

# UNDERSTANDING PHOSPHORUS, NITROGEN AND CADMIUM TRANSFER THROUGH A YOUNG STONY SOIL

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## Abstract

In Canterbury land-use intensification, particularly irrigated dairy expansion, is occurring on stony soils. Concerns exist about the ability of these soils to sustain intensified land-use, while maintaining nutrient leaching within discharge limits. Environmental models consistently predict stony soils as having a high vulnerability to leaching under intensive land use, but there is little experimental research to validate model predictions. This paper presents scoping experiments to quantify the degree of leaching vulnerability of young stony sand soils, and to determine likely key drivers for leaching.

Barrel lysimeters (460 mm in diameter by 700 mm deep) of intact soil columns were collected of a young stony sand soil from alluvium. Four lysimeters were used to study the preferential leaching of nitrogen (N), phosphorus (P), and cadmium (Cd) from a pulse (25 mm depth) of dairy shed effluent (DSE) followed by continuous artificial rainfall – both applied at 5 mm/h. A further two lysimeters were used to study the preferential leaching of N, P, Cd, and carbon (C) under simulated periodic irrigation (12–18 mm depth applied every 3–4 days). Sequential treatments of superphosphate, cow urine, and DSE were applied, with intervals of at least one pore volume (>200 mm) of drainage between each treatment.

The constant-rate experiment demonstrated that these soils have the potential for rapid leaching of N, P and Cd from an application of DSE. In contrast, no unequivocal increase in P, N and Cd leaching occurred after the DSE treatment in the simulated irrigation experiment, indicating strong sensitivity of these soils to application depth and rate of DSE. In the periodic-irrigation experiment the urine treatment resulted in rapid leaching of N, P, C, and Cd starting within 15–60 mm of drainage following the urine application. This indicates that under irrigated dairy grazing, urine will be a key driver for leaching of a range of possible contaminants.

Given the intensification of agricultural development on these vulnerable soils, the results of this scoping study confirm predictions that young stony sand soils have high potential leaching vulnerability, and we argue that these results urgently justify further research.

## Introduction

There are large areas of stony soils in the eastern plains of both the South and North Island of New Zealand, with 1.68 million hectares occurring on land of <15° slope, for which there is potential for intensive irrigated land use (Carrick *et al.* 2013). In Canterbury there is clear evidence of increasing land-use intensification on stony soils, particularly irrigated dairy expansion. However, there is concern about the ability of stony soils to sustain intensified land use, while maintaining nutrient leaching within discharge limits (PCE 2013). Environmental models consistently predict stony soils as having a high vulnerability to

leaching under intensive land use, primarily due to their low water storage capacity, and predominantly moderate-to-rapid permeability (Carrick 2002; Lilburne *et al.* 2010). Despite the potential leaching vulnerability there is very little experimental research on leaching from these soils to validate model predictions. This research has been confined to the Lismore shallow and stony soils (Di and Cameron 2002; Toor *et al.* 2004, 2005), although Carrick *et al.* (2013) indicates that there are large areas of stony soils with a lower water-holding capacity (653,000 ha) that environmental models predict to have a greater leaching vulnerability (Webb *et al.* 2007, 2010; Webb 2009; Lilburne *et al.* 2010; Wheeler *et al.* 2011).

Leaching vulnerability is determined by a number of factors, but key soil attributes are the soil water-holding capacity, as well as the soil permeability – which determines how rapidly solutes will move through the soil. The relative leaching vulnerability between different soils is often studied by comparing solute breakthrough curves (McLeod *et al.* 2008; Pang *et al.* 2008). A solute tracer is applied to the soil surface then leached by irrigation or rainfall to measure the solute concentration in the drainage with time (i.e. the ‘breakthrough curve’). Soils with high leaching vulnerability will see solute breakthrough much earlier in the drainage than low vulnerability soils. Normally the breakthrough curve is measured for at least one pore volume of drainage, where one pore volume is typically based on the soil total porosity. If the solute breakthrough occurs close to one pore volume of drainage then leaching is dominated by matrix-flow processes, where the solute is passing through the bulk of the soil matrix (soil aggregates), resulting in better filtering and buffering. If the solute breakthrough occurs well before one pore volume of drainage then leaching is dominated by preferential-flow processes, where the solutes are transported via macropores, largely bypassing the bulk of the soil matrix and resulting in poor filtering and buffering.

This paper summarises a series of scoping experiments to quantify the leaching vulnerability of young stony sand soils, and to determine likely key drivers of leaching. This knowledge then provides the basis for whether further research is needed, and what processes would be the focus.

