Biogas Digestate Application Modifies Solute Transport Conditions in Soils and Increases the Release of Phosphorus

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The application of fertilizers to soils may impair the quality of both surface and subsurface waters. Severe rainfall events that follow fertilizer application can increase P release from soils. In this study, suction plates were installed in a loamy soil with the aim of determining the P transport patterns and processes in the soil before and after the application of biogas digestate. Prior to the application of biogas digestate, the pore water concentrations of dissolved reactive P (DRP) were significantly lower than the total P (TP) concentrations, with DRP/TP ratios increasing from 0.03 to 0.89. After fertilizer application, the TP and DRP pore water concentrations increased 400-fold. The DRP/TP ratio remained almost constant at 0.83. After 220 mm of precipitation, 4.5% of the P mass applied was leached to below the 50-cm soil depth, indicating the general mobility of P in soils during high-intensity rainfall. Brilliant Blue dye tracing experiments revealed that organic-matter-rich biogas digestate obviously changes the flow and transport patterns in soils from being homogenous to moderately heterogeneous, including preferential flow. Although the P loading across the flux plane had been equilibrated prior to treatment, after the application it was found to be concentrated in preferred transport regions. The emerging conclusion is that the risk of ground and subsequent surface water pollution with P after fertilization with biogas digestate originates not only from the applied P mass but also from the shift in the flow and transport regime caused by the organic-matter-rich slurry.

Abbreviations: BB, Brilliant Blue; DRP, dissolved reactive phosphorus; TP, total phosphorus.

The anthropogenic P in landscapes originates from urban, industrial, and agricultural sources (Blaas and Kroeze, 2016). In landscapes threatened by eutrophication, the loss of P from soil into surface water is a major concern (Kleinman et al., 2009). Despite the risk of eutrophication in surface waters, there is a considerable demand for P, in the form of mineral or organic fertilizers, to increase crop health and yields in areas with a low-P soil status (Bauke et al., 2017).

There is a trade-off between the optimal supply of P in P-depleted soils and the efficient mitigation of elevated P leaching. Applied P can be fixed rapidly to the soil by adsorption to ferric and aluminum (hydr)oxides and clay minerals and by precipitation with Ca, Mg, Fe, and Al (Degryse et al., 2013). Phosphorus can be transported to surface waters through tile drainage and groundwater flow as well as surface runoff. The contribution of surface runoff and erosion may, however, be negligible in lowland watersheds, in which it occurs only during wet conditions when precipitation exceeds the pore volume (Dolezal et al., 2001) and/or the soil’s infiltration capacity (King et al., 2015b).

Recent studies confirmed that groundwater flow (Holman et al., 2008) and tile drainage flow (King et al., 2015a, 2018; Kleinman et al., 2015) can contribute significant amounts of P to surface waters in agricultural landscapes. To be transferred to adjacent surface waters, the P has to bypass the soil matrix; it is assumed that the dissolved reactive P (DRP) and total P (TP, including particle-bound P) fractions follow different pathways through the soil (Koch et al., 2018). Dissolved reactive P can be transported by preferential as well as matrix flows, while the TP fraction (e.g., particle-bound P) is exclusively transported by macropore flow (Williams et al., 2016). This phenomenon has been visualized...
using Brilliant Blue and TiO₂ as dye tracers (Koch et al., 2016). In catchments where surface runoff dominates, particle-bound P could constitute a more important fraction of the total P load than in lowland catchments (Sharpley et al., 1994).

The effect of strong rainfall events on P’s temporal export patterns is substantial. In a northeastern German lowland catchment, 53% of the DRP and TP were transported with a fast flow component after short periods of severe rainfall events (Tiemeyer et al., 2009). A high temporal variability in P export was also observed in a Spanish watershed, where runoff events contributed to 68% of the overall exported P during a 3-yr study period (Rodríguez-Blanco et al., 2013).

