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6 **Investigation of phosphorus desorption from P-saturated alum**

7 **sludge used as a substrate in constructed wetland**

8

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27 **Abstract**

28 Phosphorus (P) desorption from P-saturated alum sludge, which was used as main substrate in a
29 novel constructed wetland for wastewater treatment, was studied. Groups of batch experiments were
30 designed and conducted to explore the efficiencies of P extraction using different acids (HCl, HNO₃,
31 H₂SO₄) and bases (NaOH, KOH). The results showed that either acid or base is efficient for
32 P-extraction and the efficiency relied mainly on the concentrations of H⁺/OH⁻, not the type of acid
33 or base. Considering the efficiency, price and safety of the acids and bases tested, H₂SO₄ was
34 chosen as most suitable reagent for P-extraction. A Box-Behnken experimental design based on the
35 response surface methodology (RSM) was applied to evaluate the optimum of H₂SO₄ extraction.
36 The optimal condition for the mass of sludge, H₂SO₄ concentration and volume was 0.8 g, 0.063 M
37 and 142 ml, respectively. At such optimal condition, the maximum P-extraction efficiency of
38 98.2 % was achieved. Additionally, most of the main components of the saturated sludge, such as
39 metals (Al, Ca, Mg, Fe), TOC (total organic carbon) and nitrogen can also be extracted. Overall, the
40 results supported that H₂SO₄ seems to be an efficient and cost-effective reagent among all the
41 reagents tested for P-saturated alum sludge treatment.

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44 **Keywords:** phosphorus, desorption, acid, base, alum sludge, RSM, constructed wetland

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50 **1. INTRODUCTION**

51 In contemporary society, phosphorus (P) is a crucial element for agricultural and numerous
52 industrial activities. It is very severe that P is a non-regenerative resource and the known reserves
53 are estimated to last only about 100 years with the present utilization rate [1]. At the same time,
54 significant amount of P is consumed via various industrial- and daily life activities, thus making P
55 being one of the main contaminants in various wastewaters. The main processes of P removal from
56 wastewaters are chemical precipitation by metal salts, biological removal in bioreactors, constructed
57 wetlands and enhanced biological phosphorus removal (EBPR) etc. [2]. In line with sustainable
58 wastewater treatment technologies which are environmentally friendly, more and more efforts have
59 been made in recent years, towards recovering phosphorus from wastewater and the sludge
60 generated inevitably during the wastewater treatment [3-5].

61
62 On the other hand constructed wetland as a less energy-intensive, easy to operate and cost-effective
63 technology is increasingly employed worldwide for various wastewater treatments. In the past five
64 years, great efforts have been made at the University College Dublin, Ireland, towards developing a
65 novel constructed wetland system for wastewater, especially the P-rich wastewater, treatment [6-8].
66 The novel constructed wetland lies in the use of the dewatered aluminium-based drinking-water
67 treatment sludge (termed as alum sludge) as a substrate and a P-removing material for wastewater
68 treatment. Such reuse of alum sludge in wetland is quite attractive. The concept is also sustainable
69 as the objective of its utilization is not merely to dispose the alum sludge as a waste or find an
70 alternative disposal route, but to utilize it for the purpose of enhancing wastewater treatment
71 (particularly P removal) in constructed wetland. It has been demonstrated that more than 90% of

phosphorus can be absorbed by alum sludge cakes [7]. Previous study [9] has showed that the P adsorption capacity of the same alum sludge determined using batch isotherm tests would be 14.3 mg P/g dried sludge, implying that the lifetime of the alum sludge used in the constructed wetland for domestic wastewater treatment could be 9–40 years [8]. Even in the case of high P effluent of animal farm wastewater treatment tested, the lifetime of alum sludge can be estimated as 2.5– 3.7 years.

After use or saturation of such substrate (dewatered alum sludge), the investigation of desorption or extractability of P retained in the substrate is very crucial regarding the p-recovery as a resource. Recently, studies on P recovery technologies by the application of the solvent-extraction method have attracted considerable attention [10]. However, these methods not only use a large amount of organic solvent such as butyl-alcohol or tri-butyl phosphate to extract P but also require a very complicated procedure.