## **Methods**

The soil studied is a Selwyn stony sand, classified as a Typic Fluvial Recent Soil (Hewitt 2010; Webb & Lilburne 2011). Selwyn soils are formed on floodplains of greywacke alluvium, and have <45 cm of fines over stony sands, often with the stony sands extending to near the soil surface. Topsoils are typically 100–200 mm thick, with weakly-developed fine soil structure. The lysimeters used for the leaching studies were collected in June 2012, from a low intensity dryland sheep and beef grazing paddock near the Waimakariri River (location S43.46° E172.50°). Six undisturbed barrel lysimeters (460 mm diameter × 700 mm high) were collected, as described in McLeod *et al.* (2014). In addition, three replicate sampling pits, located 0.3–1 m distance from the side of the lysimeter sampling trench, were hand-excavated following the technique described in Hedley *et al.* (2012). The sampling pits were used to collect samples for analysis of physical and chemical attributes (Table 1).

### *Indoor leaching experiments*

In the laboratory (room temperature 20–22°C) two sets of leaching experiments were conducted: (1) constant-rate leaching of dairy shed effluent (DSE); (2) periodic irrigation, with sequential applications through time of superphosphate, cow urine, and DSE.

**Table 1** Physical and chemical soil attributes (average  $\pm$  standard deviation)

Attribute	Soil depth (cm)		
	0–15	15–30	30–70
Sand (% F.E.) <sup>1</sup>	88 $\pm$ 1	98 $\pm$ 1	92 $\pm$ 7
Clay (% F.E.) <sup>1</sup>	1 $\pm$ 1	0	0
Stones (volumetric %)	54 $\pm$ 5	67 $\pm$ 3	64 $\pm$ 4
Whole soil bulk density (g/cm <sup>3</sup> )	1.98 $\pm$ 0.09	2.10 $\pm$ 0.11	2.12 $\pm$ 0.26
Total porosity (volumetric %)	25 $\pm$ 4	21 $\pm$ 4	20 $\pm$ 10
Field capacity (volumetric %)	16 $\pm$ 4	5 $\pm$ 2	4 $\pm$ 1
Carbon (% F.E.) <sup>1,2</sup>	2.9 $\pm$ 0.9	0.7 $\pm$ 0.5	0.3 $\pm$ 0.1
Anion retention capacity <sup>2</sup> (%)	4 $\pm$ 1	2 $\pm$ 1	2 $\pm$ 1
Cadmium <sup>2</sup> (mg/kg)	0.35 $\pm$ 0.01	0.35 $\pm$ 0.00	0.36 $\pm$ 0.03

<sup>1</sup> % F.E. is the percentage of the fine earth fraction. <sup>2</sup> Measured over 0–10 cm, 10–30 cm, 30–70 cm depths.

#### Constant-rate-irrigation experiment

Four lysimeters were irrigated for 2 days to flush the cores then allowed to drain to field capacity (about 24 h). A 25-mm application (4.25 litres) of DSE was then irrigated at 5 mm/h onto three replicate lysimeters, which were then continuously irrigated with water at a rate of 5 mm/h using a drip-type rainfall simulator (McLeod *et al.* 2014). A control lysimeter received no DSE but was continuously irrigated with water at a rate of 5 mm/h. The concentrations and amount per hectare of phosphorus (P), nitrogen (N) species and cadmium (Cd) in the DSE are shown in Table 2.

Leachate samples were collected into sterile bottles every 0.5 or 1 litre of drainage until one pore volume (average of 150 mm of drainage, using total porosity data from Table 2) of leachate had been collected. Leachates were stored at 4°C prior to analysis for nitrogen species, total phosphorus (TP) and bromide tracer by Landcare Research (2014), and Cd and zinc by Hill Laboratories (2014). In this paper only the TP and Cd results are discussed. Results of the leaching of *Escherichia coli*, bromide, and ammonium (NH<sub>4</sub><sup>+</sup>-N) are presented in McLeod *et al.* (2014).

