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## **Leaching of two northern France slag heaps: Influence on the surrounding aquatic environment**

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24 **Abstract**

25 After the exploitation of coal mines in the 19<sup>th</sup> and 20<sup>th</sup> centuries in northern France, many  
26 mining slag heaps (SH) were left without any particular management or monitoring. Currently,  
27 the influence of these SHs on the quality of surrounding wetlands is hardly known.

28 The purpose of this work is to determine the water quality in the neighbourhood of two SHs  
29 located near the city of Douai and its influence on the distribution of aquatic invertebrates in  
30 local wetlands. Our approach involves (1) the spatial and temporal characterization of the water  
31 composition (anions, major elements, sulphide, DOC and alkalinity) and of the biological  
32 diversity (aquatic invertebrates) and (2), based on this chemical and biological screening, the  
33 establishment of relationships between water quality and biodiversity distribution through  
34 multivariate data analysis. The results clearly indicate that substantial leaching from the slag  
35 heaps occurs, given the very high concentrations of dissolved sulphates (in the range of 2 g L<sup>-1</sup>).  
36 While the pH remains weakly basic, indicating that the leaching water has been neutralized  
37 by the highly carbonated regional substratum, high levels of biodegradable organic matter and  
38 sulphate contents have been noticed. They sporadically cause significant drops in dissolved  
39 oxygen and the occurrence of dissolved sulphides that massively reduce biodiversity,  
40 qualitatively and quantitatively. In Summer, oxygen saturation is generally lower due to the  
41 higher rate of organic matter degradation, and the risk of anoxic episodes therefore increases.  
42 Finally, as wetlands are vulnerable environments, these preliminary results suggest that  
43 monitoring and management of these sites must be attempted quickly to avoid the degradation  
44 of those valuable habitats.

45 *Synopsis: Leaching of slag heaps introduces in the surrounding wetlands high amounts of*  
46 *sulphates that influences the aquatic biodiversity through redox processes.*

47

48 **Keywords:** Slag heap, Wetland, Acid Mine Drainage, Water quality, Biodiversity.

## 49 **1. Introduction**

50 The Hauts-de-France region faced huge changes between the 17<sup>th</sup> and the 20<sup>th</sup> century with the  
51 appearance of coal mining which has accelerated its industrial and economic development, but  
52 has also transformed its landscape (Foucher et al., 2012). Indeed, the traces left behind by  
53 former mining sites are still visible today. They take the shape of hills, called slag heaps (SH),  
54 resulting from a long accumulation of mine tailings (mainly black schist and sandstones)  
55 (Apourceau-Poly and Bertram, 2016). During this industrial period, the slag heaps were the  
56 property of the mining company, Charbonnage de France. However, when the coal extraction  
57 stopped, SHs have been rapidly abandoned, leaving in the northern landscape huge piles of  
58 natural mining material. Of anthropogenic origin, some of these slag heaps have gradually  
59 become green spaces due to a natural return of the vegetation (CPIE Chaîne des terrils et al.,  
60 2014). On their slopes and at their feet, they now shelter remarkable but fragile ecosystems.  
61 They host unique habitats, thanks to abnormally high temperatures resulting from the lower  
62 albedo of the black schist (Denimal, 2001). Hence, they allow rare and protected species to  
63 survive in the region and constitute a shelter and/or a feeding place for many others. However,  
64 they are highly sensitive to erosion, landslide and leaching. In the early years of this century,  
65 these sites have therefore been re-evaluated as Sensitive Natural Areas and have been purchased  
66 by the North Department Council, because of their value as biodiversity hotspots (Sader, 2018).  
67 Further on, the slag heaps became UNESCO World Heritage in 2012 and are now part of the  
68 biodiversity wealth of the region (Apourceau-Poly and Bertram, 2016; Gilbert, 2012). While  
69 these slag heaps were thus fostered for their biodiversity wealth, vast wetlands (and more  
70 specifically peatlands) spread out in the same area were damaged by the erection of these slag  
71 heaps. This created an important environmental problem especially since wetland areas are  
72 becoming a worldwide environmental concern: wetland destruction including habitat  
73 fragmentation and degradation is increasing while climate change increases the pressure on the

74 wetland ecosystem (Holland et al., 1995; Davis and Froend, 1999; Gibbs, 2000). They are  
75 nowadays facing a strong decline, while they have a proven added value for biodiversity and  
76 therefore a need to be protected (Gibbs, 1993; Mitsch and Gosselink, 2000). Wetlands host  
77 complex ecosystems including both aquatic and terrestrial biotopes. Moreover, the various  
78 habitats, with permanently to temporary water zones, are related to different chemical properties  
79 of the water and the soil (Akcil and Koldas, 2006). The story of the slag heaps is thus one with  
80 two faces: slag heaps offer a unique environment for many rare species, but their erection has  
81 caused habitat fragmentation and degradation of already existing environments.

82 As mentioned, the SH soils are particularly sensitive to erosion and leaching, either by rainwater  
83 or by the oscillation of underground water reservoirs (Figure 1). After such phenomena, the  
84 leaching water carries dissolved species and suspended matter from the mining hill into the  
85 surrounding wetland and therefore potentially influences this ecosystem (Duffaut, 2001). Slag  
86 heap leaching in the Hauts-de-France mine region was initially studied to investigate the impact  
87 on groundwater quality (Denimal, 2001). More general studies on post-mining issues included  
88 studies on trace metal leaching (Allan, 1995), on Acid Mine Drainage (AMD) issues (Akcil and  
89 Koldas, 2006) or on nutrient levels and litter decomposition and their impact on the ecosystem  
90 (Lee and Bukaveckas, 2002). The AMD is a common effect of SH leaching which results from  
91 the oxidation of pyrite ( $\text{FeS}_2$ ) and produces an acidic leachate source for the environment (Rose  
92 and Cravotta III, 1998). Its consequences on aquatic environments such as wetlands are today  
93 still poorly studied, specifically in the Hauts-de-France mining area. Moreover, there is a lack  
94 of knowledge on the link existing between biodiversity of these wetlands and the leaching  
95 inputs of the SHs into them.

96 **Figure 1**

97 Therefore, more studies must be carried out to better understand the diverse influences of SHs  
98 on surrounding wetlands and ponds. Invertebrates occupy a central place in aquatic ecosystems  
99 since they are ranked at the lower trophic levels of the food chain and they have a role both as  
100 consumer (phytoplankton, etc...) and food source (especially for fish and aquatic birds) (Benoit-  
101 Chabot, 2014). Information on their nature and quantity is therefore essential for assessing the  
102 ecological quality of wetlands at the bottom of slag heaps. Thus, the objectives of the present  
103 study are: (i) to establish a state of the art of the physicochemical and biological composition  
104 of these atypical environments; (ii) to assess the possible influence of slag heap leaching on the  
105 surrounding aquatic ecosystem composition and distribution; and finally (iii) to investigate  
106 potential variation of these processes in time and in space.

107

## 108 **2. Material and methods**

### 109 **2.1. Study site**

110 Two slag heaps have been selected in agreement with the Northern France Department Council  
111 that had noticed recurrent patches of water leaching into the surrounding wetlands. They are  
112 both located close to the city of Douai and are called hereafter SH I and SH II (Figure 2). Both  
113 have the same tabular shape, but SH I was formed from 1958 to 1984 having a 97-ha surface,  
114 while the other one was formed between 1912 and 1975 having a surface of 140 ha (North  
115 Department Council, internal communication). The soil surrounding both SHs is mainly  
116 occupied by vegetation (agricultural land, woods and meadows) and by water bodies  
117 (waterways, ponds and wetlands). The water levels in the ponds and wetlands are relatively  
118 stable throughout the year, although they pass through seasonal low and high-water periods.  
119 Both SHs are surrounded by a complex network of ponds and wetlands which are fed by the  
120 outflow from the slag heaps (enriched in elements from the SH, *i.e.* leaching phenomena) by  
121 rainwater and groundwater.

