Sensitivity of soil phosphorus tests in predicting the potential risk of phosphorus loss from pasture soil

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The objective of this study was to examine the effects of urine and dung additions on the phosphorus (P) chemistry of pasture land and to compare the sensitivity of two soil extraction methods in assessing the P-loading risk. In a field experiment, urine and dung were added to soil in amounts corresponding to single excrement portions and the soil samples, taken at certain intervals, were analysed for pH_{H2O} , acid ammonium acetate extractable P (P_{Ac}) and water extractable total P (TP_w), and molybdate reactive P (MRP_w). Urine additions immediately increased soil pH and MRP_w, but no such response was observed in P_{Ac} extraction due to the low pH (4.65) of the extractant enhancing the resorption of P. The P_{Ac} responded to the dung-induced increase in soil total P similarly as did P_w , which suggests that both tests can serve to detect areas of high P concentration. However, water extraction was a more sensitive method for estimating short-term changes in P solubility. In pasture soils, the risk of P loss increases as a result of the interaction of urination and high P concentration in the topsoil resulting from continuous dung excretion.

Key-words: soil testing, phosphorus, organic, inorganic, soil pH, extraction, pasture, urine, dung, runoff, leaching

Introduction

Agriculture plays a major role in non-point nutrient loading into watercourses. The Finnish Agri-Environmental Programme, established in 1995, was a step towards reduced use of nutrients in agriculture. The programme requires farms to test their soils every fifth year and included quite strict regulations on P application rates based on soil analysis. According to statistics provided by Soil Analysis Service (Viljavuuspalvelu Oy), P_{Ac} concentration in Finnish soils has increased in recent

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decades (Mäntylahti 2002). This increase ceased in the beginning of the 21st century, probably as a consequence of diminished fertiliser use, and has since decreased (Mäntylahti 2002). The P balance in the fields has decreased during the past decade from about 30 kg ha⁻¹ to 8 kg ha⁻¹ (Ministry of Agriculture and Forestry 2004). According to Granlund et al. (2005), the P load from agriculture has declined only slightly, if at all, although the P input, as manure or mineral fertilisers per hectare of farmland, has decreased (Ministry of Agriculture and Forestry 2004). In fact, the P lost from agriculture still seems to be the major pollutant in Finnish surface waters.

The high P concentration in the surface soil increases the risk for surface runoff loss of P (Sharpley and Withers 1994, Turtola and Yli-Halla 1999). In pasture soils, the defecation of grazing animals leads to P enrichment in the uppermost surface soil, especially in feeding and queuing areas (Jansson and Tuhkanen 2003). Urination, on the other hand, may enhance the risk of P loss by increasing the soil pH. Hartikainen and Yli-Halla (1996) found that an increase in pH caused by urea hydrolysis enhances the mobility of P and dissolved organic carbon in the soil. They hypothesised that at high pH, OH⁻ ions replace phosphate anions (PO₄⁻) from the sorption sites. Furthermore, a urea-induced increase in soil pH is followed by an increase in the negative charge of the adsorbing oxides, which reduces their sorption affinity. Even though the pH in their experiment later decreased, the amount of water extractable P remained far above the original level. The simultaneous dissolution of organic matter may have resulted in competition between PO_{4}^{-} and organic anions, thus diminishing the resorption of dissolved PO₄⁻ (Hartikainen and Yli-Halla 1996).

For decades, different soil phosphorus tests based on chemical extraction methods have served to estimate plant-available P reserves in soil. However, environmental concern about P has compelled research to find methods for assessing the risk of P leaching from soils. High soil P test values have been reported to indicate increased risk of dissolved P loss (e.g. Pote et al. 1996). According to Turtola and Yli-Halla (1999), routine agronomic soil tests, such as P_{Olsen} and P_{Ac} , can serve as an estimate for risk of dissolved P loss from soils. In their catchment scale study, Uusitalo and Jansson (2002) concluded that the close relationship between water extractable molybdate reactive phosphorus (MRP_w) and P_{Ac} is unaffected by soil properties such as pH, texture and organic carbon. In incubation studies, however, these P tests have been found to differ in their response to salt concentration and to a liming induced-increase in pH (Hartikainen 1989a).

