

1 Phosphorus availability of sewage sludge-based fertilizers determined  
2 by the diffusive gradients in thin films (DGT) technique

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## 30 **Abstract**

31           The plant-availability of phosphorus (P) in fertilizers and soil can strongly influence the  
32 yield of agricultural crops. However, there are no methods to efficiently and satisfactorily  
33 analyze the plant-availability of P in sewage sludge-based P fertilizers except by undertaking  
34 time-consuming and complex pot or field experiments. We employed the diffusive gradients in  
35 thin films (DGT) technique to quantify the plant P availability of various types of P fertilizers  
36 with a novel focus on sewage sludge-based P fertilizers. Mixtures of fertilizer and soil were  
37 incubated for 3 weeks at 60% water holding capacity. DGT devices were deployed at the  
38 beginning of the incubation and again after 1, 2, and 3 weeks. Two weeks of incubation were  
39 sufficient for the formation of plant-available P in the fertilizer/soil mixtures. In a pot  
40 experiment, the DGT technique predicted maize (*Zea mays* L.) biomass yield and P uptake  
41 significantly more accurately than standard chemical extraction tests for P fertilizers (e.g. water,  
42 citric acid, and neutral ammonium citrate). Therefore, the DGT technique can be recommended  
43 as a reliable and robust method to screen the performance of different types of sewage sludge-  
44 based P fertilizers for maize cultivation minimizing the need for time-consuming and costly pot  
45 or field experiments.

46

## 47 **1 Introduction**

48           The chemical form of phosphorus (P) applied to agricultural crops is a major  
49 determinant of its plant availability. Therefore, in order to improve the uptake of P by plants,  
50 substantial knowledge of the chemical form of P in fertilizers is necessary. This is particularly  
51 important for novel P fertilizers such as those obtained from waste materials (e.g. sewage  
52 sludge). Currently, several different processes for P recovery from waste water or sewage  
53 sludge are in development or already in operation (*Donatello and Cheeseman, 2013; Kabbe et*  
54 *al., 2015*). Previous pot experiments with sewage sludge-based P fertilizers demonstrated strong

55 variation in plant P availability (Römer, 2006; Nanzer et al., 2014; Severin et al., 2014; Vogel  
56 et al., 2015).

57

58 While pot experiments are useful for determining the plant availability of a P fertilizer,  
59 they are time-consuming and costly. Therefore, various simple chemical extraction methods are  
60 often used instead (EU, 2003; Kratz and Schnug, 2009; Kratz et al., 2016). These chemical  
61 extraction methods mainly differ in their pH values, and the type of organic acid used as the  
62 extractant (EU, 2003). However, despite the demand, there is currently no satisfactory  
63 extraction method available for determining the plant availability of sewage sludge-based P  
64 fertilizers. In pot experiments carried out with thermochemically treated sewage sludge ash,  
65 Kratz et al. (2010) found that neutral and alkaline ammonium citrate extraction methods were  
66 the most accurate predictors of plant P uptake and yield. However, for sewage sludge-based  
67 biochars, the neutral ammonium citrate extraction method did not show an adequate correlation  
68 to the results of pot experiments (Steckenmesser et al., 2017). This indicates that simple  
69 chemical extraction methods can be strongly influenced by the matrix of the fertilizer (Axelrod  
70 and Greidinger, 1979; Braithwaite et al., 1989).

71

72 For soil-P analysis, different chemical extraction methods (e.g. water, Olsen, CAL (=   
73 calcium acetate lactate), Colwell, Bray, Mehlich etc.) are often used (Steffens, 1994; Mundus et  
74 al., 2013; Wuenscher et al., 2015). More recently, several research groups (e.g. Zhang et al.,  
75 1998; Menzies et al., 2005; Mason et al., 2010; Tandy et al., 2011; Moody et al., 2013; Speirs  
76 et al., 2013; Mundus et al., 2013; Six et al., 2014; Santner et al., 2015; Davison, 2016) have  
77 shown that the diffusive gradients in thin films (DGT) method has a much better correlation to  
78 plant-available P in soils than standard chemical extraction tests. The DGT device consists of a  
79 binding layer, a diffusion gel and a filter (to protect the gel) in a plastic piston (Davison et al.,  
80 2016). The dissolved P fraction of the soil solution from moist soil samples diffuses through

81 the filter and diffusion gel (normally for 24 h), and is subsequently adsorbed to the binding  
82 layer. The amount of P accumulated on the binding layer depends on the diffusion of P through  
83 the diffusion layer and the resupply of labile P from the solid soil phase. This amount of  
84 adsorbed P on the binding layer is then used to calculate the diffusion-limited, time-averaged  
85 concentration of P, which we used as indicator for the plant availability of the soil-P.

86

87 The aim of our work was to develop a reliable and robust method to quantify the plant-  
88 available P in sewage sludge-based P fertilizers by adopting the DGT technique and deploying  
89 the DGT device on various fertilizer/soil-mixtures. Furthermore, we compared the DGT method  
90 with different commonly applied chemical extraction methods to quantify the plant-available P  
91 in soil fertilized with various sewage sludge-based P fertilizers. The plant-available P quantified  
92 with these methods was then compared to the yield and P uptake of maize grown on the same  
93 amended soils.

