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<b>Title</b>	Leachability and leaching patterns from aluminium-based water treatment residual used as media in laboratory-scale engineered wetlands
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<b>Publication date</b>	2010-08
<b>Publication information</b>	Babatunde, A.O., and Y.Q. Zhao. "Leachability and Leaching Patterns from Aluminium-Based Water Treatment Residual Used as Media in Laboratory-Scale Engineered Wetlands." Springer, August 2010. <a href="https://doi.org/10.1007/s11356-010-0311-5">https://doi.org/10.1007/s11356-010-0311-5</a> .
<b>Publisher</b>	Springer
<b>Item record/more information</b>	<a href="http://hdl.handle.net/10197/3127">http://hdl.handle.net/10197/3127</a>
<b>Publisher's statement</b>	The final publication is available at <a href="http://springerlink.com">springerlink.com</a>
<b>Publisher's version (DOI)</b>	<a href="https://doi.org/10.1007/s11356-010-0311-5">10.1007/s11356-010-0311-5</a>

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**Leachability and leaching patterns from aluminium-based water treatment  
residual used as media in laboratory-scale engineered wetlands**

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35 **Abstract**

36 **Concept and purpose**

37 Virtually all water treatment facilities worldwide generate an enormous amount of water treatment  
38 residual (WTR) solids for which environmentally-friendly end-use options are continually being  
39 sought as opposed to their landfilling. Aluminium-based WTR (Al-WTR) can offer huge benefits  
40 particularly for phosphorus (P) removal and biofilm attachment when used as media in engineered  
41 wetlands. However, potential environmental risks that may arise from the leaching out of its  
42 constituents must be properly evaluated before such reuse can be assured. This paper presents  
43 results of an assessment carried out to monitor and examine the leachability and leaching patterns of  
44 the constituents of an Al-WTR used as media in laboratory scale engineered wetland systems.

45 **Main features, materials and methods**

46 Al-WTR was used as media in four different configurations of laboratory scale engineered wetland  
47 systems treating agricultural wastewater. Selected metal levels were determined in the Al-WTR  
48 prior to being used while levels of total and dissolved concentration for the metals were monitored  
49 in the influent and effluent samples. The increase or decrease of these metals in the used Al-WTR  
50 and their potential for leaching were determined. Leached metal levels in the effluents were  
51 compared with relevant environmental quality standards to ascertain if they pose considerable risks.

52 **Results**

53 Aluminium, arsenic, iron, lead, and manganese were leached into the treated effluent, but  
54 aluminium exhibited the least leaching potential relative to the initial content in the fresh Al-WTR.  
55 Levels of P increased from 0.13 mg-P/g (fresh Al-WTR) to 33.9 mg-P/g – 40.6 mg-P/g (used Al-  
56 WTR). Dissolved levels of lead and arsenic (except on one instance) were below the prescribed  
57 limits for discharge. However, total and dissolved levels of aluminium were in most cases above the  
58 prescribed limits for discharge, especially at the beginning of the experiments.

59 **Conclusions, recommendations and perspectives**

60 Overall, the study indicate that when Al-WTR is beneficially reused for enhanced P removal in  
61 engineered wetlands as opposed to landfilling it, the leaching out of aluminium into the treated

62 effluent beyond the prescribed limits of 0.2mg/l may be a potential problem. However, since the  
63 results obtained indicate that most of the aluminium leached out are associated with solids, a post-  
64 treatment unit which can further reduce the level of aluminium in the treated effluent by filtering  
65 out the solids could serve to mitigate this. Notwithstanding, the use of Al-WTR as a media in  
66 engineered wetlands can serve to greatly enhance the removal of P from wastewaters and also serve  
67 as support material for biofilm attachment.

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**Key words** engineered wetlands, leaching, metals, phosphorus, reuse, water treatment residual

## **1 Introduction**

Water treatment residual (WTR) refers to the inevitable by-product obtained as a result of the drinking water treatment processes in water treatment facilities worldwide. The disposal of WTRs has become an integral part of the operation and management of water treatment facilities due to stringent regulations. Several authors have shown that common options for managing WTRs are not optimal solutions and several alternative WTRs management methods have been highlighted with major emphasis placed on reusing or recycling WTRs (Bourgeois et al. 2004; Babatunde and Zhao 2007). Currently, there are over eleven ways in which WTRs are being reused (Babatunde and Zhao 2007), but there is yet to be any reuse option that can utilize the vast amount of WTRs generated daily worldwide. Therefore, the need for a continued research into reuse/recycle options for WTRs is continuing. A recent and growing trend in research is the possible reuse/recycle of WTR in wastewater treatment. In particular, it has been demonstrated that aluminium-based WTR (Al-WTR) which is derived from water treatment facilities that use aluminium salts as coagulant can be a good adsorbent material for a variety of contaminants in wastewaters including phosphorus (P) (Babatunde and Zhao 2007). Al-WTR is the most widely generated WTR worldwide, prompting increased concerns as regards its disposal and/or alternative beneficial reuses.