122

## Figure 2

123 Four very shallow and narrow ponds were sampled at the foot of the SH I (I-01 to I-04) and of  
124 the SH II (II-01 to II-06). At the foot of SH II, a deeper and bigger pond (24.5 hectares, 2m  
125 deep in average) is also present. Twenty stations were chosen in this pond, but since the results  
126 between those stations were not significantly different, only the average of the results is  
127 reported in this paper and referred to as station II-07. Finally, a screening of a wetland located  
128 in the southern part of SH I was also performed (I-05 to I-15), in order to investigate potential  
129 concentration gradients (Figure 2).

130 Close to a third SH (SH III), a non-impacted reference station, that is recurrently monitored by  
131 the Ecology service of the North Department Council, has also been chosen: reference point  
132 III-01. According to the internal reports of the Ecology service, the wetland close to SH III is  
133 protected from the leaching waters by a clay horizon, resulting in good water quality and good  
134 biodiversity indicators (nesting and feeding sites, presence of reed bed, helophytes,  
135 hydrophytes, clear water) (North Department Council, 2012). Note further that all GPS  
136 coordinates of the sampling points are listed in the supplementary information section.

137 Two sampling campaigns have been carried out, in order to study possible temporal changes  
138 occurring in the environment around the SHs. Each sampling campaign lasted less than 24 h,  
139 in order to avoid any influences from weather (rain, drought, etc.) or changes in groundwater  
140 levels. A first sampling campaign took place by the end of March 2016 at all 42 stations,  
141 including the reference point (III-01). A second one took place by the beginning of July 2016  
142 but only at a few specific stations close to SH I (I-01 to I-04, I-09 to I-12). The second campaign  
143 was reduced compared to the first one mostly due to unforeseen events: hunting season and  
144 inaccessibility of the sites.

## 145 **2.2. Sampling, *in situ* measurements and sample pre-treatments**

146 Temperature, pH, dissolved oxygen saturation and conductivity were measured *in situ* at each  
147 station using electrodes previously calibrated [pH: combined glass and Ag/AgCl/KCl  
148 electrodes (Mettler-Toledo), dissolved oxygen saturation: Clark sensor (WTW, Oxi 340) and  
149 conductivity (WTW: ProfiLine Cond 3110)]. For the other parameters (alkalinity, anions, major  
150 elements, dissolved organic carbon and characterization of organic matter), water was sampled  
151 in a clean PFA bottle at about 20 cm depth (when possible) below the surface. A first part of  
152 the sample remained unfiltered prior to the biological analysis and was kept at 5°C in an icebox.  
153 Back in the laboratory, the aquatic invertebrates were removed from the unfiltered water  
154 samples, using a 0.5 mm sieve; aquatic invertebrates were then placed into clean glass flasks,  
155 and 70% isopropyl alcohol was added to prevent organisms from decomposing and to avoid  
156 predation by higher trophic organisms. The second part of the sample was filtered immediately  
157 in the field through 0.45 µm pore size filters (cellulose acetate membranes, Sartorius) for the  
158 determination of all parameters, except organic matter. Three aliquots were subsequently  
159 prepared for measuring: (i) major elements by addition of 400 µl ultrapure HNO<sub>3</sub> (Fisher  
160 Scientific, Optima™); (ii) sulphides by addition of 10 µL of 2N zinc acetate [guaranteed AGR  
161 (Analytical Grade Reagents)] and 10 µL of 10<sup>-2</sup> M NaOH (AGR) solution in 10 mL of the  
162 sample to stabilize the analyte; and (iii) anions and alkalinity without any treatment but kept at  
163 4°C in an icebox. The third part of the sample was filtered on a glass fibre filter (0.7 µm,  
164 Whatmann) previously pyrolyzed at 450°C for 24 hours. This aliquot was kept in the icebox for  
165 subsequent analyses of the organic carbon content.

## 166 **2.3. Chemical analysis**

### 167 **2.3.1. Sulphides**

168 The solution prepared in the field for sulphide measurements was treated by addition of ferric  
169 chloride and N,N-dimethyl-p-phenylenediamine oxalate solution to form the methylene blue  
170 complex. In order to eliminate the colour due to the presence of ferric ion in the solution,

171 ammonium phosphate dibasic solution, used as a buffer, is added after 5 min to the last solution  
172 (Expertise Center in Environmental Analysis of Quebec, 2015). All the reagents were of  
173 analytical grade (AGR). The measurements were performed by spectrophotometry (Varian,  
174 Cary 300 Scan UV-Visible) at 664 nm. The sulphide concentration was then determined by  
175 comparing the field sample result with that of a calibration curve, made in the same conditions  
176 as the field sample. The S(-II) standard mother solution was prepared under nitrogen  
177 atmosphere from  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (Aldrich) and titrated before use by potentiometry with a  $\text{Cd}^{2+}$   
178 standard solution, using a sulphide ion selective electrode (Orion) and a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference  
179 electrode. The limit of detection of this technique was  $0.2 \text{ mg L}^{-1}$  and the relative standard  
180 deviation carried out on triplicates from several samples was better than 5 %.

### 181 **2.3.2. Anions**

182 Sulphate, nitrate, chloride, phosphate and fluoride concentrations were assessed with ionic  
183 chromatography (Dionex, column Ion Pac AS18, 4x250mm). The MagIC Net 3.1 software was  
184 used to process and calibrate the analysis. Limit of detections (LOD) were  $0.05 \text{ mg L}^{-1}$  for  
185 sulphate,  $0.01 \text{ mg L}^{-1}$  for nitrate,  $0.02 \text{ mg L}^{-1}$  for chloride,  $0.04 \text{ mg L}^{-1}$  for phosphate and  $0.01$   
186  $\text{mg L}^{-1}$  for fluoride. The relative standard deviation (RSD) carried out on several triplicate  
187 measurements was better than 10 % for all species.

### 188 **2.3.3. Major Elements**

189 Elemental analyses of Ca, Fe, P, Mn, Mg, Na, Sr, K, Si and B were performed in the water  
190 samples by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Varian,  
191 Vista Pro, axial view) after multi-elemental External calibrations. Limits of detections (LOD)  
192 were  $0.1 \text{ mg L}^{-1}$  for Ca,  $0.06 \text{ mg L}^{-1}$  for Fe,  $0.2 \text{ mg L}^{-1}$  for P,  $0.01 \text{ mg L}^{-1}$  for Mn,  $0.03 \text{ mg L}^{-1}$   
193 for Mg,  $0.06 \text{ mg L}^{-1}$  for Na,  $0.01 \text{ mg L}^{-1}$  for Sr and  $0.1 \text{ mg L}^{-1}$  for K. The relative standard  
194 deviation (RSD) carried out on triplicates was better than 5% for all species.