94

## 95 **2 Material and methods**

### 96 **2.1 P-fertilizer production**

97 Different sewage sludge-based P fertilizers were prepared by low-temperature  
98 conversion and thermochemical post-treatment of sewage sludge sourced from two wastewater  
99 treatment plants in Germany. One sewage sludge was simultaneously precipitated with  $\text{FeCl}_2$   
100 and directly fermented, which resulted in an anaerobically stabilized sludge. The other sewage  
101 sludge originated from a waste water treatment plant with enhanced biological phosphorus  
102 removal (EBPR). This sludge was aerobically stabilized followed by P-precipitation with  
103  $\text{Al}_2(\text{SO}_4)_3$ . Both sewage sludges were converted to biochars by low-temperature conversion in  
104 a lab-scale reactor at 400-500°C (Weber et al., 2014; Steckenmesser et al., 2017). Hereafter, the  
105 sludges will be referred to as  $B_{\text{chem}}$  and  $B_{\text{bio}}$ , respectively. The resulting biochars were used  
106 either directly for the pot experiment or further thermochemically processed at 950°C for

107 approximately 30 min in a rotary furnace (Thermal Technology, RT1700, corundum tube,  
108 Bayreuth, Germany) to improve the fertilizer performance of the material as follows:

109

110 1. Treatment of  $B_{\text{chem}}$  with magnesium chloride ( $\text{MgCl}_2$ ; Sigma-Aldrich, Steinheim,  
111 Germany) under oxidizing (air) conditions (Adam et al., 2009; Vogel and Adam, 2011; hereafter  
112 the product is referred to  $B_{\text{chem-Mg}}$ ).

113 2. Treatment of  $B_{\text{bio}}$  with sodium sulfate ( $\text{Na}_2\text{SO}_4$ ; Applichem, Darmstadt, Germany)  
114 under reducing conditions (Stemann et al., 2015; Herzog et al., 2016; Vogel et al., 2016; hereafter  
115 the product is referred to  $B_{\text{bio-Na}}$ ).

116 3. Treatment of  $B_{\text{chem}}$  first a gaseous chloride donor (hydrochloric acid) to remove heavy  
117 metals (Vogel and Adam, 2011), followed by addition of  $\text{Na}_2\text{SO}_4$  (under reductive conditions)  
118 to enhance the P plant-availability (hereafter the product is referred to  $B_{\text{chem-Cl+Na}}$ ).

119

120 The P-bearing mineral phases of the sewage sludge-based P fertilizers were determined  
121 using X-ray diffraction (Steckenmesser et al., 2017). The biochar  $B_{\text{chem}}$  mainly contained  
122 inorganic pyro- and polyphosphates. After thermochemical treatment with  $\text{MgCl}_2$  ( $B_{\text{chem-Mg}}$ ),  
123 chlorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ) and stanfieldite ( $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ ) were detected as P phases. The  
124  $\text{HCl}/\text{Na}_2\text{SO}_4$  treatment ( $B_{\text{chem-Cl+Na}}$ ) led to the formation of calcium sodium phosphate  
125 ( $\text{CaMgNa}_2(\text{PO}_4)_2$ ). For the biochar  $B_{\text{bio}}$ , meta- or short polyphosphates were assumed. After  
126 treatment with  $\text{Na}_2\text{SO}_4$  ( $B_{\text{bio-Na}}$ ), calcium sodium phosphate ( $\text{Ca}_{13}\text{Mg}_5\text{Na}_{18}(\text{PO}_4)_{18}$ ) and  
127 whitlockite were detected.

128

## 129 **2.2 Pot experiment**

130 Three kg of a subsoil from a brown earth derived from loess were mixed with 3 kg of  
131 quartz sand, to decrease the P mass fraction ( $P_{\text{Total}} = 180 \text{ mg kg}^{-1}$ ,  $P_{\text{CAL}} = 10 \text{ mg kg}^{-1}$ , pH in 0.01  
132 M  $\text{CaCl}_2 = 6.7$  of mixture), was used for the pot experiment. The experiment consisted of six

133 treatments; five sewage sludge-based P fertilizers and one triple superphosphate (TSP)  
134 treatment. A control with no added P (P0) was also included. Four replicates were used per  
135 treatment (also for P0), and the test plant was maize (*Zea mays* L. cv. Amadeo). Based on pre-  
136 tests, a P application rate of 0.6 g per pot was adequate to achieve maximum shoot biomass of  
137 maize plants after 30 d of cultivation. Therefore, the soil/sand mixture was fertilized with 100  
138 mg P kg<sup>-1</sup> soil of each P fertilizer as well as 250 mg N (as NH<sub>4</sub>NO<sub>3</sub>), 300 mg K (50% KCl +  
139 50% K<sub>2</sub>SO<sub>4</sub>), and 150 mg Mg (MgSO<sub>4</sub>) per kg soil. Micronutrients were added as an aqueous  
140 solution containing 20 mg Mn (MnSO<sub>4</sub>), 10 mg Zn (ZnSO<sub>4</sub>), 5 mg Cu (CuSO<sub>4</sub>), 0.5 mg B  
141 (H<sub>3</sub>BO<sub>3</sub>), and 0.11 mg Mo ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>) per kg of soil.

