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Department of **Water and Environmental Regulation**
Department of **Primary Industries and Regional Development**

Treating agricultural soils with Iron Man Gypsum to reduce phosphate leaching and runoff to waterways

Mucca Dairy experiments

HEALTHY
ESTUARIES
WA

Delivering on the
Bindjareb Djilba Peel-Harvey estuary
Protection Plan

Water Science
technical series

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Summary

Many coastal sandy soils have poor phosphorus (P) retention capacity and are prone to becoming saturated with the nutrient. Loss of soluble P in runoff and leaching from P-saturated coastal sandy agricultural soils is a major cause of eutrophication in the southern estuaries of Western Australia. Adding high-P-adsorbing materials to these soils to slightly increase P-adsorption capacity offers a management option to immediately reduce P losses to waterways.

Healthy Estuaries WA is a Western Australian State Government program, building on the work of the Regional Estuaries Initiative (2016 to 2020). Both programs have sought to improve the health of estuaries in south-west Western Australia (WA) by reducing nutrient losses from their catchments. Innovative remediation options are one way to do this. This report presents scientific findings from research into soil amendments for treating high-nutrient-loss soils in catchments.

Iron Man Gypsum (IMG) is a high-P-adsorbing material that is a secondary product of titanium ore processing by Iluka Resources in Capel. At the time of publication, it was the only extensively researched material with proven effects on P mobility that was available in bulk quantities near the Peel region for trials on farms. During the past 20 years, IMG has been tested in a range of soil and water treatment situations by the CSIRO, ChemCentre and predecessors of the departments of Water and Environment, and Primary Industries and Regional Development.

While the material prevents P leaching over the long term when mixed into soils at high rates (>150 t/ha), this practice is impractical for grazing systems. Further research is needed to assess whether applying IMG at lower rates can achieve similar benefits in different soil settings. We conducted two paddock-scale experiments on a dairy farm in the Bindjareb Djilba (Peel-Harvey) catchment to investigate the benefits and potential risks of mixing IMG into soils at 60 t/ha compared with surface applied (top-dressed) IMG at 20 t/ha, and the effects of using rates of top-dressed IMG less than 20 t/ha.

We treated pasture used for cattle grazing with IMG in two adjacent replicated block experiments. The mixing experiment compared soils where IMG was applied at 60 t/ha and mixed by ploughing with IMG top-dressed at 20 t/ha with no ploughing. In an adjacent paddock, the top-dressing experiment compared soil where IMG was spread at 5, 10 and 20 t/ha with no ploughing. Ryegrass was annually direct-drill seeded in both experiments. We assessed the effects on runoff quality in both experiments in late winter using a rainfall simulator to generate runoff from waterlogged quadrants. In addition, we collected leachates from non-waterlogged soils in the top-dressing experiment throughout winter and spring using pan lysimeters and analysed them for nutrients and a broad range of other elements. These measurements were coupled with annual analyses of soils and analyses of pasture plants during the growing season.

Mixing IMG into soils, or applying it as a top-dress, immediately reduced the P lost in runoff from waterlogged soils by up to 78%, but the effectiveness depended on the application rates. Effects on runoff were similar for soils top-dressed with IMG at

20 t/ha or mixed with IMG at 60 t/ha, but decreased where soils were top-dressed with IMG at less than 20 t/ha. Despite only interacting with the surface layer of the soils, top-dressing with IMG at 20 t/ha also reduced leaching of P by 88% to less than 0.2 kg P/ha/yr, but had a minimal effect at lower rates of applied IMG. Reduced P in runoff and leachates following IMG treatment was due to lower free-P concentrations, measured as 0.01M $CaCl_2$-extractable P ($CaCl_2$-P). With IMG treatment, small increases in indicators of P-adsorption capacity, such as the phosphorus buffering index (PBI) and phosphorus retention index (PRI), were sufficient to reduce free-P concentrations without reducing plant-available P. Free-P concentrations were not predictable from other common measures of soil P availability (Colwell P) or adsorption capacity (PRI and PBI) but was broadly related to the phosphate environmental risk index (PERI). This index is derived from commonly used agronomic P analyses and could be used to highlight soils on farms with a high risk of P loss that would benefit from IMG amendment.

Top-dressing with IMG increases manganese (Mn), cobalt (Co) and sulfate (SO_4) in runoff and leachates, but not to an extent that poses a risk to aquatic ecosystems. Increases in leaching were most notable in Mn and, to a much lesser extent, in Co, cadmium (Cd) and zinc (Zn). The effect decreased with lower rates of top-dressed IMG. This contrasted with no change or reduced leaching of a range of other trace elements. Increases in Mn and Co likely originated from the applied IMG, whereas the Zn and Cd were likely mobilised from soils following IMG-induced soil changes. The increases in Mn and Co concentrations in runoff were much lower than the increases measured in leachates. Concurrent leaching of Ca with these metals mitigated any risks of Mn toxicity to pasture plants, as well as Mn and Co toxicity to aquatic organisms in downstream environments. Leaching of SO_4 from soils top-dressed with IMG also increased, but this effect is expected to diminish within a few years.

Top-dressing P-saturated pastures on sandy soils with IMG at a rate of 20 t/ha is a management strategy that can immediately reduce runoff and leaching losses of P from farms. The application method has the practical advantage of targeting the surface of soils – which is often the zone of highest P concentration – without needing to plough and reseed. Top-dressing is the cheapest method of application ($1,080 per hectare for IMG top-dressed at 20 t/ha in the Peel region), but the longevity of reduced P runoff is uncertain and likely depends on the initial amount of excess P in the surface soil. Mixing IMG with soils is necessary at higher rates of application (>40 t/ha) to avoid surface sealing, but the benefits include a greater increase in soil pH, it lasting longer and being more effective for reducing leaching. This option is more expensive (> $3,000/ha in the Peel region) but might be more suited to areas of farms with high P loading such as yards and laneways.

Further research into the effects of IMG on soil properties, plant uptake of nutrients, P loss and patterns of Mn, Co and SO_4 leaching will be carried out under Healthy Estuaries WA, alongside additional trials in different soil and farm settings. All these efforts aim to build confidence among farmers and agronomists to use IMG as a soil amendment in pasture production systems.

1 Introduction

Iron Man Gypsum (IMG) is a high-P-adsorbing soil amendment showing significant promise for improving retention of P as phosphate in sandy topsoils and reducing losses to waterways. The amendment is a dark brown loamy material with 10% iron as iron oxide minerals in a gypsum matrix (Douglas et al. 2012; Degens & Shackleton 2016). IMG is produced by Iluka Resources at its Capel production facility as a secondary product of ilmenite ($FeTiO_3$) ore processing (Wendling et al. 2012). It is the oxidised, dried, mixed and screened solid recovered from a sulfuric acid liquor that has been neutralised with $Ca(OH)_2$. The source liquor is a waste generated from washing of the ilmenite ore concentrate with sulfuric acid. At the time of publication, IMG was the only well-researched material with proven effects on P mobility that was available in bulk quantities in south-west WA for trials on farms.

Surface application (top-dressing) of IMG on pastures in Bassendean sands can increase topsoil P retention and reduce P leaching. These sands are common on the Swan coastal plain and are widely used in agricultural production. A study by Sharma et al. (2018) showed surface application of IMG at rates ranging from 10 to 50 t/ha on sandy soils minimised leaching of P by more than 80% over five years of monitoring. In this study, leaching losses were the result of fertiliser P applied during the experiment with the soils initially having negligible plant-available P. Greater reduction in leaching can be achieved where IMG is mixed into soils, but this is less practical for grazing production systems. P leaching was similarly reduced by >90% where IMG was mixed at 20 t/ha and 60 t/ha into P-saturated sandy soils under intensive dairy grazing (Degens et al. 2022). Mixing higher rates (150 t/ha) into sandy soils at a turf farm achieved >97% reduction in leached P (Douglas et al. 2010a, b). The treatment also increased accumulation of organic matter in the soils (Douglas et al. 2010a). This investigation also claimed the amendment increased the soil water-holding capacity, but this was inferred from reduced leaching of water rather than by direct measurements of water-holding capacity. Other uses of IMG have also been researched, such as for treating P in groundwater flowing to subsoil drains beneath an urban development (Degens & Shackleton 2016) and in surface water pumped from Ellen Brook (ChemCentre 2016; Department of Biodiversity, Conservation and Attractions 2018).

Many sandy soils on the Swan coastal plain have an inherently poor capacity to retain P and prevent loss to leaching or runoff (Ritchie & Weaver 1993; Bolland et al. 2003). After many decades of fertiliser application for agricultural production, large areas of these soils are now saturated with P (Summers et al. 2020) that is lost to shallow groundwater or runoff each winter. Overland flow is often the largest direct pathway of P loss to waterways (Gerritse & Schofield 1989; Ruprecht & George 1993). This typically happens when low-lying sandy soils with a shallow watertable are saturated during rainfall events. The P loss is further amplified in pasture soils by high P accumulation and the saturated-P retention capacity common in the surface few centimetres (Ryan et al. 2017).

Nothing is known of the effectiveness of top-dressed or mixed IMG in reducing the loss of P to runoff or whether this is similar for the treatment methods. In sandy soils, the greatest effect is expected to be on P loss during surface flows from saturated (waterlogged) sandy soils in winter. This might also extend to influencing P loss in runoff from intense rainfall events when soil infiltration rates are exceeded (e.g. summer thunderstorms). While P loss generally comes from washing of soluble P from the surface few centimetres of soils under saturated conditions, in unusual situations intense rainfall may also cause transport of soil particles (and associated P) from sloping sandy soils. Transport under these conditions is more dependent on factors other than P adsorption, such as local hydrology, ground cover, slope and soil management (Dougherty et al. 2004).

Adding IMG to sandy soils offers a way to improve P retention and at higher rates may yield the additional benefits of improved carbon storage. Improved P retention is expected to improve the P available for plant growth and reduce annual P loss, particularly for sandy soils with a long history of fertiliser application. This is particularly relevant for agricultural soils that have accumulated high amounts of P that exceed the requirements for pasture production. It may take some decades for the P status of these soils to ‘run down’ (Gerritse & Schofield 1989). During this process, the soils will continue to lose P in high concentrations as leachates to shallow groundwater or in runoff to waterways.

The optimal IMG application rate and most effective application methods to achieve maximum benefits in terms of reduced P losses from agricultural soils are still to be determined. Surface-applied (top-dressed) IMG of 10 t/ha was sufficient to capture leaching losses of up to 15 kg P/ha/yr (Sharma et al. 2018), while mixing IMG into soil at 150 t/ha captured up to 72 kg P/ha/yr (Douglas et al. 2010a). Mixing IMG may be more effective for minimising P losses than top-dressing IMG – particularly in situations where the whole topsoil is saturated with P due to historic fertiliser or grazing practices. However, IMG may be more effective at lower rates when applied to the surface of soils that are commonly highly P stratified (Ryan et al. 2017) due to manure deposition and surface applications of fertiliser P. This application method is likely to be effective for soils in low-lying areas that are seasonally waterlogged and frequently generate runoff during winter.

We tested the hypotheses that surface-applied (top-dressed) IMG at 20 t/ha can be as effective as IMG mixed at 60 t/ha and that lighter rates of top-dressed IMG may also be effective. Two paddock-scale experiments with replicated block designs were carried out on high-P-status sandy soils used for beef and dairy production. The mixing experiment compared soils where IMG was applied at 60 t/ha and mixed by ploughing with IMG top-dressed at 20 t/ha with no ploughing. In an adjacent paddock, the top-dressing experiment compared soil where IMG was spread at 5, 10 and 20 t/ha with no ploughing. We measured the improvement in P retention and soil quality as well as the agronomic benefits of the treatments by monitoring soils, plants, leachates and runoff. These included comprehensive analyses that enabled monitoring and assessment of any environmental and production system risks.

2 Design and methods

We conducted the experiments on two adjacent paddocks on Rob Giura's property (Mucca Dairy) at Keysbrook, 20 km north-east of Mandurah. This property is in the upper part of the Nambeelup Brook catchment of the Bindjareb Djilba (Peel-Harvey estuary).

2.1 General site description

Both sites had pastures dominated by ryegrass that were used for hay production during spring and grazed in early winter, then grazed again in summer through autumn.

The soils were regionally mapped as sandplains and broad rises with mostly grey siliceous sands variously underlain by deep bleached horizons, clays or iron-organic hardpans at depth (>1m). Towards the south-west of the experimental sites the soils were deep grey imperfectly drained siliceous sands of the Bassendean series (212 Bs_B6 after Van Gool 1990). These transitioned to the north and east to deep bleached grey sandy sands sometimes with pale yellow B horizons (212 Bs_B1 after Van Gool 1990), clays or weak iron-organic hardpans at depths greater than 1.5 m (212 Bs_B4 after Van Gool 1990).

2.2 Climatic conditions

The first year of the experiment (2018) was a wet one, with 702 mm of rainfall being recorded on the property. We used rainfall recorded by the Bureau of Meteorology at nearby Cloon (site 9242) to assess rainfall during the experiment relative to other years. In 2018, the rainfall at Cloon was 70 mm greater than the median and marginally less than the 90th percentile for the 24-year record at this site. In contrast, the second year of the experiment was a dry one, with 508 mm recorded on the property. At Cloon, the 2019 rainfall was 60 mm below the median and marginally above the 10th percentile.

2.3 Experiment site descriptions

Hand auguring inspection of the mixing experiment site revealed mostly gradational siliceous sands. These graded from grey to light brown with mottling over coffee rock (at >1.1 mbgl) in the north, transitioning to generally grey topsoils with yellowish-brown subsoil sands overlying mottled clayey sands (> 1.5 mbgl) in the south. The depth to coffee rock and thickness of the overlying bleached sandy horizons generally increased upslope to the north.

In contrast, soils at the top-dress experiment site were mostly deep siliceous sands. Grey sand topsoils with light grey sand subsoils overlaid light brown sands at below 0.3 to 1.1 mbgl, with reddish-brown mottling that typically increased with depth. Beneath this were brown sands in the permanent watertable, typically at 0.6 to

1.2 mgbl. Coffee rock was absent beneath the site, but iron concretions were found in some of the deeper mottled sands.

We took pre-establishment samples from both sites and found the topsoils (0–10 cm) to be acidic extremely-low-P-buffering sands with moderate to high P status. Soil pH (in 0.01M $CaCl_2$) was similar, ranging from 4.7 to 5.6. Phosphorus buffering index (PBI) and plant-available P (Colwell P) were also similar, although tended slightly higher on the top-dress site with much greater variation. PBI ranged from 2.7 to 12.9 on the mixing experiment site, but from 5 to 38 on the top-dress site. Similarly, Colwell P ranged between 15 to 44 mg/kg on the mixing site but ranged from 23 to 80 mg/kg on the top-dress site.

The land surface of the mixing site gently sloped to the south (Figure 1) and was flatter and more low-lying than the top-dress site. In contrast, the top-dress site had greater relief given it was transected by a slight dune ridge – the land gently sloping to the east and west either side of it (Figure 2).

Depth to the watertable across the mixing site varied from <0.1 mbgl in winter to >1 mbgl in summer. This rendered the soils prone to periodic waterlogging. In contrast, the depth to watertable across the top-dress site was generally greater. During winter, this varied from 0.1 to 0.2 mbgl in soil zones 1 and 3 to 0.5 mbgl in soil zone 2 (Figure 2). A remnant spoon drain crossed part of the experiment and intersected the two plots. This carried flows during wet periods but most surface water flowed in drains along the paddock's southern and northern boundaries.

2.4 Experimental design

We sourced IMG for each experiment direct from Iluka Resources Ltd's stockpile at Capel as separate single 20-tonne loads.

2.4.1 Mixing experiment

The mixing experiment was a randomised replicated block design covering 1.6 ha that compared untreated soils (with and without tillage) with either IMG tilled in at 60 t/ha or IMG top-dressed at 20 t/ha. Each plot was 12 m x 130 m with 2 m buffer zones (Figure 1)). The tillage treatments were nested in the untreated plots as split plots of 6 m width.

We applied the treatments in early April 2018. IMG was spread in 5 t/ha passes using a wide-gate Marshall multi-spreader with a cleated feeder-belt feeding twin hydraulic spinners. The width of the plots was determined by the throw width of IMG from the spreader. Mixing of the IMG with the topsoil (0–10 cm depth) was carried out with two passes of a disced speed tiller (with offset non-scalloped discs). The speed tiller was also similarly passed over untreated soils to serve as controls.

2.4.2 Top-dress experiment

The top-dress experiment was a randomised replicated block design covering 1.7 ha that compared untreated pasture soils with soils treated with 5, 10 or 20 t/ha of IMG spread on the surface. Each plot was 12 m wide x 145 m length with 2 m buffer zones (Figure 2).

We spread the IMG in March 2019 in 5 t/ha passes using the same method described above. Spot measurements of the IMG application rate (using 1 m^2 catch plates) indicated it varied from 4 to 6 t/ha for each pass, with most IMG being within 5 m of the centre for each spreader pass. Mostly this was a result of variation in the feed of the material from the belt – with the IMG bridging and falling onto the spinners in waves. We carried out the spot measurements by collecting and weighing the IMG settling on 1 m^2 carpet squares placed in the centre of each pass and took several measurements 2 m and 4 m from the centre. Each pass was aligned with the longitudinal centre of each plot, that later formed transects for soil sampling and placement of lysimeters.

2.4.3 Agronomic management during experiments

Both sites were annual sown with Abundant® ryegrass – a tetraploid variety of Italian ryegrass (*Lolium multiflorum* var. *westerwoldicum*). This was typically carried out in May to early June using a 22 run narrow-point direct drill with 150 mm tine spacing set at nominally 10–12 mm depth but with a practical range of 5–25 mm. Other volunteer pasture plants growing were mainly Balansa clover (formerly *Trifolium balansae* now *Trifolium michelianum*) and Wimmera ryegrass (*Lolium rigidium*) with minor capeweed (*Arctotheca calendula*) and kikuyu (*Pennisetum clandestinum*).

Both experimental sites were annually fertilised in spring with an organic fertiliser (mostly composted manure) and occasional applications of urea for at least 10 years prior. The composted fertiliser was applied at a rate of 1 tonne/ha (equivalent to 0.75 tonnes air-dry material/ha) annually supplying an average of approximately 16 kg total N/ha, 4 kg total P/ha and 8 kg K/ha. This was based on analysis of air-dry samples from two batches during the experiment that found this fertiliser contained 2–3% total nitrogen (TN), 0.7–1% total phosphorus (TP) (with half of this being HCO_3 extractable), and 1–1.5% available potassium (K). In the first year we applied compost to both the mixing experiment and top-dress experiment after the runoff simulations. However, in the second winter we applied the compost two weeks before the runoff simulations.

Cattle were grazed intermittently on the experimental site during winter, depending on pasture growth, and again in summer after hay making. Grazing was withheld each spring to capture maximum pasture growth. In early summer the pasture was cut and baled as hay. Some of this hay was fed back to cattle on the site, with most going to other paddocks.

