharpley et al., 2013). In Flanders, these measures have led to a 50% decrease in P emissions

60   to the surface water between 2000 and 2017 (Personal communication, Flemish Environmental Agency

61   (VMM)). Despite these efforts, the P concentrations did not decrease proportionately and over 75% of

62   the measurement points in Flanders still exceeded environmental limits of 0.14 mg phosphate-P L^{-1} in

63   2017 (Van Peteghem, 2018). This lack of effect is also observed in other lowland regions across Europe,

64   e.g. in The Netherlands, Germany and Poland (Amery and Vandecasteele, 2015). All these regions are

65   characterized by high P peak concentrations occurring during summer. These peaks are   not

66   geographically or temporally linked to erosion, fertiliser input, sediment resuspension or dilution (Baken

67   and Smolders, 2016). This suggests that the process of internal loading of P contributed to river P and that

68   managing P concentrations in surface waters should include other measures beyond managing P

69   emissions only.

70   The process of internal loading of streams by sediment P is deduced from static laboratory experiments

71   and corroborated by a weight of statistical evidence of field data (Banaszuk and Wysocka-czubaszek, 2005;

72   Bowes et al., 2003; Schulz and Bischoff, 2008; Smolders et al., 2017; van Dael et al., 2020). As far as known,

73   no direct experimental evidence has been given quantifying internal P loading in streams at low DO

74   concentration in sediments with high P/Fe ratio. The net P exchange between sediments and water has

75   been measured by mass balance studies in river segments before and these studies show that sediments

76   generally act as a net P sink (Macrae et al., 2003; Weigelhofer, 2017). However, none of these studies

77 were focused on the interaction between DO and the sediment P/Fe ratio. The locations in those studies

78 had been chosen based on other characteristics than those important to determine the effect of reductive

79 dissolution of Fe.

80 Against this background, this work was set-up (1), to determine the net sediment/water P flux as a

81 function of the DO concentration and sediment P/Fe ratio and (2), to quantify the effect of an enhanced

82 oxygen input on the P concentration in a stream. The hypothesis was that DO concentration and the

83 sediment P/Fe ratio are the main actors controlling P concentrations in lowland systems. First, net

84 sediment/water P exchanges were measured with Short Term P Additions (STPAs): a phosphate stock

85 solution was spiked with a non-reactive bromide (Br^-) tracer and injected in the stream, the upstream and

86 downstream water composition allow to calculate the net P uptake/release in a section downstream of

87 the injection point. Four different streams with contrasting sediment P/Fe ratios were selected. Seasonal

88 variation was examined by repeating the STPA in both summer (low DO concentration) and winter (high

89 DO concentration). Secondly, a two-week aeration experiment was executed in one of the four streams

90 and the downstream effect of this intervention on the P and DO concentrations was monitored. At the

91 same time pre-aeration parameters of the stream were also monitored and correlated with P and DO

92 trends. The results of this study can demonstrate the importance of a good DO balance in order to prevent

93 P release during summer. It can be used by policy makers as an argument that limiting P inputs in the

94 environment alone will not be sufficient to lower water P concentrations on a short term and that the DO

95 needs to be managed as well.

96 **Material and methods**

97 *Study sites*

98 The study sites are located in the Flemish region of Belgium. The regional climate is described as an

99 oceanic climate with a wet winter period (Köppen, 1884), the long term (1981-2010) average annual

100   precipitation is 850 mm and average of yearly average temperature 10.8°C (KMI, 2019). The precipitation

101   is almost evenly distributed throughout the year, but higher temperatures during summer result in lower

102   water flow velocities. Most surface waters are fed by groundwater base flow (75%) the rest is attributed

103   to surface runoff (Zomlot et al., 2015). As Flanders is a lowland region with a small slope (<1%), the risk of

104   erosion is limited, with the exception of the southernmost part.