142

143 The pot experiment was conducted in Mitscherlich pots (height: 18 cm, diameter: 20  
144 cm) in a growth chamber with 16 h light at 25°C, 8 h dark at 18°C, and light intensity of 150  
145 W m<sup>-2</sup>. After 1 week of pre-germination, three seeds were sown in each pot and harvested after  
146 30 d. Pots were watered daily to maintain 60% water-holding capacity (WHC). The above-  
147 ground biomass was harvested from each pot, weighed (fresh weight) and then chaffed.  
148 Biomass yield was determined after drying the plant material at 105°C. The P concentration of  
149 the dried plant material was determined using ICP-OES (Varian 720-ES, Waldbronn, Germany;  
150 wavelength 213.6 nm) after digestion with nitric acid, perchloric acid, and sulfuric acid under  
151 an increasing temperature (up to 220°C) for 6 h. The derived residue was dissolved in 5 M HCl  
152 and filtered. Homogenized soil samples were collected from each pot after harvest and air-dried  
153 at room temperature for 1 month before analysis.

154

### 155 **2.3 Chemical extraction tests for soils and fertilizers**

156 Homogenized subsamples of each treatment of the post-harvest soils were extracted in  
157 triplicate using three chemical extractants to quantify the extractable P: water (soil : solution  
158 ratio 1 : 10, 60 min), calcium acetate lactate (CAL, Schüller, 1969; soil : solution ratio 1 : 20,

159 120 min), and sodium bicarbonate (*Olsen* et al., 1954; soil : solution ratio 1 : 20, 30 min). The  
160 P fertilizers were also extracted with water ( $P_W$ ; fertilizer : solution ratio 1 : 100, 30 min), 2%  
161 citric acid ( $P_{CIT}$ ; fertilizer : solution ratio 1 : 100, 30 min) and neutral ammonium citrate ( $P_{NAC}$ ;  
162 fertilizer : solution ratio 1 : 166, 60 min) and carried out according to the EU regulation No.  
163 2003/2003 (*EU*, 2003) in triplicate. The extracted P concentrations from these chemical  
164 extraction tests were analyzed using ICP-OES (Thermo iCAP 7000, Dreieich, Germany).

165

## 166 **2.4 DGT experiments**

167 Post-harvest soil samples were also analyzed with DGT devices equipped with a  
168 ferrihydrite binding layer. After a 24 h conditioning period of the soil at 60% of the WHC, the  
169 soils were brought to 100% WHC, transferred into the DGT devices and deployed for 24 h at  
170 25°C (*Davison*, 2016). Following the extraction of P from the binding layer with 1 M HNO<sub>3</sub>, P  
171 concentrations were analyzed with ICP-MS (Thermo iCAP Q, Dreieich, Germany) and used to  
172 calculate the DGT P ( $P_{DGT}$ ). The DGT measurements were carried out in duplicate.

173

174 Additional DGT measurements were also performed with the fertilizer/soil mixtures in  
175 order to predict the performance of the various P fertilizers using a simple and rapid test. The  
176 different P fertilizers were mixed with the same soil/sand mixture and nutrients (N, K, Mg, S,  
177 micronutrients) that were used for the pot experiment (see above). Specifically, 15 g of the  
178 soil/sand mixture were mixed with 1.5 mg P from the respective P fertilizer for each experiment  
179 (= 100 mg P per kg of soil) in 50 mL plastic containers. These DGT measurements were also  
180 carried out in duplicate. Other nutrients were added to the fertilizer/soil-mixtures using the same  
181 nutrient : soil ratio as applied in the pot experiment. The soils were maintained at 60% WHC  
182 using deionized water and stored at 22°C. At the start of the incubation experiment, and after  
183 1, 2, and 3 weeks, DGT devices were deployed. As with the pot experiment, the water content  
184 was increased to 100% WHC before DGT deployment.

185

## 186 **2.5 Statistics**

187 For statistical analysis of the pot experiment, chemical extraction tests and DGT  
188 experiments, an ANOVA and a Tukey test were performed ( $P < 5\%$ ) with the software R  
189 (version 3.4.0).

190

## 191 **3 Results**

### 192 **3.1 Plant P availability in soils from pot experiment**

193  $B_{\text{chem-Cl+Na}}$  (49% P uptake relative to TSP) and  $B_{\text{bio}}$  (44%) showed the highest dry  
194 matter yield and P uptake by maize of the sewage sludge-based P fertilizers in the pot  
195 experiment (Tab. 1), followed by  $B_{\text{bio-Na}}$  (31%) and  $B_{\text{chem}}$  (26%). On the other hand,  $B_{\text{chem-Mg}}$   
196 (7%) only resulted in comparable yield and P uptake to the P0 treatment (i.e. no P added; 4%).  
197 With the extraction tests,  $B_{\text{bio}}$ -amended soils after harvest showed the highest extractable P  
198 values of the sewage sludge-based P fertilizers with all three tests (water, Olsen, and CAL  
199 extractions), with CAL showing an even higher value than TSP. Additionally, the P values of  
200  $B_{\text{chem-Cl+Na}}$  were relatively high for these three chemical extraction tests. Soils with  $B_{\text{chem-Mg}}$ ,  
201  $B_{\text{bio-Na}}$  and P0 treatments had the lowest values of extractable P. Figure 1 shows the plot of P  
202 uptake by maize plants compared with P values obtained with water, Olsen and CAL extractions  
203 in the post-harvest soils of the treatments with the applied P fertilizers. Phosphorus uptake by  
204 maize showed a modest correlation with the chemical extraction tests in the pot experiment,  
205 with the Olsen extraction performing the best out of the three extraction methods. Furthermore,  
206 the standard deviations of the chemically extracted P concentrations were high for some soil  
207 samples (%RSD values range from 1 to 52 %). In contrast, the DGT results showed a superior  
208 correlation with P uptake by maize with much lower deviation of the measured values (RSD <  
209 10%) compared to the results of the chemical extraction tests.

