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A comparison of alum sludge with peat for aqueous glyphosate removal for maximizing their value for practical use

Yae Wang, Baiming Ren, Yaqian Zhao, Anthony English and Martin Cannon

ABSTRACT

This study compares and contrasts the glyphosate removal efficiency of alum sludge (waterworks residue) and Irish peat in aqueous solution. Organic phosphonate of glyphosate aqueous solution was removed in pot tests separately filled with peat and alum sludge, while effluent samples were taken from each pot to analyse the concentration of phosphorus (P) and COD (chemical oxygen demand); physical and chemical analysis for both media before and after use was carried out subsequently. The results show that the P removal capacity of alum sludge was significant (>99%), while the removal capacity of peat was considerably less than 10% after 10 weeks. Both materials significantly reduced the levels of COD, but it was noted that peat had a marginally greater initial P removal capacity ($68 \pm 22\%$) and did perform better than alum sludge ($57 \pm 12\%$). Moreover, pre-treatment is a crucial step to harness the full potential of peat. Overall, this study provides a scientific clue for sorbents selection when considering alum sludge and peat to maximize their value in practice.

Key words | adsorption, Irish peat, organic phosphonate, waterworks residues

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INTRODUCTION

Contaminants such as phosphorus (P) are among the most extensive pollutants that enter the water system and are a direct cause of eutrophication. Conventionally, P in natural waters is found in three forms of phosphates: orthophosphate, polyphosphate and organic-phosphate. Glyphosate ($C_3H_8NO_5P$) or (N-(phosphonomethyl)glycine) as an organic phosphonate and an active ingredient in pesticide is largely used worldwide especially in Ireland, since agriculture plays an integral role in Irish economy (Hu *et al.* 2011). Therefore, there are increased concerns about its impacts on the environment, in which glyphosate enters via various routes during its manufacture, use and runoff after use etc. However, alum sludge is an easily, widely, locally available by-product of potable water production in towns, cities and metropolis, and is currently disposed of as a waste worldwide. It has been gaining considerable attention during the last decade and so far it has been preliminarily studied as a potential adsorbent for the removal of various pollutants and metals

in wastewaters (Liu *et al.* 2017; Maqbool *et al.* 2016). On the other hand, peat is an abundant natural resource in Ireland (the third largest peat deposit worldwide) and is an accumulation of partially decayed vegetation or organic matter (OM) that is unique to natural areas called peatlands, or bogs (Irish Peatland Conservation Council).

Notwithstanding both peat and alum sludge have been studied and used in Ireland for various contaminants removal as they are both easily, locally and widely available materials in this country. For example, Sen Gupta *et al.* (2009) investigated the absorption capacity of copper and nickel on Irish peat moss. Babatunde *et al.* (2010) described the removal of P and OM from wastewaters using an Irish alum sludge-based four-stage novel constructed wetland system. Moreover, from the literature worldwide, numerous studies have been conducted to investigate the use of peat and alum sludge as a pollutant absorbent for wastewater treatment. Brooks (1980) first proposed the use of peat for residential

wastewater treatment. Since then, peat had been tested for the adsorption of phosphate (Xiong & Mahmood 2010), thallium ions (Robalds *et al.* 2013), arsenic (Oliveira *et al.* 2015), Malachite green (Hemmati *et al.* 2016), etc. from domestic and industrial effluents, while alum sludge has been investigated for various adsorptions as well, including P, Cr, Pb, As, etc. (Zhou & Haynes 2011; Zhao *et al.* 2015; Maqbool *et al.* 2016). Regarding P adsorption in aqueous media, published data show that the capacity for peat is in the range of 0.097 to 8.91 mg/g (Niedermeier & Robinson 2007; Xiong & Mahmood 2010), while for alum sludge it followed the order: orthophosphate > pyrophosphate > triphosphate > organic phosphate and the range is from 3.3 to 85.9 mg/g (Babatunde *et al.* 2010; Hu *et al.* 2011; Maqbool *et al.* 2016).