105   Four streams were selected across Flanders based on the size and accessibility of the streams, contrasting

106   molar sediment Fe/P ratios and contrasting TDP concentrations. The location of the selected streams is

107   shown on Figure 1, as is the sediment P/Fe ratio in Flemish sediments. The streams were a subset from

108   the streams used by van Dael et al. (2020), so sediment parameters such as the cation exchange capacity

109   (CEC) and C/N ratio were known and were similar for all streams. Land use is comparable for all streams,

110   intensive agriculture is the most important one within a 2 km radius of the sampling points. The remaining

111   land use is dominated by pasture; except for stream 2, where residential and industrial areas, hence

112   sealed soils, comprise the second most important land use (Zomlot et al., 2015). Selected properties of

113   the stream sediments and water are given in Table 1, showing that all streams and sediment

114   characteristics were rather similar except for the sediment P/Fe ratio and TDP concentration.

115   *Short term P additions*

116   The net phosphate exchange between sediment and overlying water was measured with a spike mass

117   balance approach in four streams (Table 1). Short term additions of P were carried out in each stream.

118   The additions were executed according to the Stream Solute Workshop (1990) as described by

119   Weigelhofer et al. (2013). The additions were executed in all four streams in 2017 during summer when

120   the DO concentration is expected to be lowest and P release might occur. An additional STPA was

121   executed in stream 3 in the winter of 2018, the details of injection characteristics for each STPA are given

122   in Table 2. In short, a concentrated solution of monoammonium phosphate (MAP: $NH_4H_2PO_4$, 30-90 g P L$^-$

123　[1]and sodium bromide (NaBr, 8-80 g Br L^{-1}, Table 2) was injected into the stream at a constant flow rate

124　(0.5-2.8 mL s^{-1}) using a peristaltic pump; thereby obtaining local dilution factors ranging about 6 x 10^3 -

125　2 x 10^5. The NaBr was used as an inert tracer to account for in-stream dilution and mixing effects.

126　Bromide is a suitable tracer due to its low background concentration and low reactivity. The addition took

127　place over a period of 3 hours and aimed to increase the background TDP concentration by a factor 3 to

128　5. Seven sampling points were defined: one 10 m upstream and the others at x=10, 30, 50, 75, 100, 150

129　and 250 m downstream of the injection point. These sampling distances varied slightly between locations

130　due to accessibility. Once before and once during the addition (after reaching plateau concentrations, i.e.

131　after 90 minutes) quintuplicate water samples were collected at each sampling point. Samples were taken

132　10 cm below the water surface and were immediately filtered over 0.45 μm (Chromafill PET, diam: 25mm).

133　Subsamples were acidified instantly (2% HNO_3) and stored in polypropylene tubes. Within a week, the

134　TDP and Fe concentrations were determined in the acidified samples, using Inductively Coupled Plasma

135　Optical Emission Spectroscopy (ICP-OES, Thermo Scientific iCAP 7000 series). Anion concentrations (Cl^-,

136　SO_4^{2-}, NO_3^- and Br^-) were determined in non-acidified subsamples with anion exchange chromatography

137　(Thermo Scientific, Dionex ICS2000). The analytical detection limits of TDP were 0.015 mg P L^{-1} and of Br^-

138　were 20 μg Br^- L^{-1}.

139　Immediately after ending the spike and reaching background concentrations, the discharge Q and channel

140　morphology were measured at each measurement point using a mechanical flow meter (Geopacks stream

141　flow meter) and a gauging rod. Simultaneously duplicate sediment samples (0-10 cm depth) were taken

142　at each sampling point. They were air-dried, sieved and crushed and analysed for oxalate extractable Fe,

143　Al, and P using the method of Schwertmann (1964). This procedure is generally used for the quantification

144　of poorly crystalline Fe and Al oxyhydroxides and the P that is sorbed on these oxides. The concentrations

145　of P, Fe and Al in the extracts were detected with ICP-OES.