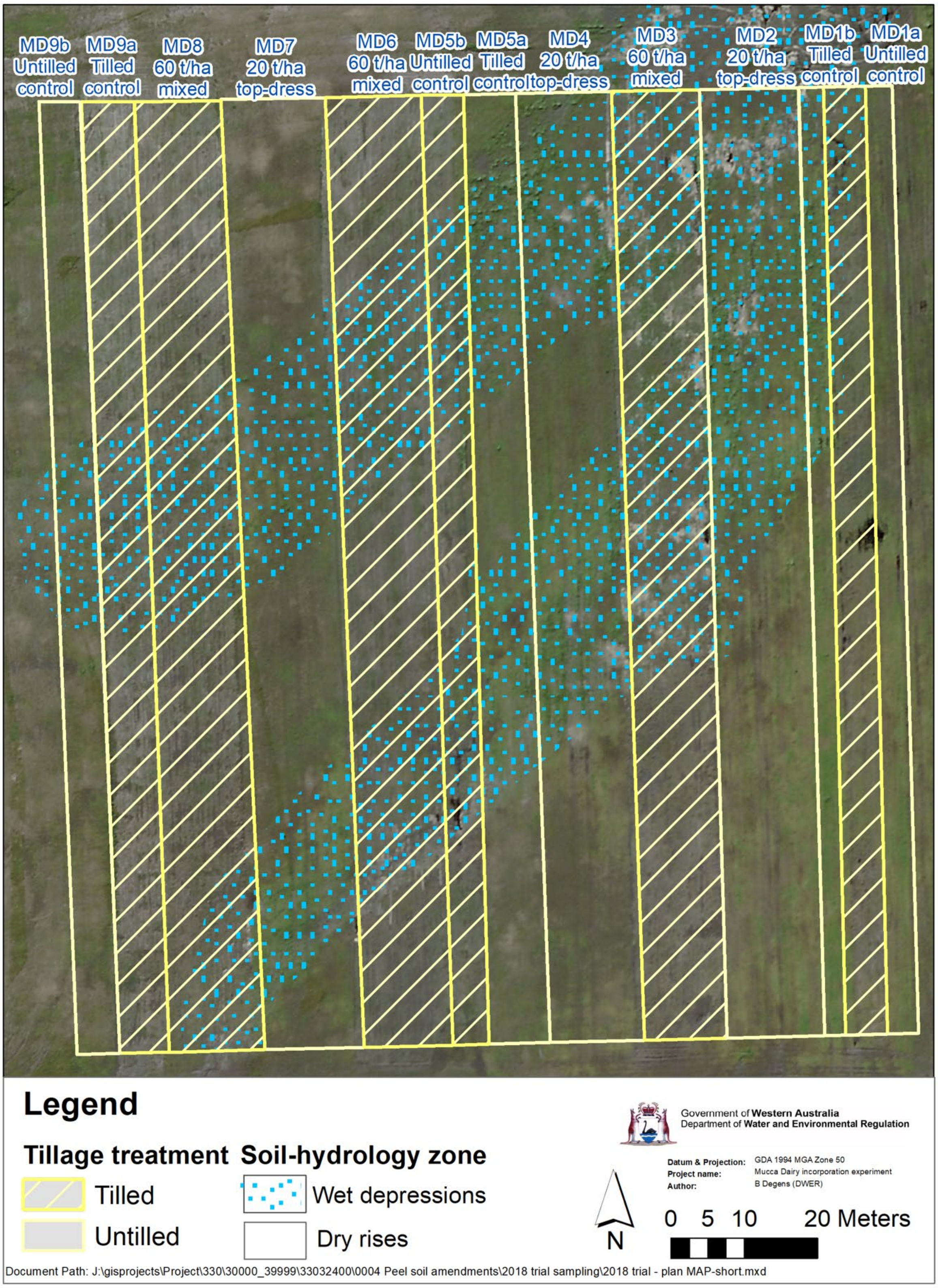


Figure 1: IMG mixing experiment design with soil-hydrology zones

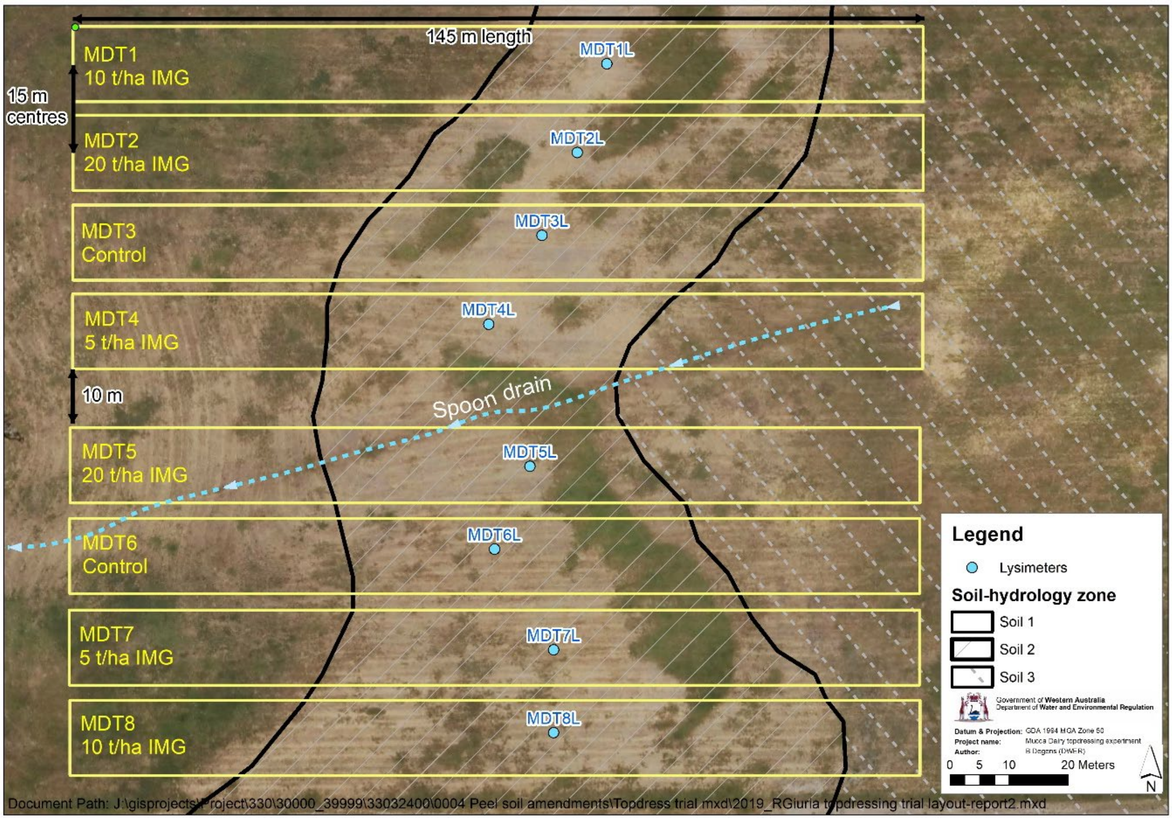


Figure 2: Top-dressed IMG experiment design with soil-hydrology zones

2.5 Sampling and analysis methods

2.5.1 Defining soil-hydrology zones

We stratified sampling and measurements in each experiment using soil-hydrology zones to separate the potential effects caused by variable waterlogging. In the mixing experiment (Figure 1), we observed that soils in minor depressions frequently became waterlogged in the first winter (wet depressions), which contrasted with soils on slight rises of approximately 5–10 cm that were less frequently waterlogged (dry rises). We identified the wet depressions by mapping areas of pooled water and surface flows across the experimental area during winter 2018 and verified these with aerial photography taken during other winters (Figure 1). We used a similar method to identify three soil-hydrology zones in the top-dress experiment (Figure 2) with these being:

- Soil zone 1: grey and black sands on a low-lying seasonally waterlogged flat to the west
- Soil zone 2: grey sands on a low-relief dune that are not seasonally waterlogged in the centre of the site
- Soil zone 3: grey and black sands on a low-lying seasonally waterlogged flat to the east.

2.5.2 Runoff assays

We carried out runoff assays in the first and second winters of the mixing experiment and in the first winter of the top-dress experiment. These were conducted in July and August when the watertable was 0.1 to 0.2 m below the soil surface with saturated overland flow frequently observed in the preceding weeks. Conditions enabled the assays to be done at random sites across all the mixing experimental plots, but only in the low-lying parts prone to waterlogging for the top-dress experiment (soil zone 1 and 3).

We used a locally designed rainfall simulator adapted from Humphry et al. (2002) to assess runoff quality from two replicate randomly placed 1 m^2 quadrants in each plot. We applied water evenly at a rate of 58–74 mm/hr to generate runoff of about 5–18 mm (average 10 mm). This application rate was necessary to initially saturate the sandy soils over 5–15 minutes and then sustain runoff for 30 minutes by saturation excess. The rate is much greater than typically experienced for an hourly rainfall rate (with an annual exceedance probability of <2%), but it is common for a 24-hour period (annual exceedance probability of 20–50%). We used a specialised spray nozzle (see details in Appendix A) at a pressure of 2 bar to achieve small droplets with an even spread across each quadrant. We collected runoff for 30 minutes (from the point we observed it to begin) using a ground-level channel and pumped it into a collection jug. See Appendix A for additional details of the simulator design and operation.

We sampled runoff water in the first and last 10 minutes for TN and TP and took a composite 30-minute sample. Samples were analysed in the field for pH, EC, temperature and in the laboratory for dissolved and total nutrients, dissolved ions and total and dissolved metals – see Appendix B.

2.5.3 Leachate sampling and analysis

We used zero-tension pan lysimeters to collect leachates from the topsoils (0–10 cm) in the dry soil rises of the top-dress experiment (soil 2, Figure 2). This was the only part of both experiments that was not seasonally waterlogged and therefore suitable for free-draining lysimeters. In April 2019 we installed eight lysimeters beneath undisturbed soil after applying the IMG and before the start of winter rainfall (Figure 2). We retrieved leachate that had collected in the drums using a hand vacuum extraction pump every two to four weeks, depending on rainfall, and measured the volumes to the nearest 50 mL. We used these to calculate total fluxes of nutrients and elements. See Appendix C for lysimeter design and sampling methods and Appendix D for an assessment of the stability of nutrients in leachates.

We measured pH, EC and temperature in the field with samples taken for nutrients, anions and metals – see Appendix B.

2.5.4 Soil, IMG and plant sampling

Sampling of topsoil (0–10 cm) for both experiments was stratified in each plot by soil-hydrology zones (Figure 2) and carried out in summer. We collected composite samples of 10 x 40 mm cores of topsoil per soil zone from centre transects in each plot, which we then mixed and sub-sampled. We submitted the samples for analysis of P chemistry, as well as standard soil properties (see details in Appendix B). In brief, this included estimation of free-P by analysing phosphate-P in a 0.01 M $CaCl_2$ soil extract (termed $CaCl_2$-P) and plant-available P using the Colwell method (Colwell P). $CaCl_2$-extractable P is widely used as an indicator of free P in the soil, otherwise known as soil solution P (Moody 2011). P-adsorption properties were assessed by analysing the PBI (Burkitt et al. 2002) and the PRI (Allen and Jeffery 1990). Both measures are indicators of soil-P-buffering capacity with PBI effectively indicating inherent, pre-development P-adsorption capacity and PRI indicating current residual capacity to adsorb further P (Bolland et al. 2003).

In addition, each summer we sampled the soils near each lysimeter in the top-dressing experiment. We used similar sampling equipment, methods and analyses to the plot sampling, except that the composite sample consisted of 10 cores taken from a 2 m x 1 m area immediately north of the lysimeter. We designed the sampling to represent the soil above the lysimeter pan and to avoid disturbing the soil around it.

We took composite samples of the IMG from the bulk truck loads delivered for each experiment. These were 10 x 40 mm diameter x 30 cm length cores from the stockpiles. The cores were combined and analysed for total element content by digestion with ICP-MS or ICP-AES depending on the analyte (see Appendix B and, for the report, Appendix E).

Over two spring seasons, in each plot of the mixing experiment, we conducted whole-plant tissue testing of specific species. In early October 2018 we sampled Balansa clover (formerly *Trifolium balansae* now *T. michelianum*) around the start of flowering. In mid-October of both years, we sampled Abundant ryegrass (*Lolium multiflorum westerwoldicum*) around 14–15 weeks after emergence. We hand-collected samples of whole-plant tops by taking 20 samples along centre transects down the length of each plot and sorting them to exclude non-target plants. See Appendix B for the analysis of the plant samples.

2.5.5 Data processing and statistical analyses

We calculated the P_{95} fertility index as the ratio: Colwell P/Colwell $P_{95\%prod}$, where $Colwell_{95\%prod}$ is the Colwell P required for 95% maximum pasture production given the PBI of each site from the formula $Colwell_{95\%prod} = 19.6 + 1.1*PBI^{0.55}$ (Gourley et al. 2019).

We calculated a proposed index of soil P environmental risk or PERI (after D. Weaver, pers. comm. 2019) from soil analyses as Colwell P/PBI (Moody 2011).

The volume-weighted concentration of constituents in leachates for each winter–spring leaching period was expressed as:

$$C = \frac{\sum_{i=1}^{n} q_i c_i}{\sum_{i=1}^{n} q_i}$$

Where:
C = volume-weighted concentration (average annual concentration)
q_i = volume of leachate for a specific period i
c_i = concentration of constituent in leachate collected for period i
n = the maximum number of leaching event samples for a year.

Results that were below analysis reporting limits (typically water quality analyses) were expressed as half the concentration of the reporting limit for the purposes of statistical analyses.

We tested the statistical significance of differences between treatments using one-way ANOVA following testing of normality using the Shapiro-Wilk test (SigmaPlot version 13). We performed two-way ANOVA to test the effects of treatments over years or treatments. We applied transformations (log normal or square root) when data was not normally distributed to allow fitting of the statistical models. We deemed the differences between means as significant when $P < 0.05$ and carried out pairwise comparisons using the Holm-Sidak test (SigmaPlot version 13).

3 Results

3.1 Topsoil properties – whole plots (summer)

The topsoils (0–10 cm) on both experimental plots were acidic medium-grained sands with moderate organic C content. Despite the differences in waterlogging, the soil properties were similar for the wet depressions and dry rises in the mixing experiment (Table 1; Table 2) and the three soil zones in the top-dress experiment (data not shown). Untreated soils in the mixing experiment had a pH_{CaCl2} that was slightly higher (range 5.0–5.8) than the untreated soils in the top-dress experiment (pH_{CaCl2} 4.4–5.0). The organic C contents were also slightly greater in the untreated soils of the mixing experiment, ranging from 3.5 to 4.2% compared with 2.4 to 3.1% in the top-dress experiment. pH and organic C were the same in the wet depressions and dry rises of the mixing experiment, but at the top-dress site, soil 2 had an organic C (average 3.1%) greater than soil 1 and 3 (average 2.4 to 2.7%).

P retention was very low in the untreated soils of both experiments, with an increase only detected in the 60 t/ha IMG treatment of the mixing experiment. PBI was <9 and PRI <0.5 in the untreated soils of the mixing experiment, marginally increasing to a PBI of >20 and PRI >3.6 in the 60 t/ha IMG treatment (Table 1; Table 2). Both PRI and PBI slightly increased where IMG was top-dressed at 20 t/ha in both experiments, but the effect was statistically significant only for PRI (Table 1; Table 2; Table 3). There were similar, small but non-statistically significant effects among the lower rates of top-dressed IMG (Table 3).

Plant-available P in the IMG-treated soils increased or remained similar over the two years of the mixing experiment, despite a slight improvement in P-retention characteristics. Untreated wet depressions and dry rises had similar Colwell P each year, which was either similar or greater in the IMG-treated soils (Table 1; Table 2). Colwell P increased in some IMG-treated soils, although not in all years or all treatments (Table 1; Table 2). These patterns indicate that greater differences may emerge over subsequent years but, at present, they are masked by variation in Colwell P across the site (being consistently greater for plots in the east than the west). In the top-dress experiment, Colwell P remained similar in the IMG-treated soils relative to the untreated soils, although overall Colwell P decreased across all treatments over the first year (Table 3).

P fertility for pasture production (P_{95} fertility index) varied significantly across each of the sites but was generally adequate. In the mixing experiment, the P_{95} fertility index averaged 1.1 to 1.3 across the site, ranging from 0.9 to 2.0 over the two years. Similarly, the P_{95} fertility index was greater than 1 across the top-dress experiment, but with a slightly larger variation (0.6–2.3 before winter narrowing to 0.5–1.9 the following summer). This was due to the decrease in Colwell P by an average of 5 mg/kg from pre-winter 2019 to summer 2020 across the experiment. These results indicated that soil P was generally more than sufficient across most of the experimental plots to achieve 95% of the maximum biomass production for high-P-demand plants such as clover (Gourley et al. 2019).

Table 1: Summary topsoil properties (0–10 cm) of the mixing experiment stratified by soil zones in the first summer after establishment

Soil-hydrology zone and treatment		CaCl$_2$-P (mg/kg)	Colwell P (mg/kg)	PRI	PBI	P$_{95}$ fertility index[2]	Colwell K (mg/kg)	SO$_4$-S (mg/kg)	pH (in CaCl$_2$)	Organic carbon (%)	CEC (meq/100g)
Wet depressions	No IMG (untilled)	8.8ab[1]	17a	0.6a	5a	0.9a	97a	101a	5.2a	3.6a	4.3a
	No IMG (tilled)	10ab	22a	0.5a	8a	1.0a	112a	82a	5.1a	3.7a	4.8a
	20 t/ha	4.3bc	21a	1.9b	12ab	0.9a	128a	254b	5.4a	4.0a	5.5ab
	60 t/ha	0.3c	23ab	3.6bc	20bc	0.9a	95a	521c	5.8a	3.0a	6.5b
Dry rises	No IMG (untilled)	14a	31ab	-0.3a	8a	1.3a	243b	112a	5.3a	3.7a	5.2ab
	No IMG (tilled)	13a	32ab	0.4a	9a	1.4ab	261b	124a	5.4a	3.8a	5.8ab
	20 t/ha	12a	59c	1.0ab	16ab	2.3b	272b	147ab	5.7a	3.5a	5.4ab
	60 t/ha	0.6c	45bc	4.0c	30c	1.6ab	164ab	512c	5.8a	3.8a	6.1b
95% target[3]			20 (17–21)				126 (109–142)	8 (6–10)			

[1] Mean values followed by the same letter are not statistically different ($P>0.05$).

[2] P$_{95}$ fertility index being the plant-available P relative to that required for a 95% production target (Weaver & Wong 2011).

[3] Concentration for 95% maximum pasture production with 95% confidence interval (Gourley et al. 2019). Note: Colwell value for PBI 10–15.

Table 2: Summary topsoil properties (0–10 cm) of the mixing experiment stratified by soil zones in the second summer after establishment

Soil-hydrology zone and treatment		$CaCl_2$-P (mg/kg)	Colwell P (mg/kg)	PRI	PBI	P_{95} fertility index[2]	Colwell K (mg/kg)	SO_4-S (mg/kg)	pH (in $CaCl_2$)	Organic carbon (%)	CEC (meq/100g)
Wet depressions	No IMG (untilled)	8.3 a[1]	18 a	-0.9 a	11 a	0.8b	124 a	101 a	5.0 ab	3.2 a	4.7ab
	No IMG (tilled)	8.2 a	28 a	0.2 ab	14 a	1.1b	156 a	85 a	5.4 ab	3.3 a	5.1ab
	20 t/ha	5.7 a	54 b	1.1 b	32 b	2.0b	210 a	200 b	5.7 a	4.0 a	5.8abc
	60 t/ha	1.0 b	38 ab	4.3 c	31 b	1.4ab	127 a	541 b	5.7 a	3.1 a	6.6c
Dry rises	No IMG (untilled)	8.6 a	18 a	0.1 ab	13 a	0.8b	177 a	93 a	4.8 a	3.3 a	4.1a
	No IMG (tilled)	5.9 a	24 a	0.4 ab	13 a	1.0b	160 a	136 a	5.2 ab	3.4 a	5.0ab
	20 t/ha	7.3 a	28 a	1.3 b	16 a	1.0b	210 a	208 b	4.9 a	3.4 a	5.2abc
	60 t/ha	0.9 b	37 ab	5.4 c	33 b	1.3ab	154 a	614 b	5.9 b	3.7 a	6.5c
95% target[3]			20 (17–21)				126 (109–142)	8 (6–10)			

[1] Mean values followed by the same letter are not statistically different (P>0.05).

[2] P_{95} fertility index being the plant-available P relative to that required for a 95% production target (Weaver & Wong 2011).

[3] Concentration for 95% maximum pasture production with 95% confidence interval (Gourley et al. 2019). Note: Colwell value for PBI 10–15.

Table 3: Average topsoil P properties before winter (pre) and in the following summer following top-dressing with different rates of IMG

Treatment	$CaCl_2$-P (mg/kg)		Colwell P (mg/kg)		PBI		PRI	
	Pre	Summer	Pre	Summer	Pre	Summer	Pre	Summer
Untreated	12.4 a	6.5 a	34 a	28 b	12 a	18 a	-0.82 a	0.42 a
5 t/ha IMG	8.2 a	5.6 a	33 a	27 b	13 a	24 a	-0.02 ab	1.12 ab
10 t/ha IMG	5.6 a	4.2 a	30 a	25 b	13 a	20 a	0.78 bc	1.38 bc
20 t/ha IMG	5.6 a	4.5 a	32 a	29 b	15 a	24 a	1.07 c	1.64 c
Significance of factors								
Time	P = 0.12		P=0.01		P>0.5		P>0.4	
Treatment	P = 0.07		P>0.9		P>0.5		P=0.04	

[1] Average values (of two replicate blocks and three soils in each) for each sampling time followed by the same letters are not statistically different (P>0.05). Results were grouped across the three soils following initial analyses finding no effect of soil zone (P>0.5).

Typically, more than 30% of plant-available P (Colwell P) was present as free-P ($CaCl_2$-P) in untreated soils of both experiments with no lasting effect of tillage. $CaCl_2$-P was reduced to less than 5% of that in the untreated soils in the first summer after mixing IMG at 60 t/ha, irrespective of the soil zone (Table 1). This effect diminished slightly after the second year, although $CaCl_2$-P remained at less than 12% of that in the untreated soils (Table 2). In contrast, no effects on $CaCl_2$-P were found in any of the top-dressed IMG treatments, initially or after several years (Table 1; Table 2; Table 3).

Across both experiments, the range of $CaCl_2$-P induced by the treatments was broadly predictable from PERI, a proposed index of soil-P environmental risk. The correlation was reasonably strong in each experiment ($r>0.77$; $P<0.01$). This relationship extended to soils with higher $CaCl_2$-P beyond the experiment site, including additional paddocks on the same property as well as another IMG experiment site near Busselton (Figure 8). PRI was also correlated with $CaCl_2$-P in each experiment ($r>0.56$; $P<0.01$) but as a negative exponential function (data not shown). In contrast, $CaCl_2$-P was poorly correlated ($r<0.26$; $P>0.4$) with Colwell P each year and across all experiments ($r<0.3$; $P>0.4$).