195           **2.3.4. Alkalinity**

196 Automatic pH-metric titrations using 0.05 M HCl were carried out (Metrohm, model 848  
197 Titrino Plus) to determine the alkalinity in our samples assuming that, according to pH values  
198 (between 6.9 and 8.5) and the other ions present (sulphate, chloride) in the solution, the  
199 measured alkalinity is related to the concentration of  $\text{HCO}_3^-$ . Indeed, at neutral pH,  $\text{HCO}_3^-$  is  
200 the dominant carbonate species and significant contributions of  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_3$  only appear  
201 at pH levels greater than 9.0 or lower than 6.0, respectively (Tarvainen et al., 2005). The LOD  
202 of this technique is estimated at  $0.1 \text{ mg L}^{-1}$  (based on a sample volume of 10 mL, a titrant HCl  
203 solution at 0.05 M and 50  $\mu\text{L}$  stepwise acid additions) with a relative standard deviation of 5%.

204           **2.3.5. Dissolved Organic Carbon (DOC)**

205 DOC content was analysed using a TOC-meter (Shimadzu, TOC-VCSH), using the NPOC  
206 method (Non Purgeable Organic Carbon). An external calibration curve, using potassium  
207 hydrogenphthalate, was previously assessed. The LOD is  $0.2 \text{ mg C L}^{-1}$  with a RSD calculated on  
208 several triplicates, lower than 5 %.

209           **2.4. Biological analysis**

210 Two biological indicators (number of aquatic invertebrate taxa and total abundance of aquatic  
211 invertebrates) were determined at each station, using 1 L water samples. The aquatic  
212 invertebrates have been sorted and then identified through a binocular microscope, using the  
213 sight hunting method and determination keys to classify them in a taxonomic family (Tachet et  
214 al., 2010). The number of taxa is defined as a group of living beings (here, aquatic invertebrates)  
215 from the same family. The abundance was equal to the total number of aquatic invertebrates  
216 listed at each sampling station including all taxa.

217           **2.5. Statistical procedures**

218 Principal Component Analysis (PCA) were performed with the R data processing software  
219 (www.R-project.org) using two packages: Corrplot and FactoMineR. The analysis of the  
220 statistical distributions of the data showed that some parameters were not normally distributed  
221 (*i.e.* not following a Gaussian distribution). Spearman correlation and PCA on ranked data were  
222 then performed to improve the robustness of the statistical analysis.

## 223 **2.6. External data**

224 As the groundwaters were not sampled, external data were provided by the French Water  
225 Agency from the piezometers 903641, 902687 and 901551 located respectively in Marchiennes,  
226 Pecquencourt and Somain (see the Supplementary Information section the for the GPS  
227 coordinates). These piezometers were selected, because of their proximity to the studied areas.

## 228 **3. Results and discussions**

### 230 **3.1. General description**

231 ***pH and conductivity*** — pH values range from 6.9 to 8.5, including the reference station III-01  
232 with a rather narrow distribution (see Table 1 and Supplementary Information for all data). The  
233 conductivity varies from 1.2 to 5.0 mS cm<sup>-1</sup> with a median value at 4 mS cm<sup>-1</sup> showing a large  
234 range of variations. These values, including III-01 (lowest value at 1.2 mS cm<sup>-1</sup>), are higher  
235 than those observed in the surrounding rivers (0.93 mS cm<sup>-1</sup> in average) and the groundwaters  
236 (0.88 mS cm<sup>-1</sup> in average) (Artois-Picardie Water Agency, 2017). This could be due to leaching  
237 processes which will be discussed later. But also, as indicated by the value of III-01, this could  
238 be due to the higher salt concentrations since evaporation occurs in these small ponds.

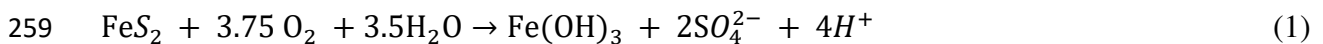
239 As no threshold values of good status for wetlands have been defined in the European Water  
240 Framework Directive, the criteria applied to rivers and ponds (Legifrance, 2015; Official  
241 Journal of the European Communities, 2000) was used in this study. Only six sampling points

242 (I-05, II-07, II-04 II-05, II-06 and III-01) have a conductivity value below the threshold value  
243 of  $3\text{mS cm}^{-1}$  indicating that most of the waters are enriched in dissolved salts provided by the  
244 SH leaching.

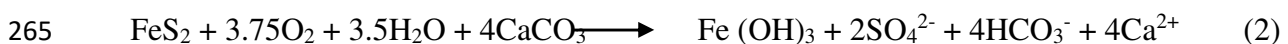
245 **Table 1**

246 ***Sulphates, cations and alkalinity*** — Concentrations of sulphate are diverse and range between  
247 900 and  $2690\text{ mg L}^{-1}$  exceeding significantly the bad-status threshold of the WFD ( $250\text{ mg L}^{-1}$ ).  
248 These concentrations were also compared to surrounding groundwaters with an average  
249 value of  $128\text{ mg L}^{-1}$  (Artois-Picardie Water Agency 2017) (no available data for rivers  
250 surrounding). At stations I-01, I-02, I-04, II-01, II-02 and II-03, the sulphate content exceeds  
251  $2000\text{ mg L}^{-1}$ , while only at the reference station (III-01) and at the most remote station of SH I  
252 (I-05) sulphate concentrations are below  $1000\text{ mg L}^{-1}$ .

253 High sulphate levels are a typical characteristic of SH leaching due to the oxidation of several  
254 sulphide minerals like pyrite (Rose and Cravotta III, 1998). When rainwater (oxygenated and  
255 with a slightly acidic pH around 5-6) or eventually water from a superficial aquifer encounters  
256 the iron sulphide minerals present in the SH, oxidation processes take place allowing the release  
257 of  $\text{H}^+$ , sulphates and Fe (III). The complete oxidation reaction involved is shown in Equation 1  
258 (Denimal, 2001):

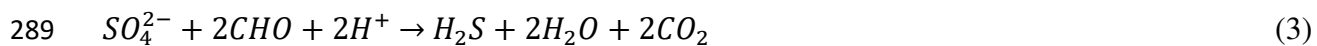


260 In our case, pH values remain quite neutral and dissolved iron concentrations are low. Indeed,  
261 iron levels range from  $< 0.06$  (LOD) to  $0.32\text{ mg L}^{-1}$ . This differs from a classic Acid Mine  
262 Drainage (AMD) and is called a neutralized AMD (nAMD) (Rose and Cravotta III, 1998). The  
263 neutral pH results from the presence of carbonate compounds in the soils (*i.e.* chinks) that buffer  
264 the leaching water (*e.g.* calcium carbonate in Equation 2).



266 Concentrations of calcium, magnesium, potassium, strontium, manganese and sodium vary  
267 from 47 to 350 mg L<sup>-1</sup> (Ca), 49 to 240 mg L<sup>-1</sup> (Mg), 13 to 39 mg L<sup>-1</sup> (K), 0.50 to 6.1 mg L<sup>-1</sup>  
268 (Sr), 0.02 to 1.0 mg L<sup>-1</sup> (Mn) and 41 to 480 mg L<sup>-1</sup> (Na), showing a wide range of variation and  
269 with several values exceeding largely those found at the reference site and in the surrounding  
270 groundwater, see Table 1 (no available data for the surrounding rivers). High concentrations of  
271 these elements can also be due to slag heap leaching followed by carbonate buffering (nAMD)  
272 (Monterroso and Macias, 1998).