146   In stream 1, the pH, dissolved oxygen (DO) and temperature (T) was continuously measured by an

147   upstream measuring station operated by the Flemish environmental agency (VMM). At the other

148   locations, the DO concentration and T was measured at the location of the spike using a field electrode

149   (YSI ProODO, optical dissolved oxygen instrument), all at 10 cm below the water surface.

150   The net P exchange between sediment and surface water was expressed by two indices, one is based on

151   the stream TDP concentrations and the second converted the TDP data to sediment/water fluxes. First,

152   the difference between the expected TDP concentration based on dilution and the actual TDP

153   concentration was calculated, the site specific dilution was derived from the Br⁻ concentrations. The

154   difference in TDP is termed ΔTDP, positive values of ΔTDP indicate net release of P by the sediment while

155   negative values point to net P uptake. For that calculation, all TDP and Br⁻ concentrations were corrected

156   for the upstream (background) concentrations by subtracting the corresponding data at 10 m upstream

157   from the injection. Assuming that all variations in the Br⁻ concentration are caused by physical processes

158   (dilution or evaporation), it is possible to calculate the expected TDP concentration due to dilution at a

159   downstream point x ($TDP_{x,\,exp}$):

$$TDP_{x,exp} = TDP_{x-1} * \frac{Br^-{}_x}{Br^-{}_{x-1}} \tag{1}$$

160   with Br^- (µg L⁻¹) and TDP (mg L⁻¹) the measured background corrected concentrations at measurement

161   points x and at x-1, the point upstream of x but downstream of the injection point. To quantify net P

162   uptake or P release between two adjacent points x and x-1, ΔTDP was calculated as

$$\Delta TDP_x = TDP_x - TDP_{x,exp} \tag{2}$$

163   There were five replicate samples at point x-1 and five at point x, data of all replicates were averaged,

164   thereby accounting for paired analyses: the TDP and Br⁻ analyses were made in the same samples,

165   therefore means of the five element ratio's $TDP_{x-1}/Br^-{}_{x-1}$ were calculated at each point, not the ratio of the

166   means. This mean ratio was then used to obtain five values for $TDP_{x,exp}$ with Eqn. 1 and five corresponding

167   values of ΔTDP_x (Eqn. 2), each time coupling the Br and TDP data of point x for the identical sample; the

168   five ΔTDP_x estimates were then averaged. Along the same lines, the standard error of the mean ΔTDP_x

169   was calculated from the replicate estimates of ΔTDP_x, thereby using n=5. Note that the spike

170   concentrations and volumetric addition rates are not used in calculating the dilution in the stream. This is

171   because the additions rates could not be determined with great accuracy with the peristaltic pump used

172   in this experiment. Flow rates varied with a factor 1.3 at a fixed pump setting in preliminary tests.

173   Therefore it was decided to use the concentrations at the first measurement point downstream from the

174   injection point as the reference value from which dilution was calculated, i.e. the ΔTDP was calculated

175   starting from the second point downstream of the injection point.

176   The second expression of the sediment water exchange of P converted TDP data to sediment-water fluxes.

177   In that calculation, it is necessary to determine the discharge Q of each stream. This discharge was

178   measured as described above at the first point downstream of the injection point. The discharges at the

179   other points downstream of that first point were corrected from the first point using the Br⁻

180   concentrations, i.e.

$$Q_x = Q_{x-1} * \frac{Br^-{}_{x-1}}{Br^-{}_x} \tag{3}$$

181   Where Q_x and Q_{x-1} (L s⁻¹) are the discharges at location x and x-1 respectively; i.e. if x-1=1, then the Q_1 was

182   the mechanically determined value. These discharges so obtained were used to obtain the net sediment

183   water flux calculation $F_{P,sed,x}$ as:

$$F_{P,sed,x} = \frac{Q_x * TDP_x - Q_{x-1} * TDP_{x-1}}{A_{sed,x}} * 86400 \frac{s}{day} \tag{4}$$