The IMG had effects on other soil properties beyond those influencing P loss, but these were detectable only at the highest rate of IMG in the mixing experiment. No significant effect on pH was found in the first year of any treatments in both experiments (P>0.1; Table 1), but a slight increase of 0.5 units emerged where IMG was mixed at 60 t/ha after the second year (Table 2). In the mixing experiment, cation exchange capacity (CEC) increased by more than 1 meq/100 g where IMG was mixed at 60 t/ha over both years (Table 1; Table 2), but there was no significant effect where IMG was top-dressed at 20 t/ha. In the adjacent top-dress experiment; however, IMG top-dressed at 20 t/ha increased the CEC by 1.4 meq/100 g, although it is worth noting the soils in this treatment started with much lower CEC. Lower rates of top-dressed IMG caused a slight, but not statistically significant increase in CEC.

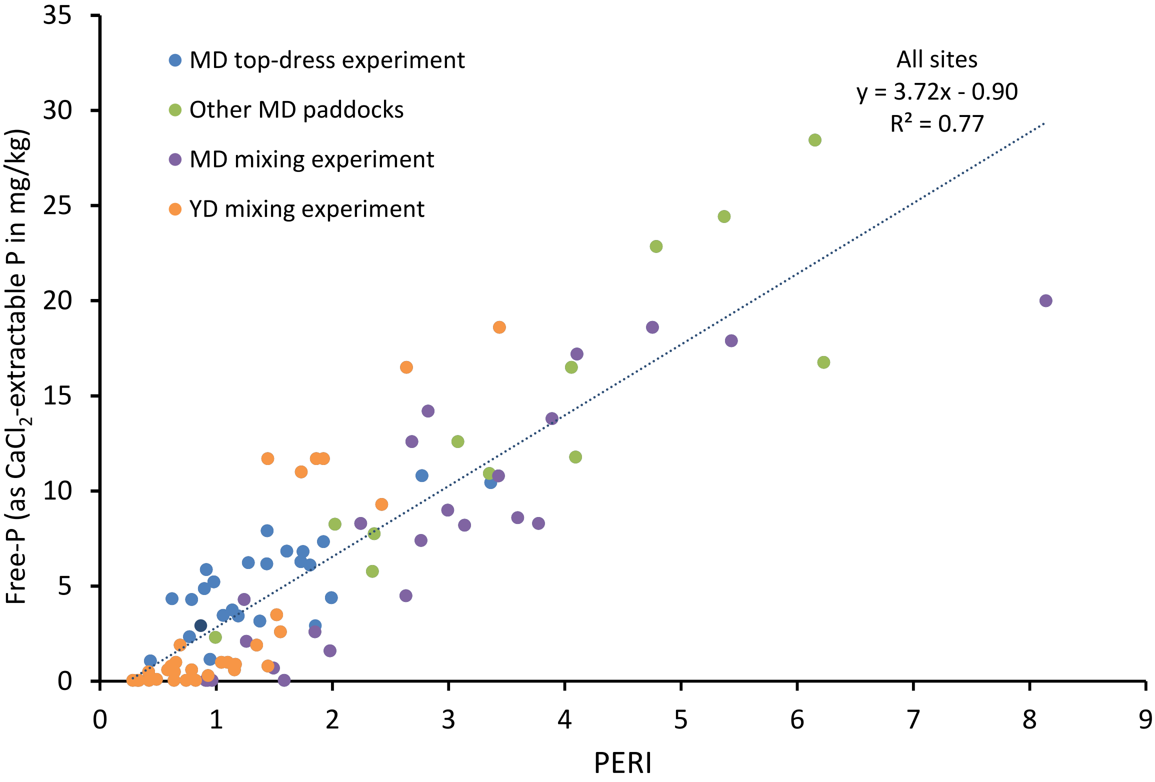


Figure 3: Free-P (as 0.01 M $CaCl_2$-extractable P) of soils as predicted by the phosphorus environmental risk index (PERI) for all 0-10 cm samples taken in the first summer year of multiple experiments at Mucca Dairy (MD) and Yoongi Downs near Busselton (YD mixing experiment)

A sustained increase in soil S was found in both experiments but was much greater with the IMG mixed at 60 t/ha than the IMG top-dressed at lighter rates. Plant-available S (as SO_4) increased by more than five-fold where IMG was mixed at 60 t/ha to more than 512 mg/kg, with this being sustained over the two years (Table 1; Table 2). The increases in plant-available S with lighter rates of top-dressed IMG were less but varied between the experiments. A concentration of more than 147 mg/kg was sustained over the two years in the 20 t/ha top-dress treatment of the mixing experiment. By comparison, after one winter, the 20 t/ha IMG application in the top-dress experiment increased plant-available S to 460 mg/kg, with an increase to 210 mg/kg measured in the 10 t/ha rate (data not shown). However, analysis results after the second winter indicated the concentrations had decreased by more than half (data not shown).

No significant effects of any of the IMG treatments were found for plant-available K and N. Colwell K was not influenced by the IMG treatments of both experiments (Table 1; Table 2), although it varied each year between the wet depressions and dry rises of the mixing experiment. Concentrations at both sites were sufficient for at least 95% maximum pasture production across most plots of both sites, except some wet zones in the mixing experiment (using guidance in Gourley et al. 2019). In the mixing experiment, Colwell K was logarithmically correlated with exchangeable K each year (r>0.8, not shown), but was not inversely related to the increase in exchangeable Ca with the IMG treatments in either year (Figure 4).

Exchangeable Mg was slightly (but not significantly) reduced with increased exchangeable Ca, particularly with IMG mixed at 60 t/ha (Figure 4). However, concentrations remained greater than 0.2 meq/100 g over the two years, which is deemed adequate for plant growth (Aitken & Scott 1999). Excess exchangeable Ca also did not result in Ca:Mg ratios exceeding 20 where Ca can hinder Mg uptake (Fenton & Conyers 2002). Extractable nitrate and ammonia did not vary between any of the soil zones or treatments of either experiment.

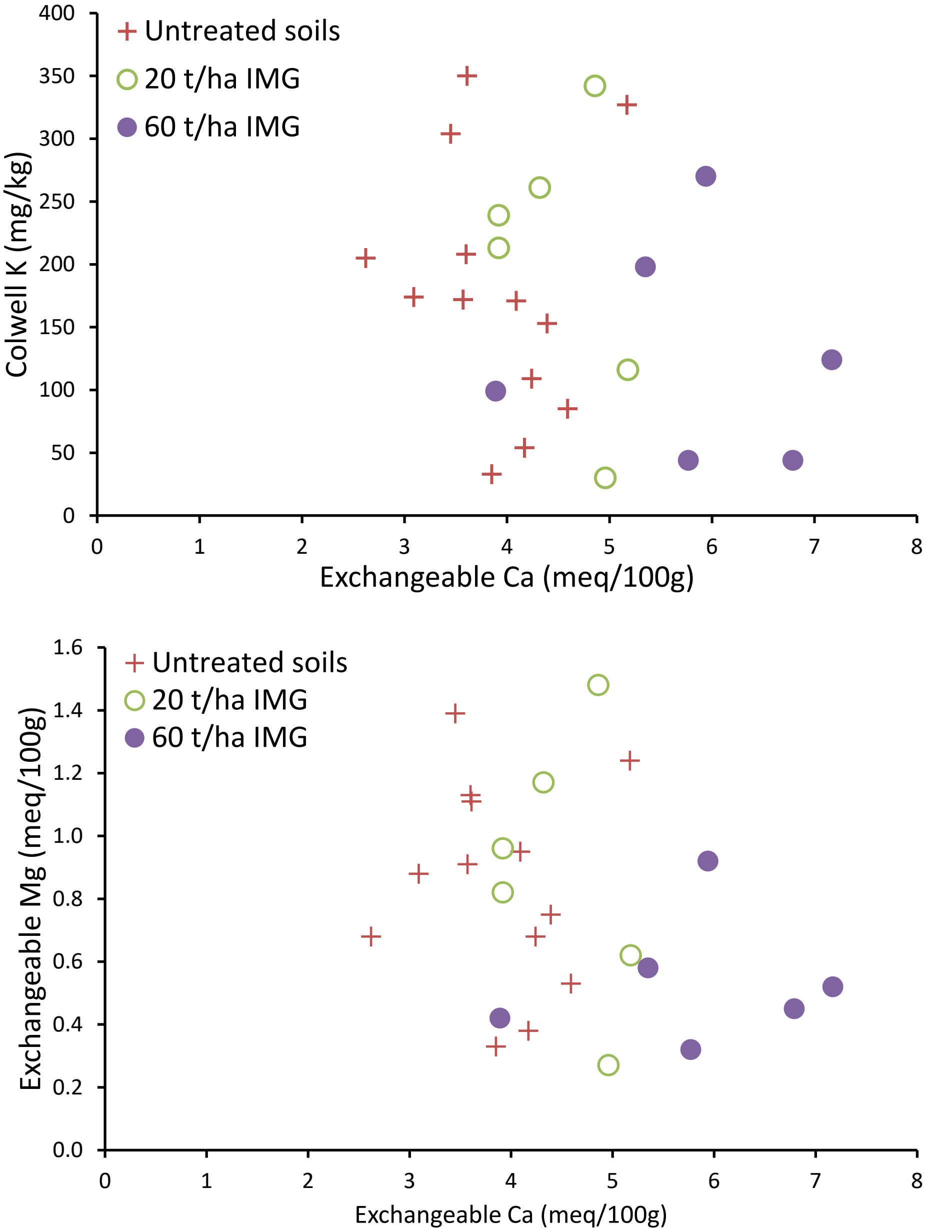


Figure 4: Colwell K and exchangeable Mg in relation to exchangeable Ca one year after IMG treatments in the mixing experiment

3.2 Plant uptake of nutrient trace elements – whole plots

Analysis of whole pasture plants in the mixing experiment found IMG did not affect the uptake of most nutrients and trace elements. In the first year, all major nutritional elements (N, P, K, S, Ca and Mg) and essential trace elements (Mn, Cu, Zn, Mo and Co) were within ranges adequate for the nutrition of the plants sampled and always below potentially toxic levels (Table A22, Table A23 in Appendix F). The patterns in the second year were similar, except that more subtle patterns of variation emerged between the wet depressions and dry rises (Table A24 in Appendix F). Over both years there no observable differences in plant growth between the untreated and IMG-treated soils, although specific biomass measurements were not carried out.

Slight effects of IMG treatment on Mn and S were only found in the first year, extending to P and K in the second year. Mn and S of both ryegrass and clover increased slightly in the 60 t/ha IMG treatment in the first year (Table A22, Table A23 in Appendix F), with Mn remaining elevated in the following year for the ryegrass that was sampled (Table A24 in Appendix F). P and K concentrations were marginally lower in 60 t/ha IMG treatment only in the second year for ryegrass, but for K this was limited to plants growing in the wet soil zone (Table A24 in Appendix E).

The uptake of most trace elements in the untreated and IMG-treated soils over two years was similar, with the exception of Co. This metal was slightly elevated in both the 20 t/ha and 60 t/ha IMG treatments of both pasture species, but only in the first year. Other elements such Cd, Se, U and Th were near or less than 0.02 mg/kg (the reporting limit) whereas Ni was below 1.6 mg/kg and Cr was below 1 mg/kg.

3.3 Winter runoff assays

3.3.1 Properties of soils in the runoff quadrants

The soil-P properties of the runoff quadrants broadly indicated conditions during the period when winter runoff was most likely. Properties such as Colwell P, PRI and PBI were generally comparable with the respective soil-zone properties of each experiment the following summer period. However, $CaCl_2$-P in the quadrants typically varied up to double the range measured in summer.

Untreated soils of both experiments had low P adsorption and were typically over-saturated with P in the surface-soil layer. PBI was slightly greater and PRI more negative in the surface soil compared with the whole topsoil, with no effect of tillage in the mixing experiment (Table 4; Table 6). The variation in surface and whole-topsoil P-adsorption properties between years was due to significant spatial variation across the plots.

Colwell P and $CaCl_2$-P were also more concentrated in the surface than the whole topsoil of the untreated soils, with a slight reduction where tilled. Colwell P and $CaCl_2$-P in the surface 2 cm was, on average, more than two times greater than that of the whole topsoil (Table 5; Table 6). Tillage slightly reduced $CaCl_2$-P in the surface of the untreated soils in the first winter, but this did not persist into the second winter and there was no effect on Colwell P (Table 5). The P_{95} fertility index (based on the Colwell P and PBI) of the untreated soils in the winter runoff sites across both experiments averaged 0.8 to 1.1, but varied locally from 0.5 to 3.0.

Table 4: Summary soil P-adsorption properties of runoff quadrants in the mixing experiment

Treatment	PBI				PRI			
	0–2 cm		0–10 cm		0–2 cm		0–10 cm	
	1st winter	2nd winter	1st winter	2nd winter	1st winter	2nd winter	1st winter	2nd winter
No IMG (untilled)	13 a[1]	12 a	16 a	5 a	-1.6 a	-2.2 a	2 a	-1.1 a
No IMG (tilled)	11 a	9 a	11 a	6 a	-0.8 a	-1.9 a	2 a	-0.9 a
20 t/ha IMG (untilled)	55 c	58 c	16 a	14 b	18 b	7.4 b	2 a	0.8 b
60 t/ha IMG (tilled)	40 c	37 b	39 b	27 c	14 b	7.8 b	17 b	6.7 c

[1] Within each winter, average values (of two replicate quadrants in three replicate plots) followed by the same letters are not statistically different (P>0.05).

Table 5: Summary soil-P availability of runoff quadrants in the mixing experiment

Treatment	$CaCl_2$-P (mg/kg)				Colwell P (mg/kg)			
	0–2 cm		0–10 cm		0–2 cm		0–10 cm	
	1st winter	2nd winter	1st winter	2nd winter	1st winter	2nd winter	1st winter	2nd winter
No IMG (untilled)	18 a[1]	22 a	8 a	9 a	48 ab	49 a	23 a	17 a
No IMG (tilled)	12 b	16 a	9 a	7 a	40 ab	32 a	21 a	17 a
20 t/ha IMG (untilled)	0.7 c	2.6 c	2 b	4 b	63 b	79 b	20 a	20 a
60 t/ha IMG (tilled)	0.1 c	0.6 c	0.1 b	0.3 c	24 c	34 a	24 a	19 a

[1] Within each winter, average values (of two replicate quadrants in three replicate plots) followed by the same letters are not statistically different (P>0.05).

Increases in PBI and PRI with top-dressed IMG treatment were clearest and concentrated in the surface 2 cm of soils and diminished with lower rates of applied IMG. The increase in surface-soil PBI when treated with 20 t/ha IMG in both experiments ranged from 41 to 46, but for the whole topsoil was much smaller (Table 4; Table 6). PRI followed a similar pattern – with the increase in surface PRI initially ranging from 9 to 16. There were smaller increases in PBI and PRI in the surface soils with IMG top-dressed at 5 and 10 t/ha (Table 6).

Where IMG was mixed at 60 t/ha the increases in PBI were similar in both the surface and whole topsoil (15 to 28) of both winters (Table 4). Similarly, both surface and whole topsoil PRI increased between 8 and 15 where IMG was mixed at 60 t/ha (Table 4). The increases in surface PBI were more than two times less where IMG was top-dressed at 20 t/ha.

The IMG treatments greatly reduced $CaCl_2$-P with generally no effects on Colwell P. $CaCl_2$-P was reduced by more than 96% in the surface soil of all the treatments, except where IMG was top-dressed at less than 20 t/ha (Table 5; Table 6) – the effect largely being sustained into the second winter (Table 5). There were similar reductions in $CaCl_2$-P of the whole topsoil where IMG was mixed at 60 t/ha but these were diminished in the top-dressed IMG treatments (Table 5; Table 6). In contrast, Colwell P in the whole topsoil was no different from the untreated soils for any of the applied rates of IMG in both experiments, although it was slightly increased in the surface soils where 20 t/ha was top-dressed in the mixing experiment.

Most properties of the whole topsoils were generally weakly correlated with that of the surface soils. Concentrations of $CaCl_2$-P in the whole and surface soils generally had the greatest correlation ($r = 0.76$; $P<0.01$), which was slightly weaker when the IMG-treated soils were excluded. These concentrations were also correlated with the PERI environmental risk index ($r>0.67$; $P<0.01$), which is derived from whole topsoil measurements of Colwell P and PBI. Colwell P in the surface and whole topsoil were strongly correlated ($r = 0.71$; $P <0.01$), but surface and whole topsoil PBI and PRI were typically weakly or not correlated ($r < 0.5$).

Table 6: Summary soil-P properties of runoff quadrants in seasonally waterlogged soil zones (1 and 3) of the top-dress experiment

Treatment	$CaCl_2$-P (mg/kg)		Colwell P (mg/kg)		PBI		PRI	
	0–2 cm	0–10 cm	0–2 cm	0–10 cm	0–2 cm	0–10 cm	0–2 cm	0–10 cm
Untreated	23 a[1]	9.2 a	63 a	22 a	18 a	10 a	-2.3 a	-0.6 a
5 t/ha IMG	7.0 b	5.0 ab	82 a	29 a	39 ab	15 a	1.7 ab	0.8 a
10 t/ha IMG	4.2 b	3.7 b	82 a	36 a	42 b	21 a	5.2 b	1.7 ab
20 t/ha IMG	1.4 b	2.5 b	71 a	22 a	59 b	17 a	14 c	2.2 b

[1] Average values (of two replicate quadrants in each of two replicate plots) followed by the same letters are not statistically different (P>0.05).

3.3.2 P and N in simulated runoff

P in runoff was dominated by soluble P in both experiments. In the first winter soluble P was reduced by up to 78% in the mixing experiment (for both IMG treatment rates), while average TP concentration in the runoff from untreated soils reduced from 0.36 mg/L to 0.09 mg/L due to reduction in soluble P (Figure 5). Significant variation in TP occurred across the untreated soils (coefficient of variation of 76%), mostly because

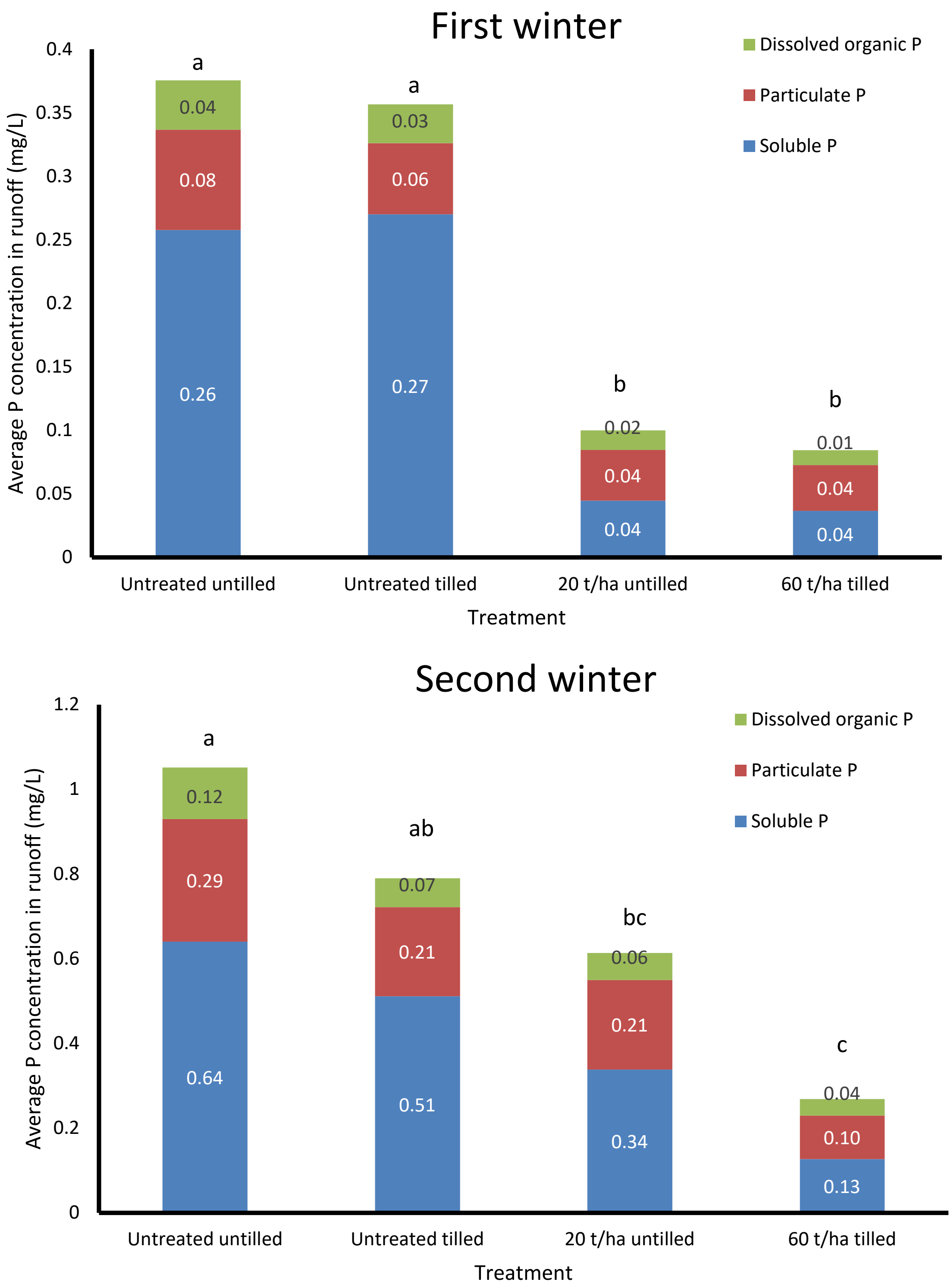


Figure 5: Average forms of P in runoff from small quadrant assays on the mixing experiment site (letters above bars followed by the same value indicate total values that are not statistically different with P>0.05)

of variation in soluble P (coefficient of variation of 92%) which comprised >65% of total P. Proportional reduction of P in runoff in the second winter remained similar (71%) where IMG was mixed at 60 t/ha, but was less than 50% where IMG was top-dressed at 20 t/ha (Figure 5). There were slight but significant (P<0.05) reductions in organic P in runoff in the IMG treatments in both years, with this comprising less than 10% of TP in runoff. In contrast, no effects of the IMG treatments on particulate P concentrations were found (Figure 5).