It has been noted that both the materials, peat and alum sludge, have been used in constructed wetlands as the main substrate for enhanced wastewater treatment (Babatunde *et al.* 2010; Jin *et al.* 2017). With the recent development of constructed wetland technology, it has become a mainstream treatment technology for the mitigation of a variety of wastewaters. In constructed wetlands, substrate and vegetation are two of the three main wetland components along with hydrology (Vymazal 2013). Studies have shown that the contribution to treatment of the overall system could be significantly enhanced by adopting alternative substrates including natural, manufactured and reclaimed materials. Peat is a natural material, while alum sludge is a water treatment by-product. Applications of both materials in constructed wetlands are generally preferable due to their low economic cost and geographical availability.

However, it is noted that the individual studies were based on different experimental conditions and there is no report for the purpose of comparison of using these two low-cost materials. Thus, knowledge of comparing the two cost-effective adsorbents for pollutant immobilization is not only necessary for the materials choice, but is also useful for beneficial reuse to maximize their value in practice. Therefore, the objective of the study was to compare and contrast the two abundant and indigenous low-cost materials, i.e. Irish peat and alum sludge, addressing their glyphosate removal capacity via pot tests.

METHODS

Raw materials

Dewatered alum sludge cake (Figure 1(a)) was collected from the Ballymore Eustace water treatment works located

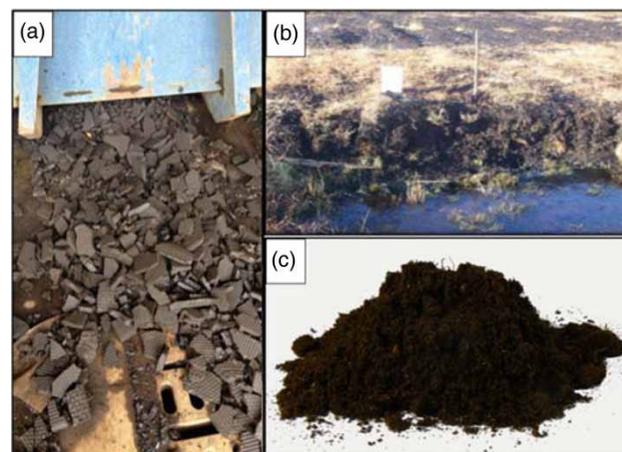


Figure 1 | Raw materials: (a) alum sludge cake; (b) ombrotrophic bogs in Co. Mayo, Ireland; (c) peat sample.

in Co. Kildare, Ireland. After collection, the alum sludge cakes were air-dried and large chunks of them were ground for further use. The nature of the plant and the characteristics of the alum sludge have been investigated and reported in our previous study (Hu *et al.* 2011). The peats used in this study were extracted from two ombrotrophic bogs in Co. Mayo, Ireland, one at Loughruseen, Castlebar and the other at Derrybeag, Kiltimagh. The initial 30–40 cm of the surface peatland layer was scraped away from both sites and an appropriate mass of the peat beneath (below 30–40 cm from the surface) was extracted (Figure 1(b)). Both peat samples were mixed evenly (Figure 1(c)) to achieve the advantages of both peat types for use in pot tests. Components of both alum sludge and peat were monitored, while the moisture content (MC) of both the materials was also measured with 69.9% for alum sludge and 80.2% for peat. Accordingly, the mass of peat used was 2.278 kg for each pot, which equals the mass of alum sludge of 1.498 kg. The P-containing contaminant used was Roundup™ Bioactive, with glyphosate as its active ingredient and a target glyphosate concentration of 50 mg/l in glyphosate aqueous solution; a natural pH of 5.2–5.6 was decided. A diluted solution that resulted in 22.2 ml of the stock solution was used to make up the 1,600 ml influent solution.

Pot setup

Four identical plastic containers were sourced and hydraulic valves were attached to each pot at 35 mm from the base of the pot. The pot was 200 mm in diameter and 250 mm in height (Figure 2). The base of the pots was filled with

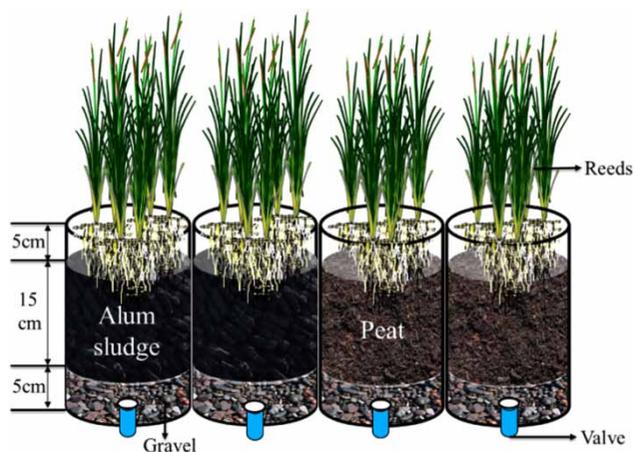


Figure 2 | Schematic of pot apparatus.