210



### 211 **3.2 Chemical extraction tests of applied P-fertilizers**

212 The water-extractable P ( $P_W$ ) was very low for the sewage sludge-based P fertilizers,  
213 with the highest  $P_W$  observed for the sodium-treated products:  $B_{\text{bio-Na}}$  (5%) and  $B_{\text{chem-Cl+Na}}$   
214 (2%; Tab. 2). The P extracted with citric acid ( $P_{\text{CIT}}$ ) and neutral ammonium citrate ( $P_{\text{NAC}}$ ) was  
215 much higher for all applied P fertilizers, with the highest  $P_{\text{CIT}}$  and  $P_{\text{NAC}}$  observed from  $B_{\text{chem}}$   
216 and  $B_{\text{bio-Na}}$ , respectively. Figure 2 shows that there is a modest correlation between the  $P_W$  of  
217 the applied P fertilizers and the P uptake by maize in the pot experiment with the same P  
218 fertilizers, even if the values for the sewage sludge-based P fertilizers were relatively small. In  
219 contrast, the extractable P of  $P_{\text{CIT}}$  and  $P_{\text{NAC}}$  showed no correlation with the P uptake by maize.

220

### 221 **3.3 DGT technique applied to fertilizer/soil mixtures**

222 Without incubation the application of the two  $B_{\text{bio}}$  products showed the highest DGT P  
223 ( $P_{\text{DGT}}$ ) values for the fertilizer/soil mixtures of the sewage sludge-based P fertilizers (Tab. 2).  
224 The  $P_{\text{DGT}}$  values increased after 1 and 2 weeks of incubation (except with  $B_{\text{chem-Mg}}$  which did  
225 not change). The  $P_{\text{DGT}}$  values of  $B_{\text{bio-Na}}$  reached their maximum after 1 week, while the other  
226 sewage sludge-based P fertilizers required 2 weeks of incubation to reach their highest  $P_{\text{DGT}}$ . In  
227 contrast, the  $P_{\text{DGT}}$  values of TSP decreased after the first week of incubation and remained at  
228 this level. In addition, Fig. 3 shows the P uptake by maize in relation to the results from the  
229 incubated fertilizer/soil DGT experiments in the corresponding pot experiment. After 2 weeks  
230 of incubation, the correlation is better than after 1 week of incubation. The  $P_{\text{DGT}}$  after 3 weeks  
231 of incubation and the correlation with P uptake by maize were not significantly different to  
232 those after 2 weeks.

233

234

235

## 236 **4 Discussion**

### 237 **4.1 Comparison of plant P availability of soils from pot experiment**

238 The results of the pot experiment show that different treatments of sewage sludge  
239 resulted in P fertilizers with different plant P availability. During the pot experiment, the plants  
240 did not take up all of the applied P. The remaining P in the amended soils can be used as an  
241 indicator for the P-fertilizer performance. For all chemical extraction tests, the soil amended  
242 with the fertilizer B<sub>bio</sub> showed the highest extractable P of the sewage sludge-based P fertilizers.  
243 It is assumed, that the biochar B<sub>bio</sub> contains—in contrast to B<sub>chem</sub>—more soluble meta- and short  
244 polyphosphates because it originated from a waste-water treatment plant with enhanced  
245 biological P removal (*Stratful et al., 1999; Steckenmesser et al., 2017*). *Torres-Dorante et al.*  
246 (2006) showed that meta- and short polyphosphates have a high plant P availability. In contrast,  
247 B<sub>bio</sub>-Na, the product of thermochemical treatment of B<sub>bio</sub> Na<sub>2</sub>SO<sub>4</sub>, allowed a much lower  
248 biomass yield and P uptake than B<sub>bio</sub>. This may be attributed to the decomposition of meta- and  
249 polyphosphates during the treatment process. In contrast to the chemical extraction methods,  
250 the DGT method showed an excellent correlation with the P uptake by maize. This correlation  
251 is in agreement with other studies (*Menzies et al., 2005; Six et al., 2014; Wang and Chu, 2015;*  
252 *Christel et al., 2014, 2016a*) that found a good correlation between the amount of added  
253 fertilizer P and adsorbed P in soil determined by DGT methods. This finding confirms the  
254 validity of using the DGT approach for P-fertilizers derived from sewage sludge.

255

256 Furthermore, the standard deviation of the respective P values were much higher for the  
257 chemical extraction tests than for P<sub>DGT</sub>. For the DGT experiments, a greater mass of soil was  
258 used compared to that for the chemical extraction tests (15 g instead of 5 g) which may be an  
259 explanation for the lower standard deviation P<sub>DGT</sub>. In addition, different P fertilizers can change  
260 the soil pH in different ways, which can negatively affect several soil P extraction methods  
261 (*Wuenschel et al., 2015*). In contrast, the DGT method is unaffected by pH within the range 3-

262 9 (Mason et al., 2005), because it uses water instead of buffer solutions as extractant. Therefore,  
263 the plant-available P can be analyzed at the native soil pH, as confirmed during P adsorption  
264 tests with iron oxide strips, which act as the DGT binding layer, in soils (Uusitalo and Yli-  
265 Halla, 1999; Mundus et al., 2013).