273 A large range of alkalinity values, from 1.51 (II-06) to 24.2 mmol L<sup>-1</sup> (I-10), are observed with  
274 several values exceeding largely those found at the reference site III-01 (2.76 mmol L<sup>-1</sup>) and in  
275 the surrounding groundwater (5.06 mmol L<sup>-1</sup> in average) (no available data for the surrounding  
276 rivers). Besides carbonates at circumneutral pH, alkalinity can also include other chemical  
277 species such as bisulphide, silicates, borates and phosphates. After quantification of phosphates,  
278 of total Si and of B, it is justified to say that, except for station II-01 where sulphides are found  
279 at high concentrations (0.9 mmol of sulphides for 2.2 mmol of alkalinity), alkalinity is primarily  
280 composed of hydrogen carbonates. Hydrogen carbonate concentration could result from the  
281 neutralisation of the AMD, especially at SH II where a significant correlation is observed  
282 between alkalinity, sulphate and major cations coming from the leaching (Figure 3). However,  
283 for SH I, alkalinity is not correlated with the released species, which can be due to several  
284 reasons. Firstly, Rose and Cravotta III (1998) described several neutralisation processes without  
285 affecting alkalinity. The acidity can indeed be neutralised by dissolution of FeCO<sub>3</sub> or silicate  
286 minerals in which case alkalinity is not affected. Secondly, in SH I and to lesser extent in SH  
287 II, the reduction of sulphates by Sulphate Reducing Bacteria (SRB) will consume protons and  
288 simultaneously produce gaseous H<sub>2</sub>S (Equation 3; Wu et al., 2013).



290 As the dissolved organic carbon concentrations are generally higher in SH I than in SH II, the  
291 bio-reduction of the sulphates may be favoured at SH I, with, as a consequence, the increase in  
292 alkalinity and a poorer correlation between alkalinity and the other slag heap leaching markers.  
293 Thirdly, the non-correlation between alkalinity and the released species may also be linked to  
294 other phenomena like photosynthesis and aerobic respiration, consuming either  $NO_3^-$  or  $NH_4^+$   
295 (Stumm and Morgan, 1996). Precipitation of various solid phases, such as metal sulphides or  
296 evaporation when the water level is low, can cause alkalinity changes too.

297 **Anions and DOC** — Nutrient concentrations ( $NO_3^-$  and  $PO_4^{3-}$ ) are possible eutrophication  
298 indicators in aquatic environments. Nitrate levels range from  $< 0.01$  to  $0.95 \text{ mg L}^{-1}$ , which is  
299 low compared to the surrounding waterbody averages ( $5 \text{ mg L}^{-1}$  for groundwaters,  $31 \text{ mg L}^{-1}$   
300 for rivers) and to the WFD threshold value of  $10 \text{ mg L}^{-1}$ , definition for a “very good state of  
301 water”. Phosphate exhibits very low concentration levels, mostly under the detection limit of  
302  $0.04 \text{ mg L}^{-1}$ . Except for a few stations, most of them display phosphate levels below the  
303 detection limit. Overall, the impact of urban and agriculture activities on our study sites are  
304 limited and do not favour eutrophication processes in the ponds and wetlands.

305 Fluorides and chlorides can have adverse effects on terrestrial aquatic ecosystems when present  
306 at high concentrations (Elphick et al., 2011; United States Geological Survey, 2009).  $F^-$  levels  
307 range from  $< 0.01$  to  $0.31 \text{ mg L}^{-1}$ , which comply with the average content of the surrounding  
308 groundwater ( $0.17 \text{ mg L}^{-1}$ ) and are below the threshold value of  $0.5 \text{ mg L}^{-1}$  above which  $F^-$  has  
309 been shown to affect aquatic organisms (Camargo, 2003).  $Cl^-$  concentrations are low (between  
310  $8.1$  and  $26.6 \text{ mg L}^{-1}$ ) and below the groundwater and III-1 levels ( $27.1 \text{ mg L}^{-1}$ ) and the WFD  
311 threshold value of  $50 \text{ mg L}^{-1}$  (Official Journal of the European Communities, 2000).

312 DOC concentrations range from 1.6 to 25.1 mg C L<sup>-1</sup> with the lowest values at stations I-04 and  
313 I-09 and all stations of SH II. At the other SH I stations and at the reference station III-01 (7.5  
314 mg C L<sup>-1</sup>), the threshold value as defined by the WFD (5 mg C L<sup>-1</sup>) is exceeded. However, the  
315 WFD threshold value for DOC must be handled with caution, because these reference values  
316 were originally determined to qualify the state of a water mass (lake, river, etc.), while we are  
317 here dealing with wetlands which are, by definition, rich in vegetation and thus in DOC. In a  
318 wetland, the WFD threshold value of DOC can be easily exceeded. The highest DOC  
319 concentrations were recorded at I-05, I-08 and I-13 with values above 15 mg C L<sup>-1</sup>,  
320 corresponding to a bad status of water bodies. As SH II is far less vegetated than SH I, it is not  
321 surprising to find lower DOC values in SH II. This observation can mainly be explained by the  
322 difference in age and maturity of both systems. In addition, vegetation maintenance is better in  
323 SH II than in SH I where vegetation overgrowth creates obstacles in the water runoff. Finally,  
324 as reported by Lee and Bukaveckas (2002), wetlands impacted by mine drainage usually show  
325 slower decomposition rates and lower nutrient levels in comparison to wetlands found in  
326 predominantly agricultural areas (Lee and Bukaveckas, 2002).

327 ***Oxygen, sulphides and total P*** — Dissolved oxygen saturation ranged from 9 to 140% with an  
328 average of about 75%. There is, therefore, a wide range of variation with very high values at  
329 some locations (I-01, 02, 03, 05, 09, 12, II-03, 05, 06 and III-01 > 90%) and very low at the  
330 surface, even anoxic at the bottom, of others (I-01, 04, II-02 < 30%). Sulphide concentrations  
331 were only detected in these three anoxic stations. Total dissolved phosphorus concentrations  
332 also seemed to be linked to dissolved oxygen concentration. Varying from < 0.2 to 0.93 mg/L,  
333 the variation in phosphate was negatively correlated to that in O<sub>2</sub>. It has been observed that in  
334 hypoxic or anoxic conditions, the reduction of iron oxides can lead to the release of phosphates  
335 in the water that were previously trapped in these oxides (Patrick and Khalid, 1974).

336 **Biological analysis** — The biological inventory highlighted the presence of several aquatic  
337 invertebrate families. Sixteen families of species, spread over all sampling stations, have been  
338 identified and quantified (Table 2), with as the most important, *Cyclops sp*, *Chydoridae* and  
339 *Daphniidae*.

340 The poorest biodiversity levels were observed at SH II stations II-01 and II-02 (respectively, 0  
341 and 1 for the taxon, 0 and 13 for the abundance), where oxygen levels were low and sulphide  
342 concentrations high, exceeding 24 mg L<sup>-1</sup>. Station II-03 showed the highest biodiversity level  
343 with 3 taxa and an abundance of 39 individuals. At this station oxygen levels were high,  
344 sulphide was not detected, and the highest levels of Ca, K, Mg, Mn and sulphates were  
345 observed.

346 At SH I, the biodiversity wealth seems higher than at SH II: the total number of taxa is 8 (I-01)  
347 and the total abundance 288 (I-08). However, large differences between the sampling stations  
348 can be observed. The lowest biodiversity levels are observed at stations I-04 and I-05  
349 (respectively, 0 and 2 for the taxon, 0 and 14 for the abundance), the highest levels at I-01 and  
350 I-08.

