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Long-term application of animal slurries to grassland alters soil cation balance

P.N.C. Murphy¹, R.J. Stevens^{1,2} & P. Christie^{1,2,*}

Abstract. Soil samples from a 32-year grassland field experiment were taken from 0–5, 5–10, and 10–15 cm soil depths in February 2002. Plots received annual treatments of unamended control, mineral fertilizer, three rates of pig slurry and three rates of cow slurry, each with six replicates. Samples were analysed for cation exchange capacity (CEC), exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), pH and Olsen P. Exchangeable sodium percentage (ESP) was calculated as a sodicity indicator. Mean ESP was generally greater for slurry treatments than the control, with a trend of increasing ESP with application rate. This was particularly marked for cow slurry. At 0–5 cm depth ESP increased from 1.18 in the control to 1.75 at the highest rate of pig slurry and 5.60 at the highest rate of cow slurry. Similar trends were shown for CEC, exchangeable Na^+ , K^+ and Mg^{2+} , Ca^{2+} and Olsen P. The build-up of soil P due to slurry applications, together with this combination of physical and chemical factors, may increase the risk of P loss to surface waters, particularly from soils receiving high rates of cow slurry.

Keywords: Phosphorus, sodicity, cation exchange capacity, phosphorus loss, infiltration, animal slurry

INTRODUCTION

The application of animal slurry to grassland is a common agricultural practice. Slurry is applied to farmland not only as a source of plant nutrients, but also as a means of recycling organic manures produced on the farm. Organic manure application alters both chemical and physical properties of soil (Shaviv *et al.* 1986; Christie 1987; Haynes & Naidu 1998; Hao & Chang 2002), which has implications for aspects of the agro-environmental system such as plant nutrient supply and nutrient loss to surface waters. Soil sodicity may be increased, which is known to damage soil structure and alter soil hydraulic properties (Shainberg & Letey 1984; Sumner 1993). Much work has highlighted the risk of nutrient loss, particularly phosphorus (P), from soils receiving organic fertilizers (McGechan 2001; Van Vliet *et al.* 2002) and this has been identified as a major contributor to the eutrophication of surface water bodies. Diffuse source pollution of surface waters by P from farming activities is a major environmental problem in Ireland (Foy *et al.* 1995; Heaney *et al.* 2001). Long-term slurry applications to grassland increased soil P status considerably and in proportion to application rates (Anderson & Wu 2001). These increased soil P levels were related to increased molybdate reactive P in the soil solution beneath the plots. The present study followed on

from Anderson & Wu (2001) and tested whether long-term slurry application alters soil cation balance. The implications this may have for P loss to surface waters from these soils are assessed.

MATERIALS AND METHODS

Forty-eight plots, each 29.75 m² in area, were established in 1970 on a clay loam (0–30 cm) grassland soil at Hillsborough, Co. Down in northeast Ireland (Christie 1987). The soil is a Dystric Cambisol developed on glacial till overlying Silurian shales and greywackes. The soil has an organic matter content of 4.25% and its hydrogeological class number within HOST (Hydrology of Soil Types) is 18 *sensu* Boorman *et al.* (1995). The site is considered typical of a large area of grassland in Northern Ireland. The plots were laid out on an established perennial ryegrass sward approximately 120 metres above sea level. Eight treatments with six replicates each were distributed as a randomized block. The treatments were:

- control with no nutrient amendment (CTRL),
- mineral fertilizer at 200 kg N, 32 kg P and 160 kg K ha⁻¹ yr⁻¹ (NPK),
- pig slurry at 50 m³ ha⁻¹ yr⁻¹ (LP),
- pig slurry at 100 m³ ha⁻¹ yr⁻¹ (MP),
- pig slurry at 200 m³ ha⁻¹ yr⁻¹ (HP),
- cow slurry at 50 m³ ha⁻¹ yr⁻¹ (LC),
- cow slurry at 100 m³ ha⁻¹ yr⁻¹ (MC) and
- cow slurry at 200 m³ ha⁻¹ yr⁻¹ (HC).

For further details, see Christie (1987). In conventional farming practice, farmers would usually be advised to make

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slurry application rates between 50 and 100 m³ ha⁻¹ yr⁻¹. The highest application rate was included in the experiment to test extreme conditions. No lime was applied to the plots during the first 20 years of the experiment and soil pH declined to varying extents in the different treatments (Christie 1987). The exceptions were the MC and HC slurry treatments in some plots in which the slurry acted as an effective liming material that maintained soil pH > 6. In November 1990 and October 1994 lime was applied to all of the acidified plots to raise their surface pH to 6.