washed gravel to an approximate height of 50 mm. After calculating the dry weight of both substrate types, the substrate with the large MC (peat) was filled into the first pot until there was only a free board of 50 mm at the top. The mass of the peat added was 2.278 kg. The allowable mass of alum sludge of 1.498 kg, which was equivalent to the dry mass of the peat, was then placed in the corresponding pot to allow the mass of substrates to be equal in both corresponding blank and active pots. Trimmed young reeds were then planted on the top of each pot.

Dosing and sampling

As shown in Figure 3, the influent of 1,600 ml per pot was divided into two doses of 800 ml. One pot of each material was dosed with the selected herbicide solution at room temperature (22 °C), while the remaining two pots were filled with tap water and used as control blanks. The pots

were drained via the valve and refilled twice weekly for a 10-week period. Each pot was drained and then individually passed through a vacuum filter using a 0.45 µm pore filter paper. The filtrate was then subjected to water quality monitoring.

Analysis

Monitoring of P and chemical oxygen demand (COD) for filtrate from each pot (named as blank peat, peat, blank alum, alum) was conducted via a Unicam Helias- α spectrometer for P and a HACH DR-2400 spectrometer for COD with standard procedure. As the P source was an organic phosphonate, the sample had to firstly undergo chemical and thermal treatment by autoclave method. In addition, samples of the alum sludge and peat before and after use in pot testing were naturally dried for examination of their physical and chemical properties. Their surfaces were observed under a scanning electron microscope (SEM) (LEO 1530 VP Germany) to visualize inner porosity, surface properties and changes to the surfaces of the four relevant particles from the four pots. The SEM was further combined with energy-dispersive X-ray (EDX) to determine the composition and relative distribution of elements particularly on the surface. The chemical components of four media were examined via inductively coupled plasma atomic emission spectrometry (ICP-AES, Profile DV, America Leeman Labs Inc.).

RESULTS AND DISCUSSION

Figure 4 represents the comparison of glyphosate concentrations in both the effluents from peat and alum sludge

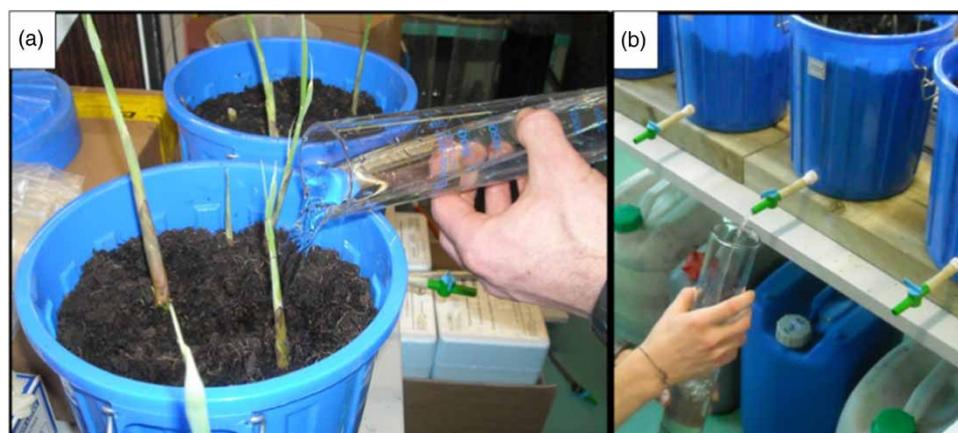


Figure 3 | Dosing and sampling.