## 351 **Table 2**

352 Aquatic invertebrate species, also those found here, can be used as bio-indicators of their  
353 environment (e.g. Health Monitoring Institute, 2004; Hodkinson and Jackson, 2005). For  
354 instance, *Cyclops sp* (found at all stations except I-04, 06, II-01, 05, 06) and *Diaptomus sp*  
355 (found only at II-06) are invertebrate species known for their tolerance to wastewater but also  
356 to eutrophication processes. More specifically, *Chironominae* (stations I-01, 03 and II-05),  
357 *Ceratopogonidae* (stations I-01 and I-06), *Culicidae* (I-05) and *Nematode* (II-05) are bio-  
358 indicators of organic or chemical polluted waters as they are tolerant to such environmental  
359 conditions. On the contrary, *Hydrophilus sp* (only found at station I-12) is a species which is

360 sensitive to water pollution by organic matter and chemicals. *Rotifera* (I-11) is sensitive to  
361 salinity, while *Ostracode* (stations I-06, 08, 09, 10, 11, 14) can tolerate salinity but it is sensitive  
362 to organic matter, industrial and metal-mining pollution (David M. Rosenberg and Resh, 1993).  
363 The salinity resistance of the *Ostracode* family as well as the high alkalinity and the relatively  
364 low leaching impact at stations I-06, 08, 09, 10, 11, 14, allowed them to develop there.

### 365 **3.2. Lixiviation influence**

366  
367 When looking at the results from the PCA (see Fig. 3 – A and C), the first axis with the most  
368 variance (PC1 with almost 50% of the data variability) fits well with the lixiviation process.  
369 For both sites taken separately, sulphates, major cations, conductivity are close on the right side  
370 of PC1. On the opposite side of the PC1 axis, the chlorides are found for both sampling sites  
371 (Fig. 3 – A and C) and the DOC is found only at SH I (Fig. 3 – A). These elements are both  
372 indicators of non-impacted waters (or less impacted) from the slag heap. A gradient of these  
373 two sources is indicated in Figure 3: the first principal component represents the mixing of  
374 lixiviates (positive part) and lake water (negative part). The distribution of the points on Fig.  
375 3B gives the relative importance of the two sources for each station. We notice that the  
376 “cleanest” stations are in the lakes (I-05 and II-07) and several nearby stations.

### 377 **Figure 3**

378 The leaching of the slags influences the water composition at the foot of the two SHs. Indeed,  
379 sulphates, Ca, Sr, Mg, Na and to a lesser extent alkalinity are correlated at both sites, indicating  
380 that all these elements are probably solubilised simultaneously during the leaching process.  
381 However, the average composition of the leaching solution after normalisation by the sulphate  
382 concentration varies between the 2 SHs as indicated in Table 3. From this table, it is clear that  
383 there exists a supplementary mineral phase supplying dissolved sodium and carbonate during  
384 the leaching or neutralization process at site I. However, at site II, a slight increase in the

385 amounts of calcium and strontium can be noticed. The two sites being only 2 km apart, such a  
386 difference was surprising. However, it appears that the two slag heaps have different histories.  
387 SH I is a relatively recent “washing slag heap”, which was build up between 1950 and 1984  
388 and contains fine particles. SH II is a more historical one (1912-1975), containing a lot of coal  
389 and a larger size of slags. In 1975, the remaining coal was extracted from these slags with a  
390 washing process and the residues were thereafter redeposited at the same place. Since the  
391 mineral composition of the soil between the two sites is different, the lixiviates composition  
392 varies as well. It may explain why for SH II, most dissolvable salts, *e.g.* the sodium carbonate  
393 phase, may already have been leached.

### 394 **Table 3**

### 395 **3.3. Hypoxia**

396  
397 Hypoxia or even anoxia has been observed at several sampling sites. This could be due to a  
398 complete consumption of dissolved oxygen for the oxidation of organic matter in the small  
399 ponds, which are full of vegetal debris. It is also possible that some water leaching from the SH  
400 was yet anoxic as all the oxygen was used for pyrite re-oxidation. This is partly supported by  
401 the fact that only stations very close to the SH were found with low O<sub>2</sub> concentration and  
402 sulphides.  
403

404 When all oxygen is consumed, anaerobic respiration leads to the reduction of iron oxides and  
405 concomitantly the release of P and the reduction of sulphates. The pH also slightly decreases  
406 due to the release of CO<sub>2</sub> from oxidised organic matter (Seybold et al., 2002). On the PCA in  
407 SH I (Fig. 3A), O<sub>2</sub> and pH are close to each other on the positive part of PC2, but opposite to P  
408 and sulphides on the same axis. This is mainly true for SH I. If for SH II the opposition between  
409 pH / O<sub>2</sub> and P / sulphides is still visible, it is not as clear as on the second principal component  
410 PC2. This lack of complete orthogonality could be the sign of a link between hypoxia and  
411 lixiviation on SH II (*e.g.* anoxic lixiviates).

412

### 413 **3.4. Chemistry and biodiversity**

414 It seems that for SH I, as it is indicated on Fig. 3.A, lixiviation from the SH and the biological  
415 diversity are unrelated. No decrease of the taxon and of the abundance is found along the  
416 lixiviation gradient. Lixiviation and aquatic invertebrate diversity and abundance seem  
417 orthogonal. Hypoxia seems to influence the invertebrate distribution much more ( $R = 0.61$  and  
418  $0.55$  respectively for  $O_2$  vs taxon and for  $O_2$  vs abundance for all campaigns). The lack of  
419 oxygen is very damaging, as it goes pair with the emerging sulphides. The toxicity of sulphides  
420 depends on the species, the exposure time and its concentration. Sulphides mainly interfere with  
421 respiration metabolism: levels reaching  $\mu\text{g L}^{-1}$  levels will affect the whole aquatic organism,  
422 but concentrations at the  $\text{ng L}^{-1}$  level are, for instance, enough to impact enzyme functioning  
423 like the cytochrome c oxidase which is a transmembrane protein complex and part of the  
424 respiratory electron transport chain of eukaryotes including aquatic invertebrates (Castresana  
425 et al. 1994). As a competitive inhibitor of the cytochrome c oxidase enzyme, excessive levels  
426 of sulphide can lead to cell asphyxia (Grieshaber and Völkel, 1998; Nicholls et al., 2013).  
427 Overall, the appearance of sulphides was shown to amplify hypoxia effects (Bagarinao, 1993).  
428 The impact and diffusion of sulphide through a cell is also directly proportional to the  $H_2S$   
429 concentration in the solution. Indeed,  $H_2S$  can easily cross membranes, whereas the hydrogen  
430 sulphide  $HS^-$  may be electrically excluded. Nevertheless,  $HS^-$  can still contribute to toxicity at  
431 high concentration (Beauchamp et al., 1984).

432 For SH II, the quality also depends strongly on the dissolved oxygen concentration ( $R= 0.90$   
433 and  $0.77$  respectively for  $O_2$  vs taxon and for  $O_2$  vs abundance). However, as it has been seen  
434 before for this site, hypoxia and lixiviation may not be as independent as it is observed for SH  
435 I. Lixiviation from the heap may be indirectly responsible for the lack of invertebrates.

436

### 3.5. Temporal variability

437  
438  
439 In July 2016, eight stations from the first campaign were sampled again: I-01, 02, 03, 04, 09,  
440 10, 11 and 12. Figure 4 compares these results to the ones obtained in March showing the  
441 change in wetland composition between these two seasons.