Composite soil samples were taken to a depth of 15 cm using half-corer augers. These cores were sectioned to depths of 0–5, 5–10 and 10–15 cm. Samples were air-dried and ground to pass a 2 mm sieve. Soil pH was measured in water with a glass electrode at a 1:2.5 soil–water ratio (MAFF 1986). Phosphorus extractable by sodium bicarbonate (Olsen P) was determined by a modification (MAFF 1986) of the method of Olsen *et al.* (1957). Exchangeable Na⁺, K⁺, Ca²⁺ and Mg²⁺ were determined by commonly used methods (MAFF 1986), except that ammonium acetate replaced ammonium nitrate. K⁺ and Na⁺ were measured with a Corning 410 flame photometer and Ca²⁺ and Mg²⁺ with a Perkin Elmer 2380 atomic absorption spectrophotometer. Cation exchange capacity was determined by compulsive exchange of Mg²⁺ on to a Ba-saturated soil sample (Avery & Bascomb 1974). Exchangeable sodium percentage (ESP) was used as a sodicity indicator and calculated as:

$$\text{ESP} = 100(\text{Na}_{\text{ex}}/\text{CEC}) \quad (1)$$

where Na_{ex} = exchangeable Na⁺ (cmol_c kg⁻¹) and CEC = cation exchange capacity (cmol_c kg⁻¹).

Means and standard errors were calculated and the significance of treatment effects was tested by ANOVA with repeated measures using the GENSTAT statistical package. Repeated measures analysis was used because values over depth were not statistically independent.

RESULTS AND DISCUSSION

Slurry treatments increased CEC from a mean of 22.8 cmol_c kg⁻¹ in the CTRL treatment to 24.2 cmol_c kg⁻¹ at the medium slurry rate and 27.0 cmol_c kg⁻¹ at the high slurry rate. Slurry application presumably increased soil organic matter (SOM) and hence CEC. Mean values for exchangeable Ca²⁺, Mg²⁺, Na⁺ and K⁺ at each depth are shown in Table 1. Thirty-two years of slurry applications have altered the exchangeable cation balance, although the interpretation of exchangeable Ca²⁺ values is confounded by the differential application of lime. Lime was applied in November 1990 and October 1994 to maintain soil pH ≥ 6.0 in the top 15 cm, so all but one of the plots receiving the high-rate cow slurry treatment and all but two of the plots receiving the medium-rate cow slurry treatment were never limed because their pH was already greater than 6.0. The highest application rate of slurry tested was included in the experiment to investigate extreme conditions, and it could be argued that the effects

of cow slurry applied at 200 m³ ha⁻¹ yr⁻¹ are only of academic interest. However, farmers may not always have closely followed advisory guidelines. For example, they may tend to spread more slurry on fields with good drainage characteristics. As a result, some fields may have received large application rates similar to the highest rate in our experiment. Some intensively managed farms may also apply slurry at higher than recommended rates because of limited land area for spreading.

All of the slurry treatments increased exchangeable Mg²⁺, the increase with cow slurry being greater than with pig slurry. On average over 0–15 cm soil depth within a slurry type, exchangeable Mg²⁺ increased linearly with rate of application (Figure 1). The HP and all cow slurry treatments increased exchangeable K⁺ and Na⁺. On average over 0–15 cm soil depth exchangeable Na⁺ and K⁺ increased linearly with application rate for cow slurry (Figure 2). Exchangeable cations decreased with depth for all treatments (Table 1).

Although we have emphasized long-term slurry application, it should be noted that these changes in soil cation balance might occur over a much shorter term. Further work using archived soil samples from the site would be required to assess whether this had occurred.

The NPK treatment had no significant effect on ESP (Table 1). The effect of slurry treatments on ESP, averaged over all depths, is shown in Figure 3. For pig slurry, only the HP treatment significantly increased ESP over the control, increasing the mean value from 1.0 to 1.5%. Cow slurry had a pronounced effect on ESP, the increase being directly proportional to the application rate (Figure 3).

Increased ESP has been related to decreased soil hydraulic conductivity and infiltration rate (Frenkel *et al.* 1978; Sumner 1993; Halliwell *et al.* 2001). The mechanism by which this may occur is by damaging soil structure (Halliwell *et al.* 2001; Collis-George 2003; Quirk 2003). The increased prevalence of Na⁺ in exchange for divalent cations increases electrostatic repulsion between soil particles. In terms of the Guoy–Chapman diffuse double layer theory, an increase in the prevalence of monovalent cations will increase the size of the double layer, as it is inversely proportional to the square of the valency of the neutralizing cation. This aids clay dispersion, which damages soil structure by breaking up tactoids and can lead to surface sealing.