The effect of IMG on soluble P in runoff was less significant in the top-dress experiment. Although IMG treatment slightly reduced soluble and total P concentrations in runoff, this was not statistically significant (P>0.3; Figure 6) due to large variation in the untreated and 5 t/ha treated soils. However, soluble P was <0.06 mg/L (and TP <0.1 mg/L) on individual quadrants with 10 t/ha and 20 t/ha. The response of runoff P concentrations to IMG application is clearer when considering soil properties (see Section 3.3.4 below).

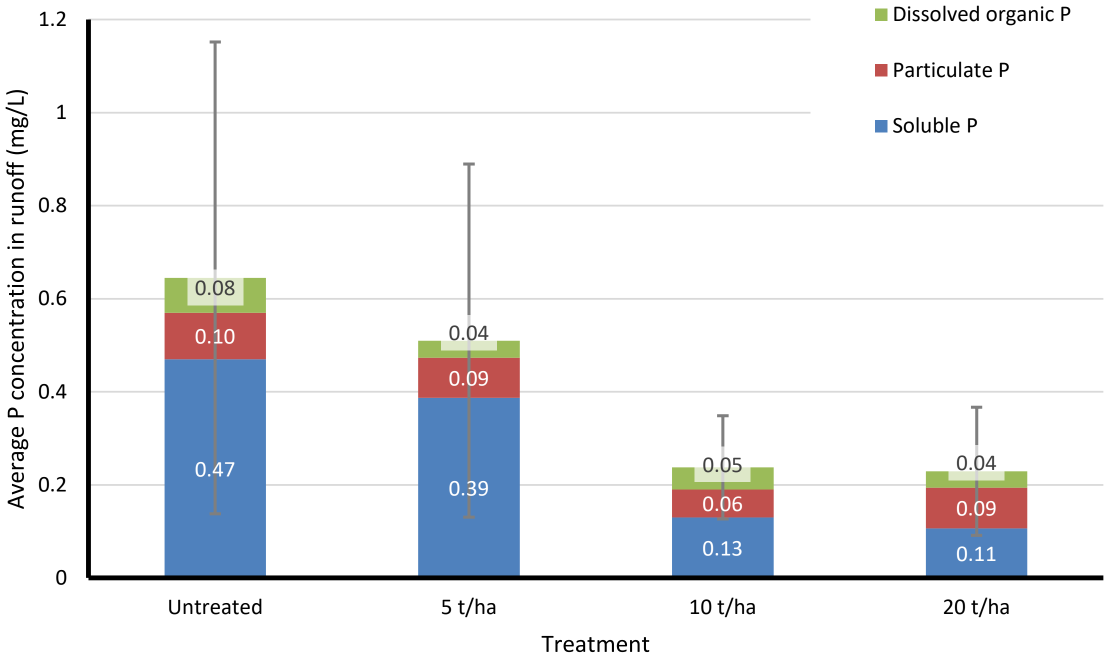


Figure 6: Average forms of P in runoff from small quadrant assays on the top-dress experiment site (bars represent standard deviation of total P that were not different; P>0.3)

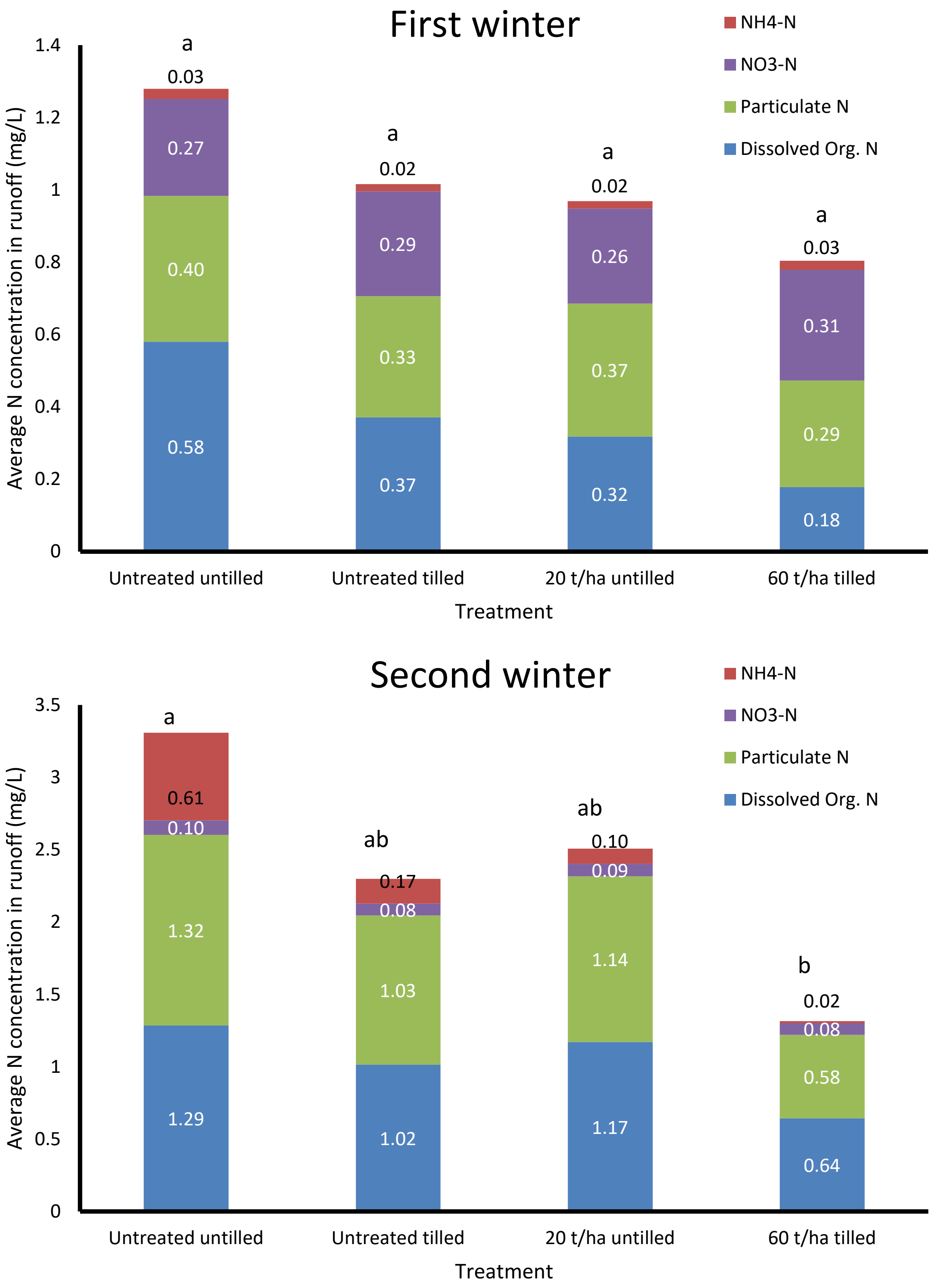


Figure 7: Average forms of N in runoff from small quadrant assays on the mixing experiment site (letters above bars followed by the same value indicate total values that are not statistically different with P>0.05)

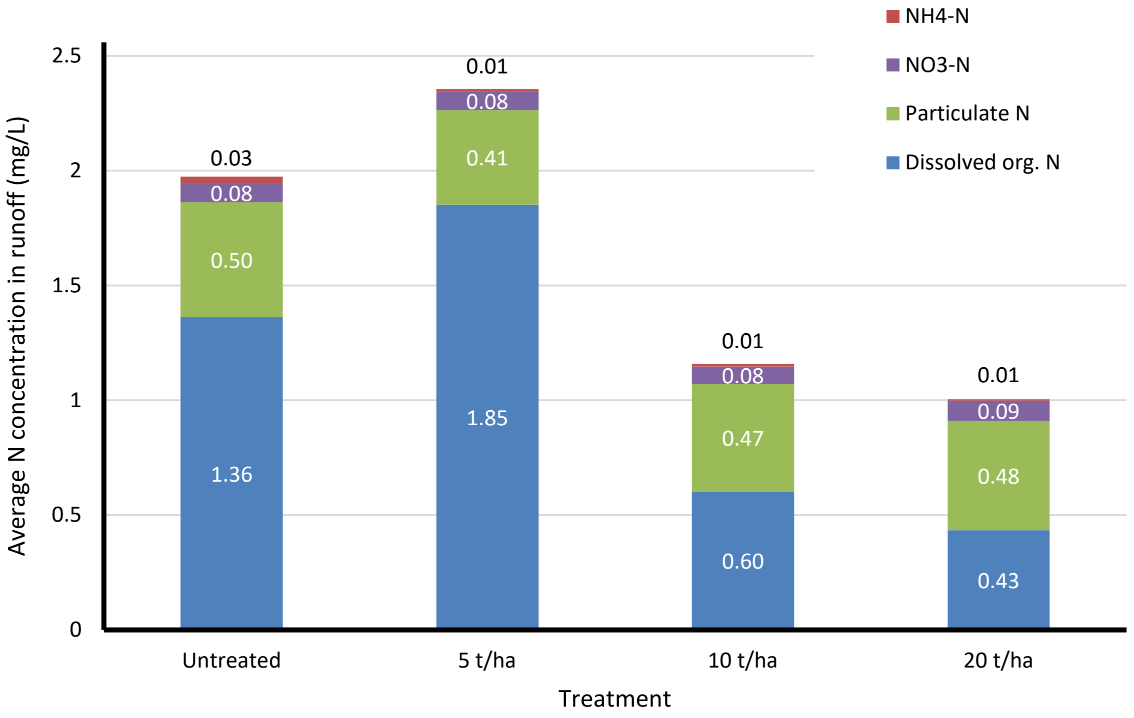


Figure 8: Average forms of N in runoff from small quadrant assays on the top-dress experiment site (note: total concentrations were not significantly different at P>0.4)

TP and TN concentrations generally decreased with increased duration of runoff – the effect being greater in untreated soils. TP decreased during each 30-minute runoff duration by an average of 0.33 to 0.44 mg/L in untreated soils and 0.03 to 0.1 mg/L in IMG-treated soils (Table 7). Similar patterns were found for TN decreases during runoff (Table 7). The greater decrease from the untreated soils corresponded with higher concentrations of soluble nutrients in the bulk runoff (i.e. soluble P, nitrate and dissolved organic N; Figure 5). This also indicated that the relative effects of IMG on soluble P is greatest on initial runoff than later in intense rain events.

3.3.3 Other effects on runoff quality

IMG treatment of soils had a slight influence on some other aspects of runoff water quality, but this did not differ between the treatment rates. The most notable was the effect on SO_4 concentrations. In the first winter of both experiments, average SO_4 concentrations in runoff from IMG-treated soils ranged from 60 to 137 mg/L, with no significant effects of application rates (Table 8; Table 9). In comparison, concentrations of SO_4 in untreated soils were less than 5 mg/L. Concentrations were still elevated in the second winter of the mixing experiment but were up to 70% less than in the first winter.

Table 7: Change in TN and TP concentrations with runoff duration (first winter) for each experiment

Experiment	Treatment	Average decrease in concentration (mg/L) from 0–10 mins to 20–30 mins	
		TP	TN
Mixing	No IMG (untilled)	0.27	1.75
	No IMG (tilled)	0.39	1.13
	20 t/ha IMG (untilled)	0.03	0.30
	60 t/ha IMG (tilled)	0.03	0.45
Top-dress	Untreated	0.41	1.45
	5 t/ha IMG	0.08	1.40
	10 t/ha IMG	0.10	0.68
	20 t/ha IMG	0.10	0.78

Ca and to a lesser extent Mg concentrations were raised in runoff from the IMG-treated soils. This resulted in hardness levels averaging 80 to 136 mg $CaCO_3$/L in the first winter of both experiments (Table 8; Table 9), thus making them moderately hard to hard waters. Hardness diminished up to 45% by the second winter of the mixing experiment, but remained more than double that in runoff from the untreated soils. As with SO_4, there were no statistical differences in runoff hardness between the IMG treatments. The increased Ca concentrations in the runoff from treated sites also did not significantly affect runoff pH, with this ranging from 6.8 to 7.8.

Soluble and total Mn concentrations were also raised in runoff from the IMG-treated soils, but with no effect of increasing rates of applied IMG (Table 8; Table 9). Average total Mn concentrations in runoff from the treated soils in the first winter of both experiments were less than 0.53 mg/L but ranged from 0.1 to 0.87 mg/L across the plots. On average, less than 25% of the total Mn was in the soluble form likely to pose greatest offsite risks (Table 8; Table 9). Concentrations generally decreased by more than half in the second winter of the mixing experiment, with a greater proportion of the Mn in soluble form. As a consequence, total Mn in runoff in the first winter, but not the second, was weakly correlated with other measures of particulate transport (e.g. particulate N: r=0.51, P=0.1; particulate P: r=0.76, P=0.04). Similarly, for runoff from the top-dress experiment, total Mn was weakly correlated with other measures of particulate transport such as particulate P (r=0.56, P=0.02), but not with particulate N (r=0.32, P>0.1).

Table 8: Concentrations and forms of selected metals and anions in runoff from small quadrants in the mixing experiment site over two consecutive winters

Treatment	Total Mn		Soluble Mn		Total Fe		Sulfate		Hardness	
	mg/L								mg $CaCO_3$/L	
Winter	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
No IMG (untilled)	0.01a[1]	0.02a	0.004a	0.010a	0.05a	0.06a	5.7a	<5a	23a	19a
No IMG (tilled)	0.01a	0.02a	0.004a	0.009a	0.07a	0.06a	<5a	<5a	18a	18a
20 t/ha IMG (untilled)	0.33b	0.10b	0.041ab	0.048b	1.08b	0.31b	60b	17b	82b	45b
60 t/ha IMG (tilled)	0.24b	0.11b	0.058b	0.031ab	0.60ab	0.29b	108b	68b	136b	89b

[1] For each winter, average values (of two replicate quadrants in three replicate plots) followed by the same letters are not statistically different (P>0.05).

Total Fe was also slightly raised in runoff from the IMG-treated soils, but the increase did not correlate with the rate of applied IMG (Table 8; Table 9). Total Fe concentrations also tended to decrease by more than half in the second winter of the mixing experiment. Increased total Fe concentrations were highly correlated with total Mn in runoff from both experiments (r=0.71, P<0.01). However, total Fe was not correlated with particulate P at both sites and for either winter at the mixing experiment site (r<0.3, P>0.25), even within the IMG treatments (r<0.42, P>0.17). There was a similar general lack of correlation with particulate N, except for a weak relationship in runoff from the top-dress experiment (r=0.48, P=0.1).

Table 9: Concentrations and forms of selected metals and anions in runoff from small quadrants with different rates of top-dressed IMG

Treatment	Total Mn	Soluble Mn	Total Fe	Sulfate	Hardness
	mg/L				mg $CaCO_3$/L
Untreated	0.02[1] a	0.009 a	0.13 a	<5 a	17 a
5 t/ha IMG	0.35 ab	0.25 a	0.71 ab	137 b	98 b
10 t/ha IMG	0.15 ab	0.02 a	0.64 ab	71 b	87 b
20 t/ha IMG	0.53 b	0.03 a	2.44 ab	96 b	111 b

[1] Average values (of two replicate quadrants in each of two replicate plots) followed by the same letters are not statistically different (P>0.05).

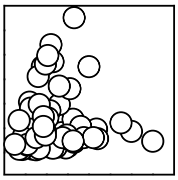
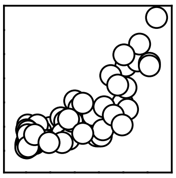
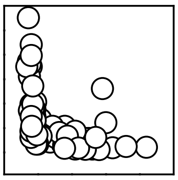
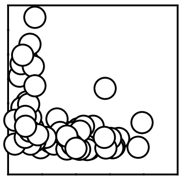
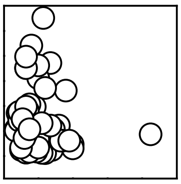
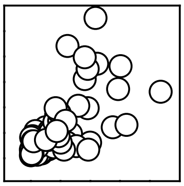
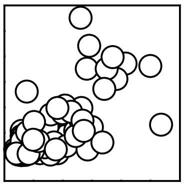
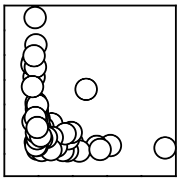
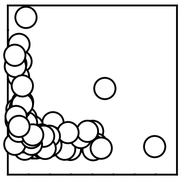
3.3.4 Influence of soil properties on P transport in runoff

Analysis of the combined measurements for both experiments showed that soil $CaCl_2$-extractable P best predicted soluble P concentrations in runoff for all untreated and IMG-treated soils. Runoff P concentrations were better correlated with $CaCl_2$-P in the surface 2 cm of soil than with $CaCl_2$-P in the whole topsoil (Table 10; Figure 9). By contrast, there was no correlation between soluble P in runoff and Colwell P in either the surface or whole topsoil (Table 10). The relationship between soluble P in runoff and surface soil $CaCl_2$-P (Figure 9) was better explained by a non-linear function (r^2=0.78) than a linear relationship (r^2=0.69).

The effects of IMG treatment were broadly evident as sites with reduced soil $CaCl_2$-P, but varied for different rates of top-dressed IMG. For example, some quadrants in the 10 and 20 t/ha treatments of the top-dress experiment had higher concentrations of P in runoff and $CaCl_2$-P in soils than quadrants with the 5 t/ha treatment (Figure 9).

P concentrations in runoff and most P-adsorption properties of the soils were generally poorly correlated. PBI and PRI was weakly correlated with runoff concentrations in the low organic loading sites, but not the high organic loading sites, and PRI was not correlated in either situation (Table 10). By contrast, PERI – a potential indicator of soil-P runoff risk – was reasonably well correlated with runoff concentrations measured across both experiments (Figure 10). This association reflected correlations between PERI and $CaCl_2$-P in soils (see Section 3.3.1).