**Table 2** Application rate and concentration of nitrogen species (total nitrogen (TN), ammonium (NH<sub>4</sub>) and nitrate (NO<sub>3</sub>)), total phosphorus (TP) and cadmium (Cd) applied to each lysimeter

Treatment applied	TN		NH <sub>4</sub>		NO <sub>3</sub>		TP		Cd	
	(mg/L)	(kg/ha)	(mg/L)	(kg/ha)	(mg/L)	(kg/ha)	(mg/L)	(kg/ha)	(mg/L)	(g/ha)
Constant-rate-irrigation experiment										
Background irrigation water	0.65	n.s.	-----	-----	-----	-----	<0.01	n.s.	<0.000053	n.s.
Dairy shed effluent	605	151	435	109	1.5	0.4	114	28	0.0026	0.704
Periodic-irrigation experiment										
Background irrigation water	-----	-----	-----	-----	-----	-----	-----	-----	<0.000053	n.s.
Superphosphate	-----	-----	-----	-----	-----	-----	-----	95	11.1*	11.1
Cow urine	4200	395	84	7.9	0.3	n.s.	1.9	0.2	<0.0011	n.s.
Dairy shed effluent	300	27.6	74	6.8	0.17	n.s.	96	8.8	0.0020	0.209

\*mg/kg, <sup>1</sup> n.s. = not significant (dashed lines = not measured)

### *Periodic-irrigation experiment*

A further two lysimeters (Lysimeter L1 and Lysimeter L2) were used to study the preferential leaching of N, P, Cd, and carbon (C) under an irrigation rate and depth similar to centre-pivot sprinkler irrigation (12–18 mm depth at 35–40 mm/h applied every 3–4 days). Sequential treatments of superphosphate, cow urine, and DSE were applied, with intervals of at least one pore volume (>200 mm) of drainage between each treatment. The concentrations and amount per hectare of P, N and Cd of each treatment are shown in Table 2.

Prior to application of the treatments the background leaching rate was measured over 84 and 104 mm of drainage for L1 and L2 respectively. Prior to the first treatment the pasture was killed by application of glyphosate, and 4 days later superphosphate was applied at the development rate of 95 kg P/ha and new ryegrass–clover pasture was then sown. The irrigation cycle started 2 days later. Although not considered treatments per se, a low rate of urea-N (31 kg N/ha) was applied at 2 and then 5 weeks following pasture sowing, as is common practice on dairy farms during pasture establishment. After a further 334 mm and 345 mm of drainage for L1 and L2 respectively, 1.7 litres (equivalent to 10-mm irrigation depth) of fresh cow urine was applied by pouring from a container held above the lysimeter. After a further 200 and 240 mm of drainage for L1 and L2 respectively, a third treatment was applied, with 1.7 litres of fresh DSE applied at the rate of 10 mm/h. Leaching was then measured for a further 170 and 240 mm of drainage for L1 and L2 respectively.

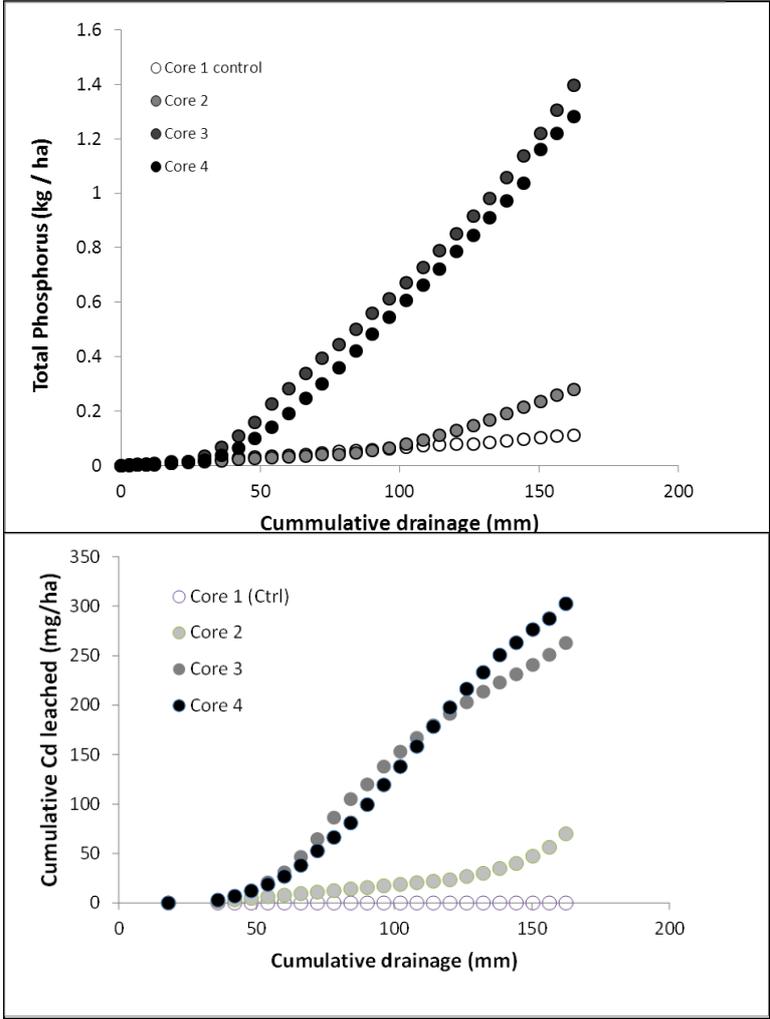
Leachate was collected in acid-washed sealed plastic containers that were placed under the lysimeters just before irrigation, and removed just before the next irrigation event 3–4 days later. Leachates were stored at 4°C until sent for laboratory analysis within one week of sampling. Leachates, urine and DSE were analysed for total dissolved nitrogen (TDN), ammonium ( $\text{NH}_4^+\text{-N}$ ), nitrate ( $\text{NO}_3^-\text{-N}$ ), dissolved organic nitrogen (DON), total phosphorus (TP), dissolved organic carbon (DOC), Cd, as well as uranium, zinc and fluoride (results not shown in this paper) using the methods described by Hills Laboratories (2014). In addition, total P, Cd and uranium in the superphosphate were analysed by Lincoln University.