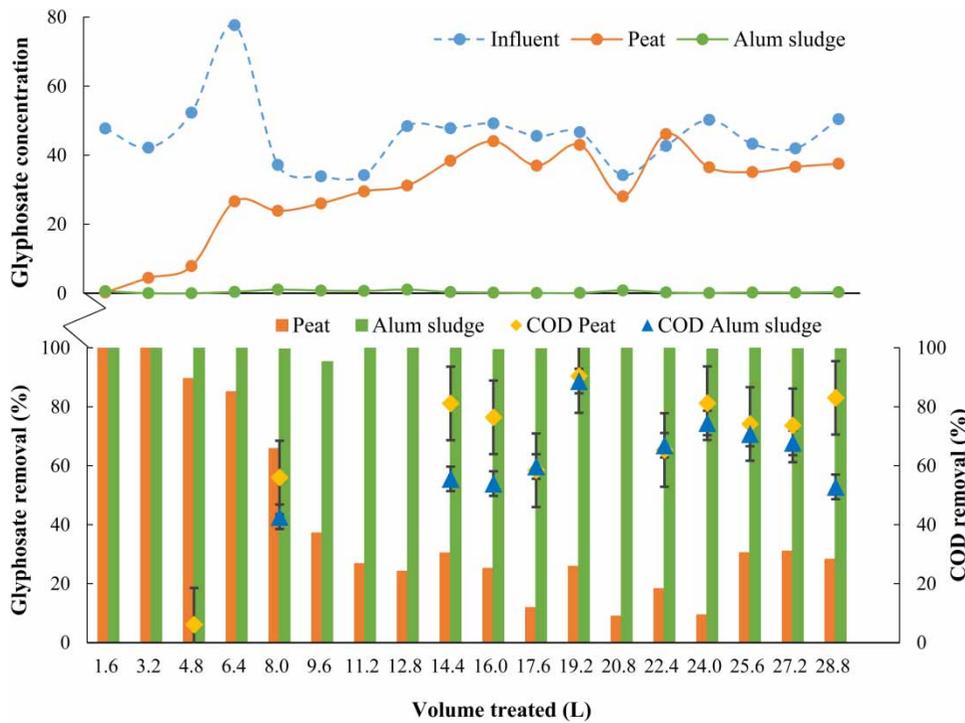


Figure 4 | Glyphosate concentration/removal and COD removal rate.

pots, alongside the influent concentration. The glyphosate concentration in peat quickly rises towards the influent concentration. In contrast, the alum sludge remains practically at zero throughout, considering alum sludge has the high glyphosate adsorption capacity of 85.9 mg/g (Hu *et al.* 2011). The smaller space between the influent line and peat line shows a steady decline in peat's adsorption capacity over time, and again the consistency of alum sludge can be clearly seen with virtually all traces of glyphosate removed. The percentage removal efficiency of both substrates was analysed; Inthorn *et al.* (2010) determined that removal efficiency of less than 10% is termed an exhaustion limit of the substrate. A similar exhaustion limit is shown in Figure 4. The peat substrate has been exhausted, as the efficiency falls below 10% on two occasions. Significantly, the degradation of peat's removal ability indicates an imminent intersection with the influent concentration line, thereby reaching theoretical saturation. It can be clearly seen from the results that at the end of the 10-week testing schedule the peat's removal capacity was practically exhausted. These findings conflict with results from other studies, such as those undertaken by Heavey (2003), which found the P removal of peat to be up to 63%, although a significant decrease in capacity after a 6-month period was observed. There are a number of reasons that the peat may have underperformed. In a study of various

filter materials, Kõiv *et al.* (2009) found P removal was only initiated when the total P inflow was greater than 1.5 mg/l. The concentrations of the polluting materials must firstly reach a significant level in order to be removed from the influent. It was observed that P was not removed during the preliminary phase of operation when the total P inflow was too low. More significantly, Brown *et al.* (2000) noted that peat adsorption is pH dependent, stating that in order for peat to offer significant adsorption capacity the pH must not exceed 8. Additionally, if the pH of the peat drops below 3, metal ions are exchanged by hydrogen ions, resulting in leaching or stripping of metals from the peat. This phenomenon enables the regeneration and recovery of the peat being used for metal removal by washing with an acidic solution of pH less than 3. Kõiv *et al.* (2009) also observed that P was not removed during the preliminary phase of operation which corresponded with Figure 4 when the total P inflow was low. It was only due to a mechanical filter malfunction that the level of total P inflow was increased. With this increase, the filter showed a sizeable reduction of total P through the system. Pollutants and contaminants removal by peat can occur through physical, chemical and biological processes. The removal of P by peat can occur through sedimentation, sorption or a combination of complex compounds (Vohla *et al.* 2011). Some quantity of P may also be bound onto the