Table 10: Linear Pearson correlation coefficients (r) between soluble P concentrations in runoff from small quadrants and various indicators of soil P chemistry in surface soil (SS; 0–2 cm) or whole topsoil (WS; 0–10 cm)

	Colwell P	$CaCl_2$-P	PERI (0–10 cm)	PRI	PBI
SS	0.05 	0.83** 		-0.52** 	-0.50** 
WS	-0.04 	0.65** 	0.63** 	-0.33* 	-0.39* 

** denotes significant at P<0.01; * denotes significant at P<0.05

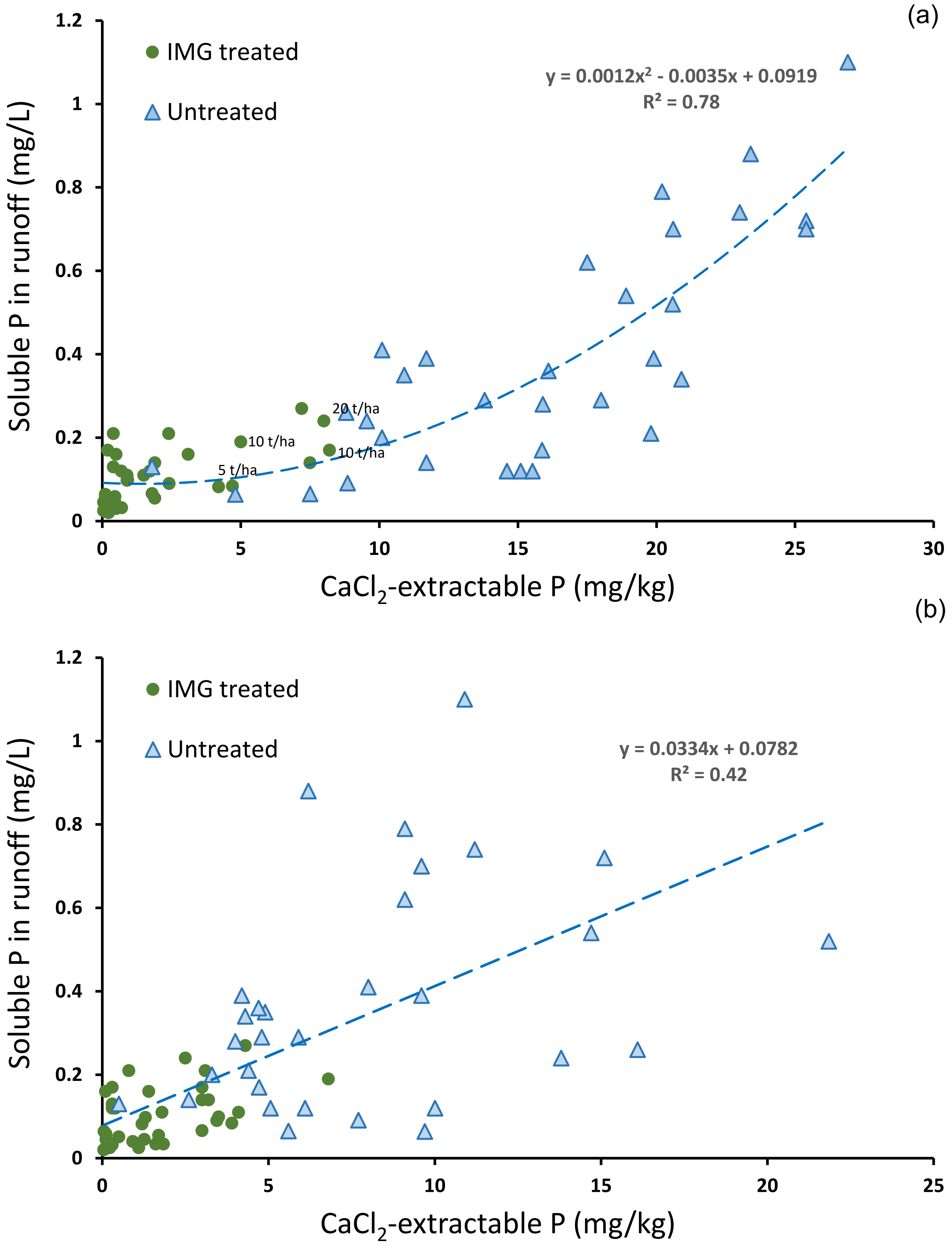


Figure 9: Soluble P in runoff from small quadrants relative to soluble P (as $CaCl_2$-extractable P) in the (a) surface and (b) whole topsoil combining both IMG experiment sites

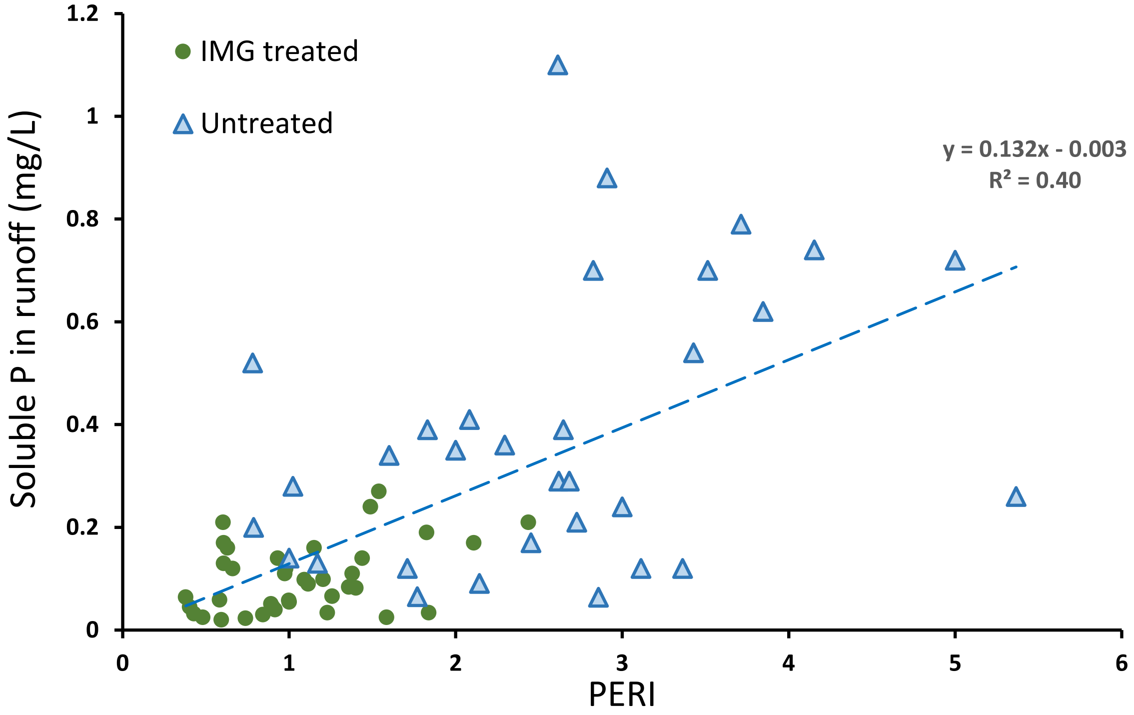


Figure 10: Soluble P in runoff from small quadrants relative to phosphorus environmental risk index (PERI) of whole topsoils combining results for two IMG experiment sites over two years

3.4 Winter-spring leaching in the top-dress experiment

3.4.1 Soil properties – lysimeters

Only the properties of the surface-soil layers at the lysimeters were different between the treatments, with these generally being similar in the subsurface soils and whole topsoils. Analysis of the properties by depth showed that:

- The PBI increased with the rate of IMG applied and was up to twice as high in the surface soils where 20 t/ha was applied compared with the untreated sites. In contrast, the PBI of the subsurface soils was similar between the treated and untreated soils (Table 11). There were similar patterns with PRI (Table 11).
- $CaCl_2$-P was initially up to 4.5 times greater in the surface of the untreated soils than the subsurface soils (Table 11). Increased rates of applied IMG incrementally reduced surface $CaCl_2$-P from an average of 13 mg/kg in the untreated soils to 4.8 to 6.5 mg/kg in the 5 and 10 t/ha treatments and 2.0 mg/kg in the 20 t/ha application. However, the treatments had no effect on $CaCl_2$-P in the subsurface soils.
- Colwell P was almost twice as high in the surface compared with subsurface soils (averages of 35.5 mg/kg versus 18.6 mg/kg) and unaffected by IMG (Table 11).

- pH, organic C and metals such as Cd were also typically greater in the surface than the subsurface-soil layers, but not different between the IMG treatments. Surface soil pH averaged 5.6 and was almost a unit greater than the subsurface, with no effect of the IMG. Organic C was 1.7 times greater in the surface (average 3.7%) compared with the subsurface soils (average 2.2%). Cd was similarly more concentrated in the surface – with an average of 0.08 mg/kg in the surface 2 cm compared with less than 0.05 mg/kg in the subsurface soils.

Table 11: Average soil-P properties by depth at lysimeters (before and after winter) with different rates of top-dressed IMG

Treatment	$CaCl_2$-P (mg/kg)		Colwell P (mg/kg)		PBI		PRI	
	0–2 cm	2–10 cm	0–2 cm	2–10 cm	0–2 cm	2–10 cm	0–2 cm	2–10 cm
Untreated	13.3 a	2.8 c	36 a	13 b	13 a	12 a	-1 a	0.7 a
5 t/ha IMG	6.5 b	3.5 c	36 a	12 b	18 ab	10 a	0 a	0.2 a
10 t/ha IMG	4.8 b	3.8 bc	49 a	22 b	26 b	18 a	1.4 a	1.1 a
20 t/ha IMG	2.0 d	2.8 dc	48 a	18 b	41 c	13 a	9 b	0.7 a
Significance of factors								
Depth	P < 0.001		P = 0.02		P < 0.001		P = 0.04	
treatment	P < 0.001		P > 0.2		P < 0.001		P = 0.003	

[1] For each property, average values (of two replicate sites) followed by the same letters are not statistically different (P>0.05).

Contrasting with the surface, the soil-P properties of the whole topsoils at the lysimeters were generally similar between the treatments. The exception was PBI, which was slightly greater in soils top-dressed with 20 t/ha of IMG (Table 12). The properties of the soils at the lysimeters were similar to those in the broader soil zone of each plot (see Section 3.1). Given the Colwell P and PBI measurements, the lysimeters had an average P_{95} fertility index of 0.8 (ranging from 0.5 to 1.5) that was similar between the treatments (P>0.1).

Table 12: Average soil-P properties of whole topsoils at lysimeters before winter (pre) and in the following summer with different rates of top-dressed IMG

Treatment	$CaCl_2$-P (mg/kg)		Colwell P (mg/kg)		PBI		PRI	
	Pre	Summer	Pre	Summer	Pre	Summer	Pre	Summer
Untreated	4.4 a	3.4 b	13	18	8 a	16 c	0.04	1.0
5 t/ha IMG	4.8 a	2.8 b	16	12	7 a	20 c	0	0.4
10 t/ha IMG	5.5 a	2.3 b	24	31	9 a	24 c	0.2	1.0
20 t/ha IMG	2.8 a	2.6 b	23	20	15 b	34 d	2.0	2.0
Significance of factors								
Time	P = 0.04		P > 0.05		P < 0.001		P > 0.05	
treatment	P > 0.05		P > 0.05		P = 0.003		P > 0.05	

[1] For each property, average values (of two replicate sites) followed by the same letters are not statistically different (P>0.05).

3.4.2 Leached nutrient concentrations

Concentrations of leached nutrients captured by the lysimeters were different between the untreated and IMG-treated soils, but not statistically different between the rates of applied IMG.

More than 80% of leached P from the untreated soils was soluble P, which is considered to be mostly phosphate-P (Table 13). The remaining was mostly organic P (average of 9% of TP) with particulate P (being mostly colloidal) comprising generally less than 5% of TP.

Average soluble-P concentrations tended to decrease with the rate of IMG application, although the effect was not statistically significant in the first winter ($P>0.1$; Table 13). In untreated soils and those with the lowest rate of top-dressed IMG (5 t/ha), average soluble-P concentrations in leachates were greater than 1.7 mg/L compared with less than 0.4 mg/L where IMG had been top-dressed at 20 t/ha. This represented a reduction in leachate concentrations approaching 90%.

Table 13: Annual average concentrations of P fractions and DOC in leachates from soils with different rates of top-dressed IMG

Treatment	Soluble P (FRP)	Organic P[2]	Fine particulate (colloidal P)[1]	Dissolved organic C
Untreated	3.07 a[3]	0.22 a	0.32 a	123 a
5 t/ha	1.77 a	0.10 a	0.07 a	74 ab
10 t/ha	1.57 a	0.11 a	0.09 a	59 ab
20 t/ha	0.31 b	0.10 a	0.01 a	37 b

[1] Fine particulate P calculated as TP – FRP – Organic P

[2] Organic P calculated as total filterable P – FRP

[3] Where tested, values followed by the same letter in each year are not statistically different between treatments ($P<0.05$)

Soluble-P concentrations tended to decrease during the winter–spring period. The greatest decline in concentrations was evident in the untreated soils, whereby a flush of soluble P of up to 8 mg/L in early winter decreased to less than 1.4 mg/L by early spring (Figure 11). Leached concentrations of soluble P where IMG was top-dressed at 5 and 10 t/ha followed a similar pattern, whereas where IMG was top-dressed at 20 t/ha, concentrations were consistently less than 0.4 mg/L (Figure 11). There were no differences in the concentrations of other fractions of leached P between the treatments and no consistent pattern of variation in concentrations during the winter–spring period.

Concentrations of N in leachate varied widely between the lysimeters irrespective of treatment, with minor effects of the IMG treatments. Annual average TN concentrations ranged from 8.4 to 41 mg/L (Table 14) and was dominated by oxidised N (mostly nitrate), making up more than 55% of the N leached on most occasions (Table 14). TN concentrations typically decreased during winter–spring, reflecting the leaching of high concentrations of nitrate in early winter (Figure A21 in

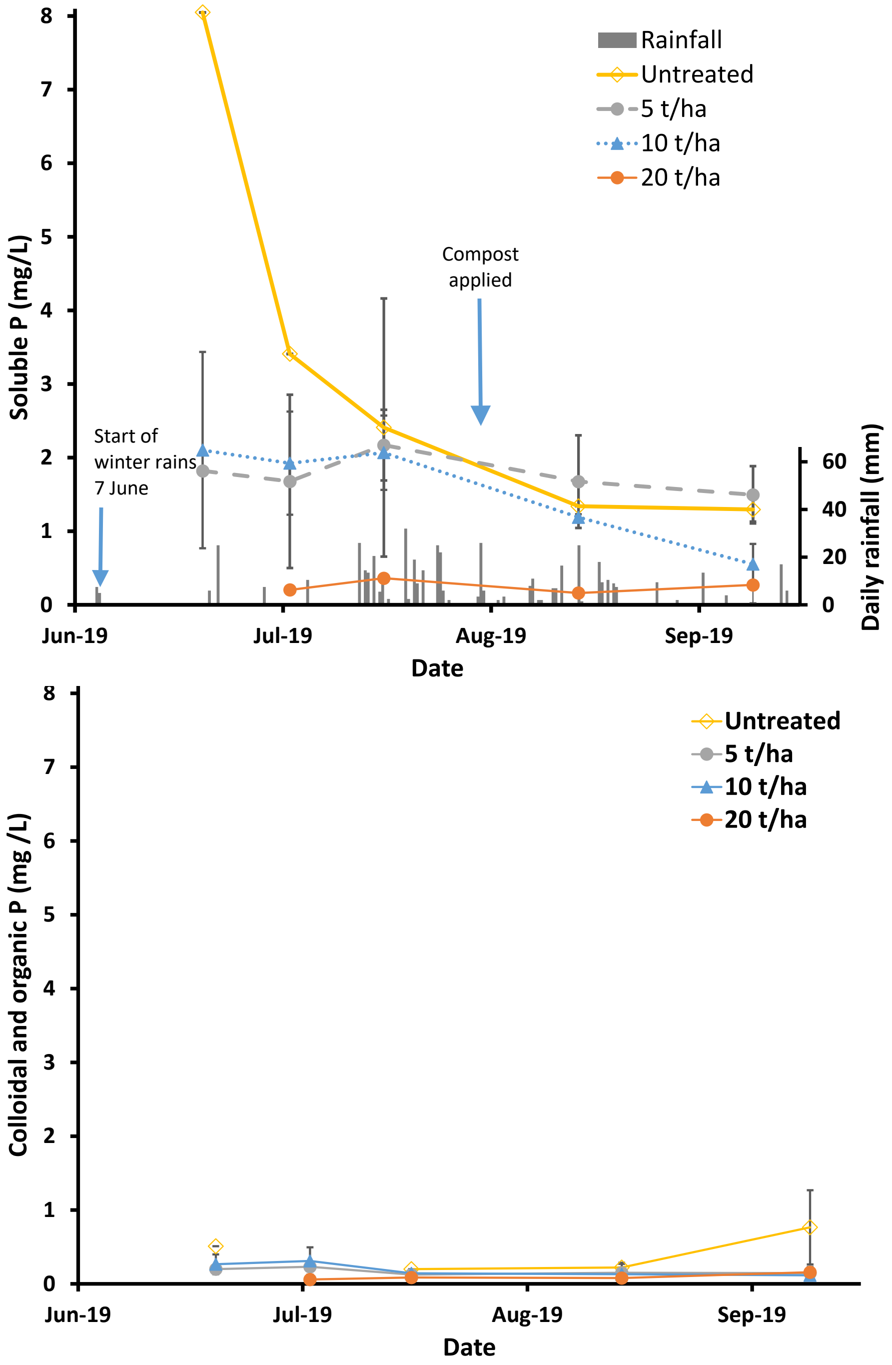


Figure 11: P in leachates from soils with different rates of top-dressed IMG in the first year after application (means with error bars representing standard deviation)

Appendix G). By contrast, concentrations of other N fractions in the treatments remained generally similar over time except for an increase in DON from late winter onwards (Figure A21 in Appendix G).

Top-dressing with IMG had effects only on DON concentrations in leachates. DON concentrations from the IMG-treated soils were reduced by up to half where IMG was top-dressed at 20 t/ha (Table 14), with minor but not significant effects at the lower top-dressing rates. These patterns and effects were also reflected in DOC concentrations.

Table 14: Annual average concentrations of N fractions in leachates from soils with different rates of top-dressed IMG

Treatment	Total N (TN)	Nitrate and nitrite (NO_x)	Ammonia (NH_4-N)	Dissolved organic N (DON)
Untreated	16.97 a[1]	7.34 a	0.57 a	9.12 a
5 t/ha	41.03 a	27.17 a	6.32 a	6.31 ab
10 t/ha	19.26 a	10.23 a	2.33 a	6.08 ab
20 t/ha	8.37 a	4.11 a	0.26 a	3.74 b

[1] Where tested, values followed by the same letter in each year are not statistically different between treatments ($P<0.05$).

3.4.3 Other leached element concentrations

Leachate concentrations of IMG constituents such as SO_4, Ca and Mn were consistently higher from the IMG-treated soils in the first winter–spring season. By contrast, other trace metals were generally similar or greater in the untreated soils. Leachate pH ranged from 3.9 to 6.6 during the year (Figure 12), with no consistent differences between the untreated and treated soils ($P>0.3$; see Table A25 in Appendix H). Salinity, indicated by Cl concentrations, varied widely between the lysimeters but with no consistent pattern across the treatments (data not shown).

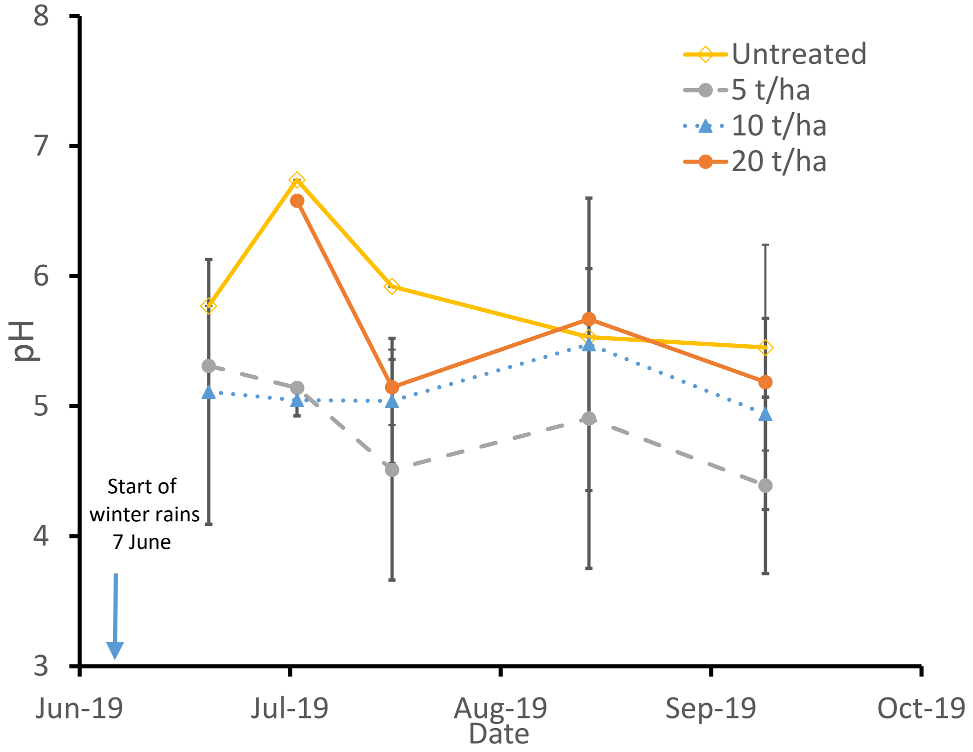


Figure 12: pH of leachates from soils with different rates of top-dressed IMG in the first year after application (means with error bars representing standard deviation)

Leachate concentrations of SO_4 and Ca increased proportional to the rate of IMG applied. The annual average leachate concentrations of SO_4 were almost twice as high where IMG was top-dressed at 20 t/ha compared with 5 t/ha (Table 15). Ca concentrations showed a similar pattern and typically exceeded 101 mg/L throughout the year. Concentrations of other cations such as Mg also increased by more than seven-fold in all the IMG-treated soils ($P<0.03$), but K remained similar compared with leachates from the untreated soils (Table A25 in Appendix H).