## **Results and Discussion**

### *Leaching under constant-rate irrigation*

Total P and Cd leached under constant-rate irrigation after the addition of DSE is shown in Figure 1. Compared with the control lysimeter, where no DSE was applied, two of the lysimeters (cores 3 and 4) showed rapid leaching of TP and Cd, beginning after approximately 40 mm of drainage. In contrast, one of the lysimeters (core 2) showed a much lower degree of leaching, not starting to leach until after 100 mm of drainage for TP and 130 mm for Cd. The rapid-leaching lysimeters (cores 3 and 4) suggest movement of contaminants by preferential-flow processes under these conditions, as detection of the contaminants in the leachate occurred well within one pore volume of drainage, whereas the lag in leaching from core 2 suggests a typical matrix-flow-dominated leaching process. We attribute this to the possible presence of a sand lens in the slower-leaching lysimeter. These lenses were observed to occur at random locations throughout the lysimeter collection trench and McLeod *et al.* (2014) suggested that they provide greater filtration (and hence slower leaching) than the surrounding stone-dominated areas. It is important that future studies on stony soils account for the field variability in stone-dominated matrix and sand lens proportions, with previous research indicating that at least 90% of the area will be stone-dominated matrix (Dann *et al.* 2009).

By the end of this experiment the rapid-leaching lysimeters (cores 3 and 4) had leached 5% of the TP applied in the DSE, whereas only 1% of the applied TP leached from the slow-leaching lysimeter (core 2). In contrast, 37–42% of the applied Cd leached from cores 3 and 4 and only 5% from core 2. The variation between lysimeters that we observed for TP and Cd, and the subsequent inferred leaching processes, are consistent with that observed for *E. coli* leaching from the same lysimeters (McLeod *et al.* 2014). McLeod *et al.* (2014) concluded that these soils have a high potential to leach *E. coli*. The results shown in Figure 1 indicate these soils have a high potential to leach TP and Cd also, not just via preferential transfer but over sustained cumulative drainage, as shown by the end of this experiment where all lysimeters that received DSE were still continuing to leach.