Threshold values of 5–15% ESP have been given for the definition of a sodic soil, but these thresholds are somewhat arbitrary and the detrimental physical effects of increased ESP act over a continuum of values, so that soils with lower ESP can exhibit sodic behaviour (So & Aylmore 1993; Sumner 1993; Halliwell *et al.* 2001). There is no generally accepted definition of a sodic soil (Sumner 1993). Lebron *et al.* (2002) found that hydraulic conductivity decreased sharply as ESP approached 5%. An ESP of only 2.2% can cause a 70% decrease in infiltration rate (Shainberg & Letey 1984). Soils with a high clay or silt content might be expected to be more sensitive to increased ESP than sandy soils.

The HC treatment resulted in soils with >5% ESP over all depths, and this might be expected to influence soil physical conditions, decreasing infiltration rate. Decreased

Table 1. The effect of treatment on exchangeable sodium percentage (ESP), exchangeable cations and cation exchange capacity (CEC), Olsen P and pH, including levels of probability.

Treatment ^a	Depth (cm)	ESP (%)	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	CEC	Olsen P ^b (mg L ⁻¹)	pH
(cmol _c kg ⁻¹)									
CTRL	0–5	1.18	0.32	0.34	0.68	12.42	27.06	14.00	6.09
	5–10	0.86	0.18	0.16	0.37	10.11	21.71	8.33	6.28
	10–15	0.83	0.16	0.15	0.31	9.34	19.77	8.00	6.32
NPK	0–5	1.28	0.33	0.44	0.32	12.57	25.71	44.33	6.09
	5–10	0.90	0.19	0.19	0.06	11.69	21.79	19.83	6.29
	10–15	0.91	0.19	0.17	0.42	10.45	21.10	34.83	6.31
LP	0–5	1.22	0.32	0.33	1.38	13.01	26.53	52.33	6.04
	5–10	0.96	0.22	0.16	0.84	11.94	23.14	26.67	6.25
	10–15	0.87	0.17	0.13	0.61	10.44	20.19	17.50	6.33
MP	0–5	1.13	0.31	0.29	1.92	13.17	27.51	100.67	6.26
	5–10	0.91	0.22	0.16	1.32	12.07	25.00	69.00	6.42
	10–15	0.94	0.21	0.15	0.98	10.60	21.93	51.00	6.46
HP	0–5	1.75	0.55	0.84	2.77	13.23	31.84	202.50	6.14
	5–10	1.42	0.38	0.45	2.09	12.00	26.87	192.50	6.24
	10–15	1.21	0.28	0.26	1.56	9.61	23.18	145.83	6.24
LC	0–5	2.58	0.65	1.03	1.84	10.97	25.72	27.50	6.11
	5–10	1.84	0.42	0.63	1.16	9.49	23.05	12.33	6.23
	10–15	1.59	0.31	0.45	0.86	8.68	19.53	9.33	6.28
MC	0–5	3.82	1.07	2.05	3.24	9.97	28.08	60.33	6.18
	5–10	4.24	1.00	1.73	2.25	8.32	23.57	27.67	6.37
	10–15	3.90	0.80	1.33	1.61	7.35	20.74	17.67	6.37
HC	0–5	5.60	1.66	3.13	4.06	10.77	29.98	138.33	6.35
	5–10	5.78	1.55	2.91	3.22	9.36	27.16	89.83	6.59
	10–15	6.29	1.48	2.67	2.57	8.08	23.65	61.00	6.59
LSD		0.464	0.102	0.206	0.251	1.524	1.907		0.188
Comparison									
Treatment ^c		<0.001	<0.001	<0.001	<0.001	0.021	<0.001	<0.001	0.430
Slurry type ^d		<0.001	<0.001	<0.001	0.504	0.132	0.347	<0.002	0.152
Slurry application rate		<0.001	<0.001	<0.001	<0.001	0.112	<0.001	<0.003	0.048
Slurry type × rate		<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.450	0.015
Soil depth		0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Treatment × depth		<0.001	0.231	0.180	<0.001	0.764	0.224	0.040	0.755
Slurry type × depth		0.009	0.034	0.098	0.999	0.433	0.685	0.016	0.672
Slurry rate × depth		0.077	0.021	<0.001	0.001	0.615	0.226	0.007	0.449
Slurry type × rate × depth		0.120	0.009	0.002	0.259	0.214	0.775	0.273	0.023