Therefore, the objective of this study was to investigate effectiveness of acids or bases extraction of phosphorus from saturated alum sludge which was adopted as a substrate in a laboratory scale constructed wetland for P immobilization from an animal farm effluent containing COD (chemical oxygen demand) of 213 ± 127 mg/l, BOD₅ (biochemical oxygen demand) of 110 ± 69 mg/l, phosphorus of 28 ± 15 mg/l ($\text{PO}_4^{3-}\text{-P}$), SS (suspended solids) of 72 ± 66 mg/l and pH of 6.8 ± 0.4 [8]. The farm possesses about 2000 livestock units of sheep, pigs, cattle and horses. The animal farm effluent is derived from all the activities on the farm and it undergoes some form of primary sedimentation before being pumped to the treatment wetland system [8]. After the preliminary

investigation, the study was focused on selecting the most suitable reagent for P desorption and optimizing the factors like mass of sludge, concentration and volume of reagent using response surface methodology (RSM) to achieve the most optimal and economical conditions. The accompanying changes of other main components of sludge such as metals, nitrogen, TOC (total organic carbon) under the optimal desorption conditions were also examined.

2. MATERIALS AND METHODS

2.1 Origin of P-saturated alum sludge

The P saturated alum sludge used in this study was obtained from a laboratory scale constructed wetland system which uses dewatered alum sludge (collected from Ballymore Eustace Water Treatment Works in Southwest Dublin, Ireland) as the substrate for a P-rich animal farm wastewater treatment. After a long time operation, the alum sludge was almost saturated with marginal P adsorption ability. The sludge was dried at room temperature and then ground and sieved to diameter <0.3 mm to provide the test samples. By using inductively coupled plasma-mass spectrometry (ICP-MS) (for testing Al, Ca, Fe, Mg and P), Eltra CS800 carbon/sulfur determinator (for testing TOC) and Kone Analyser (for testing nitrite and nitrate), the characteristics of the P-saturated sludge are listed in Table 1. As a comparison, the characteristics of the air-dried fresh alum sludge before the wetland use are jointly listed in Table 1.

[Table 1 here]

2.2 Experimental procedure

The experiments were conducted in room temperature and the procedure was as follows. Initially,

the efficiencies of P extraction by acid and base under varied extraction time were examined. A batch of 0.8 g pre-weighed sludge samples was put into a series of 250 ml flasks. Then, 150 ml of acid (HCl) or base (NaOH) with different concentrations up to 0.1 M was added to the samples, thereafter the flasks were placed on a orbital shaker (SSL1, Bibby Sterilin LTD, UK) at 225 rpm for 1-6 hours for P extraction. During the extraction period, pH was not controlled although it was occasionally monitored and the pH was slightly increased along with the extraction process. After extraction, the samples were filtered using 0.45 μ m Millipore filter paper (Millipore) before the phosphate ($\text{PO}_4\text{-P}$) analysis, which was conducted following the standard method using a Hach spectrophotometer (DR/2400).

The second set of experiments was conducted to examine the effect of different acid (H_2SO_4 , HNO_3 , HCl) or base (NaOH, KOH) with different concentrations from 0.01 M to 0.1 M on P extraction at fixed extraction time of 60 min following the same procedure described above.

The third set of experiments was designed using RSM method to optimize the H_2SO_4 extraction. RSM is a collection of mathematical and statistical techniques which can be used for studying the effect of several factors at different level and their influence on each other [11]. A Box-Behnken design [12] was chosen to evaluate the combined effect of the three independent variables, i.e. mass of alum sludge (X_1), concentration (X_2) and volume of acid solution (X_3) with extraction time being fixed as 60 min. The full experimental plan with respect to the values of the parameter in actual and coded form is listed in Table 2.

[Table 2 here]

138 Subsequently, P-extraction of the wetland used sludge with H_2SO_4 under the optimal conditions was
139 conducted. In such experiment, the characteristics of the leachate were examined to evaluate the
140 release/extraction of other components in the sludge by H_2SO_4 .

141

142 Finally, a series of 100 ml H_2SO_4 leachate were tested by adding 4 M NaOH at pH range of 4-10.5
143 and stirred 30 min to form the aluminum phosphate precipitations. This is expected as the process
144 for P recovery.