In the pasture fields, the wide spatial variability in nutrient concentrations (West et al. 1989, Anderson et al. 1992) complicates the estimation of P loss. Traditionally, agronomic soil P tests serve to asses the need for fertilisation and the sampling strategy aims to obtain a soil sample representing a larger field area. From the environmental point of view, however, identification of the specific areas that contribute substantially to P loss is important. In this study, we investigated the effects of urine and dung additions on the soil P in two upper soil layers of pasture soil. The objective was to obtain information on the risk that pasture land causes to watercourses, and to compare the sensitivity of two routine P tests (P_{Ac} used for soil testing in Finland and water extraction used in the Netherlands) in assessing this risk.

Material and methods

Site description and experimental design

The study site was located in Central Finland at MTT Agrifood Research Finland, Maaninka (63°10'N, 27°18'E). According to FAO classification, the soil type was medium-textured Dystric Regosol with an organic matter content of 5.7%. The slope of the experimental area was less than 1%. The total rainfall and pan evaporation between samplings and the soil volumetric moisture content at sampling appear in Table 1. The volumetric soil moisture was measured using a Theta Probe (type ML2, Delta-T-Devices, UK).

Table 1. Sampling dates and sum of the rainfall and pan evaporation between the samplings and the soil volumetric moisture content on the sampling days.

Sampling day	Date	Rainfall, mm	Pan evapo- ration, mm	Volumetric moisture*, m ³ m ⁻³
0	9.6.	0	2	0.329
1	10.6.	33	3	0.402
3	12.6.	11	10	0.357
5	14.6.	2	7	0.344
10	19.6.	4	16	0.334
21	30.6.	11	52	0.290
49	28.7.	71	131	0.444
77	25.8.	57	81	0.323
127	14.10.	110	61	0.375

* Measured using a Theta Probe.

The experimental field was fertilised with 224 kg N, 15 kg P and 126 kg K ha⁻¹ yr⁻¹ divided into three applications of which the first (90N-15P-25K) was applied on 20 May, the second on 11 June (80N-0P-60K) and the third on 7 July 2003 (56N-0P-42K). Before the experiment began, the study area was cut twice to simulate the first two grazing rotations. The first cut (10 cm stubble) took place on 28 May and the second cut (7 cm stubble) took place immediately before applying the treatments on 9 June 2003.

The average amount of excreta was calculated on the basis of 50 single urination and defecation samples collected from tied cows. The average weight of a single defecation was 2.47 kg (SE 0.29), and urination 2.37 kg (SE 0.30). The average surface area of a dung patch was determined by measuring the cross diameters of 15 dung patches on the pasture. The surface area of average-size urination was determined by placing paper on a fresh urine spot (6 replicates) and pressing it to the ground with a plate. The size of the wet area on the paper was measured. The properties of the dung and urine appear in Table 2.

The experimental design involved randomised complete blocks (three replicate blocks) with three treatments: control, urine and dung. A total of ten dung, urine or control patches were randomised on

1		U				
	Fresh urine	Fresh dung				
pН	8.4	6.2				
DM, %	5.32	11.7				
N, g kg ⁻¹	7.5	3.9				
K, g kg ⁻¹	12.5	1.1				
Ca, g kg ⁻¹	0.1	0.9				
P, g kg ⁻¹	0.0	1.1				

Table 2. Properties of urine and dung used in this study.

DM = dry matter.

each of the three blocks. The treatment spots were placed 1.5 m apart. The excreta were collected from grazing cows during milking one hour before applying them to the field; dung and urine were collected in separate containers, mixed, sampled and then applied. Average-size dung patches were placed in the centre of a weighed, round plastic netting (diameter 36 cm, 1.3×1.3 mm mesh net) laid on the grass stubble on the field. The dung patch was spread onto the net so that a 1-cm margin remained clear along the edge of the net. The dung was easy to spread and made immediate contact with the surface soil. The weighed urine (2.37 l)was spread evenly onto the field within the border of a collar having a size corresponding to the area of a single urination (diameter 67 cm).

Soil sampling and laboratory analyses

Soil samples from the urine and control patches were taken 0, 1, 3, 5, 10, 21, 49, 77 and 120 days after the beginning of the experiment. The sampling of soil below the dung patches began on day three and continued as above. Before the sampling, the dung patch was removed from the soil with the net and taken for dry matter (DM) measurement. The sampling depths were 0-2 cm and 2-10 cm. The samples were taken simultaneously in both layers with a square-shaped ($10 \times 10 \times 10$ cm) drill. Four square core samples were taken from each treatment patch, mixed thoroughly, and divided in two sub-samples. Aboveground vegetation, other macro-

organic matter and visible stones were removed. The samples were left to dry at room temperature (20 °C) and the analysis was carried out with the air-dried soil.