Concentrations of SO_4 and Ca were generally greatest in the first leachates collected in early winter. Thereafter they steadily decreased to almost half the initial values where IMG was top-dressed at 5 and 10 t/ha. However, concentrations remained similar throughout the leaching period where IMG was top-dressed at 20 t/ha (Figure 13).

Mn concentrations increased more than 20-fold in the leachates from IMG-treated soils but did not vary with increasing application rates. More than 95% of leached Mn was in soluble form, along with a small component of particulate Mn (most likely from washing of soil particles into the lysimeters). Average concentrations decreased slightly during the winter (Figure 13) to 1.35 to 1.44 mg/L (Table 15), with no difference between rates of applied IMG. Average concentrations weighted by leachate volume were slightly greater, reflecting the effect of higher concentrations in early winter (see Table A26 in Appendix H).

Table 15: Summary soluble Mn, SO_4 and hardness concentrations (mean ± standard deviation) in leachates from soils with different rates of top-dressed IMG

Treatment	Total Mn (as mg/L)		SO			Hardness (as mg $CaCO_3$/L)	

Treatment	Total Mn (as mg/L)		SO_4 (as mg/L)		Hardness (as mg $CaCO_3$/L)	
Untreated	0.07	±0.06 a[1]	19	±20 a	93	±38
5 t/ha	1.44	±1.31 b	612	±309 b	720	±389
10 t/ha	1.35	±0.93 b	874	±408 b	978	±479
20 t/ha	1.40	±0.59 b	1337	±120 b	1565	±144

[1] Where tested, values followed by the same letter in each year are not statistically different between treatments ($P<0.05$).

The leaching of Ca and Mg from the IMG-treated soils resulted in average hardness being more than 720 mg $CaCO_3$/L, with this increasing in proportion with the rate of applied IMG (Table 15). Hardness can mitigate the plant and aquatic toxicity of many leached metals. Hardness followed similar annual patterns as calcium – being unchanged where IMG was top-dressed at 20 t/ha but decreasing throughout winter where applied at lighter rates (Figure 13). By the end of winter, concentrations in these had decreased to 364 to 572 $CaCO_3$/L but remained at more than 1,400 mg $CaCO_3$/L where IMG was top-dressed at 20 t/ha. As with calcium, the annual average hardness leaching from the 20 t/ha soil was slightly more than double that of the 5 t/ha rate (Table 15). Average annual concentrations weighted by leachate volumes from each lysimeter were similar to the unweighted average concentrations (see Table A26 in Appendix H).

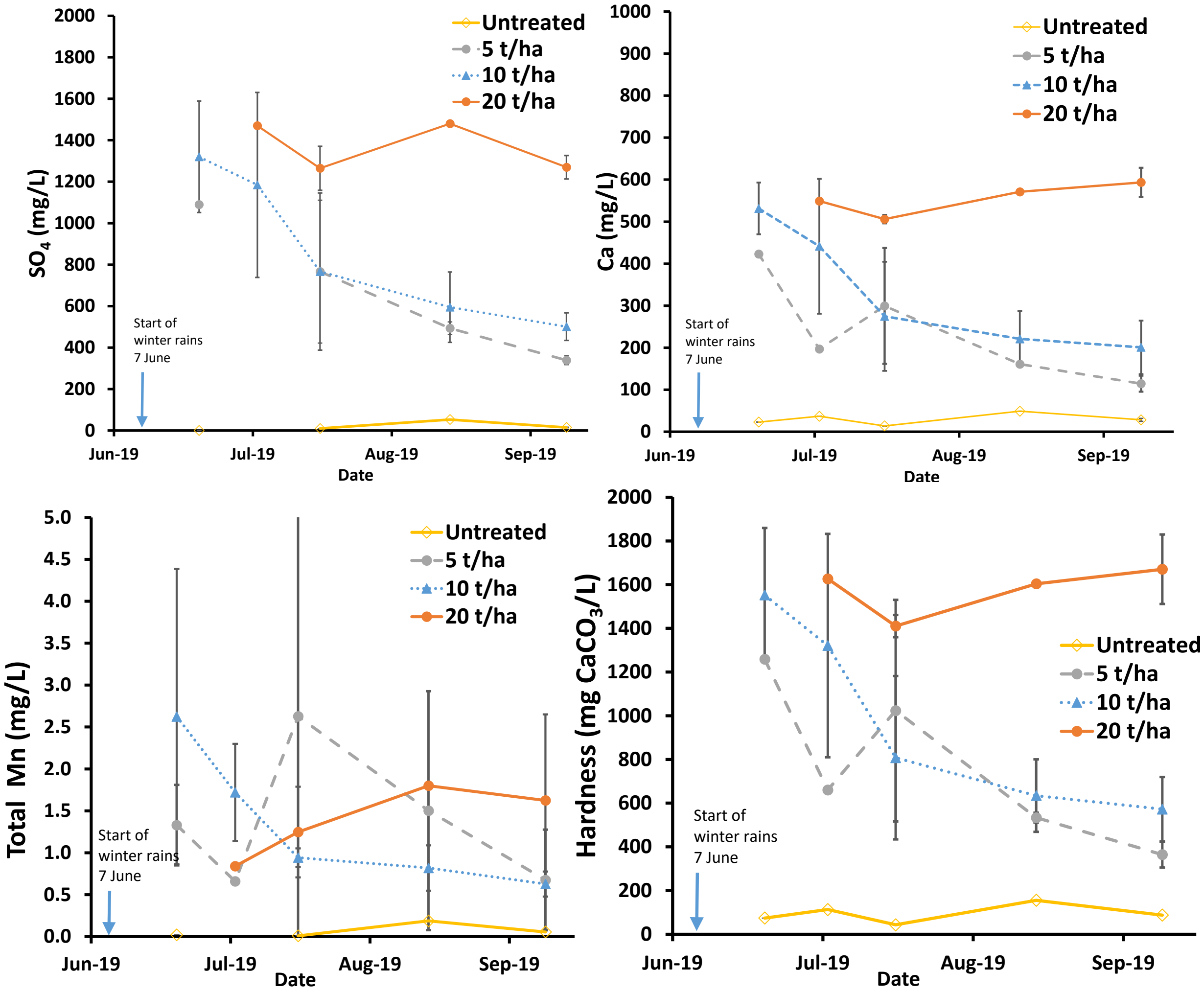


Figure 13: Sulfate, calcium, total manganese and hardness in leachates from soils with different rates of top-dressed IMG in the first year after application (means with error bars representing standard deviation)

Concentrations of all trace elements except Zn, Co and Cd in leachates from IMG-treated soils were similar or slightly less than from untreated soils. Zn concentrations increased in response to increasing IMG application (P<0.01), although not directly in proportion with the application rates – with average concentrations being less than 566 µg/L (Table 16). By contrast, concentrations of Co and Cd leaching from IMG-treated soils increased slightly (Table 16), but these were not statistically significant (P>0.1). Concentrations of Co from individual lysimeters did not exceed 3 µg/L, whereas Cd similarly did not exceed 3.7 µg/L. Average Zn (but not Cd) concentrations leaching from the IMG-treated soils exceeded the 99% water quality trigger values for the highest protection level modified for the hardness of the waters (ANZECC & ARMCANZ 2000).

There were slight reductions in concentrations of metals such as Cr, Cu, Fe and U leaching from the IMG-treated soils (P<0.1) compared with untreated soils (Table 16). Elements such as As, Fe, Pb and Zn leached in similar concentrations from untreated and IMG-treated soils.

Table 16: Annual average total metal concentrations (μg/L) in leachates from soils with different rates of top-dressed IMG

Treatment	As	Bi	Cd	Cr	Co	Cu	Fe	Pb	Ni	Th	U	Zn
Untreated	1.1	<0.05	0.2	2.4	1.4	36	803	1.2	9.7	0.2	0.4	161
5 t/ha	0.8	<0.05	1.3	1.9	3.9	18	292	1.6	10.8	0.2	0.2	336
10 t/ha	1.0	<0.05	0.7	1.6	4.2	16	252	1.0	8.0	0.1	0.2	380
20 t/ha	1.0	<0.05	1.1	1.1	3.7	12	81	0.7	7.1	0.1	0.1c	566

Correlation analysis of leached metal concentrations (Table A27 in Appendix I) showed several other aspects of the leachate chemistry. Leaching of Cr, Cu, Fe (soluble and total), Ni, Th and U was strongly correlated with the leaching of DOC ($r>0.75$, $P<0.01$). In contrast, Zn leaching was strongly-correlated with Ca, SO_4 and Mg ($r>0.67$, $P<0.01$), whereas Cd leaching was strongly correlated with Co, Mg, Mn and Cl (Table A27 in Appendix I), although the relationship with Cl was due to a single outlier. Co was strongly correlated with Mn and Cd, less so with Mg and not with Cl. In contrast, leachate pH was poorly correlated with concentrations of most metals ($-0.4 < r < 0.4$), except for weak negative correlations with Cr and Mn ($r < -0.5$).

3.4.4 Leachate fluxes

Nutrient fluxes estimated from the lysimeters indicated that soluble-P loss from topsoils reduced by 1.4 kg/ha/yr (an 88% reduction) after being top-dressed with 20 t/ha IMG. Less than 0.2 kg/ha/yr of soluble P leached from this treatment (Table 17). By contrast, there was no significant reduction in P leaching from the soils treated with 5 and 10 t/ha IMG (Table 17). A large part of the variation in P leaching (and other nutrients) was caused by variation in the volumes of leachates collected at each lysimeter, which ranged from 46 to 233 mm (being 10 to 51% of rainfall over the winter–spring period). Leaching of other forms of P (colloidal and organic) were not significantly different between the treated and untreated soils and amounted to less than 0.5 kg P/ha/yr.

Table 17: Summary P and N leachate fluxes during the first winter (kg/ha/yr as mean ± standard deviation) from soils top-dressed with IMG

Treatment	Soluble P (FRP)	Colloidal and organic P[1]	Total N	Dissolved organic N
Untreated	1.6 ±1.0 a[2]	0.5 ±0.3 a	13.2 ±1.9 ab	10.4 ±0.2 a
5 t/ha	2.0 ±1.5 a	0.3 ±0.3 a	26.5 ±4.8 a	10.5 ±12 a
10 t/ha	1.4 ±0.3 a	0.2 ±0.01 a	15.8 ±0.4 ab	5.3 ±2.2 a
20 t/ha	0.2 ±0.01 b	0.1 ±0.01 a	6.6 ±5.6 b	3.4 ±1.6 a

[1] Combined fine particulate, colloidal and organic P calculated as TP – FRP.

[2] Where tested, values followed by the same letter in each year are not statistically different between treatments ($P<0.05$).

Leaching of TN at each lysimeter ranged from 2.7 to 30 kg/ha/yr, with the higher rates being dominated by nitrate. There were no significant differences in TN or any organic and inorganic N fractions due to the IMG treatments.

Leaching of gypsum (as Ca + SO_4) and Mn increased with IMG treatment but not in proportion to the application rate. Up to 1.5 tonnes of gypsum/ha (as Ca + SO_4) leached from the 20 t/ha IMG treatment in the first winter, although this was not significantly greater than the leaching from the treatments with lower rates of IMG. (Table 18). The average rate of leaching of gypsum (Ca+SO_4) represented 7% of that applied where IMG was top-dressed at 20 t/ha, but 31% and 20% of that applied in the 5 and 10 t/ha treatments respectively (Table 18). With Mn, the leaching of less than 1.3 kg/ha/yr represented less than 0.5% of the Mn applied in the highest rate of applied IMG (being 380 kg Mn/ha in the 20 t/ha treatment).

Rates of K and Mg leaching were highly variable across the experiment site with slight effects of the IMG treatment. Leaching of Mg increased by up to 36 kg/ha/yr with the IMG treatments in the first winter, but did not go up with increasing rates of applied IMG (Table 18). By contrast, no significant increase in leaching of K occurred (Table 18).

Acidity flux from the soils (indicated by leachate pH) did not have a pattern attributable to the treatments (P>0.1). The molar flux of H+ (calculated from pH) ranged from 0.9 M H+/ha in an untreated soil to 51 M H+/ha in a 5 t/ha treatment. Instead, the flux of Cd leaching increased from 0.2 g/m^2 in the untreated soils to 0.6 to 1.3 g/m^2 in the IMG-treated soils, with no difference between the rates.

Table 18: Summary gypsum and selected element leachate fluxes during the first winter (kg/ha/yr as mean ± standard deviation) from soils top-dressed with IMG

Treatment	Gypsum (as Ca+SO_4)	Mn	K	Mg
Untreated	35 ±10 a[1]	0.05 ±0.03 a	3.9 ±2.5 a	3 ±5 a
5 t/ha	825 ±651 b	1.0 ±0.2 b	9.8 ±5.7 a	39 ±15 b
10 t/ha	1045 ±286 b	1.1 ±0.2 b	6.8 ±0.3 a	29 ±14 b
20 t/ha	1555 ±734 b	1.3 ±0.2 b	8.9 ±12 a	37 ±0.2 b

[1] Where tested, values followed by the same letter in each year are not statistically different between treatments (P<0.05).

3.4.5 Influence of soil properties on leached nutrient concentrations

Average winter–spring concentrations of leached soluble P were broadly predictable from some pre-winter soil properties. Leached P concentrations (weighted by leached volumes) were weakly correlated (P = 0.09) with $CaCl_2$-P at each lysimeter (Figure 14). Comparison with leaching over two successive years in an IMG mixing experiment in the Vasse region (Yoongarillup mixing experiment; Degens et al. 2022) indicated the relationships may differ slightly between the sites. The best relationship across all of the sites; however, was a non-linear polynomial function. This suggested that leachate concentrations, and therefore annual leachate losses from soils, increased greatly with increasing summer $CaCl_2$-P.

Leached P concentrations were less strongly, but still significantly correlated with PERI (Figure 15; r = 0.71, P = 0.05) for the top-dress experiment. Comparison with the leached P–PERI relationship in the Yoongarillup mixing experiment showed the relationship clearly differed between the sites (Figure 15). In contrast, concentrations were not significantly linearly correlated with Colwell P, PRI or PBI (r<0.5, P>0.2).

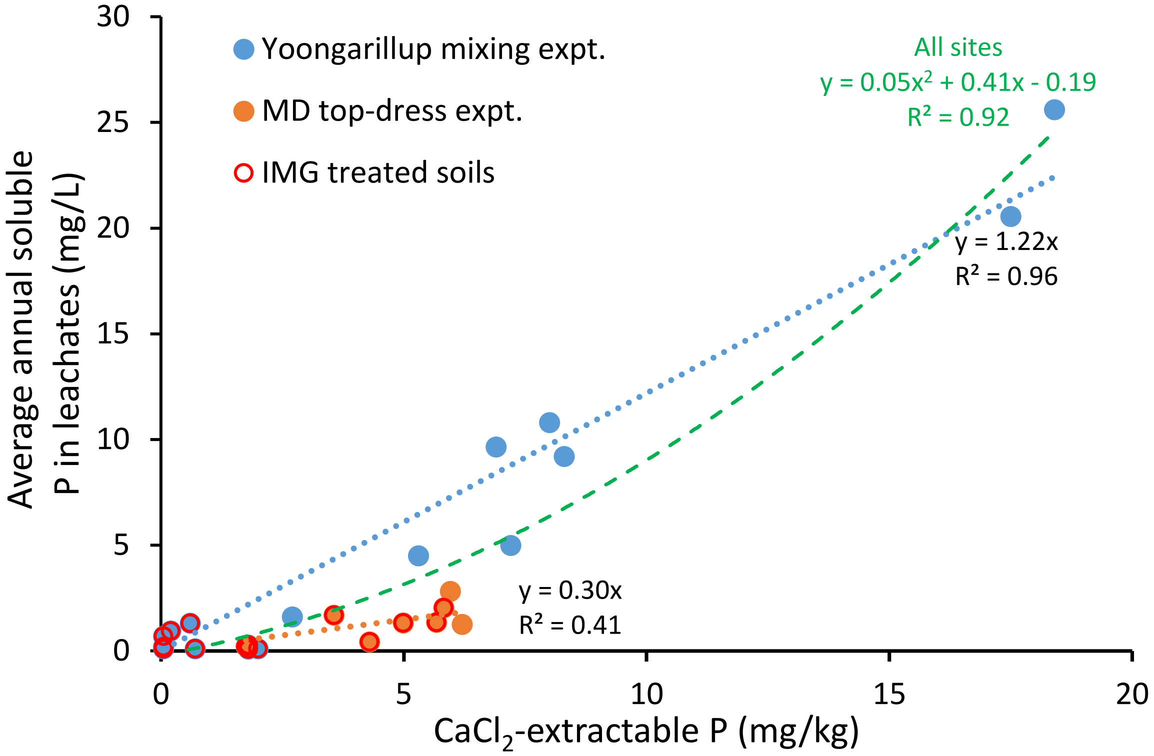


Figure 14: Average soluble P in leachates during winter–spring in relation to the previous summer $CaCl_2$-extractable P at two experiment sites

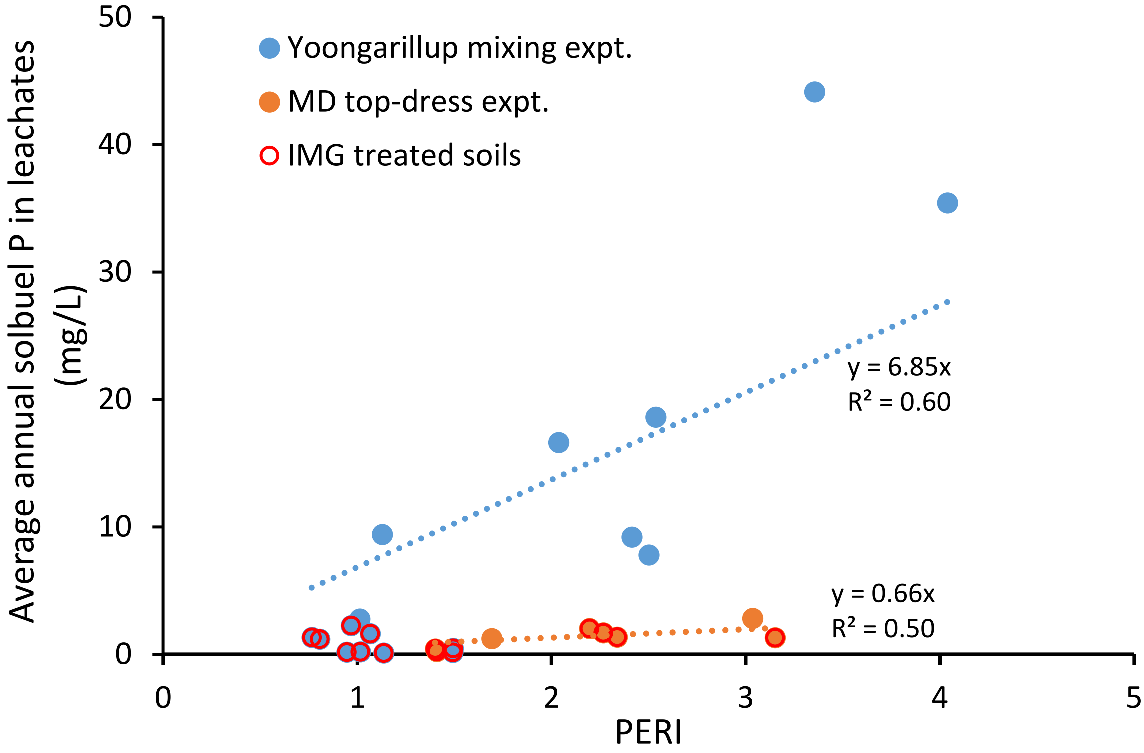


Figure 15: Average soluble P in leachates during winter–spring in relation to the previous summer PERI at two experiment sites

4 Discussion

4.1 Reduced P in runoff and leachates with IMG application

IMG application immediately reduced P lost to winter runoff. TP concentrations in intense runoff from soils reduced by up to 78% following IMG treatment – primarily because of reduced soluble P (with this being typically more than 55% of TP). In the first winter after application, reductions in TP were similar when IMG was mixed into soils at 60 t/ha or top-dressed at 20 t/ha, with more subtle effects for lower top-dressed rates. The effects persisted into the second year where IMG was mixed, even as additional nutrients were applied to the soils, but began to decrease where IMG was top-dressed.

Top-dressing of IMG has the advantage of targeting the highest P concentration zone in soils under continuous pasture production. P was highly stratified in the soils, with concentrations of free-P in the top 2 cm being typically many times greater than in the underlying soil. The concentration of P in the surface also results in this layer becoming over-saturated with P, as indicated by the negative PRI. Top-dressing with IMG maximises close contact between the amendment and these P-saturated soil layers. It is also cheaper than mixing and has the further advantage of not impacting on established permanent pastures.

