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Phosphorus Leaching from Cow Manure Patches on Soil Columns

W. J. Chardon,* G. H. Aalderink, and C. van der Salm

ABSTRACT

The loss of P in overland flow or leachate from manure patches can impair surface water quality. We studied leaching of P from 10-cm-high lysimeters filled with intact grassland soil or with acid-washed sand. A manure patch was created on two grassland and two sand-filled lysimeters, and an additional two grass lysimeters served as blanks. Lysimeters were leached in the laboratory during 234 d with a diluted salt solution, and column effluent was passed through a 0.45- μm filter, analyzed for pH, dissolved reactive P (DRP), and total dissolved P (TDP). At the end of the experiment lysimeter soil was sampled and analyzed for pH, available P, and oxalate-extractable P, Fe, and Al. The concentration of TDP in the effluent from the sand column increased to 25 mg L⁻¹ during the first weeks and remained above 10 mg L⁻¹ during the rest of the percolation. In effluent from grass + patch lysimeters TDP gradually increased to 4 mg L⁻¹. Both in the manure and in the effluent of the sand lysimeter P was found mainly in the form of DRP, but in the effluent from the grass lysimeters was found mainly as dissolved unreactive P (DUP = TDP - DRP). Earthworm activity was responsible for decomposition of the manure patch on the grass lysimeters. Manure patches and their remains were found to be a long-term source of high concentrations of P in leachates. Spreading of patches after a grazing period could reduce their possible negative impacts on the environment.

APPLICATION of animal manure to soils can be an important direct source of P in runoff (Mueller et al., 1984; Sharpley et al., 1994). When frequently applied in amounts exceeding harvest offtake, it can cause the buildup of large amounts of P in the soil profile (Lehmann et al., 2005; Nelson et al., 2005; Koopmans et al., 2006). When the P sorption capacity of the soil becomes filled, the risks of vertical transport through the profile and groundwater and surface water contamination increase (Sims et al., 1998; Schoumans and Groenendijk, 2000). Manure patches, deposited on grassland during grazing, are a concentrated source of P (Haynes and Williams, 1993). They can be an important source of P for grassland, and are often larger than the amount added via fertilizers (Williams and Haynes, 1995). When patches occur on areas where runoff is likely, increased loss to surface water becomes possible (McDowell and Stewart, 2005). Deposition of patches during grazing of stream banks can lead to a direct input of P into streams (McDowell, 2006), and of suspended sediment, N, and *Escherichia coli* (McDowell et al., 2006). The amount of P applied under a patch was estimated as 280 kg ha⁻¹ (Haynes and Williams, 1993). Due to this high P application rate, the local risk of leaching may also increase.

Twelve months after application of a manure patch in the field, Williams and Haynes (1995) found an increase of bicarbonate and resin-extractable P up to 10-cm depth below the patch. Page et al. (2005) measured plant-available P (Olsen method) on various locations in two catchments and found large spatial variability. High values of Olsen P were ascribed to livestock sheltering under trees, runoff from the cow shed, or the proximity of a gate. In all cases manure patches were the source of the high Olsen P values (Page et al., 2005).

The overall objectives of this research were (i) to study concentrations of P found in leachates from artificial manure patches created on grassland or sand lysimeters and (ii) to determine the different forms of P in manure and lysimeter leachate.

MATERIALS AND METHODS

Lysimeter Collection

Intact monolith lysimeters (10-cm depth, 24-cm i.d.) of a free-draining sandy soil were taken from a permanent grassland site on the Aver-Heino experimental farm in Heino, The Netherlands (52°26' N; 6°14' E). The soil had an organic matter content of 0.051 kg kg⁻¹, a clay content of 3%, and the pH measured in KCl was 5.6 (van Middelkoop et al., 2004). Four polyvinyl chloride casings were manually driven into the soil using a hammer, the surrounding soil was removed, and at the bottom of the casing the soil was cut with a knife. In the laboratory, the soil columns were equipped with a bottom filled with acid-washed (0.1 M HCl) sand to create a free-draining situation through an open outlet. Besides the four columns with field soil, two blank columns were filled with acid-washed sand as a zero P sorption control.