Another new and novel way of reusing Al-WTR in wastewater treatment is utilizing it as media in engineered wetland systems for wastewater treatment. Our previous studies have confirmed that Al-WTR can bring about significant improvements in P removal in engineered wetland systems due to its high P adsorption capacity (Yang et al. 2006; Babatunde et al. 2007) and it can also successfully act as a biofilm carrier in such systems (Zhao et al. 2009). This can bring about enhanced reduction of P in wastewater during treatment in engineered wetlands. In addition, Al-WTR is an easily available by-product in towns, cities and metropolis regions worldwide that utilize surface waters as

114 a drinking water source. Any attempt to reduce P in wastewaters is valuable because inputs of P to  
115 rivers and lakes from point and diffuse sources continue to pose an environmental problem that is  
116 gaining increased attention. While there are a number of ways and technologies to remove P from  
117 wastewater, most involve the use of expensive chemicals and the generation of a secondary sludge.  
118 On the other hand, engineered wetland systems are fast becoming a preferred wastewater treatment  
119 system of choice for treating a diverse range of wastewaters due to their green appeal, low cost,  
120 ease of construction and operation, low environmental footprint and good performance in terms of  
121 organics removal. However, their performance in terms of nutrient removal (especially P) is often  
122 inconsistent and poor. Therefore, the possibility of using a residual waste material such as Al-WTR  
123 in an engineered wetland system to particularly enhance P removal from wastewaters before entry  
124 into water bodies is quite an attractive and strategic initiative.

125 This current work is part of a larger project being carried out for the past five years at the University  
126 College Dublin, Ireland, towards developing a novel Al-WTR based engineered wetland system for  
127 wastewater treatment. After extensive studies on: (i) characterizing and identifying the P  
128 adsorption capacity of the Al-WTR (Yang et al. 2006; Babatunde et al. 2009) (ii) examining the  
129 removal efficiencies of other pollutants (COD, BOD<sub>5</sub>) using Al-WTR as main substrate in  
130 engineered wetland systems (Zhao et al. 2009) (iii) investigating the forms and patterns of P  
131 retained in the used Al-WTR (Babatunde and Zhao 2009) and (iv) recovering P from the P  
132 saturated Al-WTR (Zhao and Zhao 2009), the development of the novel engineered wetland system  
133 has been focused on addressing the possible release of substances from the Al-WTR into the treated  
134 effluent during such reuse. The potential leaching of the constituents of the Al-WTR becomes an  
135 environmental issue of priority when it is reused. As such, this study provides a vital background  
136 concerning such potential release and possible means of mitigating such release.

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138 Few studies have been conducted to address this concern. Cornwell et al. (1992) investigated the  
139 leaching of various metals from a WTR using Toxicity Characteristic Leaching Procedure (TCLP).  
140 It was reported that aluminium (Al) concentrations were particularly negligible for the 1.1m of  
141 rainfall permeated through the wet residual solids columns over the study period. Similarly, Hsieh  
142 et al. (2000) investigated several factors that may affect the leaching of metals from WTR during  
143 reuse. It was concluded that pH and metal solubility can affect the release of metals in the WTR  
144 while it was concluded that the particle size of the WTR has no significant effect on the metal  
145 leaching. In other studies, Hsieh et al. (2006) studied the leaching of metals and organic chemicals  
146 from WTR using a model monofill. Manganese (Mn) was reported to have the highest leaching  
147 capability, while the quantity of calcium (Ca) in the leachate was noted to increase appreciably with  
148 time. However, none of the studies evaluated the leaching tendency of the sludges in real reuse  
149 situations.

150 In this study, we seek to determine whether the constituents (particularly metals) of Al-WTR will  
151 leach out when it is being reused as a media in engineered wetland systems, particularly to enhance  
152 P removal. We also determined the levels of leached metals in the treated effluent. Four laboratory  
153 scale engineered wetland systems using Al-WTR as main media for enhanced P removal were  
154 constructed and set up to treat wastewater from an animal research farm. The levels of specific  
155 elements/metals were monitored in the Al-WTR and in the influent and effluents of the four  
156 systems over a 25 weeks period. This paper presents the data obtained during the study and  
157 discusses the potential leaching and leachability of specific elements/metals from the Al-WTR  
158 during such reuse. The leaching patterns were also examined and the inferences made would  
159 provide real and useful information for further field application of the Al-WTR as a P removing  
160 media for engineered wetlands.

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## 2 Materials and methods

### 2.1 Al-WTR and effluent samples

Al-WTR was obtained from the biggest water treatment plant in Ireland, located on the shores of a 5,000 acres Poulaphuca reservoir in Co. Kildare, Ireland. The plant uses aluminium sulphate as the primary coagulant and serves approximately one-third of the entire Irish population, producing 230,000 m<sup>3</sup>/d of potable water and generating 45-75 tonnes of Al-WTR daily. X-ray diffraction and SEM-EDX (scanning electron microscope-energy dispersive X-ray) analyses both showed that the Al-WTR is mainly composed of amorphous aluminium and it has a high P adsorption capacity (Babatunde et al. 2009). Upon collection, the Al-WTR was transported to the laboratory and air-dried. Thereafter, the Al-WTR was ground to pass a 2-mm mesh sieve and then used as the main substrate in four laboratory scale engineered wetland systems. The engineered wetlands were simulated in the laboratory using Pyrex tubes which were 900 mm in height and 95 mm in diameter.

Fig. 1 shows a schematic diagram of the set-up of the four systems labelled as 1, 2, 3 and 4 respectively. Gravel was used at the base of all the systems to act as support for the Al-WTR. Systems 2, 3 and 4 contained pea gravel up to varying depths as shown in Fig. 1. Thus the proportions of pea gravel in the systems were 0%, 20%, 40% and 60% for systems 1, 2, 3 and 4 respectively. This translates to 100%, 80%, 60% and 40% by proportion of Al-WTR in the systems 1, 2, 3 and 4 respectively. At the time of the experiments, the pea gravels were used in the systems to examine their effect on improving wastewater flow and delaying clogging. Therefore, it should be noted that each individual configuration of the systems represents a potential configuration for the final field-scale system from the point of view of delayed clogging and P removal. We have examined the influence of the pea gravel and the different configurations on P removal and delayed clogging between the systems (Babatunde, 2007). This study is concerned with monitoring the release or otherwise of substances from the Al-WTR into the treated effluent from each of the individual systems. All the systems were fed from the same feed tank which contains wastewater



191 collected from an animal research farm. The wastewater had a typical concentration (after  
192 settlement) of 322-510 mg/l (SS), 720-1523 mg/l (COD), 540-850 mg/l (BOD<sub>5</sub>), 48-73 mg/l (P) and  
193 6.7-7.4 (pH).