^aFor treatment key, see Materials and Methods; ^bOlsen P values were transformed to log_e values and analysed; ^ctreatment = fertilizer vs control vs slurry;

^dslurry type = cow vs pig. LSD = least significant difference.

infiltration rate may increase overland flow from soils, which has been identified as an important P loss pathway (Haygarth & Jarvis 1999; Heathwaite & Dils 2000). The hydrological properties of the soil surface are particularly sensitive to increases in ESP due to the low electrolyte concentration of the infiltrating water, the energy of raindrop impact, and the lack of a surrounding soil matrix (Agassi *et al.* 1981; Sumner 1993). Surface hydrology is critical in determining the distribution of water between subsurface and overland flow. Thus, the fact that treatment effects were concentrated at the surface gives further cause for concern.

Levels of ESP tended to decrease with depth for all treatments except the MC and HC, for which the trend was reversed. This decrease with depth reflects the concentration of Na⁺ at the surface due to surface application of

slurries. However, the increase in ESP with depth for the two highest rates of cow slurry suggests an increased mobility of Na⁺ in the soil profile at higher rates of application. Na⁺ leached to lower depths in the profile will exchange from solution to the solid phase. The effect of this exchanged Na⁺ on ESP may be more marked at depth, due to a smaller CEC than at the surface.

The effects of increased ESP on soil hydrology have been found to be magnified by raised soil pH (Suarez *et al.* 1984), which will tend to increase the negative charge on variable charge surfaces (Frenkel *et al.* 1978; Sumner 1993). This gives further cause for concern with soils receiving cow slurry (Table 1).

It should be noted that long-term slurry application will also increase humified SOM at the soil surface, increasing aggregate stability. This might counter the effects of

Figure 1. The effect of slurry application rate on exchangeable Mg^{2+} averaged over 0–15 cm soil depth for pig (◆) and cow (■) slurries.

Figure 3. The effect of slurry application rate on exchangeable sodium percentage (ESP) averaged over 0–15 cm depth for pig (◆) and cow (■) slurries.

changed cation balance on aggregate stability. Therefore, the effect of slurry application on soil structure and hydrology may depend on a balance between these processes.

In addition to physical effects, the capacity of the soil to sorb P anions may be decreased by the increased proportion of monovalent cations on the exchange sites (Curtin *et al.* 1987; Smillie *et al.* 1987). If slurry alters soil infiltration rate because of its Na^+ content, the environmental impact could be exacerbated because of concomitant soil P accumulation. P accumulated, particularly at 0–5 cm depth in the cow slurry treatments, to levels well beyond the agronomic optimum of 16–25 mg L^{-1} (MAFF 2000) (Figure 4). The greatest potential risk from a combination of soil physical and chemical effects is on the MC and HC treatments. It may be necessary to consider long-term strategies of controlled application to avoid such detrimental effects.

The application of lime is the usual practice in Ireland to raise soil pH and counter Al toxicity. It is necessary to

counteract the process of acidification, which is prevalent under Irish climatic conditions. However, soil pH is already greater than 6.0 in the HC treatment without lime having been applied at any time over the 32 years to all but one of the HC plots; thus the addition of lime to supply Ca^{2+} and increase soil pH further is not an agronomic option. The addition of gypsum is a possible management strategy to minimize the impact of slurry (Shainberg & Letey 1984; Halliwell *et al.* 2001; Lebron *et al.* 2002). Gypsum can provide the Ca^{2+} needed to exchange for Na^+ and K^+ and maintain a higher electrolyte concentration in solution; it has been shown to improve soil physical conditions (Shainberg & Letey 1984; Sumner 1993; Yu *et al.* 2003) and P retention (Vidal *et al.* 2003).

CONCLUSIONS

Long-term applications of pig and cow slurries increased ESP, exchangeable Na^+ , K^+ and Mg^{2+} , CEC, pH and

Figure 2. The effect of cow slurry application rate on exchangeable K^+ (◆) and Na^+ (■) averaged over 0–15 cm soil depth.

Figure 4. The effect of various slurry treatments on Olsen P over 0–5 cm soil depth. For treatment key, see Materials and Methods.

Olsen P. These effects were particularly marked for cow slurry. Treatment effects tended to be concentrated in the upper 5 cm of the soil horizon. The physical and chemical effects of increased ESP with a concurrent increase in soil P gives cause for concern with regard to P loss to surface waters from agricultural soils receiving slurry, particularly in the case of cow slurry. The effect of slurry application increased with application rate and it may be necessary to consider long-term strategies of controlled application to avoid detrimental effects. Lime or gypsum may be applied as a possible ameliorant, depending on soil pH.

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