145

146 **3. RESULTS**

147 **3.1 Phosphorus extraction by acid and base**

148 Results of phosphorus extraction from P-saturated alum sludge by HCl or NaOH at different
149 extraction time are presented in Fig. 1. The results showed that both the HCl and NaOH can be the
150 efficient reagents for P extraction. Relatively, acid (HCl) is better than base (NaOH) since more
151 than 90% phosphorus can be extracted by 0.1M HCl while 70% P extraction was obtained with the
152 same concentration when NaOH was used. Concentration of HCl or NaOH seems to be an
153 important factor to affect the extraction efficiency with high P extraction being achieved at strong
154 acid or base. From Fig. 1, it can be seen that P was mostly extracted in the initial stage and the
155 equilibrium can be reached within 60 min for both HCl and NaOH extraction.

156 [Fig. 1 here]

157

158 Yang *et al.*[13] studied the P-adsorption by alum sludge and claimed that the phosphorus and
159 aluminum can form the complex compounds through chemical reaction and precipitation. The

P-adsorption is dominated by the significant amount of reactive functional groups, such as –OH, –Cl, –SO₄ and humic substances in the sludge surface via the ligand exchange mechanism. Therefore, it is expected that the P extraction via leaching to the acid or base solution from the alum phosphate can be expressed with chemical equations shown below.

Based on the kinetic fitting using the experimental data derived from this study, the P extraction in the initial stage was found to follow a first-order reaction, which could be described as follows:

$$\log (C_t/C_0) = -(\kappa/2.303)t \quad (3)$$

where C_t =residual P concentration in the sludge (mg/g) at extraction time t , C_0 =initial P concentration in the sludge (mg/g) (at $t=0$), κ =rate constant (min^{-1}), t =extraction time (min). At 20 °C, the correlation coefficients and the rate constants κ of different solutions were calculated and showed in Table 3.

[Table 3 here]

Fig. 2 illustrated P extraction using different acids (HCl, HNO₃, H₂SO₄) or bases (NaOH, KOH) with different concentrations at extraction of 60 min. From the results, there is no obvious difference of extraction abilities between different acids or bases. The extraction efficiencies exhibited an increased trend with concentrations of H⁺ or OH[–] but no significant increasing between 0.075 and 0.1 M. As all the acids and bases used are strong types and they are all completely ionized in solution, dissolution of AlPO₄ is fully dependent on H⁺ or OH[–] (see Eq. (1), (2)), thus no striking difference within acids and bases is understandable.

[Fig. 2 here]

183

184 Interestingly, it is noted from Fig. 2 that in low concentrations under 0.05 M, P extraction is more
185 efficient by using base than that of using acid, but in high concentrations, acids are more powerful
186 than bases. For example, P extraction efficiency by 0.075 M HNO₃ and NaOH was 90% and 65%
187 respectively. The possible reasons for this may be the Al(OH)₃ inside the alum sludge, which was
188 formed during the flocculation in water treatment process. The residual Al(OH)₃ might consume
189 some acid or base when the sludge were treated/extracted by lower concentration. The reaction can
190 be described as follows.

193 Obviously, more acid was used for dissolving Al(OH)₃. As a result, the acids exhibited the less
194 efficiency for P extraction in the low concentration range. On the contrary, when concentrations are
195 high enough, the reactions mainly follow the equation (1) and (2) and humic acid in sludge is thus
196 easily released by base. As a result, the acids displayed the higher efficiency than the bases. Overall,
197 it is a rather complicated reaction because of the complexity of components in alum sludge. Stark *et*
198 *al.* [14] studied the P extraction from different sludges (collected from an incineration plant and a
199 waste water treatment plant located in Sweden) by acid or base and claimed that the use of acid
200 gave a higher P extraction for all samples. Keep in mind of this, by considering the cost of HNO₃,
201 HCl and H₂SO₄ for the reagents for P extraction, H₂SO₄ was chosen for the subsequent experiments
202 since H₂SO₄ extraction is much cheaper than HNO₃ and HCl, as shown in Table 4. In addition,
203 considering the convenience and safety of operation, H₂SO₄ is better than the others as well because

204 HNO₃ and HCl are both high volatile acids with dangerous acid mist.

205 [Table 4 here]

206

207 3.2 Optimization of H₂SO₄ extraction

208 The sludge mass, H⁺ concentration and volume of solution were selected as factors in the screening
209 test, to determine their significance in maximizing the solubilization of phosphate from used alum
210 sludge under H₂SO₄ extraction. According to a Box-Behnken design, the three-level experiments
211 were carried out and the results of experimental and predicted P extraction efficiencies are presented
212 in Table 5.