194

195 **[INSERT FIG. 1 HERE]**

196 **Fig. 1** Schematic diagram of the laboratory scale engineered wetland systems

197

198 The wastewater was introduced into the systems in batches of 6-8 daily feeding regimes and this  
199 was carried out using programmed peristaltic pumps. The designed hydraulic loading rate ranged  
200 between 1.23-1.86 m<sup>3</sup>/m<sup>2</sup>.d across the systems. The experiment was conducted for 25 weeks. At the  
201 end of the experiments, used Al-WTR samples were collected from the topmost layer of the Al-  
202 WTR in the systems. This is the Al-WTR layer that is first in contact with the wastewater passing  
203 through the system and which would reasonably be the most loaded Al-WTR layer. The sampling  
204 of the used Al-WTR was limited to the topmost layer of the Al-WTR in each system due to the high  
205 cost involved in analysing all the samples. Both the used Al-WTR samples collected and the fresh  
206 Al-WTR samples were stored in the refrigerator at  $\approx 4^{\circ}\text{C}$  until they were analysed according to  
207 standard recommendations (Pierzynski 2000). At the same time, samples from the feed tank and  
208 effluent samples from the systems were collected on three occasions during the 25-week operating  
209 period and specifically analysed for metals. The first set of samples were taken immediately after  
210 the commencement of operation (referred to as period 1), the second set was taken at about mid-  
211 way into the entire operational time (referred to as period 2), while the last set of samples were  
212 taken at the end of the experiments (referred to as period 3).

## 213 **2.2 Analytical procedures and methods**

214

215 To obtain the total metals in the Al-WTR samples, an Anton Paar MULTIWAVE microwave  
216 sample preparation system was used to digest the samples. The metals analysed were selected based  
217 on their relative presence in the Al-WTR as observed in the initial analysis obtained from the plant

operators. The use of microwave enhanced acid digestion of solid samples for elemental analysis is now well established as a routine sample preparation method (Jin et al. 1999), and it is noted to be a rapid and efficient method of sample decomposition prior to the determination of metals (Robache et al. 2000). The low volume microwave digestion allows the determination of analytes in small samples ( $< 0.1\text{g}$ ), thereby avoiding reduction in method sensitivity (Sandroni et al. 2003). Approximately 0.025 g of the Al-WTR samples (fresh and used) was weighed into clean TMF (trifluoromethylene) vessels followed by the addition of 4 ml  $\text{HNO}_3$  + 200  $\mu\text{l}$  HF + 4 ml  $\text{H}_2\text{O}$ . A built-in computer program was used to specify the decomposition program, control the MULTIWAVE, and hold a library of sample data. When decomposition is complete, the sample is transferred to a volumetric flask and the volume is made up to 15 ml. These were then sent out to a certified laboratory for total metal analysis. Total and dissolved metal analysis on samples from the feed tank (influent) and samples from the systems (effluent) was also done through the contracted certified laboratory using ICP (IRIS) and ICP-MS for the total and dissolved metals respectively. The method detection limits (MDL) are included in Table 1. All sample handling/preservation and classification were done according to standard methods (APHA-AWWA-WEF 1998).

233

234

### 235 **2.3 Leaching Potential (L.P)**

236

237 An attempt was made in this study to quantify the relationship between quantities of  
238 elemental/metals in the effluents and their corresponding quantity in the fresh Al-WTR. Following a  
239 similar work done by Hsieh et al. (2006), the leaching potential of the respective constituents of the  
240 Al-WTR was determined as a ratio of the mass of the constituent in the leachate at time  $t$ , to the  
241 corresponding mass of the constituent present in the unused Al-WTR using Eq. (1). This gives a  
242 sort of indication as to the relative potential for leaching (leachability) for the respective  
243 constituents in the Al-WTR.

$$L.P = G \left( \frac{C_{abs}}{C_f} \right) \quad (1)$$

where G is determined by Eq. (2)

$$G = \frac{1 - S}{10S} \quad (2)$$

and  $C_{abs}$  is given by Eq. (3)

$$C_{abs} = C_{eff} - C_{inf} \quad (3)$$

$C_{abs}$  (mg/l) is absolute concentration of the constituent in the effluent,  $C_f$  (mg/g) is the concentration of the constituent in the unused Al-WTR and  $S$  is the solids content.  $C_{eff}$  and  $C_{inf}$  represent the respective concentration of the constituent in the effluent and influent in mg/l. The value of G was computed to be 0.075 for a solids content of 0.57.