266

#### 267 **4.2 Chemical extraction tests of sewage sludge-based P fertilizers**

268 The extractable P in water ( $P_w$ ) of the sewage sludge-based P fertilizers is very low ( $\leq$   
269 5%) in contrast to TSP (96%). However, the  $P_w$  shows the best correlation of the chemical  
270 extraction tests with the P uptake by maize in the pot experiment ( $R^2 = 0.73$ ). Hence, this good  
271 correlation is strongly influenced by the  $P_w$  value of TSP. In contrast, the extractable P is much  
272 higher in citric acid ( $P_{CIT}$ ) and neutral ammonium citrate ( $P_{NAC}$ ), but there was no correlation  
273 with the P uptake by maize in the pot experiment. This demonstrates that these chemical  
274 extraction tests are not predictive for P plant uptake for various types of sewage sludge-based  
275 P fertilizers. Steckenmesser et al. (2017) showed a strong correlation for the P uptake and  
276 biomass yield by maize treated with chemically precipitated sewage sludge-based P fertilizers  
277 with the extractable P in 2% formic acid. In contrast to this, Kratz et al. (2010) recommend the  
278  $P_{NAC}$ -extractable P as the best indicator for plant P availability based on modified Neubauer  
279 trials with summer rye grown in soil amended with sewage sludge ash based P-fertilizers. Thus,  
280 there is no universally applicable chemical extraction test which can quantify the plant P  
281 availability of various sewage sludge-based P fertilizers.

282

#### 283 **4.3 Estimation of plant-available P in P fertilizers with the DGT technique**

284 The DGT results from the incubated fertilizer/soil mixtures have, in contrast to the  
285 chemical extraction tests, a much better correlation with the P uptake by maize in the pot  
286 experiment. For all applied P fertilizers, 2 weeks of incubation seemed to be sufficient for the  
287 formation of plant-available P in the fertilizer/soil mixtures. In contrast to the sewage sludge-

288 based P fertilizers the  $P_{DGT}$  value of TSP/soil incubation decreased in the first week. This is  
289 easily rationalized given that P from TSP ( $Ca(H_2PO_4)_2 \times H_2O$ ) is highly soluble, and is slowly  
290 converted to water-insoluble  $CaHPO_4 \times 2 H_2O$  over the incubation period (Vogel et al., 2013).  
291 Therefore, it should be noted that direct application of DGT to analyze P fertilizers is not  
292 informative because water-soluble P fertilizer (e.g. TSP) can simply saturate the binding layer  
293 too quickly, while water-insoluble P fertilizers (e.g. sewage sludge (ash)-based materials)  
294 release only negligible amounts of P without prior incubation in soil (Christel et al. 2016b).

295

296         However, the correlation between P uptake and  $P_{DGT}$  values was not as strong as  
297 measured from the actual soils in the pot experiment, even though it was the same soil with the  
298 same micro and macro-nutrients. This could be due to the absence of plant roots that lead to a  
299 lower mobilization of P from the applied P fertilizers in the fertilizer/soil mixture. Furthermore,  
300 the  $R^2$  values of the correlations in Fig. 3 are highly dependent on the  $P_{DGT}$  value of TSP. Thus,  
301 the DGT approach will not substitute pot or field experiments completely in all scenarios, but  
302 does offer a time and cost-effective screening method to support the measurement of P-fertilizer  
303 performance.

304

305         Finally, the ferrihydrite DGT binding layer can adsorb only up to approximately 50  $\mu g$   
306 of P and larger amounts of P in fertilizer/soil mixtures could possibly saturate the binding layer,  
307 even with slow-releasing, water-insoluble P fertilizers. Therefore, binding layers with higher  
308 capacities may be used, such as titanium dioxide (Panther et al., 2010), zirconium oxide (Ding  
309 et al., 2010) or magnesium carbonate (Xie et al., 2016). An alternative is a shorter deployment  
310 time of the DGT devices for incubated fertilizer/soil mixtures.

311

## 312 **5 Conclusions**

313           In this paper, we have demonstrated the potential of the DGT approach to become a key  
314 method for the determination of plant-available P in sewage sludge-based P fertilizers. The P  
315 value determined with DGT was strongly correlated with the P uptake by maize cultivated with  
316 a range of sewage sludge-based P fertilizers. Furthermore, by adopting the DGT approach an  
317 improved assessment of the plant-available P of various P fertilizers was made, compared to  
318 the conventional chemical extraction tests. We conclude that while the DGT method cannot  
319 completely substitute pot experiments, it is a suitable method for time and cost-effective  
320 screening of P-fertilizer performance.