biofilm of the peat. This study has proven that peat in its natural state performs unsatisfactorily in terms of P removal, but it is believed that peat may still be used as a low-cost adsorbent for P if pre-treatment is essential. Peat used in the research of Sen Gupta *et al.* (2009) was washed for 30 mins in HCl solution before use, as well as in the research of Hemmati *et al.* (2016) where peat was washed several times using distilled water to remove the primary impurities, etc. It can be inferred that all the pre-treatment gave a uniformity and possibly increased performance. In general, there is a wide range of pre-treatment processes that may be carried out. Some methods are simple, such as air drying, which is aimed towards increasing hydraulic conductivity as well as improved removal performance. Thermal and chemical pre-treatments, surface thermolysis, EDTA (ethylenediaminetetraacetic acid) washing have also been implemented as methods used in an attempt to improve the removal efficiencies of peat.

However, the alum sludge results surpassed expectation based on previous literature, exhibiting an average glyphosate removal of 99.8% over the 10-week test period. This result shows no trends indicating a significant change of its performance in the immediate future. To expand on the research completed in this study, it would be wiser that the testing schedule be increased to a long term basis to determine the longevity of alum sludge. However, our previous study on the long term use of alum sludge in constructed wetland has demonstrated and predicted its lifespan (Zhao *et al.* 2009), while the current study is focusing

on the comparison of the two materials. This result also indicates that Yang *et al.* (2008), who reported P removal via adsorption, found alum sludge had greater capability to remove inorganic P compared to organic P.

The results for COD are displayed in Figure 4. Since the COD data were limited to 11 results, perhaps a more accurate description would be provided with an increase in COD data over a longer period. The theoretical COD can be calculated from stoichiometry, 50 mg/l glyphosate = 23.5 mg/l COD (theoretical). In contrast to the glyphosate removal, initially the peat's removal efficiency was very good and the alum sludge removal was quite poor. As the volume treated increased there was both a decrease and an increase in removal efficiency in the peat and alum sludge, respectively. The two substrates then appeared to reach removal equilibrium of approximately 70%. Despite the poor removal of P, peat did perform better than alum sludge in terms of COD removal, demonstrating an average removal of $68 \pm 22\%$. The alum sludge had an average COD removal of $57 \pm 12\%$ after an initial poor start. It should be noted that both the sorbents (peat and alum sludge) can release some organic material, thus increasing the COD level of the effluent. Detailed consideration of COD removal should consider the effect of COD release from both the sorbents via the extra trials.

To provide an insight into the material's surface, either the raw media or the media after P adsorption in the pot were observed by SEM, as shown in Figure 5. It clearly shows the difference between the two alum sludge surfaces,