### 3 Results and discussion

#### 3.1. Changes in the element/metal concentration of Al-WTR used as substrate in engineered wetlands

Fig. 2 shows the elemental/metal concentration in the Al-WTR, before and after use in the four engineered wetland systems. It should be quickly pointed out that the level of metals in the fresh Al-WTR, particularly those of lead (Pb) and zinc (Zn) are below their typical levels in uncontaminated soils (Elliot et al. 1990; Elliot and Dempsey 1991). The metal levels are also in range with those reported for WTRs by other authors (DeWolfe 2006; Makris and O'Connor 2007). Al had the highest proportion by composition in the Al-WTR. Al (expressed as  $Al_2O_3$ ) accounted for 8.1% of the sampled Al-WTR. In separate reviews on WTRs, Babatunde and Zhao (2007) reported a mean value of 29.7% Al for Al-WTR (which is equivalent to 56.1% Al expressed as  $Al_2O_3$ ), while from Makris and O'Connor (2007), a range of 2.9 to 57% Al as  $Al_2O_3$  can be inferred. Thus the Al-WTR

269 samples used in this study can be suggested to be in the lower end of the range of aluminium  
270 concentrations in such WTRs.

271

272 **[INSERT FIG. 2 HERE]**

273 **Fig. 2** Elemental/metal concentration in the fresh and used Al-WTR samples from the four  
274 engineered wetland systems (1, 2, 3 and 4 refer to the engineered systems respectively)

275

276 The concentrations of elements/metals in the Al-WTR before and after use give an idea of whether  
277 they are leached or not. By comparing the concentrations of elements/metals in the fresh and used  
278 Al-WTR samples as shown in Fig. 2, it can be observed that the concentrations of Al, arsenic (As),  
279 iron (Fe), Pb and Mn were all decreased. On the other hand, the concentration of P, Ca, Mg, Zn and  
280 titanium (Ti) were increased. Leaching of constituents from WTR has been reported in literature  
281 (Cornwell et al. 1992), although simulated conditions were used. Hsieh et al. (2006) noted that the  
282 amount of metals retained in a WTR depends on the form of metals and the anion group that they  
283 are associated with, while Elliot et al. (1990) noted that the extent to which metals are solubilised  
284 depends on a variety of factors. Thus, the release or otherwise of any metal will be specific to the  
285 metal and several complex and interacting processes.

286 By comparing the results of analyses of fresh and used Al-WTR from systems 1, 2, 3 and 4 as  
287 shown in Fig. 2, it can be seen that there was consistency in the elements/metals that showed  
288 increase or decrease in concentration. However, the magnitudes of the increase or decrease in  
289 concentration were not the same and do not reflect the differences in the proportion of Al-WTR in  
290 the systems. For instance, system 1 had the highest proportion of Al-WTR (100%), but the increase  
291 or decrease in the concentration of the elements/metals was not always the highest. Similarly,  
292 although system 4 had the least proportion of Al-WTR in its composition, it had the same  
293 magnitude of decrease for Pb as the other systems, while the decrease in Fe was more in the system  
294 than in system 2.

295 The pH levels of the influent and effluents of the four systems did not reveal any marked difference  
296 and it ranged from 6.7-7.4 and 6.8 to 7.2 for the influent and effluent respectively. In addition, the  
297 pH did not vary greatly across the four systems. It is therefore likely that other inherent conditions  
298 that are specific to each of the systems might have influenced the increase or decrease in the  
299 concentration of the elements/metals. From Fig. 2, it can also be seen that across the systems, the  
300 relative decrease in As concentration was the highest, followed by Mn and then Al. There was also  
301 an indication of slight decrease in Pb concentrations. The release of Mn might suggest a reducing  
302 environment. On the other hand, the increase in P was highest across the systems, followed by Ca,  
303 Zn, Mg and Ti. The huge increase in P concentration in the used Al-WTR attests to the high P  
304 adsorption capacity of the Al-WTR. In our previous studies, it was shown that Al-WTR has a  
305 preferential adsorption for P (Yang et al. 2006) and the adsorption capacity of the Al-WTR can  
306 range from 10.2 mg-P/g to 31.9 mg-P/g (determined using the Langmuir adsorption isotherm)  
307 (Babatunde, 2007).

308 In all the samples analysed, the percentage of increase in P was between 1-3 orders of magnitude  
309 higher than the increases in Ca, Zn and Mg highlighting the capacity and preference of the Al-WTR  
310 for P adsorption. The increases in Ca, Zn and Mg also show the adsorption ability of the Al-WTR  
311 for other ions. Elliot et al. (1990) remarked in their study that freshly precipitated hydrous oxides  
312 have a large capacity to occlude, coprecipitate, and sorb divalent metal ions from the surrounding  
313 aqueous media, despite an unfavourable surface charge. Overall, these results indicate a  
314 simultaneous uptake and release of substances from the Al-WTR matrix when used as a media in an  
315 engineered wetland system. The uptake of certain elements from the wastewater is desirable and  
316 beneficial, in particular P. However, the potential release of some metals from the Al-WTR is not  
317 totally desirable, but caution is needed before any conclusion can be made and the release pathway  
318 needs to be established.

319

320 **3.2. Monitoring of levels of elements/metals from the leachate of the Al-WTR-based**  
321 **engineered wetland systems.**  
322

323 Table 1 shows the levels of total and dissolved metals in the influent and effluent of the four  
324 systems across the three periods. Any increase in the level of the metals in the effluents may suggest  
325 the leaching of the metal from the Al-WTR into the effluent, while decrease in the level of any  
326 metal can equally suggest uptake of the metal by the Al-WTR. In most cases, the levels of dissolved  
327 metal concentration were compared with prescribed limits. This is because metal levels associated  
328 with solids can be removed/reduced by including an in-line filtration unit in the system design.  
329 Therefore, by checking the level of dissolved metals against the prescribed limits, recommendations  
330 can be made as to whether further treatment unit will be required. From Table 1, it can be observed  
331 that the level of Al (both total and dissolved) in the effluents was always higher than that in the  
332 influent (feed) in all the cases except on one occasion. This indicates that there was some release of  
333 Al into the treated wastewater during passage through the systems. Although the influent  
334 wastewater had some background Al concentration, this is quite small, compared to the level in the  
335 effluents. In addition, based on the level of total and dissolved concentration of Al in the influent, it  
336 can be inferred that most of the Al in the influent is probably associated with the solids. The results  
337 also indicate that the relative proportion of dissolved Al to the total Al in the effluent decreased  
338 over the periods.