321

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329

330

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457 **Table 1:** Dry matter yield and P uptake by maize and water, Olsen and CAL extractable P and DGT P results from the soils after harvest in the  
 458 corresponding pot experiment. Different letters within each column indicate significant differences between treatments according ANOVA and  
 459 Tukey test ( $p < 0.05$ ).

|                          | <b>Dry matter yield</b><br>(g) | <b>P uptake</b><br>(mg P/pot) | <b>Water extraction</b><br>(mg/kg) | <b>Olsen extraction</b><br>(mg/kg) | <b>CAL extraction</b><br>(mg/kg) | <b>DGT</b><br>( $\mu\text{g/l}$ ) |
|--------------------------|--------------------------------|-------------------------------|------------------------------------|------------------------------------|----------------------------------|-----------------------------------|
| P0                       | 2.5 $\pm$ 0.3 a                | 2.5 $\pm$ 0.4 a               | 5.4 $\pm$ 0.3 bc                   | 8.5 $\pm$ 2.4 ab                   | 7.6 $\pm$ 1.0 a                  | 3.3 $\pm$ 1.1 a                   |
| B <sub>chem</sub>        | 13.5 $\pm$ 1.4 b               | 18.1 $\pm$ 1.7 b              | 6.2 $\pm$ 0.9 bc                   | 8.9 $\pm$ 4.6 ab                   | 35.6 $\pm$ 2.8 b                 | 27.8 $\pm$ 4.4 b                  |
| B <sub>bio</sub>         | 20.6 $\pm$ 0.9 c               | 30.5 $\pm$ 2.3 c              | 7.2 $\pm$ 1.4 bc                   | 15.7 $\pm$ 3.2 b                   | 49.2 $\pm$ 9.4 b                 | 54.7 $\pm$ 5.0 c                  |
| B <sub>chem</sub> -Mg    | 2.8 $\pm$ 0.6 a                | 4.5 $\pm$ 1.0 a               | 0.1 $\pm$ 0.0 a                    | 3.6 $\pm$ 0.0 a                    | 35.5 $\pm$ 7.9 b                 | 10.4 $\pm$ 2.7 a                  |
| B <sub>chem</sub> -Cl+Na | 20.6 $\pm$ 3.4 c               | 33.4 $\pm$ 7.2 c              | 6.7 $\pm$ 0.0 bc                   | 9.1 $\pm$ 3.0 ab                   | 42.1 $\pm$ 12.0 b                | 62.4 $\pm$ 3.9 c                  |
| B <sub>bio</sub> -Na     | 13.8 $\pm$ 1.2 b               | 21.6 $\pm$ 3.5 b              | 2.1 $\pm$ 0.2 ab                   | 7.6 $\pm$ 0.1 ab                   | 25.7 $\pm$ 2.7 ab                | 46.4 $\pm$ 3.2 b                  |
| TSP                      | 29.2 $\pm$ 0.8 d               | 68.8 $\pm$ 5.8 d              | 8.5 $\pm$ 2.4 c                    | 22.8 $\pm$ 5.1 c                   | 38.1 $\pm$ 10.6 b                | 135.6 $\pm$ 0.6 d                 |

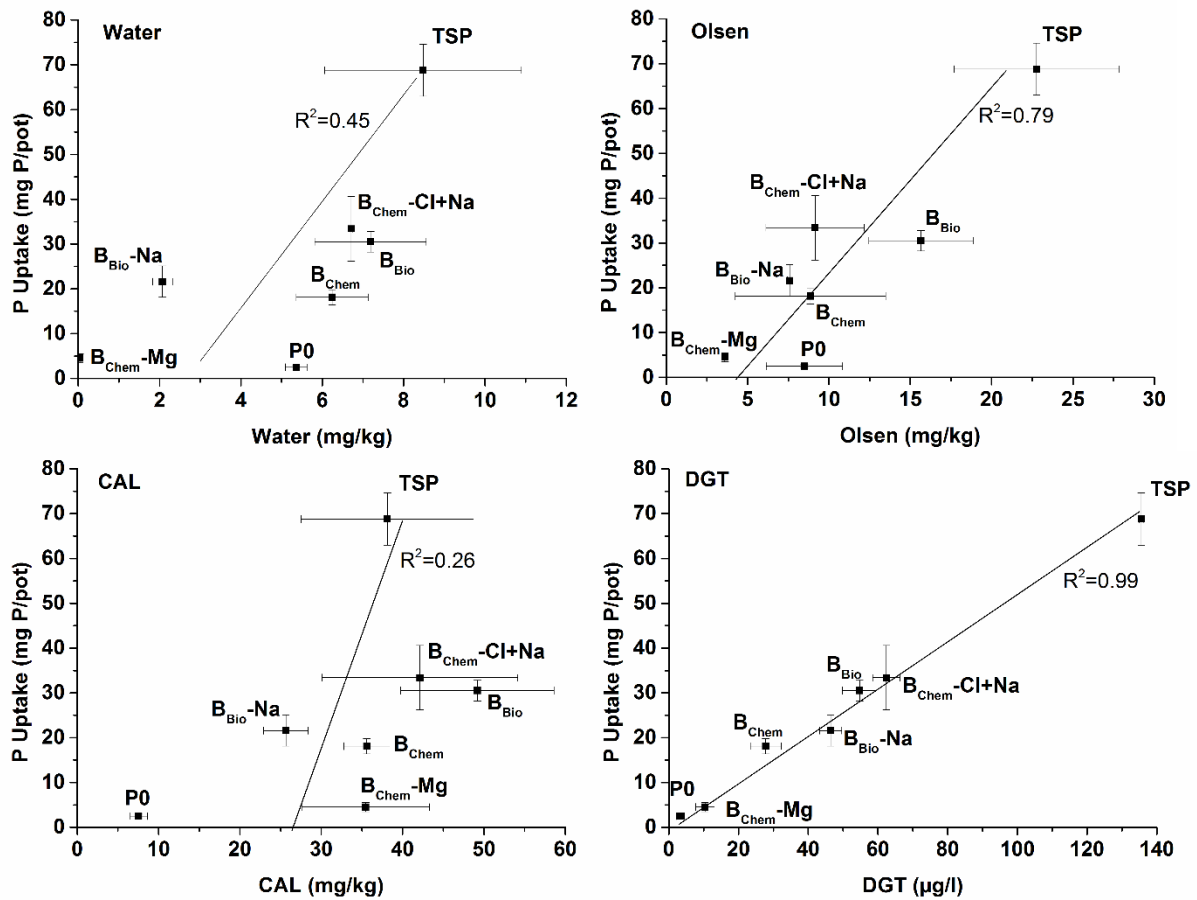
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461 **Table 2:** P<sub>w</sub>, P<sub>CIT</sub> and P<sub>NAC</sub> extracted from the applied P-fertilizers and P<sub>DGT</sub> results from incubated fertilizer-soil mixtures (direct, one, two and  
 462 three weeks). Different letters within each column indicate significant differences between treatments according ANOVA and Tukey test ( $p < 0.05$ ).