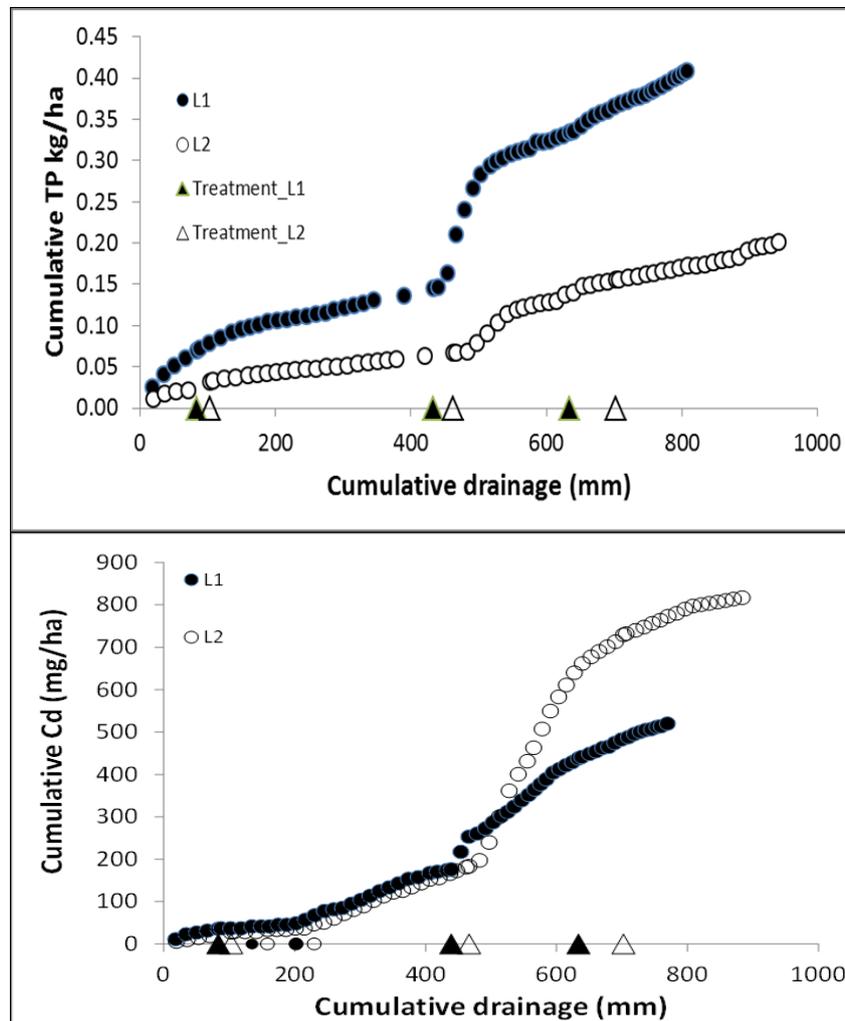


**Figure 1** Cumulative total phosphorus (kg/ha) and cadmium (Cd) (mg/ha) leached with cumulative drainage, following application of dairy shed effluent followed by constant-rate irrigation.

*Leaching under periodic irrigation*

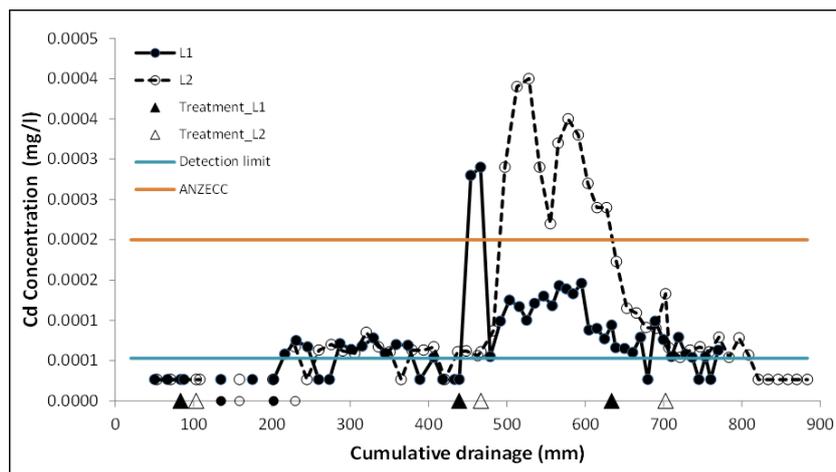
Total P and Cd leaching from the simulated centre-pivot irrigation experiment are shown in Figure 2. Prior to the application of any treatments, a small amount of TP was leaching, while no Cd was detected in the leachate. There was no clear increase in TP following the superphosphate application, although there was a low but detectable increase in Cd after the second urea-fertiliser application. The application of urine resulted in a marked increase in

leaching of both TP and Cd, indicating that cow urine will be a key driver of TP and Cd leaching in these soils. The marked increase in leaching occurred within 15–30 mm drainage (or 1–2 irrigation events) following the urine application, clearly indicating a preferential-flow-driven transfer process.



**Figure 2** Cumulative total phosphorus (TP) (kg/ha) and cadmium (Cd) (mg/ha) leached with cumulative drainage for 2 lysimeters (L1 and L2), following periodic irrigation at 3–4-day intervals. The three treatments marked by triangles along the x-axes represent (from left to right) applications of superphosphate, cow urine, and dairy shed effluent (DSE) respectively. The round symbols on the x-axis indicate the timing of urea applications (demonstrated on the Cd graph).