Lysimeter Treatment and Management

Manure was collected in the field from 10 patches made by 1-yr-old cows, immediately after defecation, in October 2004. Total wet weight was determined (13.7 kg) and the manure was thoroughly mixed. It was estimated that on collection 90% of the manure could be taken from the grass. Therefore, 11.1% (by weight) of the collected manure (1.52 kg) was used to create each artificial manure patch for the lysimeters. Two lysimeters with grassland soil received a patch, the other two served as blanks, and two patches were made on the lysimeters filled with acid-washed sand. During 234 d the lysimeters were percolated manually with 1.5 cm solution (\approx 136 mL) per week, the long-term average amount of weekly rainfall in The Netherlands. This was divided over five equal portions that were applied every weekday (Monday through Friday). The leachate from a grassland soil with a patch was assumed to simulate the soil solution leaving the rooting zone under the patch, and the leachate from the sand lysimeters was assumed

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Abbreviations: DM, dry matter; DRP, dissolved (0.45- μm filtrate) molybdate reactive P; DUP, dissolved unreactive P (= TDP - DRP); ICP, inductively coupled plasma; P-AL, P extracted in acid ammonium lactate; Pw, water-extractable P; P-ox, oxalate-extractable P; Fe-ox, oxalate-extractable Fe; Al-ox, oxalate-extractable Al; TDP, total dissolved P; TP, total P.

to simulate the solution that enters the soil surface under a patch. The lysimeters were kept at 15°C in a dark, temperature controlled, and mechanically ventilated incubation case. For the percolation, a solution was used with a composition comparable to rainwater collected from weather stations in the eastern part of The Netherlands. The solution contained 0.0398 mM NH_4^+ , 0.348 mM Na, 0.040 mM K, 0.138 mM Mg, 0.0398 mM NO_3^- , 0.250 mM Cl, and 0.414 mM SO_4^{2-} ($I = 0.141 \text{ mM}$).

Leachate Collection and Analysis

Leachate was collected by free drainage into a vessel and was sampled weekly. Samples were passed through a 0.45- μm cellulose nitrate-acetate filter and the filtrate was analyzed for pH, for dissolved reactive P (DRP) colorimetrically according to Murphy and Riley (1962), and for total dissolved P (TDP) using inductively coupled plasma (ICP).

Manure Analysis

Dry matter content of the manure was determined by drying subsamples ($n = 5$) at 105°C, and organic matter content was estimated by weight loss after further heating at 550°C. Total P (TP) content was determined by digestion of 2 g manure dried at 105°C ($n = 5$) using aqua regia (3:1, v/v, HCl/HNO_3). To collect the liquid fraction of the manure for DRP analysis, a 40-g subsample of the manure was centrifuged 20 min at 2000 g over a 0.45- μm cellulose nitrate-acetate filter, with a 2- μm Schleicher & Schuell 589/3 pre-filter (Whatman, Brentford, UK). Although the moisture content of the manure was approximately 81%, only 2 mL liquid could be collected this way from the 40 g manure. Water-extractable P in the manure was determined by mixing 2 g fresh manure with 400 mL demineralized water, and shaking 1 h horizontally at 150 movements min^{-1} . The mixture was filtered through a 0.45- μm filter, and DRP and TDP were determined in the filtrate.

Soil Analysis

At the end of the percolation period, all visible remains of the manure patches on the surface of the lysimeters were collected, dried at 40°C, weighed, digested with aqua regia, and analyzed for TP content. The soil was sampled with a 2-cm diameter gouge, which made it possible to split the soil into layers. Samples were collected from layers 0 to 2, 2 to 4, 4 to 6, 6 to 8, and >8 cm from the bottom. On some places of the sand lysimeters the surface was uneven, so less than the expected top 2 cm (8 to 10 cm from the bottom) was present. Thus, no sample of this layer could be obtained for the sand lysimeters. On average, eight subsamples of the same layer were mixed to one composite sample and three composite samples were prepared for each 2-cm layer. Samples were dried at 40°C and passed through a 2-mm sieve before analysis. The samples were analyzed for water-extractable P (Pw, 1:60 v/v extraction with demineralized water; Sissingh, 1971); ammonium lactate-acetic acid-extractable P (P-AL; Egnér et al., 1960); acid ammonium oxalate extraction (Schwertmann, 1964) followed by ICP analysis on P, Fe, and Al; pH (1:5 v/v demineralized water); and organic matter content via loss-on-ignition at 550°C.

RESULTS AND DISCUSSION

Manure Analysis

Results of manure analysis are summarized in Table 1. Total P content (8.7 g kg^{-1} dry matter [DM]) was higher than results for dairy manure from McDowell and Stewart

Table 1. Selected characteristics of the manure used in the lysimeter study.