Total P in dung was analyzed from oven-dried samples that were combusted at 450–500 °C and the ash was extracted with 4 M HCl (Kähäri and Nissinen 1978). Thereafter, the extract was evaporated to dryness in a water bath, and the residue was dissolved into 5 ml of 4 M HCl, rinsed immediately with 20 ml of deionised water and then filtrated (S&S 589/2) for analysis. Total P was determined with the ammonium vanadate method using a spectrophotometer. Total Kand Ca were determined from ash extract after dry combustion. Total N was determined using Kjeldahl digestion method.

Total P in the soil samples was determined with the H₂SO₄-H₂O₂-HF extraction method followed by ICP determination (Bowman 1988). Soil pH was measured from the water suspension according to routine agronomic soil testing in Finland. The water extraction was undertaken at a 1:50 (mass:volume) soil-to-solution ratio. One gram of soil in 50 ml of deionised water was shaken in a centrifuge tube with an orbital shaker for 21 hours and the suspension was filtered through a 0.4-um Nuclepore polycarbonate filter. Molybdate reactive P (MRP_w) in the filtrate was measured using the molybdenium blue method with a flow injection analyser. Total $P(TP_w)$ was measured from the filtrated samples after persulfate $(K_2S_2O_2)$ digestion using the ascorbic acid method (APHA 1989). The difference between TP_w and MRP_w in the filtrates is referred to as molybdate unreactive P (MUP_w) according to the nomenclature suggested by Haygarth and Sharpley (2000). MUP_w is considered mostly organic, but condensed forms may also be involved. Acid ammonium acetate extractable P (P_{Ac}) (0.5 M CH₃COONH₄+0.5 M CH₃COOH, pH 4.65; Vuorinen and Mäkitie, 1955) at a volumebased soil-to-solution ratio of 1:10, was measured using the molybdate-ascorbic acid -method with an autoanalyser. The bulk density of the air-dried soil, determined separately for each soil layer, was used to correct the per volume results to per kilogram of soil.

Statistically significant differences between the treatments were tested with analysis of variance. We used Dunnett's test to compare the P tests of urine- and dung-treated soils on the control treatment. The standard error (SE), standard error of difference (SED) and Dunnett's tests least significant difference (LSD) values for each variable were calculated over all treatments and sampling days, although the two sampling depths were analysed separately. The treatment means were compared separately on each sampling day using Dunnett's LSD (p < 0.05) value. The standard deviation (SD) was used for estimating the variation of P test results in control samples.

For the upper 2 cm of soil, the relative sensitivity with which P tests (P_{Ac} and MRP_w) respond to urine and dung treatments was calculated as a treatment-induced change in the P test result compared to the control sample ((Ptest_{treatment}-Ptest_{control})/ Ptest_{control}). The responsiveness of P tests to urine and dung additions were tested with analysis of variance, and the Student's T-test was used to calculate LSD (p < 0.05) over the sampling days and methods used. The effect of urine and dung on the two soil layers was tested separately.

Results

The total P concentration of dung and urine was 9 340 mg kg⁻¹ DM (dry matter) and 8.44 mg kg⁻¹, respectively. Thus, the amount of P added to the soil in dung patches was 2.7 g, and that in the urine was 0.02 g. The corresponding P load in the dung-treated soil was 36 g m⁻² and 0.06 g m⁻² in the urine-treated soil. Of the dung dosage applied (288 g DM) as much 250 g remained on day 21 whereas on day 120, the amount had decreased to 172 g. In the beginning of the experiment, the weather was dry except for a heavy shower shortly after the application of dung and urine (Table 1), which caused a little spreading of the dung. During the dry period, the surface of the dung patch dried, slowing the movement of P into the soil. However, already 10 to 21 days after the dung was applied to the soil,

several large holes underneath the patch indicated biological activity.