The chemical composition of biogas digestate from slurry and energy crops has been the subject of numerous studies, which have identified the presence of considerable amounts of N, P, and other macronutrients such as K, S, and Ca (Kirsch, 2009). The application of (organic) fertilizers can increase P leaching. This risk is highest immediately after the application of the fertilizer (Kleinman et al., 2009; King et al., 2015b). Although the effect of organic fertilizer application (e.g., manure, slurry, or biogas digestate) on DRP and TP leaching has already been studied (Ball Coelho et al., 2012), there is a lack of in situ experimental approaches at the pedon scale. Earlier studies have concentrated on the field scale by analyzing P fluxes from tile drainage systems. Various studies from tile-drained field sites suggest that P leaching losses follow regular patterns under a homogeneous rainfall regime (without severe events; Hoover et al., 2015), which is probably related to low percolation rates and low vertical spreading of digestate (Colombani et al., 2017). It is likely that under moist soil conditions, severe rainfall events would cause the applied organic P fertilizers to be rapidly exported through the soil profile and, hence, to tile drains and adjacent surface waters. Likewise, long drought periods can cause a cracking of fine-textured soils, which might increase the potential for macropore flow (Simard et al, 2000). This idea is supported by model studies that show a significant decrease in losses of P from the soil the more time passes without precipitation after fertilizer application (Vadas et al., 2011).

Lysimeters are valuable instruments for analyzing transport processes in undisturbed soils as a function of fertilizer management, crop rotation, and soil type. However, their installation is expensive, complex, and time consuming. The use of in situ suction plates in the field for short-term applications has the advantage of being cheaper and completely flexible. Suction plates are an innovative sampling approach for collecting percolating pore water, originating from both matrix and macropore flows, from the soil at a given depth. In contrast to suction cups, the large cross-sectional area ensures the sampling of various transport regions, including preferential flow (Ciglasch et al., 2005). Suction plates have been used in a variety of long-term (Frank et al., 2017) and short-term studies (Siemens et al., 2003) to investigate the vertical transport of nutrients and pollutants in soils. They have also been used in laboratory experiments with soil columns (Willich and Buerkert, 2016). In the current investigation, the objective was to assess the effect of heavy rainfall events and biogas digestate application on the transport of P, including DRP and TP. We wanted to gain a better understanding of the spatiotemporal patterns of vertical P transport in soils by installing multiple suction plates. In addition, the dye tracing technique, using Brilliant Blue, was used to analyze the effect of digestate application on flux field generation.

Table 1. Soil physical properties at the study site including particle size distribution (clay, silt, sand), pore size distribution (micropores, mesopores, and macropores), bulk density, and organic matter content.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Clay (≤2 μm)</th>
<th>Silt (2–63 μm)</th>
<th>Sand (63–2000 μm)</th>
<th>Micropores (≤0.2 μm)</th>
<th>Mesopores (0.2–50 μm)</th>
<th>Macropores (&gt;50 μm)</th>
<th>Bulk density (g cm⁻³)</th>
<th>Organic matter (%)</th>
</tr>
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<tbody>
<tr>
<td>m</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>% (v/v)</td>
<td>%</td>
<td>%</td>
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<tr>
<td>0.00–0.30</td>
<td>8.4 ± 0.61</td>
<td>28.8 ± 0.7</td>
<td>62.8 ± 0.2</td>
<td>7.6 ± 1.77</td>
<td>24.9 ± 4.3</td>
<td>13.5 ± 2.1</td>
<td>1.31 ± 0.3</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>0.30–0.42</td>
<td>8.4 ± 0.9</td>
<td>28.5 ± 0.7</td>
<td>63.2 ± 0.4</td>
<td>7.6 ± 0.1</td>
<td>20.7 ± 0.5</td>
<td>12.4 ± 1</td>
<td>1.57 ± 0.02</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>0.42–1.00</td>
<td>12.9 ± 1.8</td>
<td>31.3 ± 3.1</td>
<td>56.5 ± 2.5</td>
<td>11.5 ± 0.1</td>
<td>18.25 ± 1</td>
<td>3.5 ± 0.6</td>
<td>1.77 ± 0.02</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

† Mean ± standard deviation.
were 74.4 ± 10.8 mg kg\(^{-1}\) soil and 9.8 ± 9.8 mg kg\(^{-1}\) soil from the 0- to 35- and 35- to 50-cm depths, respectively.