442 The concentrations of Ca, K, Mg, Mn, Na and Sr drastically decreased for all stations between  
443 March and July: a 30% to 70% decrease is systematically recorded (Mg and Sr behaviour is the  
444 same as Ca; see Supplementary Information for complete data set). As previously mentioned,  
445 these elements are usually carried together with sulphate during the leaching process. However,  
446 sulphate concentrations do not really change with time. Complex geochemical processes such  
447 as dissolution of gypsum, precipitation reactions of alkaline earth elements with a high amount  
448 of carbonates, water exchange between overlying and groundwater must have been involved.  
449 These phenomena must have been induced by a lack of precipitation, leaching, temperature  
450 increase or water evaporation in the small ponds.

451 A general decrease of dissolved oxygen saturation and pH, coupled to an increase of alkalinity,  
452 was noted. This could indicate that the respiration process exceeded the primary production in  
453 these ponds. Indeed, the low water level, the high amount of sediments and particulate organic  
454 matter from the microphytes and tree leaves (based on field observations) seem to accelerate  
455 the degradation process when the temperature raises.

456 In parallel, the sulphide concentrations increased at station I-03 and I-12 and decreased at  
457 stations I-04 and I-10. We therefore suppose that the reduction of sulphates into sulphides has  
458 not been intensified by the increase in temperature and the pluviometry decline. Regarding  
459 biodiversity, the number of taxa decreased except at I-09, as well as the abundance except at I-  
460 09, I-10 and I-11. Therefore, it seems that the decrease of the biodiversity is linked to  
461 degradation processes of organic matter caused by the activity of micro-organisms. These  
462 processes reduce the dissolved oxygen concentration and may produce micro-niches of high

463 dissolved sulphide concentrations. This biogeochemical evolution could therefore lead rapidly  
464 to an eutrophication of the water system (Science for Environment Policy, 2015).

465  
466  
467  
468  
469

#### Figure 4

#### 4. Conclusion

470 This study was conducted with the aim of assessing the potential influence of slag heap leaching  
471 on the surrounding aquatic environment, in the Hauts-de-France region. We endeavoured to  
472 determine the existence or the absence of a link between the chemical composition of surface  
473 waters and the biodiversity distribution of each studied zone. One of the main findings relates  
474 to the presence of sulphates, which are the first indicators of a mining waste leaching. These  
475 sulphate concentrations, which are far above the surrounding background concentrations, are  
476 the results of pyrite oxidation contained in the slag heaps soil. Most of the studied areas are  
477 enriched in dissolved salts provided by the SH leaching. More precisely, the composition of the  
478 water around the two slag heaps reveals a typical example of a neutralized acid mine drainage,  
479 with a clear neutral pH and low Fe levels. This was especially confirmed by the presence of  
480 carbonate compounds from the soils, high enough to buffer the leaching waters, and by the high  
481 concentrations of many typical sub-products of such SH leaching (Ca, Mg, K, Mn, Na). At three  
482 sampling stations, located very close to the SH, a reduction of sulphate to sulphide coupled with  
483 anoxia and with phosphate release has been evidenced. This phenomenon might be amplified  
484 in the case of high amounts of organic matter. According to our results, this has led to a decrease  
485 in composition and distribution of aquatic invertebrates, thus in biodiversity. Most likely, the  
486 appearance of sulphides (partially under H<sub>2</sub>S) intensifies the impact of hypoxia in such  
487 ecosystems. Nevertheless, it is difficult to predict whether the ecological imbalance observed  
488 at these sampling stations constitutes an isolated case or if it is an indication of what would  
489 happen in future on a larger scale in the rest of the wetlands. Despite these three cases, the

490 invertebrate inventories generally reveal a good biodiversity richness at most of the studied  
491 areas: this was mainly linked to good oxygenation conditions of the aquatic environment and  
492 to the absence of sulphide. At these stations no influence from SH lixiviation was noticed. From  
493 March to July, increasing temperatures coupled with a pluviometry decline do not seem to  
494 promote sulphate reduction into sulphide. Even though dissolved oxygen and pH tend to be  
495 lower in Summer. Furthermore, loss of biodiversity in July seems only to be related to low  
496 dissolved oxygen levels, resulting from higher degradation rates of organic matter by micro-  
497 organisms. However, the latter processes may cause, if not controlled and managed, rapid  
498 eutrophication of the ecosystem. Finally, the same leaching signature (high sulphate levels,  
499 nAMD) is observed in the aquatic environments surrounding both SHs. However, due to a  
500 difference in age and maturity between the two SH systems and, to a lesser extent, to a  
501 difference in vegetation maintenance, some variations were highlighted, especially regarding  
502 DOC levels and the lixivate composition (explained by an historical difference in the SH  
503 treatment process).

504 In future, it would be crucial to continue a scrutiny and scientific monitoring of these very  
505 particular and fragile wetlands (including sediments and micro-organisms), especially to better  
506 understand their evolution over time during low and high-water periods and during seasonal  
507 changes. In addition, monitoring the water fraction migrating to groundwater reserves located  
508 beneath the slag heaps would be welcomed as a complementary research approach. Finally,  
509 from an operational point of view, it would be necessary to propose remediation actions to  
510 prevent possible harmful effects on these wetlands. For instance, more vegetation maintenance  
511 around the area and/or the use of pumps could be interesting levers, in order to guarantee a  
512 better water circulation, as it was the case in the past during the exploitation of the coalmines.

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## 519 **Appendix A. Supplementary Information**

520 The Supplementary Information include 4 tables and can be found in the online version.

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642 **Figure 1:** Overview of the slagheap leaching process (after Thompson, 2015)

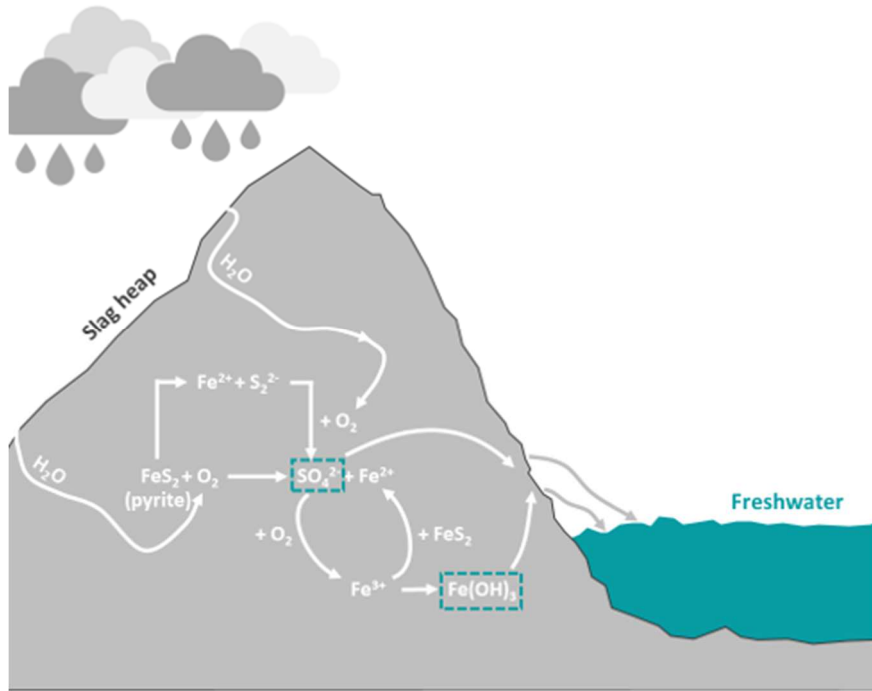
643 **Figure 2:** Sampling map for the two slag heaps: SH I and SH II, both close to the city of Douai.

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647 are not shown here.