Properties	Average ($n = 5$)	Standard deviation
Moisture content, kg kg^{-1} fresh wt.†	0.814	0.006
Dry matter content, kg kg^{-1} fresh wt.†	0.186	0.006
Organic matter content, % of DM‡	57.1	0.19
Total P, g kg^{-1} DM§	8.7	0.17
DRP in centrifugate, mg L^{-1} ¶	4.5	1.28
DRP in 200:1 extract, mg L^{-1}	5.8	0.43
TDP in 200:1 extract, mg L^{-1}	6.0	0.50
Water-extractable TDP, g kg^{-1} DM#	6.7	0.41
Water-extractable TDP, g kg^{-1} fresh wt.#	1.2	0.08

† After drying at 105°C.

‡ Determined via loss-on-ignition at 550°C.

§ Determined after aqua regia digestion.

¶ DRP, dissolved (0.45- μm filtrate) molybdate reactive P.

Calculated from TDP (total dissolved P) in 200:1 extract and dry matter content.

(2005), who found 5.5 g kg^{-1} , but was only somewhat above the range of 6.0 to 8.6 g kg^{-1} for 68 dairy manure samples, reported by Kleinman et al. (2005b). The high TP content could be caused by a higher P concentration in the pasture, since this influences P content in the manure (Haynes and Williams, 1993). On the field where our lysimeters were obtained, van Middelkoop et al. (2004) found an average value of 3.6 mg kg^{-1} DM for the P content of the grass. The concentration of water-extractable TDP in the manure was relatively high: 6.7 g kg^{-1} DM, or 77% of TP in the manure. This could be due to the high extraction ratio we used: 200:1 on basis of wet weight, or 1075:1 on basis of DM. McDowell and Stewart (2005) found that 36% of TP in fresh dairy manure was water-extractable, after shaking three times at a 100:1 ratio. Using a 200:1 ratio on basis of dry weight, Kleinman et al. (2005b) found an average Pw content equal to 60% of TP for 68 dairy manure samples that were stored and handled under different conditions; for seven fresh manure samples they found a slightly higher value of 70%. In the 200:1 extract, TDP was almost completely in the form of DRP (96.7%, Table 1).

Centrifugation at 2000 g yielded only 2 mL of solution from 40 g manure (5%), which is much less than the moisture content (0.814 g kg^{-1} fresh wt.) of the manure (Table 1). Although a 2- μm pre-filter was used, some plugging of the 0.45- μm filter may have occurred during centrifugation, which reduces the solution yield.

The lysimeters received 1.52 kg wet manure, corresponding to 0.283 kg DM and 2.46 g P. The surface of the lysimeters was 0.0452 m^2 , giving 34 g m^{-2} wet manure. In the field this would correspond with a local application of 544 kg P ha^{-1} on a place where a manure patch is deposited. In a previous field experiment, van Middelkoop et al. (2004) found for five patches on the plot where the lysimeters were collected, a lower average weight (0.97 kg), a smaller surface area (0.0322 m^2), but a comparable rate of 31 g m^{-2} wet manure; the application rate for P was 429 kg P ha^{-1} . Haynes and Williams (1993) gave 280 kg P ha^{-1} as an example for the rate of P application under a patch. These rates are high, but in the field physical breakdown or activities of fungi, bacteria, beetles, and earthworms may cause mineralization and dispersion of the manure in patches, and thus of

deposited P (Haynes and Williams, 1993). Besides, a positive influence of N applied via an artificial manure patch on grass dry matter yield, on an area four times the size of the original patch, was found by Deenen and Middelkoop (1992). Thus, under field conditions it may be expected that P deposited via patches may also be partly taken up by the grass around a patch, decreasing the risk of leaching below the patch itself. For further decrease of the leaching risk in the field, patches could be regularly dispersed, e.g., at the end of grazing periods.