The soil water retention curve allowed the calculation of various pore size classes. The pore size was determined using ceramic suction plates (at pH 1.8 and 2.48, corresponding to 60 and 300 hPa) and a pressure membrane apparatus (at pH 4.2, corresponding to 15,000 hPa, Table 1).

The experiment was conducted in September 2017 on a field sown with winter wheat (Triticum aestivum L.), 4 wk after germination. The soil surface had a minimal slope and was at a hilltop location; it was not disturbed by the experimental setup. Prior to the beginning of the experiments, 604 mm of precipitation had been measured in the year 2017 (data provided by the German Weather Service). The topsoil’s initial soil water content was 16.4% (v/v).

**Experimental Design and Laboratory Analysis**

Suction plates (EcoTech Bonn, circular borosilicate glass suction plate with a 7.5-cm diameter, a 10-μm membrane filter, and a polytetrafluoroethylene [PTFE] tube) were installed in an undisturbed soil profile with the dimensions 2.5 by 2.5 by 1.2 m (length by width by depth). Six 0.5-m-deep horizontal holes were drilled into the profile wall, 0.2 m away from each other (Fig. 1). The holes were chopped to a rectangular shape using scrapers and hand shovels, with the top of the hole being located at the 0.5-m soil depth. Before installation, the suction plates were conditioned by watering and applying a thin layer of a soil suspension to ensure a proper connection to the soil. Two suction plates were carefully installed into each mini-tunnel, and close contact to the soil was ensured by fixing each plate to a holder. Finally, the wells were refilled with the excavated soil material.
The suction plates were chosen to collect particles up to a size of 10 µm to assure the determination of DRP and particle-bound P; the particle size range for P-binding colloids and clay minerals is <20 to 300 nm (Boł et al., 2016). A 10-µm membrane was also used to prevent clogging of the suction plates.

Each suction plate was connected to a sample bottle. All 12 sample bottles were connected to the same vacuum pump to evacuate the sampling system at a constant (Leinemann et al., 2016) pressure head of ~200 hPa. A 2.5- by 1.0-m wooden collar was placed on the soil above the suction plates to allow precise irrigation and to prevent surface runoff. This setup was used for three consecutive experiments.

The first experiment took place on 26 and 27 Sept. 2017. Rainfall was simulated manually by using watering cans with a sprinkler cap. Tap water was used for irrigation. Forty millimeters of rainfall was applied during a 15-min period every 2 h. To avoid inundation of the soil surface, the precipitation intensity was reduced to 20 mm every 2 h after a total applied precipitation of 200 mm. We irrigated for a total time of 16 h in 1 d. The total amount of water applied in the first experiment was 900 L, which corresponds to a total precipitation of 360 mm. All the irrigation water was applied directly to the irrigation area (see Fig. 1). Water samples were extracted every 2 h from the evacuated sample bottles. The initial water sample was taken 5 h after the onset of irrigation; at that time, it was possible to collect the minimum sample size for chemical analysis, 60 mL per sample, from at least three sample bottles.