648 **Figure 3:** PCA results for site I (A and B) and site II (C and D). Samplings performed in March

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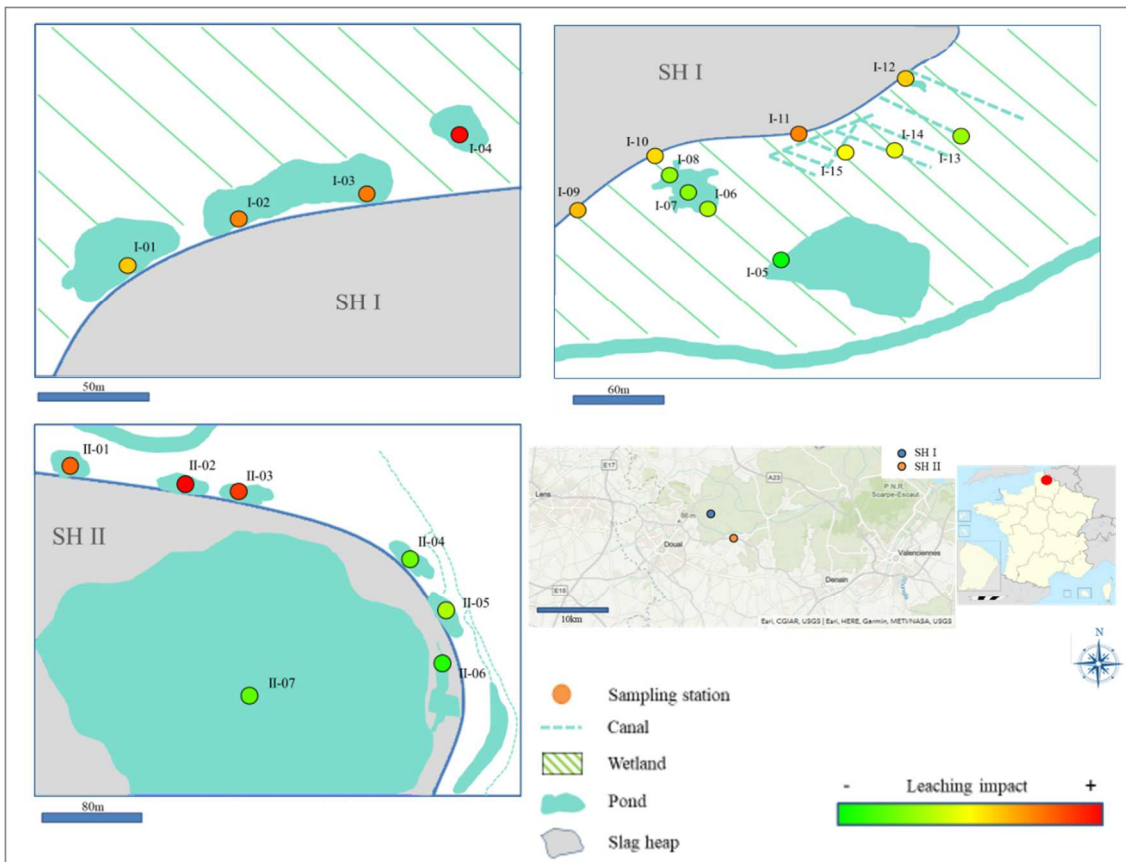
651 **Figure 4:** Temporal evolution of the wetland composition between March and July 2016.



652

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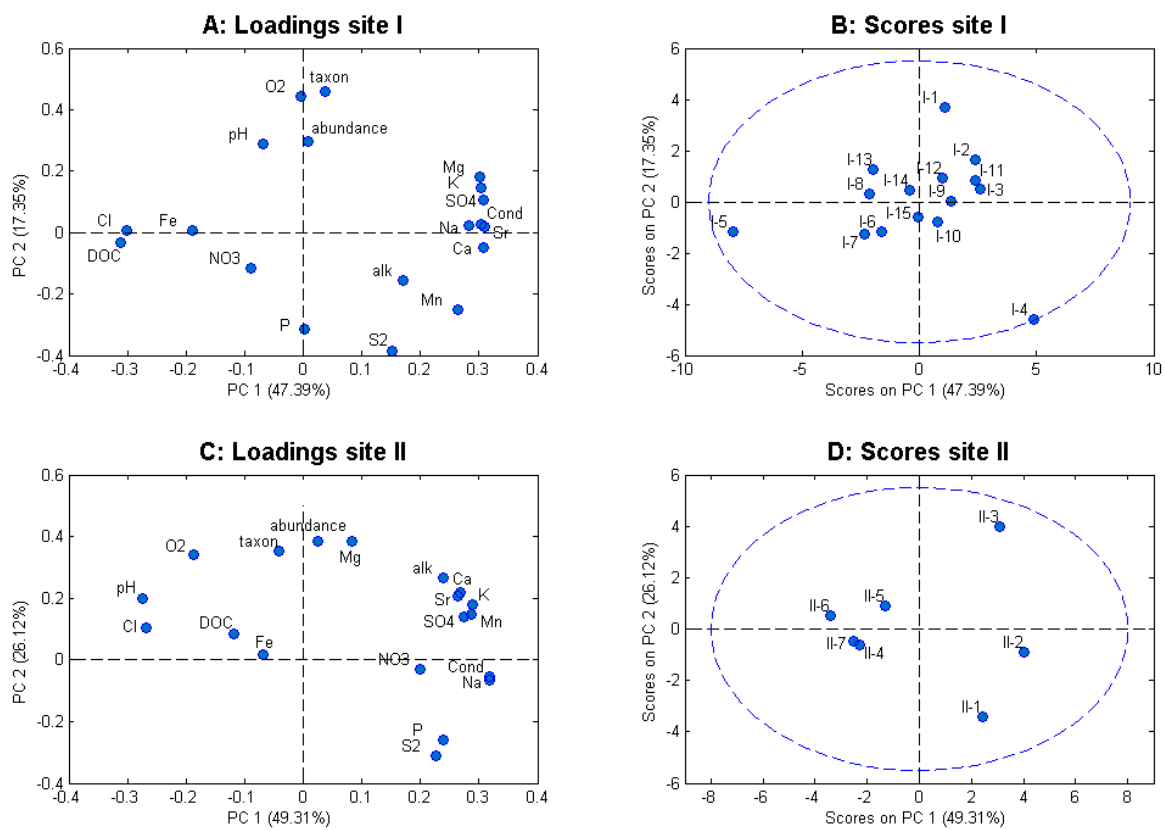
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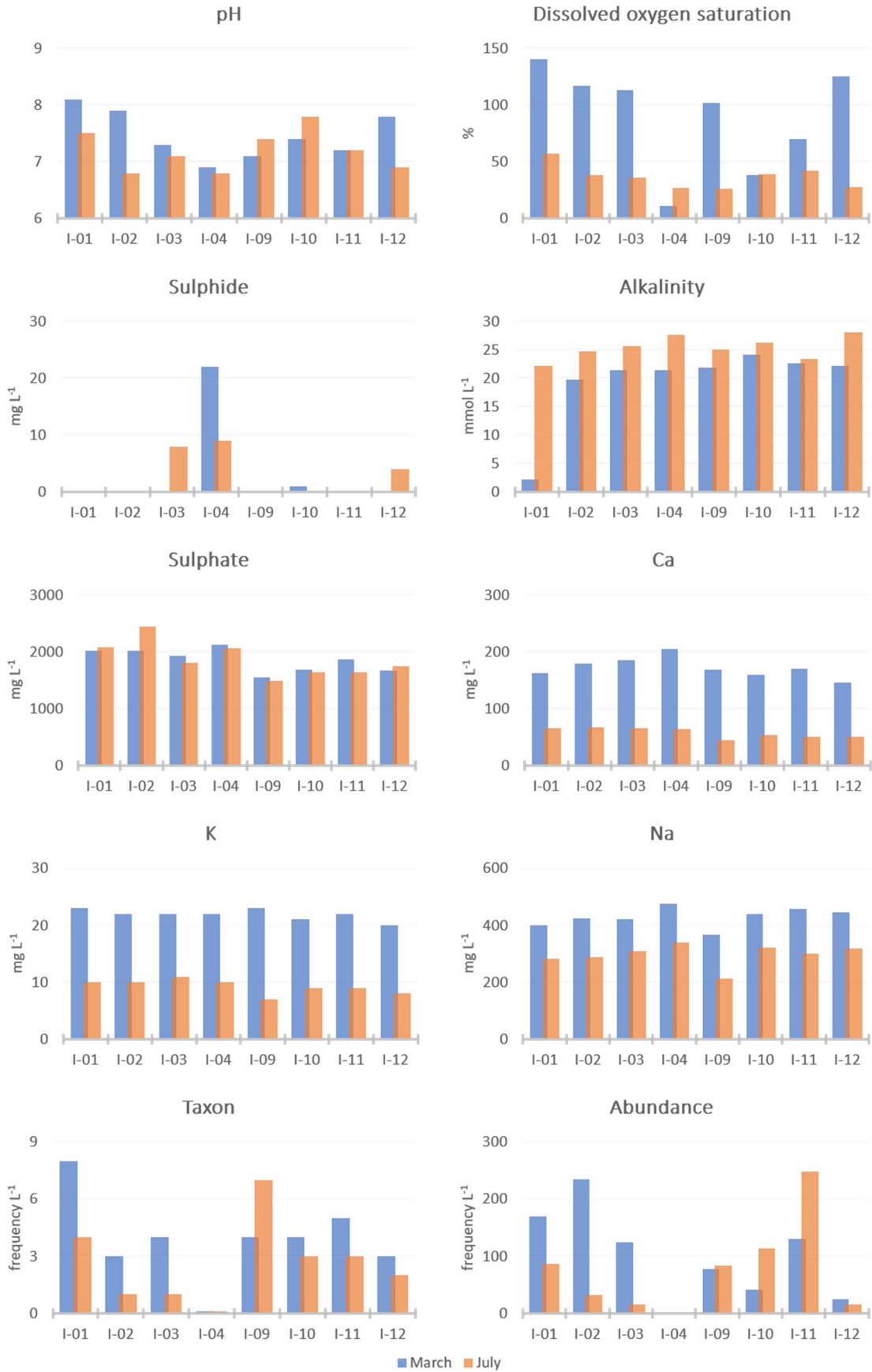
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667