339

340 **[INSERT TABLE 1 HERE]**

341

342 For instance, from Table 1, the proportion of dissolved Al to total Al for system 1 decreased from  
343 1.2 during the first period to 0.4 and 0.7 during the second and third period respectively. This may  
344 suggest that Al leached to a great extent at the beginning of the experiment. Over the three periods,  
345 levels of dissolved Al monitored in the effluent from all the systems ranged from 58 µg/l to 1106  
346 µg/l. The prescribed limit for Al for discharge into all waters is 200 µg/l (EPA 1997; UK Technical

347 Advisory Group 2008). This limit was exceeded in about 66.7% of all of the sampling cases with  
348 most of the exceedances occurred during the early stages of the experiment.

349 The level of As (total) in the effluent was relatively stable over time. However, although the level of  
350 dissolved As changed over time in the effluent, the result suggests that most of the As in the  
351 effluent was held in the solid phase. Notwithstanding, the level of dissolved As in the effluent  
352 ranged from 3 µg/l to 63 µg/l. Except on one occasion, the dissolved As levels were all below the  
353 prescribed limits of 50 µg/l for discharge into freshwaters (EPA 1997; UK Technical Advisory  
354 Group 2008). Ca in the influent wastewater was mostly in the soluble form, probably associated  
355 with CaCO<sub>3</sub>. However, from Table 1, it can be seen that there was a huge reduction in the level of  
356 Ca in the effluent exiting all the systems as compared to the Ca levels in the influent. It was also  
357 noted that there was a corresponding huge increase in the concentration of Ca in the used Al-WTR  
358 samples from all the systems as shown in Fig. 2. This implies that the Ca ions were removed from  
359 solution, possibly by adsorption/precipitation on the Al-WTR.

360 The level of total Fe in the influent was in most cases, higher than the level in the effluent, but the  
361 inverse was mostly the case for dissolved Fe. It can be suggested that most of the Fe is held in the  
362 solid phase in the influent and possibly filtered out onto the Al-WTR. Hence the level in the effluent  
363 is mostly lower than the level in the influent. The higher level of dissolved Fe in the effluent than in  
364 the influent may however suggest some release/dissolution of Fe held in the solid phase in the  
365 influent into the effluent. It should however be noted that at all times, the concentration of Fe in the  
366 effluent were very well below the prescribed limits of 1.0 mg/l for discharge into all waters (EPA  
367 1997; UK Technical Advisory Group 2008).

368 The concentration of dissolved Pb in the effluent ranged from <1 µg/l to 5 µg/l and this is clearly  
369 below the prescribed limit of 50 µg/l for discharge into freshwaters (EPA 1997; UK Technical  
370 Advisory Group 2008). Mg levels were decreased in the effluents but increased in the used Al-WTR  
371 samples. This has potential benefits as the increase in the Mg level of the Al-WTR can increase its

micronutrient value. To some extent, Mn may have leached from the Al-WTR into the effluent samples. This is however a bit difficult to ascertain, since the influent also contain some level of Mn which was higher than the level in the effluent in some instances. There were also decreases in the level of Zn (both total and dissolved) and this can be explained by the ability of the Al-WTR to further adsorb Zn from the aqueous solution, based on the increase in Zn concentration in the Al-WTR as shown in Fig. 2.

### 3.3. Leaching Potential (L.P)

The L.P covering ten elements/metal for the systems over the three periods is shown in Table 2. In calculating the L.P, only values of dissolved concentration were used, thus excluding metals/constituent associated with the solid phase. Analysing across the periods, it can be seen that Mn has the highest L.P during the first period, while Zn had the highest L.P in the second (excluding system 3) and third period (excluding system 4). Using system 1 as a typical case, the pattern of L.P in decreasing order was Mn > Ti > Al > Fe in the first period, Zn > As > Al in the second period and Zn > As > Pb > Fe > Al in the third period (note that only constituents that appear to be leached during each period of assessment were ranked. Constituents are deemed leached if the level of the respective metal is higher in the effluent than in the influent). It can be observed that relatively, Al had the lowest L.P (for the elements that leached).

[INSERT TABLE 2 HERE]

It can also be seen that the leaching of As was observed over time, while the intensity of leaching of Mn decreased over time. Similar, but slightly different patterns were also observed for the other systems. For instance, the pattern for system 2 was Mn > Ti > Fe > Al in the first period, Zn > As > Pb > Al in the second period, and Zn > As > Pb > Fe > Al in the third period. In this case, it can also be observed that Al had the lowest L.P across all the periods while there was an increase in the



leaching intensity of As observed over time. The intensity of leaching of Mn similarly decreased over time. The slight differences in the L.P. for the different metals in the systems may be due to differences in the prevailing conditions in the systems. However, it is very useful to note that, relative to the initial level of constituents in the fresh Al-WTR, Al had a relatively low L.P. as compared to the L.P for all the other metals that were leached. This is in agreement with the findings of other authors (Cornwell et al. 1992; Hsieh et al. 2006) which showed that Al leached out in very small quantities from WTRs. It can thus be reasonably inferred that, although Al did leach out from the Al-WTR used in this study, the relative quantity leached out is small. It should however be stressed that due to its high content in the fresh Al-WTR, the concentrations of Al in the effluent were above the limit values allowed for disposal in the majority of the cases.