The second experiment was conducted from 2 to 3 Oct. 2017. Fifteen liters of biogas digestate (animal slurry from cattle, co-fermented with energy crops (Zea mays L.) and grass silage) from a conventionally worked local farm (Gut Dummerstorf) was applied manually, using a dipper, 15 min prior to the onset of irrigation. The total amount of P applied to the irrigation area was 4.8 g m⁻², which corresponds to a P fertilization of approximately 48 kg P ha⁻¹. The analysis of the digestate revealed liquid mass contents of 5.05 ± 1.92% organic matter, 0.38 ± 0.12% N, 0.08 ± 0.03% P, 0.21 ± 0.01% K, and 0.12 ± 0.05% Mg. After application of the digestate, 40 mm of precipitation was applied twice to a total precipitation of 360 mm. All the irrigation water was applied manually, using a dipper, 15 min prior to the onset of irrigation. The total amount of P applied to the irrigation area was 4.8 g m⁻², which corresponds to a P fertilization of approximately 48 kg P ha⁻¹. The analysis of the digestate revealed liquid mass contents of 5.05 ± 1.92% organic matter, 0.38 ± 0.12% N, 0.08 ± 0.03% P, 0.21 ± 0.01% K, and 0.12 ± 0.05% Mg. After application of the digestate, 40 mm of precipitation was applied twice to a total precipitation of 360 mm. All the irrigation water was applied directly to the irrigation area (see Fig. 1). Water samples were extracted every 2 h from the evacuated sample bottles. The initial water sample was taken 5 h after the onset of irrigation; at that time, it was possible to collect the minimum sample size for chemical analysis, 60 mL per sample, from at least three sample bottles.

Slight indications of siltation were observed on the soil surface during both experiments, but the infiltration process was not altered.

The water samples collected in both experiments were subdivided into two samples. One sample was filtered immediately in the field using a 0.45-µm cellulose acetate membrane filter (Carl Roth). Dissolved reactive P concentrations in the filtered samples were measured colorimetrically (Specord40, Analytic Jena) (Murphy and Riley, 1962). The unfiltered samples were also analyzed colorimetrically to determine the TP concentrations after alkaline digestion (Koroleff, 1983). The measured volumes, suction plates contributing to the overall flow, and the concentrations of DRP and TP are provided in Supplemental Fig. S1.

The third experiment was a dye tracer experiment using Brilliant Blue (Flury et al., 1994), conducted from 10 to 11 Oct. 2017. A metal collar (0.7 by 0.7 m) was inserted into the soil and 24.5 L with a Brilliant Blue concentration of 4 g L⁻¹, corresponding to 50 mm of precipitation, was applied (Fig. 1). The collar was placed into the 2.5- to 1.0-m irrigation area where the biogas digestate was applied. Twenty-four hours after applying the dye tracer, five vertical soil profiles with a spacing of 0.1 m were prepared successively by cutting the soil profile with a spade. Each soil profile was photographed and analyzed by conversion into black and white images using Adobe Photoshop CC and Adobe Lightroom CC (Adobe Systems). The methodological approach used in the dye tracer experiment was described comprehensively by Koch et al. (2016).

Laboratory pretests were conducted prior to the field experiments to ensure that both the dissolved and particulate P fractions could be captured with the suction plates. The ability of the suction plates to collect particles of the required sizes was tested using a TiO₂ suspension (Tiona AT-1, Cristal Global, average particle size 0.3 µm with 75% of the particles being in the range of 0.2–0.4 µm [information supplied by Cristal Global]). Jiang et al. (2015) investigated the P content of soil aggregates ranging from <0.45 to ≥0.45 µm and found a significant increase in the overall P content with decreasing aggregate size. Thus, it can be assumed that the TiO₂ is a satisfactory representation of the relevant fraction for the transport of P-enriched soil colloids. The TiO₂ from the test suspension was found in the filtered water samples collected using a −200 hPa pressure head. The pretest confirmed that the suction plates with 10-µm pore size allowed particles in the range of 0.3 µm through and are thus considered suitable for differentiating between TP and DRP.

Results and Discussion

Dissolved Reactive and Total Phosphorus

The mean DRP and TP concentrations (± standard deviation) in the pore water were 0.07 ± 0.05 and 0.10 ± 0.09 mg L⁻¹ before digestate application (Fig. 2). These concentrations increased significantly (p < 0.001, Mann–Whitney U-test) to 0.34 ± 0.21 mg L⁻¹ DRP and 0.37 ± 0.21 mg L⁻¹ TP after application of biogas digestate. ** Significant at p < 0.01.
after the application of biogas digestate. The DRP and TP concentrations were significantly different before the application of biogas digestate ($p < 0.001$, Mann–Whitney $U$-test) but not after it ($p > 0.1$, Mann–Whitney $U$-test).