Following the urine application the Cd leaching concentrations (Figure 3) spiked to above ANZECC/ARMCANZ water quality guidelines (ANZECC 2000). In contrast to the constant-rate-irrigation experiment the application of DSE resulted in no marked increase for the TP or Cd leaching. Also in contrast to the constant rate experiment, where Cd and TP leaching appeared to be related in each lysimeter, the leaching pattern in the periodic irrigation experiment differed between TP and Cd, with greater leaching of TP occurring in L1, while great leaching of Cd occurred in L2. The application depth and rate used in the periodic-irrigation experiment followed the best-management-practice guidelines for DSE application that are recommended for this type of soil (Houlbrooke *et al.* 2011). The contrast in leaching with the constant-rate experiment indicates that leaching derived from DSE applications will be strongly influenced by the irrigation practice, and the degree of leaching observed in the constant-rate experiment has the potential to be minimised by best management practice.



**Figure 3** Concentrations of cadmium (Cd) in the leachate, compared with the ANZECC water quality guideline. The three treatments marked by triangles along the  $x$ -axis represent (from left to right) applications of superphosphate, cow urine, and dairy shed effluent (DSE) respectively. The round symbols on the  $x$ -axis indicate the timing of urea applications. L1 = Lysimeter 1, L2 = Lysimeter 2.

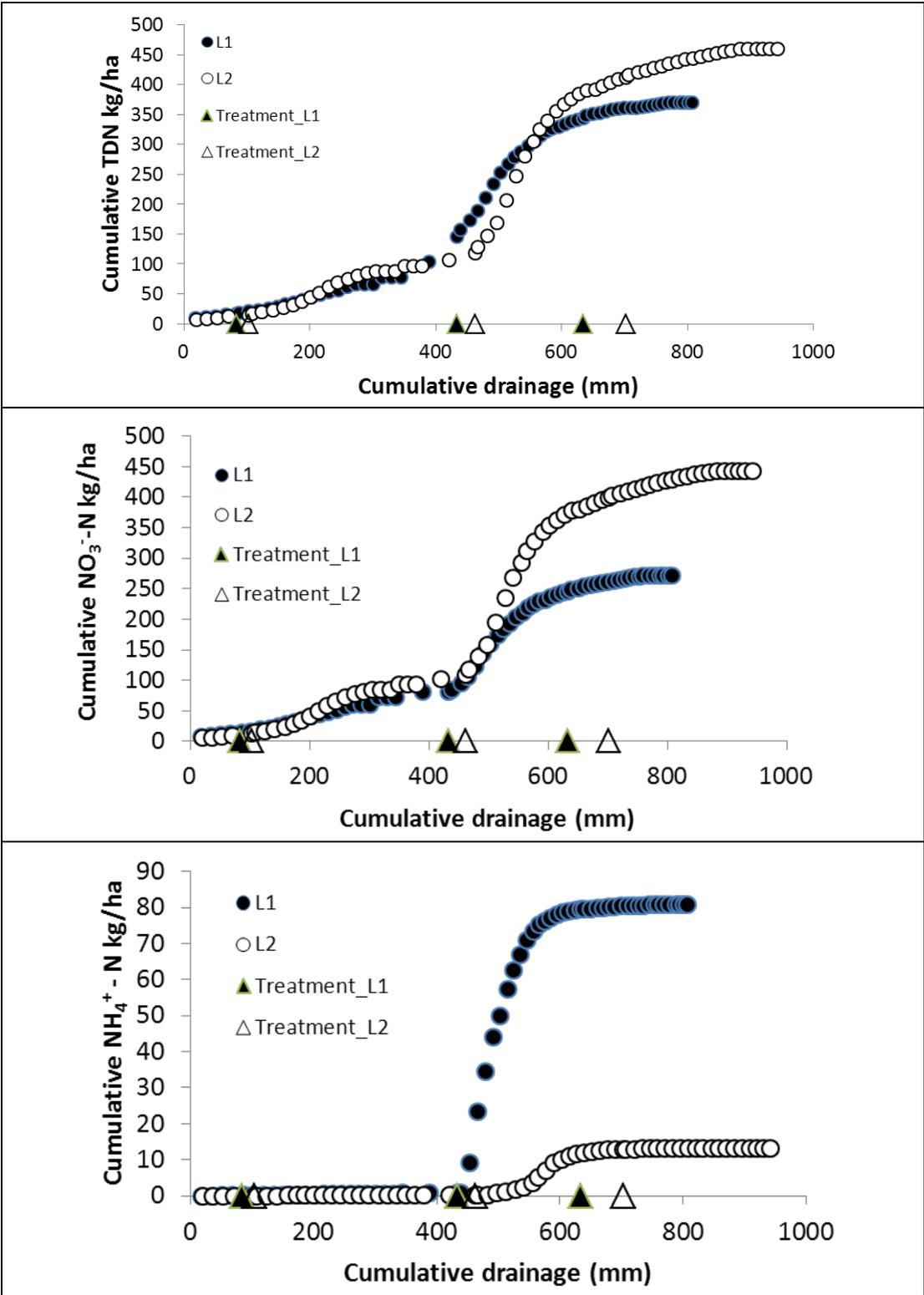
Leaching of nitrogen during the periodic-irrigation experiment is shown in Figure 4. The results indicate TDN leached throughout the irrigation trial, with both lysimeters following a similar pattern, but L2 leached about 78 kg TDN/ha more by the end of the experiment.