Leachate losses of P from the sandy soils could also be reduced by top-dressing, based on an average reduction of 88% in soils treated with 20 t/ha IMG. This would represent up to 2 kg P/ha/yr being retained in the IMG-treated soils, rather than it being lost from the farming system to shallow groundwater. In other investigations, applying top-dressed IMG could reduce P leaching losses by up to 17 kg P/ha/yr (Sharma et al. 2018). A much greater reduction was achieved in this case because the untreated soils were regularly fertilised with P and there was little plant growth to take up P – leaving more P available for leaching. Most of the reduction in P leaching in our experiment was probably by direct contact of IMG with the soil surface, with shallow mixing caused by cattle trampling and shallow disturbance during direct drill seeding. Cattle trampling was observed to cause localised depressions of up to 3 cm, which would gradually mix the surface few centimetres of the sandy soil over the long term. These findings indicate that the effectiveness of IMG in reducing leaching – particularly at the lower rates of top-dressing – is likely to increase in subsequent years, with further surface-soil mixing by cattle trampling and annual reseeding.

The effect of IMG for reducing P in runoff depended directly on the reduction in free-P concentrations – indicated by $CaCl_2$-P – in the surface few centimetres of soils. Results from the multiple runoff simulations over two years and both experiments indicated that this relationship was consistent over time and strongest for the surface-soil layer. This is the layer in closest contact with runoff and where lower rates of IMG can have a strategically greater effect (noting top-dressed IMG had the greatest effect). Runoff P concentrations were also predicted from the free-P concentrations ($CaCl_2$-P) of the whole topsoil (0–10 cm) given these were correlated with the concentrations in the surface soils. By contrast, other measures of soil P such as

Colwell P or P-buffering capacity or status (PBI, PRI) were poor predictors of runoff P. Other investigations have found that runoff P typically correlates with whole-topsoil P characteristics, such as $CaCl_2$-P, but can also be correlated with measures of plant-available P (Sharpley 1995; McDowell & Sharpley 2001; Dougherty et al. 2006; Burkitt et al. 2010). This was probably because these correlations were for soils that were mixed before runoff measurements were carried out, thereby removing any effects of P stratification where surface properties can differ from the whole topsoil (Ryan et al. 2017).

Reduced free-P in the surface few centimetres of the soils where IMG was top-dressed also reduced P loss by leaching. The measurements of $CaCl_2$-P each summer at each lysimeter indicated that average soluble P in the following winter–spring leachates could be linearly reduced with every mg/kg reduction in $CaCl_2$-P. This type of relationship has similarly been found in other soils where $CaCl_2$-P was a strong predictor of P in leachates from soils (Hesketh & Brookes 2000; McDowell & Sharpley 2001). Our results indicate there may be a general non-linear relationship between average P concentrations in leachates and soil $CaCl_2$-P that can be applied across soils, but this needs further investigation. A non-linear response is plausible given other research has found an exponential relationship across soils between $CaCl_2$-P and the concentration of P in soil solution (being leachable P) when the former was <2.5 mg/kg (Moody 2011).

Large benefits can be realised by applying materials that locally increase P adsorption in the surface of P-stratified soils without significantly increasing the P adsorption of the whole soil. However, this highlights that ongoing management of P will be important to maintain runoff and leaching benefits. Top-dressing with IMG (at 20 t/ha, 10 t/ha and 5 t/ha) only increased the PRI and PBI in the surface 2 cm of soil with no measurable effect on the whole topsoil (0–10 cm). Other investigations with top-dressed IMG only showed measurable increases in PRI and PBI in whole topsoils at rates greater than 50 t/ha (Sharma et al. 2018). Similarly, we found that increases in PBI and PRI at field scales were generally only detectable when mixing IMG with soil at 60 t/ha. This increased average PBI from 7 to 23 and average PRI from 0.2 to 3.5 in the first year, with similar effects also measured in the second year. In agronomic terms, the increases in PBI are small and represent an improvement from very low to moderately low P-adsorption capacity (Gourley et al. 2019).

Our results using runoff assays are likely to reflect the water quality for intense local runoff events from saturated sandy paddocks. These are typically winter rainfall events when the watertable is near the soil surface, generating 5 to 15 mm of runoff. Runoff assays have been widely used to indicate localised runoff P risk (Dougherty et al. 2004), which are then broadly extrapolated to paddock scales (Cornish et al. 2002; Sharpley & Kleinman 2003). However, there are many processes at the quadrant scale that limit direct extrapolation to catchment-scale runoff (Nash et al. 2021). Concentrations in runoff are typically higher in initial runoff following a period of saturation (Sharpley et al. 1981; Pote et al. 1996) and can also be less with higher-intensity rainfall (Dougherty et al. 2008). This was reflected in our experiment, with runoff P (and N) concentrations consistently decreasing during the 30-minute runoff periods. This pattern is attributed to the initial rapid mobilisation of P from soil during early runoff, combined with a slower process of P supply by desorption that dominates as runoff continues (Nash et al. 2021). The nutrient concentrations measured in drainage at broader scales likely tends towards those measured in later stages of runoff from quadrant assays.

4.2 Predicting runoff and leaching benefits

Our results show that PERI is useful to broadly indicate free-P as $CaCl_2$-P – the key soil property driving runoff or leaching P risk of soils. PERI is derived from properties commonly measured at paddock scales and therefore could be useful as a first-stage, broad identifier of areas likely to have high free-P. However, further investigation is needed to evaluate whether PERI provides a consistent measure of P runoff risks across soils and seasons (i.e. summer measurement to assess winter risk). The index has been proposed as a surrogate index for soil-water P (free-P) concentrations (Moody 2011; Moody et al. 2013) and may be comparable to the extent of P saturation of soils increasingly used to predict runoff P risk (Sharpley 1995; Nair et al. 2004; Kleinman 2017). These indicators variously attempt to provide a measure of saturation of P sorption broadly defined as sorbed P / P sorption capacity (Kleinman 2017).

PERI of soils in winter was reasonably correlated with soluble-P concentrations in runoff from the two experimental sites over two years, but weaker with concentrations in leachates. Runoff correlations were primarily attributed to the stronger correlation between PERI and $CaCl_2$-P, particularly in the whole topsoil in winter. This was much weaker for the sites where leaching was measured. Stronger correlations between PERI and $CaCl_2$-P have been reported in Queensland and northern NSW soils under grain and horticultural tree cropping (Moody 2011; Moody et al. 2013), although these were for soils that had a much wider range of PBI classes and Colwell P values than investigated here. Our finding of a poor correlation of PERI with leachate P concentrations is unexpected and requires further investigation.

Given that PERI can be determined from paddock-level Colwell P and PBI measures, soils with a risk of high P runoff could be broadly identified using routine agronomic test results. Such soils could then be investigated further with follow-up analysis of the amounts of $CaCl_2$-P to gauge the amount of IMG required to mitigate P runoff risk. Free-P can be readily carried out as part of routine testing by several commercial soil testing laboratories in WA for a minimal fee per sample.

Other measures of soil-P status (e.g. Colwell P) were consistently poor predictors of $CaCl_2$-P, in both summer and winter soils. This was possibly because these do not reflect the extent of P saturation in P-saturated soils. Our results are similar to findings for a range of soils in Queensland and northern NSW (Moody 2011; Moody et al. 2013), but contrast with those for typical pastures elsewhere in Australia (Dougherty et al. 2006; Burkitt et al. 2010). Specific relationships might also be evident only across a broader range of soils, or with higher concentrations of plant-available P – as has been found elsewhere (Hesketh & Brookes 2000; McDowell &

Sharpley 2001). Another possibility is that the much greater $CaCl_2$-P in our soils is more independent of Colwell P during each winter–spring period in soils where the P-adsorption capacity has been exhausted. Under such conditions, seasonal fertiliser P application, organic P mineralisation and leaching processes have a much bigger influence on free-P than adsorption and desorption reactions.

4.3 Factors influencing the effectiveness of IMG

This experiment shows that the effectiveness of IMG for reducing runoff and P leaching is initially influenced by the application rate and – to a lesser extent – whether it is mixed with soils.

The longevity of IMG benefits for P loss depend on maintaining low amounts of free-P in soils (indicated by $CaCl_2$-P), which is a function of IMG adsorption capacity, ongoing P application and P removal via grazing livestock. PRI and $CaCl_2$-P remained similar over two years where IMG was mixed at 60 t/ha in both the surface (of winter runoff plots) and whole topsoil, which indicates little change in the effectiveness of IMG P adsorption. However, where IMG was top-dressed at 20 t/ha, the effectiveness of the P adsorption appeared to reduce in surface layers from runoff quadrants in winter, but remained unchanged in the whole soil sampling in summer.

Disturbance from seeding operations is likely to have reduced the initial effectiveness of the top-dressed IMG treatment on runoff concentrations measured at the quadrant scale, which was not evident where IMG was mixed in by ploughing. Subsurface soil (that had not been in contact with IMG) was likely brought to the surface by the passage of direct-drill tines at 1 to 2.5 cm depth each year. This would have disrupted the IMG cover, increased mixing of the IMG and thus increased small-scale variation in the concentrations of free-P in the surface, leading to greater runoff P concentrations from runoff quadrants in the second year. The variable effects at different rates of top-dressed IMG might also have been partly caused by seeding disturbance. Further monitoring of the surface-soil layer is needed to determine whether these effects subside as the IMG is gradually mixed with the surface soil over multiple years. Such sampling would also determine the persistence of the P-retention benefits of surface-applied IMG over the long-term.

A single rate of top-dressing with IMG may not address all runoff risks. Therefore it may be beneficial to tailor rates to the P status of soils, particularly those with high P status. IMG top-dressed at 20 t/ha in both experiments did not consistently reduce soluble P in runoff to below 0.1 mg P/L in all quadrants. Again, variability in free-P reductions (indicated by $CaCl_2$-P) might be due to disturbance during seeding in soils with high initial P status. Quadrants with high free-P after treatment with 20 t/ha of IMG also had a PERI exceeding 1.5. This indicates that the soils had high P status before treatment and therefore the effectiveness of the top-dress IMG may have been more sensitive to soil disturbance. As discussed earlier, the effects of annual seeding may reduce with time or perhaps could be mitigated using higher initial application rates.

Greater capture and retention of P in the surface soil with top-dressed IMG probably contributed to more variable effects on runoff P than where the IMG was mixed with soils. Top-dressing with IMG at 20 t/ha was initially as effective in reducing P loss to runoff as mixing IMG at 60 t/ha; however, the effect started to decline and was more variable in the second winter. We had expected top-dressing with IMG to have greater and more consistent effect on runoff P concentrations due to the higher concentrations of IMG in the surface-soil layer. If 20 t/ha is assumed to eventually mix with the surface 2 cm, the IMG content of this layer would be approximately 8% by weight. In comparison, 60 t/ha mixed through 10 cm by ploughing results in an IMG content of less than 5% in the surface 2 cm (equivalent 12 t/ha top-dressed). This is also seen in the greater PBI and PRI of the surface soils where IMG was top-dressed at 20 t/ha that persisted over the two winters in the mixing experiment. However, despite no change in the PRI or PBI of these, $CaCl_2$-P in surface soil where IMG was top-dressed at 20 t/ha had increased slightly by the second winter – contributing to the increase in runoff P concentrations. This could reflect the greater effectiveness of the top-dress IMG in capturing any P in from manure and compost fertiliser or water running over the site in the surface few 2 cm of soils.

The adsorption capacity of IMG in field conditions is uncertain. Batch adsorption tests indicate a maximum P-adsorption capacity of 21 kg P/tonne (Wendling et al. 2012), although this is likely to be lower under field conditions. During the short-term batch tests, dissolution of Ca and SO_4 increases the ionic strength, which should improve P interaction with adsorptive surfaces. Furthermore, P is also likely to be reduced by precipitation of calcium phosphates given the higher pH of pure IMG compared with IMG mixed with soils. Both factors can elevate the apparent P adsorption during laboratory tests (Barrow 1984; Allen & Jeffery 1990). However, in the field these factors may be less significant or only transient during the first few years while the gypsum is dissolving.

Mixing IMG with composted fertiliser applied to paddocks (top-dressed) each year may mitigate the risk of P saturation of surface-soil layers over the long term. Compost has been applied to the soils in both experiments for at least a decade to primarily meet N and K requirements and is also the main fertiliser P input. Average P_{95} fertility indices greater than 1 across both experiment sites indicated that the P added in compost was slightly more than the P removed by grazing and lost by leaching (and runoff). Continued annual application is expected to gradually increase free-P and could be mitigated by mixing IMG with the material during the composting process. Such practice is common in the northern United States, where composted broiler waste is mixed with flue gypsum. Mixing of the waste or other manures with flue gypsum at rates of >15% by weight followed by incubation for three days can greatly reduce water-soluble P (Dou et al. 2003). The additional mineral iron in IMG would amplify this benefit.

Unexpectedly, tilling to break up stratification of the P in the soil did not reduce P losses. Tillage has been suggested as an immediate option to reduce P runoff risk in soils with P-saturated surface layers by inverting these or mixing with higher-P-adsorbing subsurface soil (Sharpley & Kleinman 2003; Kleinman 2017). Our results suggest that tillage to mix high-P surface soils with subsurface soils has little effect on reducing P in runoff where the subsurface soils also have limited P-adsorption capacity. Tillage had little effect on surface P-adsorption properties (indicated by PBI and PRI) but slightly reduced free-P in the first winter. This effect diminished by the second winter. Poor mixing of the soil by speed tilling is considered unlikely as the same machinery mixed 60 t/ha of IMG through the soil profile with no bias for greater P adsorption in the surface soils.

4.4 Other production system benefits and risks

The reduction in free-P following IMG treatment did not influence soil measures of plant-available P or P uptake, with leaf P remaining adequate over much of the site. Plant-available P remained similar even though free-P (indicated by $CaCl_2$-P) was reduced throughout the topsoil, where IMG was mixed at 60 t/ha, or only at the surface, where IMG was top-dressed. Sufficient P for plant growth was also reflected in plant-tissue P concentrations. These were similar initially and marginally lower only with IMG mixed at 60 t/ha in the second year, but consistently remained within the adequate range. For all treatments, it is expected that with increased P retention there will be a trend for increasing plant-available P in soils. This is emerging in the mixing experiment and further monitoring is required to confirm. The increase in plant-available P reflects the greater capacity for the soils to retain applied P which in the untreated soils, is either leached or washed off.

IMG improved soil pH by 0.5 units and slightly increased cation exchange capacity when mixed at 60 t/ha, but it had few other detectable benefits for soil properties aside from the changes in soil-P chemistry. The effect on pH was attributed to the weak liming effect of IMG, which has an equivalent neutralising capacity of less than 6% pure $CaCO_3$ despite having a pH of 8.5–9 (Appendix E). Mixing IMG at 60 t/ha was equivalent to mixing 2.9 t/ha of pure limesand in the topsoil (with 100% neutralising value). For a poorly buffered sand, the increase in pH was smaller than expected – this might be due to the neutralising effect becoming available only as the gypsum dissolves to expose what are probably minor carbonate minerals in the IMG. There was no detectable liming effect with IMG top-dressed at 20 t/ha, probably because this was equivalent to applying less than 1 t/ha pure limesand to the surface soil.

Applying IMG slightly affected the plant uptake of S and K in the mixing experiment, but not to any extent that influenced plant health. Uptake of S by ryegrass and clover increased initially only where IMG was mixed at 60 t/ha, despite soil-extractable SO_4 concentrations being consistently five-fold greater than in the untreated soils over both years. Uptake of K was slightly depressed in the highest IMG rate only for plants in wet soil zones, although all soil zones irrespective of treatment had similar Colwell K in summer. This was possibly due to high Ca concentrations in the soils (evident in leaf Ca concentrations) competitively excluding K uptake rather than a deficiency induced by initial displacement and increased leaching of K.

Plant uptake of Mg was not affected by the IMG treatments over the first two years, yet the status of this nutrient for plant growth needs to be monitored further. Applying IMG increases the concentrations of Ca in soils, which displaces Mg from charged surfaces (the exchangeable Mg) and increases Mg concentrations in leachates. Long-term effects of this on exchangeable Mg – an indicator of Mg available for plant growth – will depend on the longevity of very high concentrations of Ca leaching through soils. There were only slight effects of this on exchangeable Mg over the first two years, which were more prominent where IMG was mixed at 60 t/ha. The amounts of leached Mg can be readily replaced with a single application of Mg-based fertiliser. Mixing IMG with soils may increase Mg leaching, with leachate concentrations in this investigation for 20 t/ha top-dressed being much smaller than where mixed at the same rate in another experiment (Degens et al. 2022).

Although IMG slightly increased Mn uptake in plant tops, Mn status remained in the normal range. The concentrations of Mn in leachates where IMG was top-dressed at 20 t/ha were within the range (0.3–6 mg/L) that affects most plants growing in solutions with the lower Ca concentrations typical of most soils (Kopittke et al. 2010). However, the increase in soil Ca with the applied IMG, clear in the leachate Ca concentrations, probably limited the uptake of Mn and, consequently, any potential toxicity effects. High Ca concentrations are known to prevent Mn toxicity in plants, although the mechanisms remain unclear (El-Jaoual & Cox 1998). The main pathway of long-term Mn risks to grazing animals is through ingestion of Mn taken up by plants and ingestion of plants with IMG adhering to leaf surfaces immediately after application (Hagen 2018). Slight increases in plant Mn contents are not detrimental to animals consuming the grass, as hay with concentrations up to double this pose no long-term risks to animal health (Hagen 2018). Avoiding application of IMG to dense, tall pasture (green or dry) or withholding grazing until the first winter rains would provide further protection against ingestion of any IMG adhering to grazed leaves. While direct ingestion of soil containing IMG is potentially greatest with top-dressed IMG, this does not pose any risks to cattle health over the long term where the soil Mn content is assumed to remain unchanged by leaching (Hagen 2018). Mn is a micronutrient that may be deficient in alkaline soils or after liming and can be corrected with an application at 1 to 3 kg Mn/ha in a soluble sulfate form. Applying IMG at 20 t/ha would add up to 480 kg of Mn/ha, which is well in excess of what is required to overcome any deficiency; however, concentrations in leachates indicate the Mn in IMG is far less soluble. Further investigations are needed to evaluate whether the Ca in leaching from the IMG protects against Mn toxicity in plants and to understand the extended pattern of Mn availability from IMG in subsequent years.

There were slight effects of IMG on plant uptake of Co but not other elements. Plant uptake of essential elements such as Cu, Cr and Zn remained similar as did non-essential elements such as Cd, U and Th. Increased Co in plants or soils is a benefit to grazing animals – this element is frequently added to animal diets to overcome deficiencies (Hagen 2018). Co is a micronutrient that is lacking in many Australian agricultural systems and is regularly administered directly to livestock (Judson & McFarlane 1998). Pastures are typically fertilised with up to 80 g Co/ha for several years to build up soil levels followed by regular annual applications of 50 g Co/ha in susceptible areas. Application of 20 t/ha of IMG would apply 5.24 kg Co/ha but the solubility of this (and therefore availability to plants) would likely be far less than the Co in fertilisers.

4.5 Environmental risks of runoff and leachates from IMG-treated paddocks

The risk of IMG constituents moving offsite varied with the rate and method of IMG application. With minimal transport of particulates, surface transport risks were primarily limited to dissolved Ca, SO_4 and Mn. The risk of particulates washing off was greatest in the first winter after IMG was applied. However, top-dressing IMG on pasture soils did not increase particulate P transport in either of the experiments (with intensive simulated rainfall), despite a slightly higher particulate Fe transport compared with where IMG was mixed. These results indicate that adsorption and transport of P on particulate Fe after IMG treatment is minimal, even when the soils are saturated. The slight increases in total Fe measured in runoff were limited to sites where other particulates from the soil surface were also lost (shown by correlations with particulate N transport). Loss of particulate Fe (and the high correlation with particulate Mn) also indicated the risk of fine IMG particle transport that – while greatest in the first winter – diminished by more than half in the second winter. The transport risk in the first winter was probably accentuated by the limited soil contact time before winter rainfall, particularly where IMG was top-dressed.

IMG treatments increased Mn concentrations in runoff and leachate, but total concentrations posed no risk to aquatic organisms in downstream environments. Total Mn concentrations were less than 1.44 mg/L in leachates from soils top-dressed with IMG and less than 0.87 mg/L in runoff generated during intensive rainfall simulations. These concentrations are much less than the water quality guideline limit of 1.9 mg/L (ANZECC & ARMCANZ 2000), ensuring a 99% probability of protecting all aquatic organisms in soft waters (hardness < 60 mg $CaCO_3$/L). Preliminary results of aquatic toxicity testing with eight species also indicated that Mn is not toxic at concentrations less than 4 mg/L in freshwater with 100 mg $CaCO_3$/L hardness (Nice H & Degens B, unpublished data). Hardness was increased in leachates and runoff from the IMG-treated soils to at least 80 mg $CaCO_3$/L when concentrations of Mn were greatest. Increasing hardness also reduces the toxicity of Mn to aquatic organisms (Peters et al. 2011) and significantly mitigates the risk of aquatic toxicity of Mn in runoff and leachates.