The increase in pH caused by the addition of urine was greatest in the upper 2 cm soil, but a minor increase also occurred in the layer immediately below (2–10 cm) (Table 3). This response was observed in both layers immediately after the urine addition, but disappeared in the 0–2 cm soil layer after ten days, and in the 2–10 cm layer after five days. The dung seemed to increase the pH on day 3, but its immediate effect remained unclear because no sampling took place until three days after the addition. Starting from sampling day 49, the pH of the upper 2 cm soil in the dung-treated spots began to rise. In the control samples, the pH seemed to decrease during the first three days, but began to increase after 21 days. Also, in the 2-10 cm layer, the pH rose slightly in all treatments towards the end of trial.

Table 4 shows that the urine addition did not affect the soil total P at either sampling depth. On the contrary, in the dung-treated samples, total P increased in the 0-2 cm soil layer towards the end of the monitoring period. The dung decomposed on the soil surface slowly, which explains its late effect on soil P.

Table 3. Mean pH in 0–2 cm and 2–10 cm layers of control and in urine- and dung-treated samples collected on various sampling days.

Sampling day	0–2 cm				2–10 cm					
	Control	Urine	Dung			Control	Urine	Dung		
0	5.5	7.1 *				5.7	6.1*			
1	5.5	6.7 *				5.8	6.0*			
3	5.1	6.5 *	5.6 *			5.7	6.0*	5.8		
5	5.3	6.5 *	5.5			5.6	6.0*	5.7		
10	5.2	5.6 *	5.2			5.6	5.7	5.7		
21	5.2	5.5	5.6			5.6	5.4	5.6		
49	5.3	5.6	5.8 *	SE	0.11	5.6	5.5	5.7	SE	0.08
77	5.4	6.1 *	6.0 *	SED	0.16	5.8	5.6	5.8	SED	0.12
120	5.5	6.3 *	6.2 *	LSD	0.36	5.9	5.9	6.1	LSD	0.27

Stars indicate statistically significant difference (p = 0.05) between the control and urine or dung treatment. SE = standard error. SED = standard error of the mean. LSD = Dunnett's test least significant difference.

Table 4. Soil total P, g kg⁻¹, in 0–2 cm and 2–10 cm layers of control and in urine- and dung-treated samples collected on various sampling days.

Sampling		0–2 cm					2–10 cm				
day	Control	Urine	Dung			Control	Urine	Dung			
0	1.55	1.61				1.55	1.54				
1	1.56	1.59				1.52	1.54				
3	1.63	1.73	1.63			1.56	1.59	1.59			
5	1.61	1.64	1.65			1.65	1.59	1.61			
10	1.61	1.66	1.66			1.58	1.58	1.59			
21	1.63	1.68	1.65			1.62	1.64	1.55			
49	1.53	1.52	1.68	SE	0.05	1.58	1.51	1.50	SE	0.05	
77	1.50	1.51	1.74*	SED	0.07	1.50	1.48	1.51	SED	0.07	
120	1.52	1.60	1.81*	LSD	0.15	1.49	1.53	1.58	LSD	0.16	

Stars indicate statistically significant difference (p = 0.05) between the control and urine or dung treatment. SE = standard error. SED = standard error of the mean. LSD = Dunnett's test least significant difference.

In the upper soil layer of the control samples, the mean MRP_w (0–2 cm) calculated over all the sampling days was 12.8 mg kg⁻¹ (SE 0.68), and MUP_w was 5.6 mg kg⁻¹ (SE 0.34), comprising 31% of the TP_w. The mean P_{Ac} value (12.3 mg P kg⁻¹, SE 0.34) was very close to the concentration of MRP_w. The SD for mean P_{Ac} was 1.1 mg kg⁻¹. For mean TP_w, MRP_w and MUP_w, the SD was 3.7, 2.9 and 1.5 mg kg⁻¹, respectively. In the 2–10 cm layer of the control samples, MRP_{w^2} MUP_w and P_{Ac} concentrations were lower than in the upper 0–2 cm soil layer: 8.7 (SE 0.30), 3.2 (SE 0.12) and 9.1 (SE 0.19) mg kg⁻¹, respectively. In this layer, the proportion of MUP_w of TP_w was 27%. The SD of mean P_{Ac} calculated from the 2–10 cm control samples was 0.5 mg kg⁻¹. For mean TP_w, MRP_w and MUP_w, the SD was 1.3, 1.1 and 0.5 mg kg⁻¹, respectively. According to Finnish