Following the application of superphosphate, there was an increase in TDN and  $\text{NO}_3^-$ -N leaching that coincided with the second urea-fertiliser application and the first increase in Cd leaching (Figure 2). While this increase in N-leaching looks to be linked to the side-dressings of urea fertiliser, it may also be the result of organic matter mineralisation that is likely to have occurred when the lysimeters were re-grassed prior to the superphosphate application.

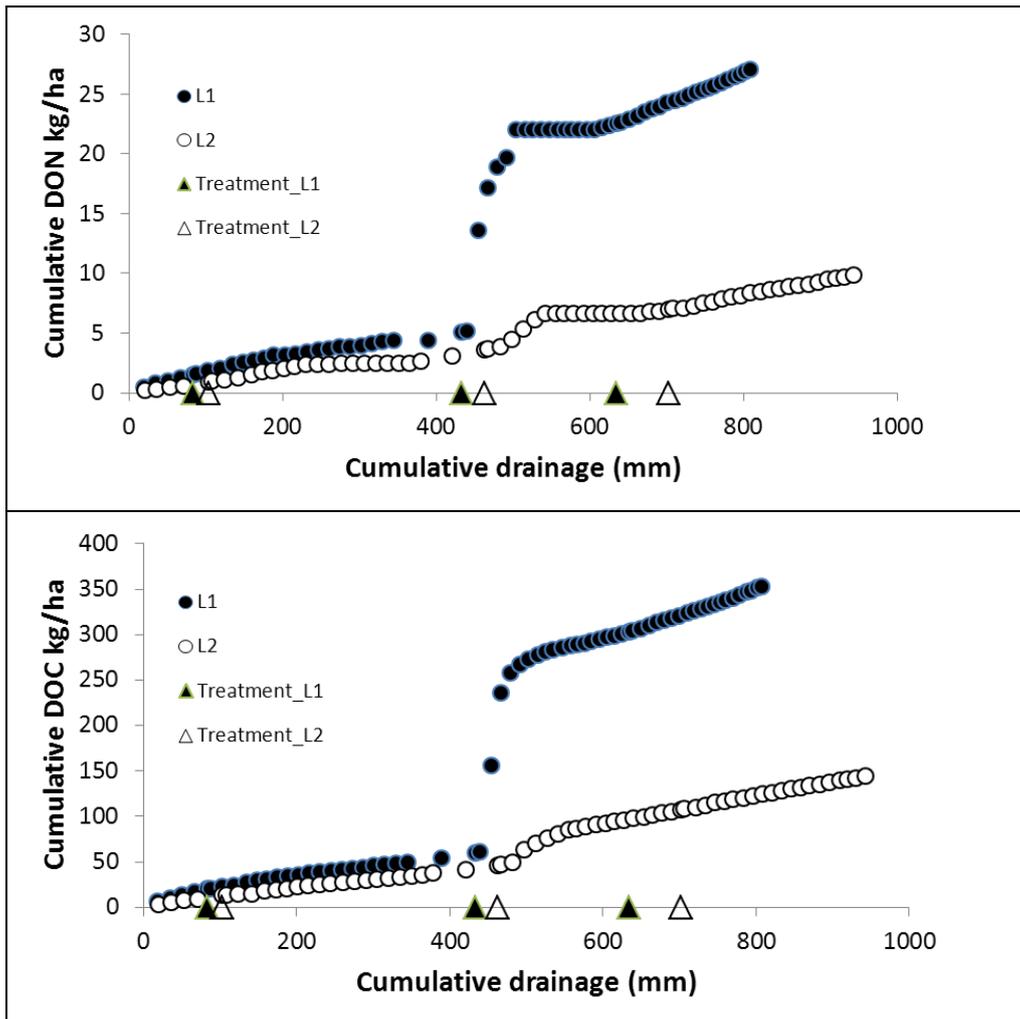
The application of urine resulted in a marked and rapid leaching in all forms of N, further indicating that cow urine will be a key driver of leaching for a range of contaminants in these soils. The marked increase in leaching occurred within 15 mm (L1) and 60 mm (L2) of drainage following the urine application. This clearly indicates a preferential-flow-driven transfer process, with both lysimeters showing an increase in TDN and  $\text{NO}_3^-$ -N in the leachate from the first irrigation event following the urine application. The strong degree of preferential flow is particularly highlighted in L2, with  $\text{NH}_4^+$ -N, DON, and DOC all showing a marked and rapid increase in the first leachate event (Figures 4 and 5). This reflects a direct transfer of raw urine from the soil surface to the lysimeter base in L1, but a slightly slower transfer of raw urine in L2 where the urine mostly leached in the  $\text{NO}_3^-$ -N form. The increase in DON and DOC following urine application may also reflect organic matter solubilisation by the urine (Lambie *et al.* 2012), which we postulate may also be a mechanism behind the TP and Cd leaching observed in Figure 2. The increased leaching of DON is of interest, as it has been previously identified as an overlooked pathway of nitrogen loss (van Kesse *et al.* 2009), with Wachendorf *et al.* (2005) estimating that possibly around 10% of urine N leached maybe DON.