184   Where $F_{P,sed,x}$ (mg P m⁻² day⁻¹) is the average sediment-water P flux between sampling point x-1 and x and

185   A_{sed} (m²) is the sediment surface area between those points, between two sampling points x and x-1. That

186   area was estimated by taking a depth profile across the width of the stream with a gauging rod (at 20 cm

187 intervals) at each sampling point. The area between two sampling points was then estimated by

188 interpolating both profiles over the length of the segment. The average P flux over the entire stream

189 section ($F_{P,sed,total}$) was then calculated by a weighted average of the fluxes for each segment:

$$F_{P,sed,total} = \frac{\sum_x F_{P,sed,x} * A_{sed,x}}{\sum_x A_{sed,x}} \tag{5}$$

190 The paired sampling was, again, taken into account to estimate the mean $F_{P,sed,x}$ and its standard error.

191 First, the five $Q_{x-1}Br_{x-1}$ products were calculated and these products were averaged to infer five replicate

192 data of Q_x according to (3). If x-1=1 (first sampling point), then Q_1 was the mechanically determined value

193 with one single value. Second, the means of five corresponding Q_xTDP_x products, not products of means,

194 were calculated and the same was done for the corresponding products at x-1. Both means of products

195 were then used in (4) to infer the average flux per segment. The error on the flux was calculated from the

196 square root of the sum of squared standard error of both Q_xTDP_x and $Q_{x-1}TDP_{x-1}$ divided by the area.

197 Finally, the standard error on $F_{P,sed,total}$ (i.e. a weighted average) was calculated from the square root of

198 the sum of squared errors of the fluxes multiplied with the square of $A_{sed,x}$, then divided by the sum of the

199 total area.

200 *Oxygen injection*

201 An in-stream oxygenation experiment was executed to identify the potential role of enhanced DO

202 concentration on reducing P release from the sediment. This was performed in August 2019 in stream 3.

203 During two weeks, air was injected at a rate of 120 L min⁻¹ using a compressor (Hydroponics Aquaculture

204 air pump, 120 L min⁻¹). To maximize oxygen exchange between the injected air bubbles and the water

205 column, the air was dispersed into small bubbles by eight porous, ceramic diffusers (Aquaculture

206 technologies, 10 cm ceramic diffusers) that were deployed at the bottom of the stream. The stream is

207 about 2 m wide and the diffusers were placed in the centre in two rows of four diffusers with about 80

208 cm between the rows and between each diffuser within a row.

209   During this aeration, daily quintuplicate water samples were collected at several distances from the air

210   injection point (x = -10, 5, 50, 100 and 200 m downstream). The samples were treated identically as in the

211   STPA experiments and were analysed for TDP, Fe and Mn and several other elements using ICP-OES. At

212   each sampling location the DO concentration, temperature (T), total dissolved solids (TDS) and pH were

213   also measured daily, using a field probe (Eijkelkamp aquaprobe AP-700). The flow rate was estimated

214   using a floating device with which the surface velocity was measured. This velocity was then multiplied by

215   a factor of 0.85 to correct for resistance at the sediment-water interface (Intermountain Environmental,

216   n.d.). Rainfall data for the period of the aeration were collected from the Flemish Environmental Agency

217   (Vlaamse Milieumaatschappij, 2019). The effects of oxygenation on the DO and TDP concentration at each

218   sampling point was used to infer the treatment effects, expressed as the differences with the background

219   (10 m upstream) concentration denoted as:

$$\Delta TDP_{oxyg,x} = TDP_x - TDP_{-10\,m} \qquad\qquad (5)$$

$$\Delta DO_{oxyg,x} = DO_x - DO_{-10\,m,} \qquad\qquad (6)$$

220   in which TDP_x and DO_x are the measured TDP and DO concentrations at each sampling point, $TDP_{-10\,m}$ and

221      $DO_{-10\,m}$ are the background TDP and DO concentrations measured 10 m upstream of the injection point.