|                          | <b>P<sub>w</sub></b><br>(%) | <b>P<sub>CIT</sub></b><br>(%) | <b>P<sub>NAC</sub></b><br>(%) | <b>P<sub>DGT</sub> direct</b><br>( $\mu\text{g/l}$ ) | <b>P<sub>DGT</sub> 1 week</b><br>( $\mu\text{g/l}$ ) | <b>P<sub>DGT</sub> 2 weeks</b><br>( $\mu\text{g/l}$ ) | <b>P<sub>DGT</sub> 3 weeks</b><br>( $\mu\text{g/l}$ ) |
|--------------------------|-----------------------------|-------------------------------|-------------------------------|--|--|---|---|
| B <sub>chem</sub>        | 0 $\pm$ 0 a                 | 93 $\pm$ 6 b                  | 30 $\pm$ 1 a                  | 17.8 $\pm$ 1.4 a                                     | 31.1 $\pm$ 2.1 ab                                    | 61.2 $\pm$ 2.7 b                                      | 56.1 $\pm$ 8.5 b                                      |
| B <sub>bio</sub>         | 1 $\pm$ 0 a                 | 33 $\pm$ 3 a                  | 25 $\pm$ 5 a                  | 49.0 $\pm$ 10.6 a                                    | 133.2 $\pm$ 7.1 c                                    | 181.0 $\pm$ 6.9 c                                     | 177.5 $\pm$ 36.1 c                                    |
| B <sub>chem</sub> -Mg    | 0 $\pm$ 0 a                 | 73 $\pm$ 2 bc                 | 53 $\pm$ 2 b                  | 9.9 $\pm$ 6.9 a                                      | 7.4 $\pm$ 0.4 ab                                     | 7.8 $\pm$ 0.5 a                                       | 11.5 $\pm$ 0.0 a                                      |
| B <sub>chem</sub> -Cl+Na | 2 $\pm$ 0 a                 | 58 $\pm$ 14 ab                | 31 $\pm$ 5 a                  | 33.1 $\pm$ 5.6 a                                     | 67.2 $\pm$ 9.2 abc                                   | 90.6 $\pm$ 7.6 b                                      | 80.7 $\pm$ 6.4 b                                      |
| B <sub>bio</sub> -Na     | 5 $\pm$ 0 a                 | 66 $\pm$ 0 b                  | 70 $\pm$ 3 c                  | 78.2 $\pm$ 22.8 a                                    | 112.7 $\pm$ 11.7 bc                                  | 106.3 $\pm$ 10.8 b                                    | 112.2 $\pm$ 14.8 bc                                   |
| TSP                      | 96 $\pm$ 5 b                | 100 $\pm$ 0 c                 | 49 $\pm$ 0 b                  | 1193.1 $\pm$ 145.7 b                                 | 678.2 $\pm$ 36.8 d                                   | 542.9 $\pm$ 27.1 d                                    | 664.4 $\pm$ 18.4 d                                    |

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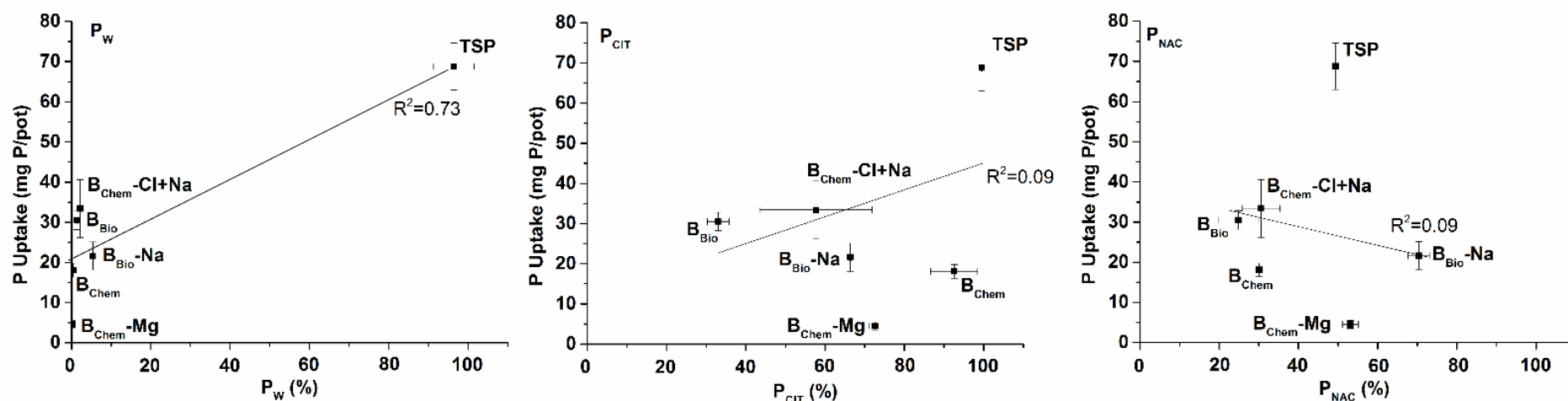
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466 **Figure 1:** Water, Olsen and CAL extractable P and DGT P results of the fertilized soils with  
467 different sewage sludge based P-fertilizers, analyzed after harvest, in relation to the P uptake  
468 by maize in the corresponding pot experiment. The vertical and horizontal lines show the  
469 standard deviation of each point.