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669 **Table 1:** Overview of the water composition for the first campaign (March 2016)

670 **Table 2:** Overview of the biological diversity in the water samples. The number of aquatic

671 invertebrates collected in 1 L of water is shown.

672 **Table 3:** Sulphate-normalised average concentrations of total dissolved Ca, K, Mg, Na, Sr

673 and alkalinity. \* and \*\* indicates the significance of the ratio difference between site I

674 and site II with a 5% and 1% error respectively.

675 **Table 1:** Overview of the water composition for the first campaign (March 2016)

	min.	max.	mean	reference site III-01	groundwater
<i>In situ measurements</i>					
pH	6.9 (I-04)	8.5 (I-13)	7.7	7.7	7
Conductivity (mS cm <sup>-1</sup> )	1.2 (III-01)	5.0 (I-04)	3.6	1.2	0.88
Dissolved oxygen saturation (%)	9 (II-02)	140 (I-01)	75	98	25
<i>Alkalinity (mmol L<sup>-1</sup>)</i>					
Alkalinity	1.51 (II-06)	24.2 (I-10)	13.7	2.76	5.06
<i>Sulphides (mg L<sup>-1</sup>)</i>					
Sulphide	< 0.2	30 (II-01)	3.3	< 0.2	-
<i>Dissolved organic matter</i>					
DOC (mg C L <sup>-1</sup> )	1.6 (I-04, I-09)	25.1 (I-05)	8.6	7.5	1.6
<i>Major elements (mg L<sup>-1</sup>)</i>					
Ca	47 (I-05)	350 (II-03)	169	189	147
Mg	49 (I-05)	240 (II-03)	131	60	15
K	13 (I-05)	39 (II-03)	21	2.5	6
Sr	0.5 (I-05)	6.1 (II-02)	2.4	1.1	-
Mn	0.02 (II-06)	1.03 (II-03)	0.29	0.03	0.01
Fe	< 0.06	0.32 (II-04)	0.09	< 0.06	0.03
P	< 0.2	0.93 (II-02)	0.26	< 0.2	-
Na	41 (II-04)	480 (I-04)	307	55	25
<i>Anions (mg L<sup>-1</sup>)</i>					
NO <sub>3</sub> <sup>-</sup>	< 0.50 (I-12, II-06)	0.95 (II-05)	0.68	< 0.50	5
PO <sub>4</sub> <sup>3-</sup>	< 0.10	1.17 (II-01)	0.26	0.80	0.03
F <sup>-</sup>	< 0.01	0.31 (II-05)	0.13	0.21	0.17
SO <sub>4</sub> <sup>2-</sup>	899 (I-05)	2693 (II-03)	1732	979	128
Cl <sup>-</sup>	8.1 (I-09)	26.6 (I-05)	15.0	27.1	27.1

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678 **Table 2:** Overview of the biological diversity in the water samples. The number of aquatic  
 679 invertebrates collected in 1 L of water is shown.

Taxonomic group	SH I						SH II						SH III									
	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	01	02	03	04	05	06	01
<i>Cyclops sp</i>	69	61	35		13		8	65	28	13	62	12	10	16	7	13	20	19				8
<i>Diaptomus sp</i>																						10
<i>Orthoclaudiinae</i>						2		3														
<i>Chironominae</i>	1		2																		3	
<i>Ceratopogonidae</i>	3					3																
<i>Culicidae</i>					1																	
<i>Chydoridae</i>	30	8						30	15	11	21	12	40	30	11			8		10	6	5
<i>Daphniidae</i>	62	165	88			80	140	181	33	15	40		61	40	24			11			10	6
Nematode																					3	
<i>Cyphon sp</i>								1														
<i>Hydrophilus sp</i>												1										
<i>Graptodytes sp</i>	2																					
Collembola	1																					
<i>Rotifera</i>											6											
Ostracode						1		8	2	2	2			7								
<i>Driops sp</i>	1																					
Total taxon	8	3	3	0	2	4	2	6	4	4	5	3	3	4	3	0	1	3	1	3	3	3
Total abundance	169	234	125	0	14	86	148	288	78	41	131	25	111	93	42	0	13	39	19	16	26	19

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687 **Table 3:** Sulphate-normalised average concentrations of total dissolved Ca, K, Mg, Na, Sr and  
 688 alkalinity. \* and \*\* indicates the significance of the ratio difference between site I and site II  
 689 with a 5% and 1% error respectively.

	SH I	SH II	
Sulphates	1	1	
Ca	0.21	0.26	*
Alkalinity	1.1	0.21	**
K	0.031	0.029	
Mg	0.29	0.33	
Na	1.0	0.26	**
Sr	0.0013	0.0019	**

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