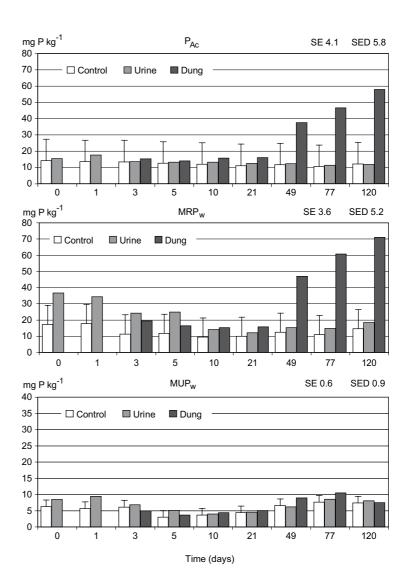


Fig. 1. Acid ammonium acetate extractable (P_{Ac}) and water extractable inorganic (MRP_w) and organic (MUP_w) phosphorus concentrations in the upper 2 cm soil layer in control and after urine and dung additions. Error bars stand for Dunnett's least significant difference between control and treatment.

soil P classification system based on the P_{Ac} and the organic matter content of soil, the P status of both soil layers was satisfactory in the beginning of the experiment (Viljavuuspalvelu 1998). In farms committed to Agri-Environmental Program, the maximum P-fertilisation of long term pasture soil having satisfactory P-status would be 8 kg ha⁻¹ y⁻¹ (Ministry of Agriculture and Forestry 2007).

In the urine-treated samples, the rise in pH had no noticeable effect on P_{Ac} (Figure 1). In the very beginning of the experiment, the concentration of P_{Ac} was somewhat elevated in the surface layer (0–2 cm) in urine-treated soil, but because a similar trend was also found in the control sample, it was probably attributable to the P fertilisation applied to the field prior to the trial. On day 3, the P_{Ac} decreased to the baseline level of the control samples. In contrast, the MRP_w closely followed the pH changes in the upper 0–2 cm soil layer: the MRP_w increased immediately after the addition of urine (Fig. 1). The increase in the MUP_w was similar to that of MRP_w, but smaller. The peak MUP_w

concentrations were measured on day 2 after the addition of urine. In the upper soil layer (0–2 cm), TP_w exceeded P_{Ac} in all treatments. It should be taken into account, however, that acid ammonium acetate extracts are analysed only for inorganic P.

In the dung-treated samples, an increase in P_{Ac} , MRP_w and MUP_w could not be seen in the upper 0–2 cm soil layer until day 49 (Figure 1). As for the MUP_w, the differences levelled off on sampling day 120. At a depth of 2–10 cm, no urine-induced effects on the P test values could be observed (Table 5) despite the increase in pH (Table 3). In contrast, the addition of dung tended to increase all P values (P_{Ac}, MRP_w and MUP_w) from sampling day 49 onwards at this depth. However, this response was statistically significant only for P_{Ac}.

Fig. 2, representing the responsiveness of P tests to urine and dung additions, shows that throughout the experiment the increase in P extractability due to urine addition was more pronounced in water extracts than in acid ammonium acetate extracts. Acid ammonium acetate extracts are analysed only

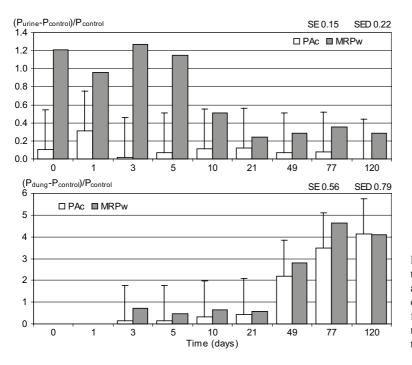


Fig. 2. Responsiveness of P tests (P_{Ac} and MRP_w) to urine and dung additions in the 0–2 cm soil layer. Error bars stand for Student's T-test least significant difference between the two methods.