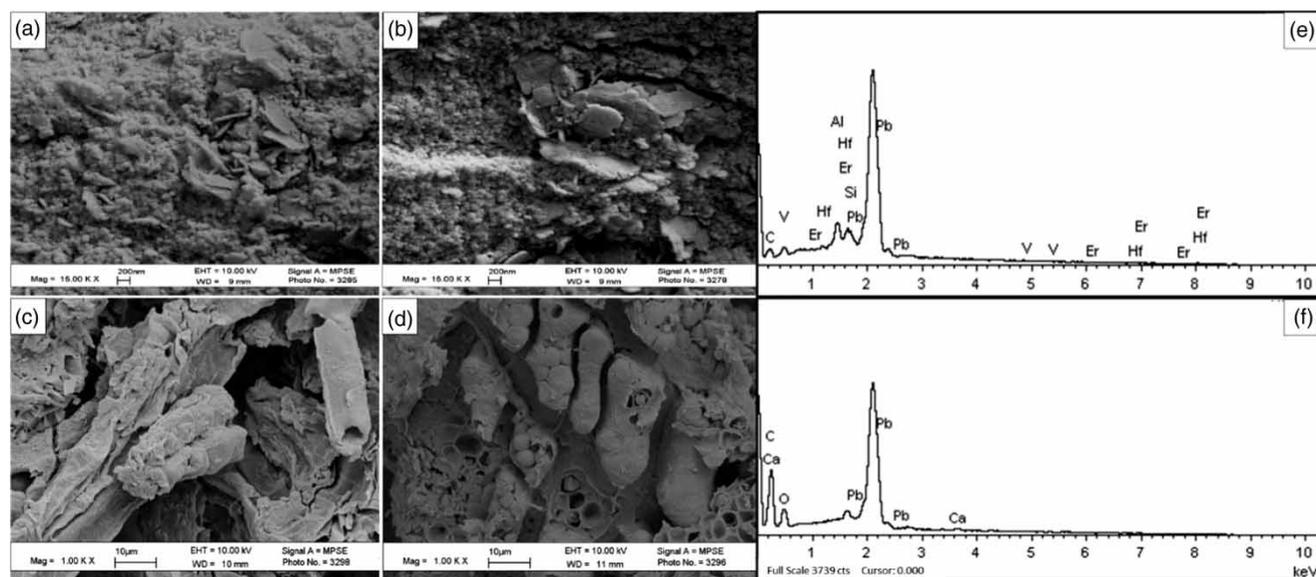


Figure 5 | SEM-EDX image: (a) raw alum sludge; (b) alum sludge after pot test; (c) raw peat; (d) peat after pot test; (e) alum sludge EDX; (f) peat EDX.

before adsorption (Figure 5(a)) the sludge particles have a porous structure, relating to the potential to adsorb P ions from the aquatic solution. However, following the adsorption for 10 weeks, the particle surface (Figure 5(b)) becomes much smoother than that of the original particles. The honeycomb holes in peat (Figure 5(c)) demonstrate the porous property. Qualitative assessment of the elemental distribution on the surface of the alum sludge and peat by the SEM-EDX (Figure 5(e) and 5(f)) showed the predominance of aluminium, and this was expected to highly influence its P adsorption ability. Ippolito *et al.* (2003) found similar results using SEM-EDX. The elemental composition of the four media (alum sludge and peat before and after use) is given in Table 1. The aluminium sulphate coagulant used during the water treatment process is reflected in the composition of the alum sludge. The aluminium component in the alum sludge is about 130 times greater than peat, and only the cuprum levels in the alum sludge are comparatively low. In the last decades, aluminium has been known to play a key role in P adsorption/precipitation by solid matrices via ligand exchange by phosphate ion reactions, with aluminium oxides forming inner-sphere complexes (Ippolito *et al.* 2003). Hence, substrates that are particularly rich in aluminium can effectively remove P by adsorption and/or precipitation of chemically stable phosphate phases. Table 1 further shows the good retention of P in the pot. It can be inferred that Al oxides particles would provide an excellent material for construction of P removal which corresponded to Arias *et al.* (2006), who addressed the covering quartz particles with Al oxides to provide high capacity adsorption and immobilization of P, as well as Ronkanen *et al.* (2016), who significantly found that the additional P was successfully retained in columns with accumulated metals. It is also noted in Table 1 that the cuprum levels in both the alum sludge and peat after use were considerably increased. The reason behind this was not clear and it deserves further investigation. However, it is noted from the Roundup formulation of the pesticide label that the

CuO additive occurred as Cu source. This may possibly cause the observed Cu increase.

CONCLUSIONS

The results clearly show that the P removal capacity of the alum sludge cake was significant, while the removal capacity of peat was considerably less than expected. At the end of the 10-week pot testing schedule, the peat's removal capacity was practically below 10% while alum sludge exhibited an average glyphosate removal of 99.8%. This result shows no trends indicating a significant change of its performance in the immediate future. It was found that both materials significantly reduced the levels of COD in the influent, and it was noted that peat had a marginally greater initial removal capacity. Despite the poor removal of P, peat did perform better than alum sludge in terms of COD removal at $68 \pm 22\%$ while alum sludge had an average of $57 \pm 12\%$ COD removal after an initial poor start. The different behaviour lies in the fact that peat in its natural state has poor P removal characteristics; in order to harness the full potential of peat, it must undergo pre-treatment prior to being used as an adsorbent material.

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Table 1 | The major chemical composition of the four media

Element (mg/g)	Alum sludge	Alum sludge (blank)	Peat	Peat (blank)
Al	131	131	1.12	0.85
P	1,165	744	372	235
Cu	73.4	31.1	116	2.8
Fe	15.3	16.7	2.8	2.7
Ca	9.3	3.0	5.3	3.5

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