222   The standard deviation of the ΔTDP and of ΔDO values were derived from the square root of the sum of

223   squared standard deviations of each term.

224   The water composition data of samples from location x = -10 m from all four streams and all sampling

225   times were used to construct a model to determine the most important factors controlling the TDP

226   concentrations in surface water (JMP pro 14.0.0, statistical software). The available data are TDP, pH, DO

227   concentration, ICP-OES detected elements (Fe, Mn, Ca, K, Na, Mg) and stream and environmental

228   parameters (Flow velocity, T, precipitation). Many of the parameters exhibited high multicollinearity,

229   leading to extremely large variance inflation factors (VIF). This made the use of standard least squares

230   regression unreliable. Partial least squares analysis (PLSA) with one response variable (TDP) was used as

231   an alternative, since it allows to evaluate a large number of correlated variables and a limited number of

232   observations. The NIPALS algorithm was applied to produce coefficient estimates for all explanatory

233   variables and holdback was used as a validation method.

234   **Results**

235   *Stream characteristics*

236   The stream characteristics of the four sites are shown in Table 1. The two eastern streams (1 and 2) are

237   characterized by very high sediment Fe concentrations and annual mean low TDP concentrations

238   (Baetens, 2016). The western streams (3 and 4) have lower sediment Fe concentrations and higher annual

239   mean TDP mostly due to large peaks occurring during summer. The sediment oxalate-extractable P

240   concentrations are slightly larger in sediments 1 and 2, than in sediment 3 and 4, but the P/Fe molar ratio

241   in streams 1 and 2 is well below the 0.12 cut-off value whereas it is above in streams 3 and 4 . The average

242   pH and DO concentration is similar for all streams, with the exception of stream 3 which has a lower DO

243   concentration. The values for the TDP concentration at the moment of the spike reflect these long term

244   averages, with larger TDP concentrations in stream 3 and 4 than in stream 1 and 2. The annual TDP peak

245   is also clearly visible comparing summer and winter TDP data from stream 3 (Table 2). The discharge in

246   stream 3 shows a strong seasonal variation as well.

247   *Short term P additions*

248   The STPAs were executed to determine whether or not there was a difference in sediment P uptake

249   among different sediments. The difference between the expected (based on dilution) and measured TDP

250   (ΔTDP) for the summer observations in the four streams is shown in Figure 2. These values indicate a net

251   P uptake in streams 1, 2 and 4 and a net release in stream 3. The sediment-to-water P fluxes for each

252   stream display the same trends (Table 3), i.e. stream 3 shows a positive P flux indicating that the sediment

253   acts as a P source, while the other streams are a sink with negative flux. The winter observation in stream

254   3 indicated a flux that was not significantly different from zero. The results show that low sediment P/Fe

255   ratios lead to net P uptake (stream 1 and 2), regardless of the DO concentration. The high sediment P/Fe

256   ratio streams show a net P release in case the DO concentration is low, such as in stream 3 in summer,

257   but not at higher DO concentrations such as in stream 4 or stream 3 in winter. Stream 2 and 3 had

258   substantially lower DO concentrations during summer than the other two streams, so they were more

259   likely to use alternative electron acceptors such as Fe hydroxides. Iron concentrations in solution were

260   also largest for these two streams. The TDP concentrations were particularly large in stream 3 and also

261   exceeded environmental limits in stream 4. In stream 3, the DO concentration was significantly higher in

262   winter than in summer, while the Fe and TDP concentration were substantially lower.

263   *Oxygen injection*

264   First, several parameters were measured the water samples upstream of the injection point in order to

265   better understand the effect of different stream parameters on the DO and TDP concentration (Table 4).