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## 410 **Conclusions**

This study examined the leachability and leaching patterns of elements/metals from engineered wetland systems set-up using an aluminium based-water treatment residual as the media. Results reveal that aluminium, arsenic, iron, lead and manganese leached out in varying quantities, while phosphorus, calcium, magnesium, zinc and titanium were adsorbed. Phosphorus increased from 0.13 mg-P/g in the fresh Al-WTR to 33.9 mg-P/g – 40.6 mg-P/g in the used Al-WTR. Dissolved levels of lead and arsenic in effluents range from <1 µg/l to 5 µg/l and 3µg/l to 63 µg/l respectively, and these were below the prescribed limits of 50µg/l (except arsenic on one instance) for their respective discharge into freshwaters. However, dissolved levels of aluminium ranged from 58 µg/l to 1106 µg/l with about 66.7% of samples above prescribed limit of 200 µg/l for aluminium. While the use of the aluminium based-water treatment residual as the media in engineered wetland showed great promise particularly for phosphorus removal, a post-treatment unit may be required to reduce aluminium levels in the treated effluent.

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## Acknowledgements

Financial support obtained from the Environmental Protection Agency Ireland (*grant no: 2005-ET-MS-38-M3*) is hereby acknowledged. Mr. Patrick Kearney, Section head technician, Water and Effluents Laboratory, UCD and Dr Dave Healy of University College Cork are also thanked for their assistances.

## References

- APHA-AWWA-WEF (1998) Standard methods for the examination of water and wastewater, 20<sup>th</sup> ed., American Public health association, Washington, DC.
- Babatunde AO (2007) The development of an alum sludge based tidal flow constructed wetland for optimizing phosphorus and organic matter removal from wastewaters, PhD dissertation, University College Dublin, Ireland.
- Babatunde AO, Zhao YQ (2007) Constructive approaches towards water treatment works sludge management: An international review of beneficial re-uses. *Crit. Rev. Environ. Sci. Tech.* 37: 129-164.
- Babatunde AO, Zhao YQ, Yang Y, Kearney P (2008) Reuse of dewatered aluminium- coagulated water treatment residual to immobilize phosphorus: Batch and column trials using a condensed phosphate. *Chemical Engineering Journal* 136:108-115.
- Babatunde AO, Zhao YQ (2009) Forms, patterns and extractability of phosphorus retained in alum sludge used as substrate in laboratory-scale constructed wetland systems. *Chemical Engineering Journal* (in press) doi:10.1016/j.cej.2009.03.020
- Babatunde AO, Zhao YQ, Burke AM, Morris MA, Hanrahan JP (2009) Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environmental Pollution* (in press) doi:10.1016/j.envpol.2009.04.016
- Bourgeois JC, Walsh ME, Gagnon GA (2004) Comparison of process options for treatment of water treatment residual streams. *Environ. Eng. Sci.* 3:477-484.
- Cornwell DA, Vandermeiden C, Dillow G, Wang M (1992) Landfilling of water treatment plant coagulant sludges. Project No. 512, AWWA research foundation. Denver, Colorado, USA.
- Dayton EA, Basta NT (2001) Characterization of drinking water treatment residuals for use as a soil substitute. *Water Environ. Res.* 73:52–57.
- DeWolfe J (2006) Water residuals to reduce soil phosphorus, AWWA research foundation.
- Elliot HA, Dempsey BA, Maille PJ (1990) Content and fractionation of heavy metals in water treatment sludges. *J. Environ. Qual.* 19:330–334.
- Elliot HA, Dempsey BA (1991) Agronomic effects of land application of water treatment sludges. *J. Am. WaterWorks Assoc.* 4:126-131.
- EPA (1997) Environmental Quality Objectives and Environmental Quality Standards: The aquatic environment- A discussion document. Environmental Protection Agency (EPA), Ardcavan, Wexford, Ireland.
- Hsieh H, Tian P, Raghu D (2000) Leaching of metals from water treatment plant residuals. *Practice periodical of hazardous, toxic, and radioactive waste management*, 4:134-139.
- Hsieh H, Raghu D, Tian P (2006) Leaching studies on a model monofill of water treatment plant residuals. *Env. Eng. Sci.* 23:230-238.
- Jin Q, Liang F, Zhang H, Zhao L, Huan Y, Song D (1999) Microwave technique in analytical chemistry. *Trends Anal. Chem.* 18: 479-484.