Phosphorus in Leachate

Figure 1 shows the concentrations of TDP measured in the effluent of the lysimeters. In effluent from sand + patch lysimeters TDP increased to a level around 25 mg L^{-1} , and after 50 d it decreased and varied between 10 and 20 mg L^{-1} (Fig. 1). On both the blank and the grass + patch lysimeters TDP varied between 1 and 2 mg L^{-1} during Days 1 through 50 and then decreased. For the grass + patch lysimeter TDP started to increase after Day 80 up to 4 mg L^{-1} , while without patch TDP remained below 0.5 mg L^{-1} (Fig. 1). Kleinman et al. (2002) found concentrations of TP in runoff after poultry manure application up to 21 mg L^{-1} , comparable to the TDP concentration found during the first 50 d in the leachate from the sand lysimeters. Nelson et al. (2005) determined DRP in $0.45\text{-}\mu\text{m}$ filtered soil solution at 45-cm depth in a field that received large amounts of swine waste in the past, and found maximum concentrations exceeding 18 mg P L^{-1} .

The cumulative amounts of P found in the effluent over the whole period are summarized in Table 2. Seven times more TDP was found in the effluent from the sand + patch lysimeters than in the grass + patch lysimeters, probably due to retention of P in the soil of the grass lysimeter. From the sand lysimeters, P almost completely leached as DRP (93%), corresponding with the fact that Pw of the manure was almost completely (96.7%) in the form of DRP (Table 1). The grass and grass + patch lysimeters showed the opposite, where less than 30% of TDP in the leachate was in the form of DRP, indicating

Table 2. Summary of data on effluent of lysimeters and P in remains of patch collected from the lysimeter surface (averages, with standard deviation of duplicate values per treatment in parentheses).

Property	Sand + patch	Grass + patch	Grass
Cumulative TDP leached, mg^\dagger	215 (17)	30 (1.2)	6 (2.5)
Cumulative DRP leached, mg^\ddagger	201 (10)	8 (0.7)	2 (0.4)
Cumulative DUP leached (TDP - DRP), mg^\S	14 (7.0)	22 (0.5)	4 (2.0)
DRP leached, % of TDP	93 (2.7)	26 (1.2)	29 (4.5)
pH $^\parallel$	7.5 (0.4)	7.3 (0.3)	7.0 (0.7)
TDP leached, % of applied	9 (0.7)	1 (0.05)	—
P in remains of patch, % of applied	76 (8)	22 (1)	—
DM in remains of patch, % of applied	68 (16)	15 (1)	—

† Total dissolved ($0.45\text{-}\mu\text{m}$ filtrate) P.

‡ Dissolved molybdate reactive P.

§ Dissolved unreactive P.

$^\parallel$ Average value of 33 measurements in effluent per lysimeter, during whole percolation period.

that dissolved unreactive P (DUP) was more mobile in this soil than DRP (Chardon et al., 1997). On average, 24 mg more TDP leached from the grass + patch than from the grass lysimeters, of which 6 mg was DRP and 18 mg was DUP (Table 2). Immobilization of P in transportable bacteria could have been responsible for the dominance of DUP in leachate of the grass + patch lysimeters. Toor et al. (2005) irrigated 70-cm-deep lysimeters with dairy farm slurry, which contained mainly DRP (86% of TDP). In the lysimeter leachates (filtered through a $0.45\text{-}\mu\text{m}$ filter), 92% of TDP occurred as DUP. In contrast, Kleinman et al. (2005a) found with 30- to 50-cm-deep intact soil columns that P leached mainly as DRP before poultry manure application, but mainly as DUP thereafter. However, this can possibly be ascribed to direct transport of DRP from the poultry manure via preferential flow through the columns.

More TDP leached from the grass + patch lysimeters than from the grass lysimeters (24 mg ; Table 2), which would correspond locally with approximately 5 kg ha^{-1} . For the rotational grazing system of the experimental farm where the lysimeters were collected, van Middelkoop et al. (2004) estimated that 5% of the soil surface is covered with manure patches yearly, so on a field scale the increased leaching due to patches would be small ($0.25 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Obviously, the percentage covered strongly depends on the grazing intensity. The small amount of P with which leaching increases can be ascribed to the large capacity of the grassland soil to bind P. However, this capacity would not have been used, and thus the effect on leaching could become much larger, when transport is possible via preferential flow paths. Under field conditions, earthworms attracted by a manure patch like the deep burrowing *Lumbricus terrestris* L., may be responsible for preferential flow paths, leading to fast transport of P to drainage pipes (Stamm et al., 1998; Shipitalo and Gibbs, 2000). Moreover, it may be expected that there is a prolonged effect of patch application on leaching as part of the P was still present in the patch at the end of the experiment, and we did not observe a decline in P leaching.