213 [Table 5 here]

214

215 The following second-order fitting polynomial equation was then obtained after the data fitting.

216
$$E(\%) = 88.04 - 15.9X_1 + 13.33X_2 + 12.83X_3 - 6.75X_1^2 - 9.62X_2^2 - 8.06X_3^2 + 11.66X_1X_2 + 13.56X_1X_3 - 10.83X_2X_3 \quad (6)$$

217
$$(R^2 = 99.8\%; \quad \text{adj } R^2 = 99.4\%)$$

218 Where $E(\%)$ is the P extraction efficiency and R^2 is the coefficient of determination. The average
219 values of efficiency and SD (standard division) obtained from the triple experiments and the
220 responses predicted via Eq. (6) are jointly shown in Table 5. Obviously, a good agreement of the
221 data between the experimental and the predicted is obtained. This can be confirmed with coefficient
222 R^2 value of 0.998. R^2 is defined as the ratio of the explained variation to the total variation and is a
223 measure of the degree of fit [15]. If R^2 value is higher than 0.8, it indicates that the model explained
224 the reaction well [16].

225

226 Minitab-14 was used to determine optimum conditions of the operating variables. The
227 maximum efficiency of P extraction obtained is 97.4 %, correspondingly the maximum values of
228 the process variables in coded values were given as follows: $X_1=-1.00$, $X_2=0.167$ and $X_3=-0.16$.
229 According to relation between X_i and ψ_i , the actual values of tested variables are shown in Table 6.
230 To validate the modeled results, three additional experiments using the optimum operation
231 conditions (Table 6) were conducted. The replicate experiments yielded an average P extraction
232 efficiency of 98.2 %. This clearly demonstrated that this model is effective to optimize the H_2SO_4
233 extraction.

234 [Table 6 here]

235

236 **3.3 Extraction of other chemical components of the sludge by H_2SO_4**

237 Table 7 presents the results of the extraction of aluminum (Al), calcium (Ca), iron (Fe), magnesium
238 (Mg), nitrite and nitrate in the P-saturated alum sludge by H_2SO_4 under the optimal operational
239 conditions. It is very clear that all of them can be extracted via the release into solution except for
240 the iron, implying that H_2SO_4 has a high leachability not only for phosphorus but also for other
241 main chemical components of the sludge such as metals, nitrogen and TOC. Therefore, it is
242 confident to claim that the wetland used sludge after H_2SO_4 extraction can be disposed without a
243 risk for environment.

244 [Table 7 here]

245

246 **3.4 P recovery by deposition**

247 The H_2SO_4 extraction makes it possible for both PO_4^{3-} and Al^{3+} being released from the sludge to the

acidic solution. The molar ratio of $\text{Al}^{3+}/\text{PO}_4^{3-}$ is 2, which is suitable to form AlPO_4 by deposition. Therefore, through adjusting pH of extraction solution by adding NaOH and keeping gentle mixing for 30 min, the precipitates were formed. Such results are showed in Fig. 3. By monitoring the P concentrations in H_2SO_4 extraction solution before and after NaOH adjustment to form AlPO_4 deposition, the P reduction in proportion of P concentration before NaOH adjustment was expressed as AlPO_4 deposition efficiency in percentage, showing in Fig. 3. It is seen from Fig. 3 that the suitable pH range is 5 to 7, allowing over 98% P being deposited.