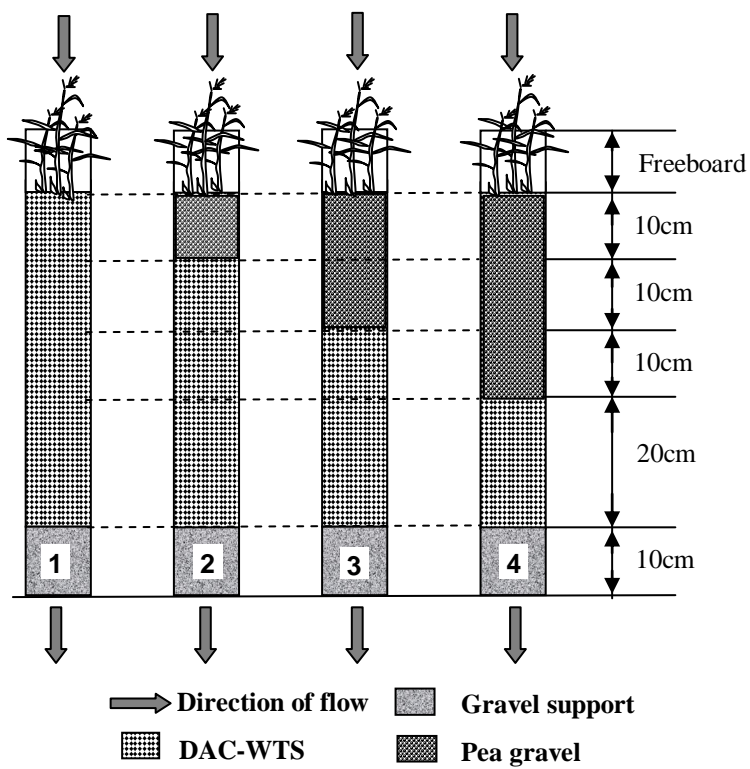
- Makris KC, O'Connor GA (2007) Beneficial utilization of drinking-water treatment residuals as contaminant-mitigating agents. In: D. Sarkar, R. Datta and R. Hannigan, Eds, Concepts and applications in environmental geochemistry, Elsevier, Amsterdam pp 609–635.
- Pierzynski GM (2000) In: Methods of soil phosphorus analysis for soils, sediments, residuals and waters. Ed. Pierzynski, G.M., Southern Cooperative series bulletin No. 396
- Robache A, Mathe F, Galloo JC, Guillermo R (2000) Multi-element analysis by inductively coupled plasma optical emission spectrometry of airborne particulate matter collected with a low-pressure cascade impactor. *Analyst*, 125:1855-1859.
- Sandroni V, Clare MM, Donovan A (2003) Microwave digestion of sediment, soils and urban particulate matter for trace metals analysis. *Talanta*, 60:715-723.
- UK Technical Advisory Group on the Water Framework Directive (2008). Proposals for Environmental Quality Standards for Annex VIII substances. Final report SR1-2007.
- Yang Y, Zhao YQ, Babatunde AO, Wang L, Ren YX, Han Y (2006) Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Sep. Purif. Technol.* 51:193–200.
- Zhao YQ, Zhao X.H, Babatunde AO (2009) Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial. *Bioresour. Technol.* 100: 644-648.
- Zhao X.H, Zhao YQ (2009) Investigation of phosphorus desorption from P-saturated alum sludge used as a substrate in constructed wetland. *Sep. Purif. Technol.* 66:71-75.

509    **LIST OF FIGURES**

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- Fig. 1    Schematic diagram of the laboratory scale engineered wetland systems
- Fig. 2    Elemental/metal concentration in the fresh and used AI-WTR samples from the four  
              engineered wetland systems (1, 2, 3 and 4 refer to the engineered systems respectively)

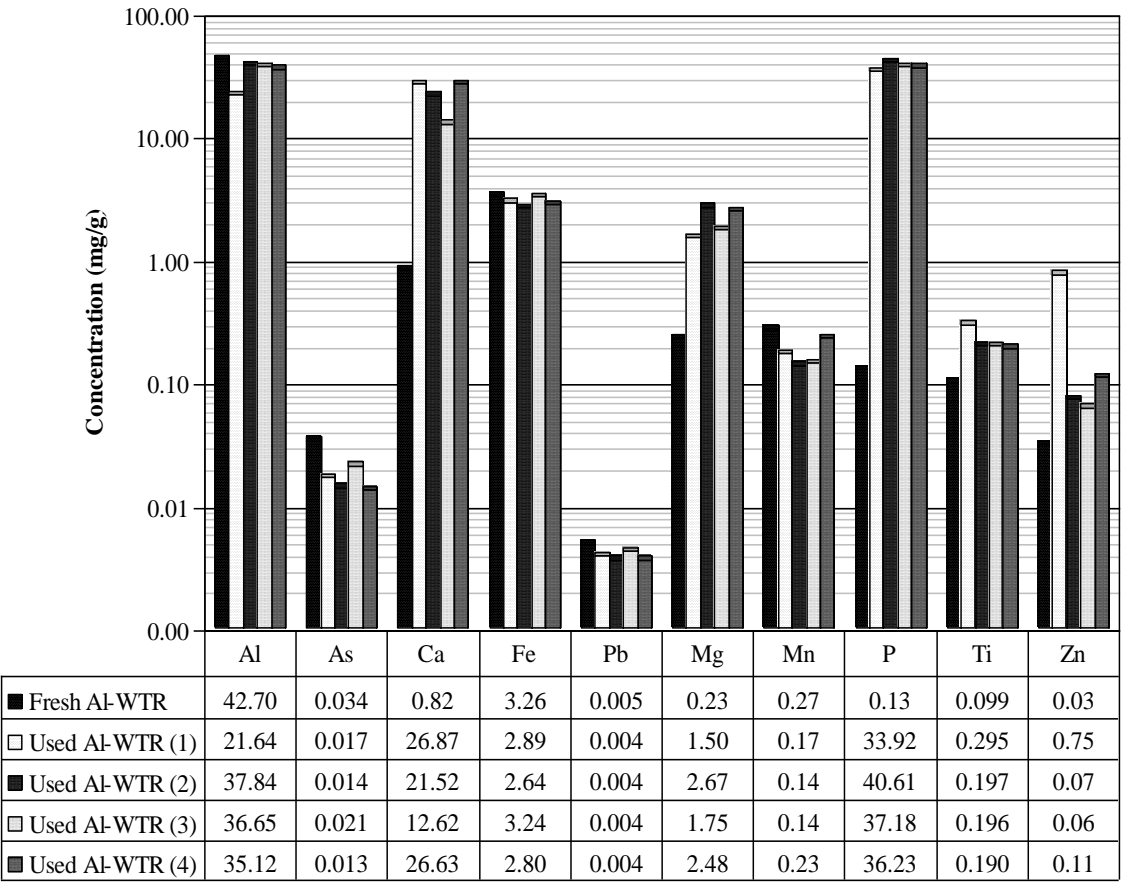
537 **Fig. 1**



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Fig. 2



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Table 1. Levels of individual elements/metals in the influent and effluent of the four systems across the