In the first experiment, the P concentrations increased steadily along with the rainfall events, with initial mean DRP and TP concentrations of 0.001 and 0.04 mg L$^{-1}$, respectively (Fig. 3a and 3c). The maximum DRP and TP concentrations of 0.12 and 0.13 mg L$^{-1}$, respectively, were measured after 18 h after beginning the experiments, 1.5 h after the final irrigation. After reaching their maximum concentrations, a constant decrease in DRP and TP concentrations was observed.

In contrast, the time variation curves were erratic following the application of biogas digestate and showed no clear trend in P concentrations, either increasing or decreasing (Fig. 3b and 3d). The mean initial DRP and TP concentrations after the application of biogas digestate were 0.39 and 0.40 mg L$^{-1}$, respectively, which corresponds to an approximately 400-fold increase. After the application of biogas digestate, the maximum and minimum mean concentrations of DRP and TP were 0.52 and 0.68 mg L$^{-1}$ (11 h after the initial irrigation) and 0.17 and 0.22 mg L$^{-1}$ (13 h after the initial irrigation), respectively.

The results confirm an increase in the release of DRP and TP after the application of the biogas digestate and are in accordance with previous studies in which digestate from biogas production using household waste or crop residues (mixed with manure and/or sewage sludge) was applied (Sharpley and Moyer, 2000; Cherobim et al., 2017; Young et al., 2017). Long-term runoff analyses from an agricultural field site under organic fertilization (swine manure) showed increased P leaching and a severe impact from storm events (30–60 and >60 mm of precipitation; Tomer et al., 2016). Likewise, an increase in tile drainage losses of DRP were recorded from a clay loam soil, independent of rainfall events. The application of compost increased the tile drainage P losses 2.7- and 5.3-fold, under different tillage practices (Zhang et al., 2017).

Initially, the vertical P transport was dominated by the TP fraction, but with increasing rainfall and percolation water, the proportion of DRP increased markedly. Immediately after the final irrigation, the DRP/TP ratio decreased rapidly. The development of the DRP/TP ratios before the application of biogas digestate (Fig. 4a) indicates DRP mobilization processes. After the application of biogas digestate, the release of P was dominated by the DRP fraction throughout the entire irrigation process; after the application of biogas digestate, roughly 87% of the TP originated from DRP. Our results agree with those of previous studies and highlight that DRP and TP follow different pathways in the soil (King et al., 2015b; Julich et al., 2017; Koch et al., 2018). Dissolved reactive P is transported through the soil matrix and also through preferential flow, while TP is transported exclusively by preferential flow. These results confirm the importance of macropore flow for the transport of TP, which had already been shown in northeastern Germany on different spatial scales, from a soil profile to a mesoscale watershed (∼3000 km$^2$) (Tiemeyer et al., 2009; Koch et al., 2016, 2018). Our study indicates that the contribution made by matrix flow and DRP to the total release of P increases with increasing rainfall and percolation duration.

The data presented highlight that without the application of biogas digestate, TP transport has a greater impact on the overall transport of P. Furthermore, shorter rainfall events will enhance the transport of particulate P rather than DRP. After the application of biogas digestate, DRP was the main contributor of P leaching through the soil. We assume that DRP’s dominance originates from the P composition of the fertilizer applied. It should be pointed out that the determination of the various P fractions in the
liquid biogas digestate has not yet been done. The available analytical data are derived from dry mass (Li et al., 2014; Bachmann et al., 2016) and cannot be transferred to the liquid digestate.

For all suction plates, the DRP and TP loads varied significantly (Table 2, $p < 0.05$, Mann–Whitney U-test) before and after biogas digestate application (Fig. 5). Before and after biogas digestate application, the total DRP loads were 0.68 and 2.56 mg (0.13 and 0.48 kg ha$^{-1}$), respectively, related to the same amount of percolated water. The total TP loads were 0.91 and 2.74 mg (0.17 and 0.52 kg ha$^{-1}$) before and after biogas digestate application, respectively, taking a similar volume flux as the calculation basis. Thus, the DRP and TP loads increased threefold by the application of biogas digestate. The observed short-term DRP loads prior to the application of biogas digestate were on the same order of magnitude as the total annual mean DRP outputs in the observed watershed (Koch et al., 2018) with the severe rainfall regime used in this study.