[Fig. 3 here]

4. DISCUSSION

In Ireland, due to the nature of the geographic distribution of residents, there is huge potential of application of small wastewater treatment systems. In line with the development of a novel constructed wetland system of reuse dewatered drinking water treatment sludge as wetland substrate for P-rich wastewater treatment, P extraction from the wetland used/saturated alum sludge was studied. It has been noted in the literature that P extraction from P-rich sludges using different methods has been reported. However, these sludges or sludge ash are mainly derived from wastewater treatment processes. For example, Takahashi *et al.*[17] have found that phosphorus and various heavy metals in the incinerated wastewater treatment sludge can be extracted when the pH of the ash fell below 2.0 by adding sulfuric acid. Hong *et al.*[10] revealed that phosphorus in the waste-activated sludge incinerator ash was completely extracted by 1 M HCl at the $L_{\text{acid}}S$ ratio of 6.4:1. Liao *et al.*[18,19] have reported that by using microwave treatment for only 5 min, about 80% of total phosphorus in the sewage sludge could be released into solution. However, it is not the

270 case for P-saturated alum sludge since it has been demonstrated that microwave treatment is weak
271 for P extraction according to our previous study [20]. The knowable reason for this lies in that the
272 main type of phosphorus in sewage sludge is organic-phosphorus, which can be easily released by
273 microwave heating. Comparing with sewage sludge, alum sludge has a strong affinity with P due to
274 its nature of abundant aluminum, which serves as coagulant in the main process of water treatment
275 system. Ippolito *et al.* [21] studied the P retention mechanisms of a WTR and they rejected the
276 hypothesis that P-loaded WTR will readily release P to solution. Therefore, it is more difficult to get
277 P being released/extracted. Nevertheless, this study mainly focuses on trying to explore a simple,
278 efficient, cost-effective alternative to address the puzzle of P extraction from the wetland used alum
279 sludge. From the results of this study, H₂SO₄ extraction is demonstrated to be a suitable method.

280 However, it should be pointed out that the optimal condition for H₂SO₄ extraction determined
281 by response surface methodology in this study may prove inadequate to even partially extract a
282 significant portion of total P from the substrate-WTR in real and field situation since the
283 pH-buffering capacity of the wastewater in the wetland may be much greater than the current
284 testing system that simply utilizes air-dried WTR in contact with an acidic solution.

285 Actually, H₂SO₄ extraction adopted in this study for the special case of P extraction from
286 substrate-WTR is a solvent-extraction approach. As shown in Tables 6 and 7, approximately 100%
287 of the total P and the metal-Al which seems to be the backbone of the WTR particles are extracted
288 from the WTR, suggesting that near complete dissolution and not extraction is taking place upon the
289 use of the strong sulfuric acid. Fortunately, both P and Al released from the sludge are suitable to
290 form AlPO₄ by deposition, as illustrated in Fig. 3. According to the studies of Makris *et al.* [22, 23],
291 the immobilized P by WTR was at least in the form of an organo (TOC)-Al-P amorphous moiety

292 which involved adsorption mechanism of intraparticle phosphorus diffusion [24]. Thus, the
293 extraction of P along with all other elements in the saturated WTR including metal and TOC are
294 understandable.

295 Regarding the application of WTR as raw material for wastewater treatment, it should bear in
296 mind that the characteristics of the WTR may vary significantly due to the differences in the quality
297 of the raw water and the varied treatment chemicals and processes in practice [23,25]. Therefore,
298 caution should be paid to use such the material for difference wastewater treatment.

299

300 **5. CONCLUSIONS**

301 In relation to the beneficial reuse of dewatered alum sludge as main substrate in constructed
302 wetland for P-rich wastewater treatment, studies of P desorption from P-saturated alum sludge was
303 described in this paper. Different acids (HCl, HNO₃, H₂SO₄) and bases (NaOH, KOH) as P
304 extraction reagent have been tested. The results indicated that both acid and base were efficient for
305 P-extraction and the efficiency mainly relied on the concentrations of H⁺/OH⁻, not the type of acid
306 or base. H₂SO₄ was then chosen as most suitable reagent for P-extraction. According to the response
307 surface methodology, which was applied to optimize the extraction process, the optimal condition
308 for the mass of sludge, H₂SO₄ concentration and volume of 0.8 g, 0.063 M and 142 ml, respectively,
309 could be determined. At such optimal condition, the maximum P-extraction efficiency of 98.2 %
310 was achieved. Additionally, most of the main components of the saturated sludge, such as metals
311 (Al, Ca, Mg, Fe), TOC and nitrogen can also be extracted, thus providing an environment-safe
312 sludge for final disposal.