	Sampling day	Control	Urine	Dung		
P _{Ac}	0	9.8	9.1			
	1	9.2	9.6			
	3	9.0	7.8	9.0		
	5	8.8	8.3	10.1		
	10	8.7	9.9	10.2		
	21	8.0	8.3	8.4		
	49	9.3	10.4	12.3 *	SE	0.6
	77	9.6	9.1	12.0 *	SED	0.9
	120	9.3	9.1	13.4 *	LSD	2.0
MRP _w	0	10.1	8.9			
w	1	9.7	10.3			
	3	9.1	6.9	9.2		
	5	8.0	8.0	9.8		
	10	7.3	7.6	9.4		
	21	6.9	5.9	7.6		
	49	8.4	8.4	11.4	SE	1.0
	77	8.9	7.2	11.7	SED	1.4
	120	10.3	9.8	15.8 *	LSD	3.1
MUP _w	0	3.3	2.6			
w	1	3.3	3.6			
	3	3.3	2.9	2.7		
	5	2.4	2.5	2.6		
	10	2.7	3.0	3.2		
	21	3.1	2.8	3.4		
	49	3.8	3.8	4.7	SE	0.3
	77	4.0	4.1	4.3	SED	0.4
	120	2.6	4.7 *	4.0 *	LSD	1.0

Table 5. Acid ammonium acetate extractable (P_{Ac}) and water extractable phosphorus inorganic (MRP_w) and organic (MUP_w) phosphorus concentrations, mg kg⁻¹, in the 2–10 cm soil layer in the control and after the urine and dung additions.

Stars indicate statistically significant difference (p = 0.05) between the control and urine or dung treatment. SE = standard error. SED = standard error of the mean. LSD = Dunnett's test least significant difference

for inorganic P and are therefore compared with MRP_w. The difference was statistically significant on sampling days 0, 1, 3, and 5. Both tests reacted similarly to the dung addition and there were no statistically significant differences between them, although the increase in MRP_w due to the dung addition was larger than in P_{Ac}, except on sampling day 120. In the 2–10 cm soil layer, there were no statistically significant differences in the responsiveness of the P test to urine or to dung treatment (data not shown).

Discussion

As expected, the urine addition increased pH in the upper 2 cm of soil. However, the statistically significant difference of pH values between the control and the urine-treated samples disappeared after day 10. This supports the findings of Hartikainen and Yli-Halla (1996), who reported that a urea-induced pH increase levelled off and began to decrease after 8–14 days when all the urea had hydrolysed. The

nitrification following the rapid increase in NH₄-N lowered the soil pH to values 0.5-1 units below the initial value. In addition, Haynes and Williams (1992) demonstrated that during the first 30 days after the addition of sheep urine, the large fluctuations in soil pH and ionic strength were mainly ensued by N transformations. In this present study, the pH in the urine- and dung-treated samples remained higher than in the control samples throughout the monitoring period. The uptake of nutrients by pasture vegetation likely counteracted the decrease in pH by two factors. Firstly, the rise in pH that occurred towards the end of the trial in all treatments can be attributed to the reduced salt concentrations raising the pH values measured in H₂O. Fertilisation, in turn, increases the salt concentration of the soil solution and lowers the pH_{H20} . In line with this, the immediate decrease in the pH observed in the control samples on day 3 coincidences with the second application of fertilisers. Secondly, the uptake of NO_{2}^{-} by plants is known to enhance the release of OH⁻ from roots. However, the effect of N fertilisation on pH during the trial began to fade when the plants growing at the study site utilised the nutrients in the soil. By measuring the pH in the salt solution instead of in water, more stable pH values would have been obtained.

When the effect of urine on soil P was measured, the two P tests gave dissimilar outcomes. A sudden rise in pH caused by the urine addition was reflected as elevated MRP_w, but no noticeable effect was observed in P_{Ac} . This is attributable to the fact that the buffered acid ammonium acetate solution extracts the soil P at a low pH of 4.65, which enhances the retention of P in soil. The water extracted depends on the actual pH in the soil. Hartikainen (1989b) demonstrated that a pH increase evoked without earth alkaline carbonates may increase P_w more than does liming with conventional earth alkaline carbonates containing agents.