It was apparent from the remains of the patches that were collected after leaching of the lysimeters was stopped

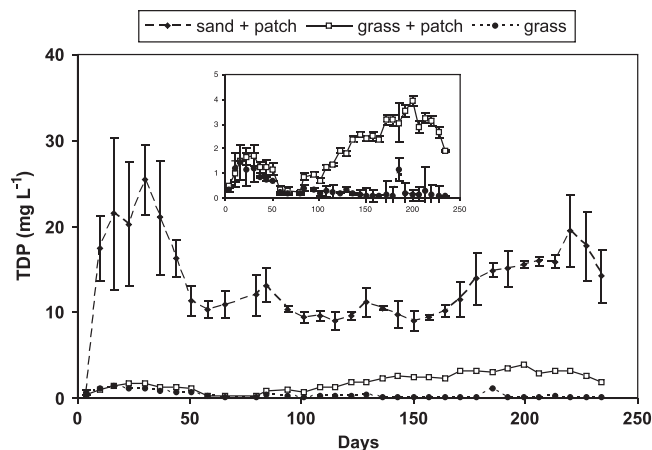


Fig. 1. Concentration of total dissolved P (TDP) in effluents of lysimeters; mean of duplicate columns with standard deviation. Inset shows details from grass lysimeters. Note different scales of y-axes.

Table 3. Selected properties of soil layers of grass + patch (g+p), grass (g), or sand + patch (s+p) lysimeters at the end of the experiment. Mean and standard deviation (s.d.) of six values (two lysimeters \times three composite samples).

Depth cm	P-AL [†]			Al-ox [‡]			Fe-ox [‡]			P-ox [‡]			PSI [§]		
	g+p	g	s+p	g+p	g	s+p	g+p	g	s+p	g+p	g	s+p	g+p	g	s+p
	mg kg ⁻¹														
0–2	648	174	NA	892	987	NA	2322	2297	NA	1421	670	NA	62	28	NA
s.d.	68	12	–	76	93	–	88	257	–	81	62	–	6.2	1.4	–
2–4	449	176	19	941	1020	13	2396	2395	45	1016	632	21	42	25	51
s.d.	76	59	12	35	52	1.7	142	113	9	96	38	9.5	3.4	1.0	18
4–6	307	166	15	968	1020	15	2321	2347	55	784	594	21	33	24	47
s.d.	46	18	4.6	65	28	1.7	154	176	25	31	36	2.9	2.5	0.9	15
6–8	250	209	19	990	1074	16	2255	2482	79	708	632	27	30	24	45
s.d.	33	83	4.0	40	57	1.0	124	230	26	40	44	5.8	1.1	1.3	15
8–10	236	171	22	961	1063	16	2375	2470	88	701	618	29	29	24	47
s.d.	31	27	3.3	49	92	2.4	117	310	31	24	70	5.9	0.4	0.8	18

[†] Phosphorus extracted in acid ammonium lactate (pH = 3).

[‡] Oxalate-extractable Al, Fe, and P.

[§] PSI = $100 \times [P/(Fe+Al)]$ -ox (molar ratio).

|| The term NA indicates that no sample was available due to uneven soil surface.

that 76% of the P that was applied via the patches was still present on the sand lysimeters, including 68% of the DM applied. For the grass lysimeters these data were much lower (22% of TP and 15% of DM; Table 2). Biological activity of earthworms that were present in the grass columns after collecting the lysimeters in the field can probably explain the disappearance of material from the patches. Excrements of earthworms were clearly visible on the surface of the grass lysimeters at the end of the experiment. The earthworm *Eisenia foetida* (Savigny) was shown to mix cattle slurry through the top 17.5 cm of a sandy soil (Opperman et al., 1987). Sharpley et al. (1979) found that activity of surface-casting earthworms increased the infiltration rate of pasture soils, which led to a decrease in P and N runoff from soil. On the other hand, surface casts accounted for a large part of the annual loading of particulate P in runoff. The overall effect of the absence of earthworms and their casts was a substantial increase in runoff P and N (Sharpley et al., 1979). From the sand lysimeters it can be concluded that a manure patch and its remains are a long-term source of a very high (TP > 10 mg L⁻¹) concentration of P in passing water like infiltrating rainwater or surface runoff. In a field study, Williams and Haynes (1995) found that it was 12 mo after application before all visible remains of cattle manure had gone from the soil surface. In a previous field experiment on the same plot as where our lysimeters were collected it

was found that manure patches had disappeared completely after 3 mo, which may be explained by biological activity (van Middelkoop et al., 2004). Breakdown of a patch is also strongly influenced by weather conditions after deposition. High temperatures promote the formation of a crust, which partially protects the patch from the eroding effects of raindrops (Haynes and Williams, 1993), but will also protect it from complete drying. McDowell and Stewart (2005) found that air-drying until moisture content was <2% of that in fresh manure (20 d at 25°C) caused a shift of P from pools extractable with water, bicarbonate, or NaOH to more recalcitrant pools, thus reducing the risk of transport.