The spatial analysis revealed that there was a profound difference in the spatial distribution of P fluxes before and after digestate application. Before the application of biogas digestate, no clear spatial pattern was detectable, and the loads were more or less homogeneously distributed across the suction plates. After fertilization, the P fluxes became more concentrated, and a heterogeneous pattern manifested; Suction Plates 3 to 8 showed significantly higher DRP and TP loads than before the biogas digestate application (Mann–Whitney U-test, $p < 0.05$). This is a surprising result since the biogas digestate was homogeneously applied to the soil surface.

Biogas digestate from slurry and energy crops carries approximately 5% organic matter in its liquid mass and about 95% organic matter in the dry mass (Al Seadi et al., 2008). The digestate used in this study had an organic matter content of 5.05 ± 1.92% in the liquid mass. While cellulose and organic acids are broken down during the digestion process (Al Seadi et al., 2008), other complex structures like lignin, and strongly hydrophobic components, such as alkanes, remain in the digestate. We postulate that the digestate’s hydrophobic compounds induced a shift in the soil’s flux and transport regimes. Before application, the P transport was dominated by a uniformly distributed matrix flow; afterward, however, the main mechanism of P leaching was preferential flow—or better said, “preferred transport.” The idea of rapidly transported dissolved P is supported by the high initial P concentrations following the application of the biogas digestate (Fig. 2). It is likely that this P originated from the slurry applied at the soil surface.

In total, 12 g of P was applied to the irrigation area (2.5 m$^2$). The leached fraction, as captured with the suction plate and extrapolated to the experimental area, was 0.54 g P. This is synonymous with a 4.5% recovery rate. The low recovery rate underlines the rapid binding of P to soil, even when being exposed to a severe rainfall regime.

### Brilliant Blue Dye Tracing

Having observed more concentrated flux and P transport in soils after organic manure application, we conducted a dye tracer test to obtain more insight into the transport situation. Using Brilliant Blue dye tracing after applying biogas digestate showed a widespread dye tracer coverage of the upper soil horizon (Fig. 6 and 7). Before the application of the biogas digestate, 57% of the upper 30 cm and 7% of the subsoil (0.3–0.7 m) were stained by Brilliant Blue. After applying biogas digestate, 31.1% of the first 30 cm, 4.3% of 30- to
Our study showed a rapid increase in the pore water concentrations of DRP and TP and changes in the spatial distribution of P transport following the application of biogas digestate and severe rainfall events (>200 mm within 1 d). The data show that in the early stages of severe rainfall events, leaching of P increases, with a dominant proportion of TP. The longer severe rainfall events last, the more DRP is mobilized. We assume that the energy input at high flux rates causes P remobilization, although definite conclusions cannot be drawn at this point. The application of biogas digestate (P equivalent of 48 kg P ha\(^{-1}\)) caused a 400-fold increase in pore water P concentrations, with a clearly dominant DRP fraction immediately after fertilization. The risk of groundwater contamination with P following the application of biogas digestate originates not only from a surplus of mobile P but also from a flux regime shift with preferential flow pathways. In view of the (unrealistic) high rainfall intensities chosen, the P loads observed express a P leaching potential for the soil studied.

Further research should focus on the short- and long-term effects of organic fertilizers on the physical properties of soil (hydrophobicity, porosity, aggregate stability) to fully understand and depict nutrient and water flow pathways after the fertilizers’ application.

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Supplemental Material
The supplemental material shows a graph in which we combined total sample volume with the number of active (water delivering) suction plates and mean P concentrations. The graphics shows that the sample volume increases with rainfall duration, as expected, and decreases after irrigation is stopped (irrigation without digestate application). The flow pattern changed after digestate application and the sample volume no longer matched the irrigation regime.

References