266   The redox active cation (Fe and Mn) concentrations correlated positively with TDP whereas negative

267   correlations were found with DO concentration and flow velocity of the stream. The non-redox reactive

268   cations show a strong association with the electric conductivity. The correlations in Table 4 are confirmed

269   by the time trends over the entire monitoring period (Figure 3, panel c-e). The TDP concentration is clearly

270   inversely related to the DO profile and the flow velocity profile.

271   In figure 4, the effect of direct oxygen addition on the downstream TDP concentration was analysed. The

272   DO concentration increases clearly at the injection point and then gradually drops back to the background

273   DO concentration. The same trend can be observed for the TDP concentration, albeit with a downstream

274   lag phase. The increase in the DO concentration due to aeration was 1 mg DO L^{-1} at x = 5 m on average

275   over 9 days. This increase achieved an average decrease of 0.3 mg P L^{-1}. The efficiency of the oxygenation

276   was largely dependent on the flow velocity at the time of sampling: a lower flow velocity enhanced the

277 increase in DO concentration which subsequently yielded a larger decrease of the TDP concentrations

278 (Figure 3, panel a-b).

279 *Factors affecting TDP concentrations*

280 The PLSA lead to a model with 5 factors in which 99.6% variation was explained for the explanatory

281 variables and 93.3% for the response variable, TDP in this case. The variable importance plot (VIP, Figure

282 SI1) shows that the most important variables (with a VIP > 0.8) are the DO concentration, Flow velocity,

283 DO*DO and Flow velocity*Flow velocity. Other variables which have a significant correlation with the TDP

284 concentration such as Fe and Mn (Table 4) are not significant in the PLSA model. This stresses the

285 multicollinearity that confounds the individual effect of the different variables.

286 **Discussion**

287 *The net sediment-water P flux*

288 The STPA results confirm that stream sediments generally act as a P sink, since most fluxes are negative

289 (Table 3). Other research also reported sediments acting as a P sink rather than a source (Eugènia Marti

290 and Francesc Sabater, 1996; Macrae et al., 2003; Weigelhofer, 2017). The net P uptake fluxes obtained

291 here range 5-39 $\mu g\ m^{-2}\ s^{-1}$ and are generally larger than those found in a similar study by Macrae et al.

292 (2003) i.e. 1-21 $\mu g\ m^{-2}\ s^{-1}$. The larger net uptake fluxes found here might be explained by the larger stream

293 size here compared to the small ditches in the study from Macrae et al. (2003), i.e. larger stream size

294 ensures more water renewal and contact with the added spike which leads to larger P fluxes. The net P

295 uptake fluxes in natural systems are even smaller and are about 1 $\mu g\ m^{-2}\ s^{-1}$ (Hill, 1982; Munn and Meyer,

296 1990; Weigelhofer, 2017), higher values found here are likely caused by the large concentrations of P that

297 were added during the STPA in this study. Different P spike concentrations and P addition rates logically

298 affects the magnitude of the flux. However, stream 3 with the largest background concentration (and,

299 hence, the largest spike concentration) could still be identified as a source.

300   *Effect of the sediment P/Fe ratio on net P fluxes*

301   The much lower sediment P/Fe ratios of streams 1 and 2 than those of stream 3 and 4 (Table 1) suggest

302   that stream 3 and 4 should be much more susceptible to P release. The P fluxes of streams 1, 2 and 3

303   (summer) confirm this hypothesis, i.e. streams 1 and 2 have a negative flux indicating net P uptake and

304   stream 3 shows a net P release. The net P uptake in stream 4 despite the high sediment P/Fe does not

305   obey that trend, most likely because of the large DO concentration in stream 4, even during summer),

306   that ensured sufficient Fe(III) (oxi)hydroxides to immobilise P to the same extent as in streams 1 and 2.