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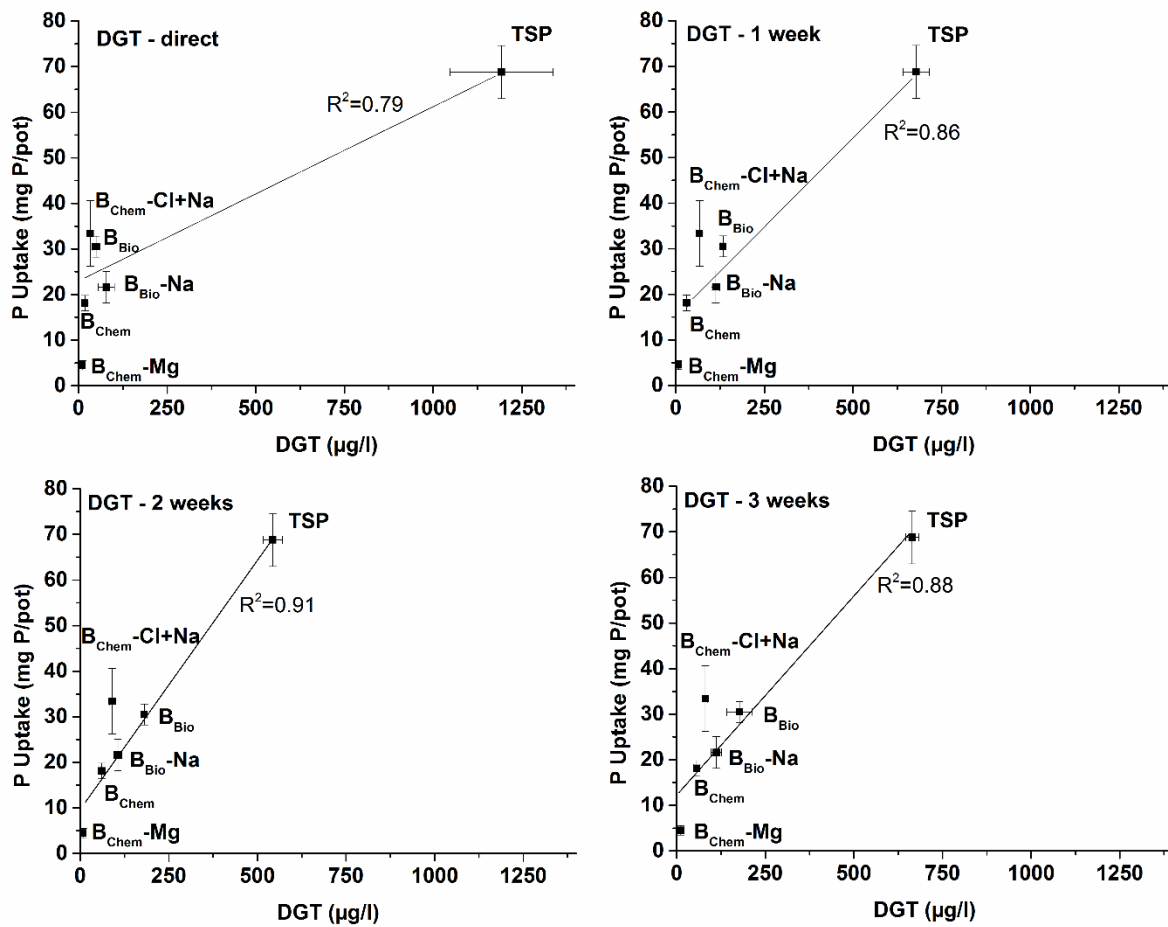
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474 **Figure 2:** Water (P<sub>w</sub>), citric acid (P<sub>CIT</sub>) and neutral ammonium citrate (P<sub>NAC</sub>) extractable P of the applied P-fertilizers in relation to the P uptake by  
475 maize in the corresponding pot experiment with these fertilizers. The vertical and horizontal lines show the standard deviation of each point.

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478 **Figure 3:** P<sub>DGT</sub> results of the incubated fertilizer-soil mixtures (direct, one, two and three  
479 weeks) in relation to the P uptake by maize in the corresponding pot experiment with these  
480 fertilizers. The vertical and horizontal lines show the standard deviation of each point.

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