Parameter		Element/metal						
		Al	As	Ca	Fe	Pb	Mg	Mn
		MDL( Tot)	<0.05mg/l	<0.05mg/l	<0.05mg/l	<0.05mg/l	<0.05mg/l	<0.05mg/l
		MDL( Dis)	<2µg/l	<1µg/l	<120µg/l	<2µg/l	<100µg/l	<1µg/l
Tot. Conc <sup>a,1</sup>	mg/l		0.16	<0.05	87.99	0.90	<0.05	14.96
Tot. Conc <sup>a,1</sup>			0.41	<0.05	13.96	0.20	<0.05	1.52
Tot. Conc <sup>a,2</sup>			0.48	<0.05	16.47	0.16	<0.05	1.64
Tot. Conc <sup>a,3</sup>			1.50	<0.05	15.69	0.35	<0.05	4.53
Tot. Conc <sup>a,4</sup>			0.52	<0.05	25.13	0.25	<0.05	7.58
Dis. Conc <sup>a,1</sup>	µg/l		<2	4	85 990	28	<1	21 990
Dis. Conc <sup>a,1</sup>			490	3	11 050	57	<1	1578
Dis. Conc <sup>a,2</sup>			479	4	14 530	121	1	1776
Dis. Conc <sup>a,3</sup>			1106	5	16 060	271	5	9081
Dis. Conc <sup>a,4</sup>			505	4	30 160	231	3	14 390
Tot. Conc <sup>b,i</sup>	mg/l		0.16	<0.05	60.29	0.94	<0.05	11.57
Tot. Conc <sup>b,1</sup>			0.42	<0.05	10.75	0.80	<0.05	2.08
Tot. Conc <sup>b,2</sup>			0.23	0.07	18.86	0.70	<0.05	6.02
Tot. Conc <sup>b,3</sup>			0.31	<0.05	36.32	0.27	<0.05	11.75
Tot. Conc <sup>b,4</sup>			0.14	0.07	41.97	0.20	<0.05	10.04
Dis. Conc <sup>b,i</sup>	µg/l		34	5	52 030	547	<1	16 880
Dis. Conc <sup>b,1</sup>			172	35	6968	488	1	2459
Dis. Conc <sup>b,2</sup>			174	18	16 190	648	2	8890
Dis. Conc <sup>b,3</sup>			250	4	39 660	197	2	19 230
Dis. Conc <sup>b,4</sup>			58	4	46 890	151	3	16 730
Tot. Conc <sup>c,i</sup>	mg/l		0.18	<0.05	43.32	0.57	0.05	9.73
Tot. Conc <sup>c,1</sup>			0.40	<0.05	15.33	0.43	<0.05	6.45
Tot. Conc <sup>c,2</sup>			0.71	<0.05	18.55	0.83	<0.05	6.01
Tot. Conc <sup>c,3</sup>			0.31	<0.05	29.76	0.35	<0.05	9.30
Tot. Conc <sup>c,4</sup>			0.26	0.11	31.34	0.29	<0.05	8.40
Dis. Conc <sup>c,i</sup>	µg/l		16	5	43 780	238	<1	16 480
Dis. Conc <sup>c,1</sup>			291	27	13 650	407	2	9676
Dis. Conc <sup>c,2</sup>			616	63	14 000	706	2	8489
Dis. Conc <sup>c,3</sup>			203	36	29 280	266	2	14 380
Dis. Conc <sup>c,4</sup>			142	41	32 580	210	2	13 150

Tot =Total, Dis=Dissolved, a, b and c refers to the first, second and third period of sampling, 1, 2, 3 and 4 refer to the system

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Table 2 Leaching potentials for the elements/metals across the four systems for the three periods

Element /metal	Period 1				Period 2				1
	1	2	3	4	1	2	3	4	
Al	0.0009	0.0008	0.0019	0.0009	0.0002	0.0003	0.0004	0.00004	0.0005
As	-0.0022	0.0000	0.0022	0.0000	0.0670	0.0290	-0.0022	-0.0022	0.0491
Ca	-6.858	-6.539	-6.349	-5.109	-4.124	-3.279	-1.132	-0.470	-2.757
Fe	0.0007	0.0021	0.0056	0.0047	-0.0014	-0.0115	-0.0081	-0.0091	0.0039
Pb	0.0000	0.0000	0.0625	0.0312	0.0000	0.0156	0.0156	0.0313	0.0156
Mg	-6.7322	-6.6669	-4.2576	-2.5066	-4.7563	-2.6352	0.7751	-0.0495	-2.2441
Mn	0.0808	0.1003	0.1706	0.2661	-0.0683	-0.0322	0.1739	0.0725	-0.0358
P	-7.903	-7.929	-7.824	-7.810	-79.076	-45.273	-94.209	-94.229	-165.78
Ti	0.0032	0.0024	0.0017	0.0009	-0.325	-0.1871	-0.3591	-0.4046	-0.8046
Zn	-0.0505	-0.0505	0.2067	0.0433	0.3558	0.3413	0.1490	0.1274	0.0938

Note: negative value indicate that there was no leaching observed and level of the metal in the influent was higher than in the effluent

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