307   These results show that P release only occurred when a low DO concentration and high sediment P/Fe

308   coincide (Stream 3, Figure 2, Table 3). These conditions facilitate P release as a result of reductive

309   dissolution of Fe (oxy)hydroxides (van Dael et al., 2020). This theory is confirmed by the fact that the Fe

310   concentrations in stream 3 are a factor 3 larger during summer than during winter (Table 3), pointing to

311   Fe reduction. The combinations of a low DO concentration with a low sediment P/Fe ratio (stream 2) or

312   of a high DO with a high sediment P/Fe ratio (stream 4) still yield net P uptake. In the first case, there is

313   Fe reduction, but sufficient Fe(III) remains to buffer the P concentration, while in the second case Fe is

314   not reduced since oxygen is still available to act as an electron acceptor. Differences in the DO

315   concentration among sites relate to different biological activity of the sediments (van Dael et al., 2020) or

316   a more turbulent flow leading to a more rapid oxygen exchange between sediment and water column

317   (Higashino et al., 2008; Sundby et al., 1986). Stream 2, for example, has a much lower DO concentration

318   than stream 1 even though the temperature was higher when sampling stream 1. A possible explanation

319   is a more laminar flow in stream 2 than in stream 1, the monitoring data of the Flemish Environment

320   Agency suggest no larger BOD in stream 2 suggests compared to the other streams (details not shown).

321   Other stream and sediment characteristics can also affect the P fluxes. Stream depth affects the

322   sediment/water ratio and, hence, the P concentrations in the water and the net P fluxes. Increasing water

323   depths lower oxygen transport to the sediment, leading to more Fe reduction and P release. Other

324   sediment characteristics such as the CEC or C/N ratio can also affect the P concentration next to the P/Fe

325   ratio (van Dael et al., 2020). The streams here were selected to keep these sediment and stream

326   characteristics as similar as possible to minimise these confounding effects.

327   *Effect of the DO concentration*

328   A comparison of the winter and summer data of stream 3 also point to P release as a result of Fe

329   dissolution; the DO concentration in winter is considerably larger, while the dissolved Fe concentration

330   and sediment P/Fe ratio are smaller. This indicates oxidation and precipitation of the Fe, which was

331   dissolved during low DO conditions in summer. This precipitation leads to an increased P binding capacity,

332   preventing P release in winter. In the winter STPA, no significant net flux was measured in stream 3. From

333   these results, it is clear that for a sediment to release P, both a low DO concentration and a high P/Fe ratio

334   are necessary. The results of the monitoring study confirm the importance of DO on the P concentration

335   in stream 3, showing similar time trends (Figure 3, panel c-e) and a high correlation coefficient between

336   the P and DO concentration (Table 4).

337   The direct oxygen additions in stream 3 act as final proof that reductive dissolution of ferric iron is at least

338   partially responsible for P peaks in lowland streams during summer. Air injection with diffusers increased

339   DO concentrations and decreased TDP concentrations (Figure 3, panel a-b). Other studies have found

340   similar responses, where aeration of the P rich water bodies decreased TDP concentrations as a result of

341   adsorption on (oxy)hydroxides (Grochowska and Gawrońska, 2004; McQueen et al., 1986). The study by

342   McQueen et al. (1986) noted a six-fold increase in P removal from the water column when the

343   hypolimnion of a stratified lake was aerated compared to when it was not. The study from 2004 used

344   aeration and destratification as a remediation technique for a previously polluted lake. In that case,

345   hypolymnetic aeration also increased DO concentrations over the entire depth profile and enhanced P

346 removal from the water column. These studies show that the use of oxygenation as a remediation

347 technique for P is not a new concept. This study here is, however, first to observe this in streams.