Both tests reacted similarly to the dung addition and exhibited a subsequent increase in soil P extractability. The increase that took place between sampling days 21 and 49 resulted from the P added to the soil in the dung rather than from the pH changes. Single additions of excreta more than tripled the P_{Ac} and TP_{w} in the 0-2 cm soil layer in 50 days. There were no sings of decreasing P solubility towards the end of the experimental period, which supports the results of Chardon et al. (2007), who found manure patches to be a source of P for a long time after deposition. Repeated dung additions may result in very high soil P status, especially in areas where cattle tend to congregate. Yli-Halla et al. (1998) reported P_{Ac} concentrations as high as 1240 mg l⁻¹ soil near the dairy station and 144 mg l⁻¹ soil in the feeding area. West et al. (1989) found that five-year grazing by cattle formed a distinct zone of nutrient enrichment around the water source. One should bear in mind, however, that the P in fresh dung is highly mobile (McDowell and Stewart 2005) and is prone to leaching before the dung is incorporated into the surface soil, especially in areas where runoff is likely (Dou et al. 2000). The decomposition of dung on the soil surface is largely affected by weather and biological activity in the soil. In this experiment, the surface of the dung patch dried, owing to the low rainfall, which may have reduced the movement of P into the soil. The net used in this experiment to some extend prevented the action of soil fauna. On the hotspot areas resulting from spatial excreta deposition, cattle trampling may accelerate the mixing of the dung with the uppermost soil layer, which decreases the risk of direct runoff. On the other hand, the effect of grazing on the soil's physical properties may promote the generation of surface runoff (see e.g. Bilotta et al. 2007).

The water extractable P in dung is composed largely of inorganic P. However, data published in the literature vary considerably due to the different extraction procedures and sample-to-solution ratios used in dung analyses (He et al. 2004, Chardon et al. 2007). In the present study, the composition of dung was not analysed in detail, but the smaller increase in MUP_w in the dung-treated samples over that of MRP_w suggests that the majority of the TP_w that ended up in the soil with the dung was in inorganic form. Even though the P in dung can be considered to be mostly inorganic, Chardon et al. (2007) found that dissolved unreactive P dominated in the leachate from a manure patch deposited on permanent grassland soil. They suggested that the

bacterial immobilisation of P may be responsible for this phenomenon.

In Finland, P fertilisation recommendations are based on routine tests where the Ac extracts are analysed only for inorganic P. However, Toor et al. (2003) suggested that in favourable conditions, a part of the unreactive P in leachate may be mineralised to inorganic P. In previous studies, the addition of urea has been reported to increase the solubility of organic matter as well as inorganic P (Hartikainen and Yli-Halla 1996, Shand et al. 2000) and organic P (Shand et al. 2000). The dissolution of organic matter in turn can retard the re-sorption of PO₄-P (Hartikainen and Yli-Halla 1996). In this study, the urine-induced increase in MUP, over that of the control samples lasted five days. In the dung-treated soil, the MUP_w was higher than in the control samples on sampling days 49 and 77. Towards the end on the experiment, however, the increasing trend was similar in all treatments, suggesting a seasonal pattern in MUP_w concentrations. Hence the analysis of MUP_w offers additional information on P chemistry and possibly on the risk of P loss.

The variation in the results from the untreated control samples was larger for MRP_w than for P_{Ac} during the experiment. Fertilisation and subsequent changes in salt concentration are most likely to cause greater fluctuation in water extractable P forms compared to PAc. Hartikainen (1989b) found a decrease in P_w after the addition of nutrient salts, but P_{Ac} was unaffected. These findings, together with the fact that P_w reacted with great sensitivity to the changes in pH, suggest that water extraction is a more sensitive method, and thus provides a more reliable estimate for P that can be leached by rainwater. One should bear in mind, however, that the effect of urine on pH diminished after ten days. If the urine addition is not repeated, the MRP_w measured immediately after the urine addition will exaggerate the long-term P-loading potential of soil. Thus, the sensitivity of water extraction to environmental changes may lead to misinterpretations, especially in situations where the assessment of P loss risk is based on only a few samples taken simultaneously.

Acid ammonium acetate extraction, found to provide a good estimation of plant-available P in acidic Finnish soils (Saarela 2002), is also reported to be a suitable indicator for critical source areas of P load in pastures (Jansson and Tuhkanen 2003). Our results support this conclusion. However, Whalen et al. (2000) reported that the incubation of acid soil with cattle manure increased the soil pH and the effect persisted during the 8-week experiment. According to Hartikainen (1989a), P_{Ac} is highly dependent on pH in limed soil and may overestimate the plant-available P. Further, Sharpley et al. (2004) suggested that the use of acid-based routine soil tests such as the Mehlich-3, may overestimate the risk of P loss from heavily manured soils. These findings suggests that the areas of high dung-loading and the interaction of urine and dung on the hotspots of pastures should be investigated more carefully before recommending the use of P_{Ac} as an indicator for hotspot areas in a pasture.