The application of DSE resulted in no increase in leaching of nitrate and ammonia (Figure 4) with a slight increase in leaching of DON (Figure 5). Leaching of TDN and  $\text{NO}_3^-$ -N forms appeared to follow a continued leaching curve from the prior application of urine. The limited N-leaching apparent from the DSE application is consistent with that observed for TP and Cd, and further indicates support for the best-management-practice guidelines for DSE irrigation

on this type of soil (Houlbrooke *et al.* 2011). However, it is important to note that the leaching of DON following DSE application amounts to approximately 5 kg/ha of DON leached from L2, and this is 10–20% of the TDN applied as DSE.



**Figure 4** Cumulative total nitrogen (TDN), nitrate (NO<sub>3</sub><sup>-</sup>-N) and ammonium (NH<sub>4</sub><sup>+</sup>-N) (kg/ha) leached with cumulative drainage, following periodic irrigation at 3–4-day intervals. The three treatments marked by triangles along the x-axes represent (from left to right) applications of superphosphate, cow urine, and dairy shed effluent (DSE) respectively. L1 = Lysimeter 1, L2 = Lysimeter 2.



**Figure 5** Cumulative dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) (kg/ha) leached with cumulative drainage, following periodic irrigation at 3–4-day intervals. The three treatments marked with triangles along the x-axes represent (from left to right) applications of superphosphate, cow urine, and dairy shed effluent (DSE) respectively. L1 = Lysimeter 1, L2 = Lysimeter 2.

As observed with TP and Cd there was a marked difference in the leaching behaviour of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, DON, and DOC between the two lysimeters. TP,  $\text{NH}_4^+$ -N, DON, and DOC showed the greatest leaching in L1, while Cd and  $\text{NO}_3^-$ -N showed the greatest leaching in L2. Post-leaching sampling and analysis of the two lysimeters showed a higher sand content at the 50–70 cm depth of L2, compared with L1, supporting our hypothesis in the constant-rate experiment that the presence of high-sand-content lenses can significantly influence the nature of the leaching process in these soils. This is reflected by L2 having much less evidence of direct leaching of raw urine, as shown by the lower levels of  $\text{NH}_4^+$ -N, DON, and DOC leaching. Instead N-leaching was dominated by transformation of the urine-N into the  $\text{NO}_3^-$ -N form, consistent with the sand lens having higher water content and slower water movement, relative to the surrounding stone-dominated areas.

## Conclusions

Our results confirm the high-leaching-vulnerability assessment of young stony sand soils for a range of possible contaminants. In the periodic-irrigation experiment the cow urine deposition was the key driver of leaching, with increased leaching of N, P, C, and Cd starting within 15–60 mm of drainage. Relative to the urine effect, the leaching from the superphosphate and DSE application was low. However, in contrast, under constant-rate irrigation, rapid leaching

of P and Cd was observed after DSE application, highlighting the sensitivity of these soils to DSE management practices.

There was high variability in leaching processes between different lysimeters, with the presence of sand lenses suggested to result in lags in leaching and/or change in chemical species in the leachate, in comparison to the strong preferential flow that was apparent in lysimeters with a stone-dominated subsoil matrix. Future studies on stony soils should account for the field variability in stone-dominated-matrix and sand-lens proportions, with previous research indicating that at least 90% of the area will be stone-dominated matrix.

This scoping study confirms model predictions that young stony sand soils have high potential leaching vulnerability, and further research is urgently needed to validate these results and ascertain the extent of leaching risk under field conditions.

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