Soil Analysis

Table 3 shows data of P-AL and oxalate extractable Al, Fe, and P (Al-ox, Fe-ox, and P-ox, respectively). As expected, both P-AL and P-ox were strongly increased in the grass + patch lysimeters when compared with the grass lysimeters. The increase diminished with depth, but remained visible up to the layer of 8 to 10 cm. Total P showed a pattern comparable to P-ox; on average P-ox was 92% of total P for all treatments (data not shown). Remarkably, below 2-cm depth Al-ox tended to be lower in the grass + patch treatment than in the grass treatment; for Fe-ox this was only the case in the layers from 6 to 10 cm. This could be due to leaching of Al and

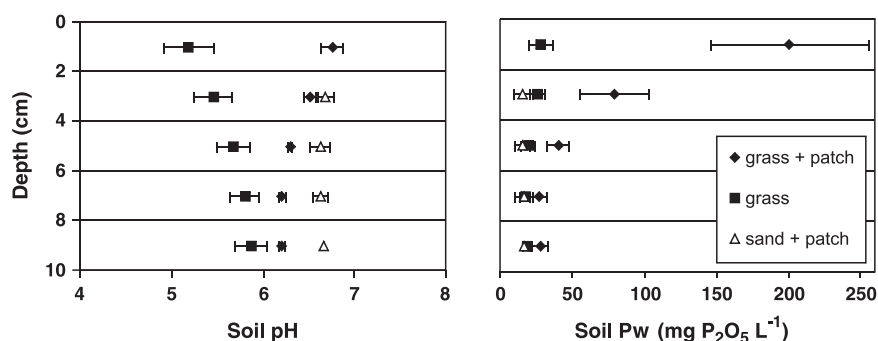


Fig. 2. Soil pH and water-extractable P (Pw) in different layers of lysimeters, sampled after leaching ended. Mean and standard deviation for six values (two columns \times three composite samples).

Fe bound to dissolved organic carbon, in turn mobilized from the soil by the high pH in the manure leachate (Table 2) (Dolfing et al., 1999). Comparing data of the grass + patch columns with data from the grass columns showed that soil pH was also strongly increased by the patch, e.g., in the 0- to 2-cm layer from 5.2 in the grass lysimeter to 6.8 in the grass + patch lysimeter (Fig. 2); the pH increased in all soil layers. In the sand + patch lysimeter the pH was approximately 6.7 in all layers. Soil pH in the sand + patch column was comparable with the grass + patch column. Water-extractable P also increased very strongly in the grass + patch lysimeter, especially in the top 0 to 4 cm. Haygarth et al. (1998) found a large build-up of Olsen extractable P in the first 2 cm of permanent grassland soil. Even after manure from the patch would have disappeared from the soil surface, this buildup of P would form a continuous risk for P loss via runoff, since this was often found to be correlated with Pw in the surface layers of the soil (Yli-Halla et al., 1995; Pote et al., 1996; Davis et al., 2005).

SUMMARY AND CONCLUSIONS

The P in the manure used for creating patches was for a large part (77% of TP) water-soluble and, when placed on a lysimeter filled with acid-washed sand, percolation caused high concentrations ($>10 \text{ mg L}^{-1}$) of TDP in the effluent for a long period. This makes patches from this type of manure a long-term source of P, which can be transported via surface runoff or leaching into the soil. Leaching of P from the sand lysimeter was almost completely in the form of DRP, as was the case with Pw in the manure. When the manure patch was placed on a grass lysimeter, earthworm activity caused disappearance of manure material from the soil surface. In the field this would probably reduce the direct risk of runoff. The grassland soil studied could retain most of the P leached from the patch. Phosphorus in the effluent from the grass lysimeters was mainly in the form of DUP, independent of the presence of a manure patch. Thus, although inorganic P dominates in the manure and in leachate from the patch, organic forms seemed to dominate P transported to soil layers below 10-cm depth.

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