National agronomic soil test data provide extensive information on the P_{Ac} status of Finnish farmland. The samples taken for this analysis are usually a mixture of sub-samples representing large field areas, and the sampling is advised to be done while avoiding the spots that differ in productivity from the surrounding field. These areas, however, are most likely of environmental interest especially in pasture fields. When sampling grassland soil, the uppermost surface soil is often removed prior to analysis, which can result in the underestimation of soil P status. Similarly, in soils with a high gradient in P concentrations between the uppermost few centimetres and the layer below, sampling at too great a depth can result in errors caused by mixing P-enriched topsoil with a larger volume of soil (Turtola and Yli-Halla 1999). Sharpley et al. (1978) suggested a sampling of 0-1 cm surface layer, when estimating the contribution of surface runoff from pasture lands to P load. Our results support this suggestion, as the increase in easily soluble P concentrations duo to urine or dung additions took place mainly in the upper 0-2 cm soil layer.

Conclusions

In pasture land, where P is enriched in the uppermost soil layer, the urine-induced increase in P_w leads to a risk of P loss. This risk is pronounced in river banks, which should be taken into account before recommending grazing in buffer zones. Critical areas in pastures where P is concentrated can be detected with water extraction and acid ammonium acetate extraction if the sampling is conducted carefully for environmental purposes. Water extraction is, however, a more sensitive method and P_w can provide a more accurate estimation of short-term changes in P solubility. The sensitivity of water extraction, however, may lead to misinterpretations if the conclusions are based on only one or two samples taken simultaneously. According to this study, P_{Ac} can provide adequate information on hotspots in pastures, especially in situations were the amount of soil analysis that can be conducted is limited. However, the effect of a urine-induced increase on pH and the subsequent increase in easily soluble inorganic and organic P may go undetected with buffered acid ammonium acetate extractant. The effect of repeated dung additions on the soil properties of the hotspot areas of a pasture should be investigated in grater detail.

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SELOSTUS

Uuttotestien herkkyys laidunmaan potentiaalisen fosforikuormituksen arvioinnissa

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Maan fysikaalisten ja kemiallisten olosuhteiden muutokset sekä muutokset maan fosforitilassa voivat edistää fosforin (P) huuhtoutumista maasta ja sitä kautta myös vesistöjen rehevöitymistä. Tutkimuksen tarkoituksena oli selvittää sonta- ja virtsalisäysten vaikutusta laidunmaan fosforitilaan sekä verrata kahden uuttotestin, vesiuuton ja happaman ammoniumasetaattiuuton, herkkyyttä muutosten seurannassa. Aineisto kerättiin MTT:n Maaningan tutkimusasemalla sijainneesta kenttäkokeesta. Sontaa ja virtsaa levitettiin koeruuduille keskimääräistä kertaeritystä vastaavat määrät ja koeruuduista (virtsa, sonta ja kontrolli) otettiin 0-2 cm ja 2-10 cm syvyyksiltä maanäytteet tietyin aikavälein. Maanäytteistä määritettiin pH_{H2O}, vesiliukoinen kokonaisfosfori (TP_w) ja epäorgaaninen fosfori (MRPw) sekä viljavuusanalyysin fosfori (PAC), jota Suomessa käytetään fosforilannoitustarpeen ennustamiseen. Eri käsittelyjen vaikutukset olivat pääasiassa havaittavissa vain maan pintakerroksessa (0-2 cm). Virtsa nosti maan pH:ta välittömästi lisäyksen jälkeen ja MRP ...: n pitoisuudet seurailivat kiinteästi pH:n muutoksia maassa. Vastaavaa nousua ei juurikaan ollut havaittavissa P_{Ac}:n pitoisuudessa. Tämä johtuu viljavuusuuttoliuoksen (hapan ammoniumasetaatti) alhaisesta pH:sta (4,65), joka edistää fosforin pidättymistä maahan. Molemmat testit reagoivat samalla tavoin sontalisäyksen aiheuttamaan maan kokonaisfosforipitoisuuden kasvuun. Tulosten mukaan vesiuutto on viljavuusanalyysin uuttoa herkempi menetelmä tarkasteltaessa lyhyen ajan muutoksia maan helppoliukoisen fosforin pitoisuuksissa. Laidunmailla virtsan aiheuttama pH:n nousu lisää liukoisen fosforin määrää, mikä yhdessä sontalisäysten aiheuttaman pintamaan fosforipitoisuuden nousun kanssa kasvattaa fosforin huuhtoutumisriskiä.