348 The efficiency of oxygenation as a measure for remediating high P concentrations has been questioned at

349 length. Several studies reported a lack of response in lakes after aeration treatment (Gächter and Müller,

350 2003; Hupfer and Lewandowski, 2008). This lack of reaction was attributed to excessive organic matter

351 concentrations which exhaust the DO stock more rapidly than it can be replenished by an aeration

352 treatment. There are also other factors that obscure the direct effect of increasing the DO on the TDP

353 concentration. Large sulphide concentrations in the sediment can lead to irreversible Fe(II)S formation

354 (Hupfer and Lewandowski, 2008). This leads to a loss in P sorption capacity and in these cases increasing

355 the DO concentration will most likely have little effect on the P concentration. These factors will limit the

356 applicability of aeration as a P mitigation technique to sediments with a low S content and a limited

357 organic matter concentration that does not exhaust the DO stock. Our study did not encounter such

358 problems, so it is clear that DO exhaustion due to rapid OM mineralisation or Fe(II)S do not occur in this

359 case.

360 *The effect of the flow velocity*

361 The effect of the flow velocity on P release is mostly indirect. The total P concentration (TP) can increase

362 with increasing flow velocity due to sediment resuspension (Jarvie et al., 2012). In this study, however,

363 the focus was on chemical P release from sediments and therefore, water samples were filtered to obtain

364 the dissolved P fraction only. The main role of the flow velocity on the DO concentration is that an

365 increased flow velocity increases mixing in the water column and, hence, increases oxygen exchange

366 between water and sediment (Figure 3 panel c-e, Sundby et al., 1986). This concept is used when installing

367 weirs in small streams in order to enhance DO concentrations. Weirs locally increase flow velocities and

368 turbulence, thereby enhancing oxygen exchange and mixing. Multiple studies have found positive effect

369   of weirs on DO concentrations in field studies (Alp and Melching, 2011; Baylar et al., 2010; Butts and

370   Evans, 2008). These results are confirmed by the PLS model showing that the DO concentration and flow

371   velocity were the most important parameters in controlling the P concentration in solution.

372   The effect of the flow velocity on the P concentration is not merely a seasonal dilution effect. It might be

373   assumed that a higher flow velocity (and flow rate) simply causes a dilution of solutes. From Table 4 it is

374   clear that the dilution effect is indeed the main factor controlling the redox inactive cations. They are

375   extremely highly correlated with the EC, showing that the water volume is the main regulator. However,

376   the correlation between EC and the redox active cations is not significant, indicating that other

377   mechanisms than dilution control their presence in solution. Combined with the strong correlation of the

378   Fe and Mn concentrations with the DO concentration, it can be assumed that reductive dissolution is the

379   main mechanism determining Fe and Mn in solution. The P concentration is also strongly correlated with

380   the DO concentration and with the redox active cations, so it can be assumed that P release is a result of

381   this reductive dissolution as well. Hence, any P sorbed to Fe or Mn (oxy)hydroxides will be released when

382   these minerals are reduced. Even though the flow velocity has a positive effect on the DO concentration,

383   the efficiency of aeration can be impeded by large flow velocities (figure 3, panel c-e, Table 4). The

384   experiment here showed that high flow velocities are the main obstacle for an efficient oxygenation effect

385   on TDP in streams.

386   **Conclusion**

387   The combination of the STPA, the monitoring study and the direct oxygenation experiments have

388   conclusively proven the importance of the sediment P/Fe ratio and the DO concentration on the P

389   concentration in lowland streams. It is now clear that under specific circumstances stream sediments can

390   act as a P source. The mechanism of reductive dissolution of Fe (oxy)hydroxides is controlling the P

391   concentration in anoxic summer periods in these streams. This implies that internal loading will remain a

392   long term problem even when future P inputs are limited. Managing the TDP concentration requires

393   managing the DO concentration, i.e. reducing BOD and nutrient input. As shown recently, the net release

394   of P from sediments to the overlying water enlarges at higher mineral N input, i.e. the legacy P in many

395   lowland streams can remain a burden to the water TDP concentration at sustained N input, especially in

396   slow-flowing lowland streams with a high P/Fe ratio. This study shows that management of P

397   concentrations in lowland streams requires more than limiting the P inputs alone and that enhanced DO

398   is key to avoiding the summer peaks, a message that must be conveyed to regulators.

399   **Acknowledgements**

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