313

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440 **FIGURES**

444
445 Fig. 1 P extraction by HCl or NaOH extraction at different time

450
451 Fig. 2 P extraction by different acid or base with different concentrations

Fig. 3 Mean values of P deposition efficiency under different pH

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487
488

TABLES

Table 1 The chemical components of the alum sludge (*DM denotes dry mass)

Chemical composition	Unit	Fresh alum sludge	P-saturated alum sludge
Total organic carbon (TOC)	% in DM*	12.8	6.9
H ₂ O (moisture content)	% in DM	22.64	21.46
Aluminum (Al)	mg/kg DM	42,880	63,020
Calcium (Ca)	mg/kg DM	1,964	16,460
Iron (Fe)	mg/kg DM	2,465	3,758
Magnesium (Mg)	mg/kg DM	46	2,377
Phosphorus (P)	mg/kg DM	154	38,590
Nitrate as NO ₃	mg/kg DM	42	366
Nitrite as NO ₂	mg/kg DM	0.4	3.2

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Table 2 Range and levels of actual and corresponded coded variables for RSM

Variables	Symbols		Levels		
	Actual	Coded	-1	0	1
Mass of alum sludge (g)	ψ_1	X_1	0.8	1.6	2.4
Concentration of H ₂ SO ₄ (M)	ψ_2	X_2	0.04	0.06	0.08
Volume of H ₂ SO ₄ solution (ml)	ψ_3	X_3	100	150	200

Note: $X_1=(\psi_1-1.6)/0.8$, $X_2=(\psi_2-0.06)/0.02$, $X_3=(\psi_3-150)/50$

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Table 3 Correlation coefficients (R^2) and rate constants (κ) of reactions

	HCl			NaOH		
	0.01 M	0.05 M	0.1 M	0.01 M	0.05 M	0.1 M
R^2	0.6091	0.9819	0.9877	0.8801	0.9858	0.9854
κ (min ⁻¹)	0.0006	0.0159	0.1243	0.0007	0.0030	0.0277

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Table 4 Cost estimation for P extraction with different acids

Acid	Price (Euro/tonne)	Cost (Euro/g P)
HNO ₃	214	7.21×10^{-3}
HCl	51	2.17×10^{-3}
H ₂ SO ₄	32	7.06×10^{-4}

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Table 5 RSM for the three experimental variables in coded units and its experimental and predicted response

Run no.	Coded factors			P extraction efficiency (%)	
	X ₁	X ₂	X ₃	Experimental	Predicted
1	-1	-1	0	87.42	85.90
2	-1	1	0	88.34	89.24
3	1	-1	0	31.68	30.78
4	1	1	0	79.25	80.76
5	0	-1	-1	31.73	33.37
6	0	-1	1	79.91	80.69
7	0	1	-1	82.48	81.69
8	0	1	1	87.33	85.69
9	-1	0	-1	90.00	89.86
10	1	0	-1	31.68	30.94
11	-1	0	1	87.67	88.40
12	1	0	1	83.59	83.72
13	0	0	0	87.33	88.04
14	0	0	0	88.18	88.04
15	0	0	0	88.61	88.04

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Table 6 Optimum value of the process parameter for maximum P extraction efficiency

Parameters	Optimum values
P extraction efficiency (%)	97.4
Mass of alum sludge (g)	0.8
Concentration of H ₂ SO ₄ (M)	0.063
Volume of solution (ml)	142

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Table 7 Extraction of other components of the sludge by H₂SO₄

Chemical components	H ₂ SO ₄ leachate	Release efficiency
Aluminum (Al)	346.4 mg/L	99.62 %
Calcium (Ca)	74.8 mg/L	82.35 %
Iron (Fe)	8.984 mg/L	43.34 %
Magnesium (Mg)	10.88 mg/L	82.94 %
Nitrate as NO ₃	1.7 mg/L	100 %
Nitrite as NO ₂	<0.05 mg/L	100 %
TOC	378.9 mg/L	99.53 %

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