Factors affecting soil particle transport are more significant for Mn transport in runoff than IMG application rates (at least up to 20 t/ha). The Mn loss where IMG was mixed at 60 t/ha was similar to where it was top-dressed at 20 t/ha, despite three times greater near-surface IMG concentrations in the latter. Using IMG content analysis (Appendix E), surface-soil Mn was increased by more than 3 g/kg when top-dressed at 20 t/ha (assuming mixing in the surface 1 cm) compared with an increase of 0.9 g/kg in the same surface layer when mixed at 60 t/ha throughout the top 10 cm. Most of the top-dressed IMG was likely to be on the soil surface in the first winter. However, animal hoof impact, soil invertebrate activity and machine traffic over several years will eventually mix IMG into the surface few centimetres of the soil. The lack of a significant effect of the exposed IMG on surface transport suggests that most Mn washing off the soil was largely due to transport of soil particles containing Mn rather than particles of IMG. Correlations between total Mn and particulate forms of nutrients in runoff in the first winter also confirm this.

The risk of Mn leaching is also similar irrespective of the IMG application rate and much less than if IMG is mixed with soils. Concentrations of Mn in leachates where IMG was top-dressed at 20t/ha were at least eight times less than where IMG was mixed at the same rate in a similar pH sandy soil (Degens et al. 2022). This is probably because Mn concentrations in leachates is dependent on contact with topsoil layers and the pH of these. Greater concentrations of Mn are likely where IMG contacts with lower pH soil increasing the solubility of the Mn in the IMG (Degens et al. 2022). Surface-soil pH at the lysimeters was a unit greater than the subsurface pH, as is common elsewhere (Ryan et al. 2017), and may explain the lower concentrations of Mn leaching from surface-applied IMG.

IMG application had no effect or reduced the leaching of most trace elements except Co, Cd and Zn, which were elevated slightly. Another IMG mixing experiment in sandy soils near Busselton had a similar finding, but only Co was elevated (Degens et al. 2022). Increased retention of trace elements contrasted with the increased leaching of protons (acidity) from the soils, but corresponded with reduced leaching of DOC. The latter correlation is presumably due to a high affinity of the metals with DOC through the formation of organo-metal complexes, which is well known for elements such as Cu, Pb or Zn (Degryse et al. 2009) and likely also extends to other elements such as Cr, Fe, U and Th. The mechanism by which DOC is retained in the top-dressing experiment is probably not related to direct adsorption onto minerals such as the iron oxides in IMG, given that IMG was not mixed with the soil. However, increased Ca in soil solutions can increase the retention of DOC in soils through increased cation bridging (Münch et al. 2002; Oste et al. 2002).

Patterns of increased Cd and Zn in leachates from the IMG-treated soils indicate an effect induced by IMG rather than due to the metals in the applied IMG. Leaching of Cd but not Zn has been previously found with IMG top-dressed on acidic sands (Sharma et al. 2018), but neither was increased in leachates where IMG was mixed into soils in other investigations (Douglas et al. 2010b; Degens et al. 2022). The leached amount of both metals in the first year was less than their total amount applied in the IMG, with the leached Cd equivalent to <0.07% of Cd in IMG and leached Zn equivalent to 10–28 % of the Zn in the applied IMG (see composition in Appendix E). While the increase in Zn corresponded with increasing IMG rates, this was not the case for Cd. This indicates that the applied IMG was perhaps not the main source of leached Cd but might have contributed to increased Zn leaching.

Correlations indicate that increased Zn and Cd originated from the soils rather than the Zn and Cd in the applied IMG. Zn and Cd concentrations in leachates correlated with Mg leaching and to a lesser degree with Ca (and SO_4) leaching. This suggests the origin of the metals is possibly exchangeable forms of Zn and Cd, behaving similar to exchangeable Mg. Displacement or exchange of such metals is typical where Ca solutions are increased in soil solutions (Degryse et al. 2009). The duration of this effect may be short, particularly since the increased Ca concentrations depend on dissolution of gypsum in the applied IMG. Further monitoring would indicate whether Ca and Zn continue to leach once leaching of Ca from the applied IMG has been exhausted. The effect of increased Ca leaching existing metals in soils is also possible following the standard practice of applying agricultural lime.

While Zn is an essential trace element in agricultural production systems, Cd is considered an environmental contaminant mostly originating from historic superphosphate applications (McLaughlin et al. 1996). The soils at the lysimeters contained initial Cd levels ranging from 0.02 mg/kg to 0.062 mg/kg – small compared with concentrations more than eight times these in other sandy soils with a history of being fertilised with Cd-containing superphosphates (Mann et al. 2002). Applying IMG at 20 t/ha added 0.41 mg Cd/m^2 compared with more than 3.7 mg Cd/m^2 already present in the surface 10 cm of the soil.

In contrast with Cd, the increase in Co leaching was likely due to the Co in the applied IMG, most probably controlled by dissolution of Mn minerals. Co leaching was strongly correlated with patterns of Mn leaching, which has been linked with the degree of soil contact (Degens et al. 2022). The lack of correlation with DOC leaching is consistent with the low affinity of Co to DOC (Degryse et al. 2009). Soil retention of the Co released from the IMG is probably limited by high concentrations of Ca that can reduce Co adsorption, and by the lack of Co-adsorbing Mn minerals (McLaren et al. 1986).

The ecological risk posed by the slight increase in Co concentrations in leachate up to 4.2 µg/L is unclear but likely negligible. Although not measured, the average Co in runoff was estimated to be less than 6 µg/L, using total Mn in runoff water and a Co:Mn ratio in IMG of 88 (see Appendix E). Concentrations of Co measured in runoff in the following year were also consistently less than 1.5 µg/L (unpublished data). As with Mn, the aquatic toxicity of Co can depend on the mitigating effect of hardness (Diamond et al. 1992; Pourkhabbaz et al. 2011), although this likely has no effect on chronic toxicity (Nagpal 2004). More recent research indicates that Co aquatic toxicity can also be reduced in water with DOC >10 mg/L depending on the size of the organic molecules (Watanabe et al. 2017). In this experiment, the DOC concentrations in soil leachates were more than four times greater and may confer some protective complexing of dissolved Co. Average Co concentrations in leachates and runoff were less than the low reliability trigger limit for the 90% protection level of 2.8 µg/L, but slightly exceeded the moderate reliability trigger of 90 µg/L (ANZECC & ARMCANZ 2000). These guidelines apply to soft waters (hardness <60 mg $CaCO_3$/L) and so there is strong possibility that the very high hardness of the leachate and runoff waters could mitigate any toxicity risks – even if diluted 10-fold. Further investigation is required to establish the toxicity of Co to aquatic organisms in south-western Australia when in complex mixtures with DOC and elevated hardness.

Similar factors also mitigate the toxicity of any Zn and Cd in leachates, in the unlikely event that this discharges to a drain, stream or wetland with no mixing with groundwater. Hardness reduces the toxicity of Cd and Zn (Warne et al. 2015), with hardness-modified trigger values for the 99% protection level being 1.0 µg/L and 35 µg/L respectively, using the minimum average leachate hardness of 720 mg $CaCO_3$/L. While the undiluted concentrations of Cd were mostly below this, DOC may have conferred some protective complexing of dissolved Zn and reduced the toxicity of the leached Zn. DOC has been widely shown to reduce the aquatic toxicity of metals such as Cd and Zn, often playing a much greater role than hardness (Wood et al. 2011). It is likely that DOC complexation alone mitigates any Cd and Zn risks, with concentrations exceeding 37 mg C/L being more than 10 times greater than most fresh waters on which the guidelines have been derived (Warne et al. 2015).

Increases in SO_4 concentrations in runoff and leachate with IMG application are also not expected to increase risks to aquatic ecosystems. Initial concentrations were typically about 10 times greater in leachates than runoff, indicating that offsite risks associated with shallow groundwater transport of SO_4 are more critical than direct runoff. The main risks lie with microbial reduction of SO_4 to H_2S under low redox groundwater conditions, which poses a hazard where this groundwater discharges. This is only likely to arise in permanent groundwater systems that can support sustained SO_4 reduction with negligible Fe minerals (which would trap dissolved sulfide) and with minimal mixing (that would otherwise dilute SO_4 and H_2S). Seasonal groundwater systems that dry out annually are unlikely to develop sufficiently low redox conditions for significant SO_4 reduction. The geochemistry of Fe can also greatly limit free H_2S and sulfides in groundwater, typically through rapid sequestration as sulfide minerals (e.g. FeS, FeS_2). Monitoring has found no evidence of SO_4 reducing conditions within the shallowest 1 m of the aquifer at the site (Degens 2023, unpublished data), although conditions in a deep aquifer similar to this site typically favour SO_4 reduction, but also can contain Fe minerals (Degens et al. 2021). Discharge and formation of H_2S in wetlands is a natural process, with multiple mechanisms often active in mitigating H_2S toxicity, including soil metal sequestration, microbial oxidation and plant root detoxification (Lamers et al. 2013).

The Pb contained in the IMG was immobile and not leached or available to plants. Previous laboratory investigations have found that the Pb in IMG was difficult to extract and mostly immobile. Less than 1% could be extracted at very low pH and corresponded with extraction of iron (Sharma et al. 2019). This suggests the Pb was embedded within the iron mineral matrix of IMG and would be largely non-reactive while this remains stable in soils. Our results and the results of other investigations also confirm this with Pb leaching being unchanged with IMG application (Degens et al., 2022; Sharma et al. 2018). Later analyses of metal concentrations in plants in our experiment found that Pb uptake from soils was also unchanged by IMG application, which is similar to the findings of other experiments (Sharma et al. 2018).

Concentrations of SO_4 in leachates varied seasonally and likely reflected rates of gypsum dissolution in the IMG. Average yearly concentrations in leachates of up to 1,337 mg/L were similar to those from the same rate of top-dressed IMG at Bullsbrook (Sharma et al. 2018), but greater than where IMG was mixed at 20 t/ha near Yoongarillup (Degens et al. 2022). However, all investigations exhibited the same pattern of seasonally decreasing concentrations – indicating an exhaustion of leachable SO_4 during each winter–spring leaching period. This is consistent with a slow rate of gypsum dissolution whereby summer drying, followed by slow wetting up with late Autumn rains (in warm soils), enables much greater initial dissolution and leaching that slows through late winter. Despite the higher concentrations in leachates, the total loss of $CaSO_4$ was less than 1.5 t/ha/yr, indicating the leaching period is likely to last at least 10 years for the highest application rate. In runoff, average concentrations of SO_4 were less than 110 mg/L irrespective of the IMG application rate. Possibly this was because runoff concentrations are limited to the dissolution of gypsum during runoff events. Any soil-accumulated free SO_4 most likely leached during wet-up of the soils.

4.6 Cost and benefits

Prospects for the adoption of IMG as a soil amendment to reduce P losses will depend on the cost-benefit ratio to the farmer, as well as to the environment. The economic costs of applying IMG depend on supply, transport and application costs – factors which need to be considered in relation to the benefits of improved P retention and how long it lasts.

Current costs indicate the on-farm P-retention benefits of IMG in the Peel are not likely to be immediately attractive to farmers, purely from an economic perspective. Projecting these benefits to farmers over 10 years, the value of the retained P at 2023 fertiliser prices ranges from $284/ha for paddocks losing 5 kg P/ha/yr to $1137/ha for paddocks losing 20 kg P/ha/yr (Table 19). Except for soils with large P losses, the cost of applying IMG under the simplest application regime (top-dressed at 20 t/ha) is typically more than double the cost of replacing the P lost from the farm (Table 19). These estimates assume IMG is effective for 10 years. If we extend the estimates out to 15 years, the value of the saved P increases by more than $122/ha. Much of the benefits of IMG treatment relate to preventing the loss of P to waterways, at least in the short-term.

Reducing the costs of IMG application by >80% is necessary for IMG to be immediately economically attractive to many landholders with average losses of <10 kg P/ha. Application costs include purchasing, transporting and spreading IMG, which was in the range of $1,172–$1,280/ha where IMG was top-dressed at 20 t/ha (using freight and spreading pricing for 2023). Naturally the costs are more than three times higher if IMG is mixed at 60 t/ha. This study assumed an IMG price of $20/tonne (excluding GST) from Iluka Resources Ltd in Capel. Transport comprises most of the cost, which is about $30–$35/tonne from Capel in 2023. Spreading costs are based on contractor rates of up to $9/tonne, including mobilisation and loading. Subsidising application costs by removing supply and freight costs (leaving on-farm spreading costs only) brings the costs into balance with the benefits. Where there are greater losses of P from soils the need to reduce costs is less, yet realising the benefits of the saved P in terms of greater pasture production rates will determine the viability of IMG in these situations.

The longevity of the IMG benefits remains a significant uncertainty for costing long-term benefits. As discussed above (Section 4.3), the laboratory-measured maximum adsorption capacity of IMG might be 21 kg P/tonne which for 20 t/ha carries a maximum P adsorption of 410 kg P/ha. However, this capacity is when P would begin to leach at concentrations like unamended soils. Using a 10-year lifespan assumes a reasonable overall P retention of between 50 and 200 kg P/ha, for scenarios with ongoing annual losses between 5 and 20 kg P/ha. The results in this report indicate that the longevity of top-dressed IMG benefits, at least for runoff loss, may be more limited than mixed IMG – but extended monitoring is needed to verify this.

Table 19: Estimated costs and benefits to farmers of improving on-farm retention of P.

Scenario	**Annual soil P loss via leaching and/or runoff (kg P/ha)**	**Benefits of retained P in soils over 10 years ($/ha)[1]**	**IMG treatment cost ($/ha)**	**Cost: benefit ratio**	**Cost of reduced P loss based on subsidy ($/kg)**
IMG top-dressed at 20 t/ha, no subsidy	5	$ 284	$ 1172[a]	4.1	
	10	$ 569	$ 1172	2.1	
	20	$ 1137	$ 1172	1.0	
IMG top-dressed at 20 t/ha with no supply cost to farmers	5	$ 284	$ 180[b]	0.6	$ 19.84
	10	$ 569	$ 180	0.3	$ 9.92
	20	$ 1137	$ 180	0.2	$ 4.96

[1] Present value of future saved P in the year that the IMG is applied, estimated using an annual discount rate of 2% (i.e. equivalent return on the money if invested elsewhere) with a 10-year return period with a P price of $6.33/kg (estimated from the value of P in single superphosphate priced at $576/tonne including GST in 2023).

[a] Treatment cost includes purchase, freight from Capel to the mid-part of the Peel region and spreading.

[b] Treatment cost for spreading only.

On-farm reduction in P loss is more cost-effective than off-farm removal of P from waterways. IMG reduces P losses at-source with the costs of intervention (by way of subsidy or incentive to farmers) ranging from $4.96/kg P to $19.84/kg P (Table 19). In comparison, effective in-stream treatment costs for P removal are estimated to range from $100 to more than $1,800/kg of P removed. The upper cost estimate is the minimum cost for treating water using high-P-adsorbing clays (Tulipani et al. 2023). There is significant uncertainty in the lower cost estimate, being in-drain treatment, which depends on the longevity and effectiveness of the ongoing P removal of any P-adsorbing media. These costs indicate that subsidising on-farm amendment costs in high-P-loss areas is more effective than treating P in drains and waterways.

About 136,000 ha of the Bindjareb Djilba (Peel-Harvey) catchment (65% of the coastal 210,000 ha) is suitable for amendment to improve P retention (sandy soils with low P-adsorption capacity, Summers et al. 2020). Applying IMG at 20 t/ha to 10% of this area (assumed to contain soils with the highest P losses) would require 272,000 tonnes of IMG at a total cost of $15.9 million. This could be achieved over 10 years with 1,360 ha treated annually for $1.6 million each year, equating to a cost of about \$5 to \$20/kg of P that would otherwise reach the estuary or require more expensive treatment. Other marginal benefits of IMG seen so far add little value but might support farmer acceptance of its use. These include the application of S and the trace elements Co, Zn and Mn, as well as a slight improvement in soil pH. Mn deficiency is common after liming and thus IMG may be a useful and cheap form of Mn to apply when liming.

5 Concluding comments

Applying IMG to pasture soils had immediate benefits for reducing P washed off or leached from the site, but its effectiveness and longevity depended on the rates and application methods. IMG top-dressed at 20 t/ha was as effective as IMG mixed into soil at 60 t/ha – both reduced the P washed off soils in runoff in the first winter by up to 78%. The top-dressed IMG also reduced P leaching by 88% in the first winter. Rates of top-dressed IMG less than 20 t/ha; however, had limited effects on P in runoff and leaching. The effects of IMG on runoff and leaching were primarily driven by the material increasing surface-soil P adsorption, which had the effect of reducing free-P without reducing plant-available P.

P concentrations in runoff were consistently related to concentrations of free-P in soils indicated by $CaCl_2$-P – highlighting the major controlling influence of this property. While the specific relationship may vary between sites, it is expected that reducing $CaCl_2$-P in soils will consistently reduce the P concentration in runoff. The sensitivity of this measurement will be useful for monitoring the performance of IMG treatment. For example, the top-dressed IMG's effectiveness for reducing runoff-P declined in the second winter and corresponded with increases in $CaCl_2$-P in the surface soils. Similarly, initial spatial variation in the reduction in $CaCl_2$-P in the surface 2 cm of soil following top-dressing – particularly at rates less than 20 t/ha – corresponded with variable effects on runoff P. Some of this variation was probably due to disruption of the surface IMG layer during annual seeding, exposing soil with high $CaCl_2$-P to runoff. This effect would be expected to decrease with time as the IMG gradually mixes with the soil surface with successive years of re-seeding.

Top-dressing with IMG targets the highest P concentration zones in soils under pasture production, enabling reduced P losses while improving pH and providing S and Ca. This application method maximises close contact between the soil amendment and P-saturated soil layers. It is cheaper than mixing the IMG into soils and carries the additional advantage of being easy to do in paddocks with existing permanent pastures. Applying IMG can also address soil S deficiency in P-saturated paddocks (P_{95}>1.5), with annual testing indicating this is typically more than 25% of paddocks in the Peel region (Summers et al. 2020).

IMG applied at higher rates (>40 t/ha) will need to be mixed into soils to avoid surface sealing, but the benefits to P retention are likely to last longer. This is largely because the higher rates achieve greater initial increases in P-adsorption capacity. Tilling to mix IMG into soils is a more intensive practice but can be opportunistically carried out during pasture renovation operations, along with liming of soils to address acidity. Tilling sandy soils alone did not achieve any measurable reductions in P loss in this study, contrasting with findings from studies elsewhere in the world (Sharpley & Kleinman 2003; Kleinman 2017). Mixing higher rates of IMG into soils is likely to extend the longevity of benefits to soil-P retention (and runoff-P loss) more than top-dressing with lower rates but carries significant up-front costs of more than $3,000/ha. However, there were other benefits of mixing higher rates of IMG, including raising soil pH by up to 0.5 units and slightly increasing its capacity to retain cations. Mixing IMG can also have other benefits to water quality, with increased retention of organic N and P, but has no effects on leaching of ammonia and nitrate (Degens et al. 2022). Applying IMG may increase organic C retention in soils, initially evident as reduced leaching of DOC, but this may take several years to be detectable and is likely to be more effective where IMG is mixed with soils.

As well as reducing P in runoff, top-dressing of IMG can also reduce leaching of P to less than 0.2 kg P/ha/yr, despite interacting with only the surface layer of the soil. Leached P losses were only significantly reduced at the highest rate of top-dressed IMG in the first winter; however there were emerging effects at lighter rates that may become clearer in subsequent years. The relationship of leachate P concentrations with free-P (as $CaCl_2$-P) indicates that winter-spring P losses are broadly predictable from summer soil analyses of free-P, at least in a system where there is soluble fertiliser P applied.

The longevity of IMG effects on runoff will depend on management of P use in the farming system. While the IMG application rate determines the overall increase in P-adsorption capacity achieved, ongoing management of P applications to soils will determine how long surface-soil P characteristics can be maintained to minimise runoff or leaching. This hinges on the judicious use of fertiliser P in accordance with soil testing. Mixed IMG is likely to provide a longer duration of benefits to leaching (and soil seepage at groundwater discharge zones; Figure 16) than top-dressed IMG for any rate of application, mostly because of the distribution of P-retention capacity throughout the soil.

Indicators of soil-P runoff or leaching risk can be useful to identify areas where soil amendments could be targeted on farms. See Figure 16 for an illustration of our general understanding of IMG effectiveness on both leaching and runoff arising from this study. Topsoils with high concentrations of free-P (indicated by $CaCl_2$-P) are at risk of leaching high concentrations of P to shallow groundwater. Similar concentrations are likely flushed to runoff where groundwater seeps through these soils during rain events (Figure 16). In low-lying areas prone to saturation, soils that have accumulated high concentrations of free-P in the surface few centimetres are at risk of increasing P concentrations in runoff.

At a farm level, paddocks with high concentrations of $CaCl_2$-P in soils can be broadly identified using the phosphorus environmental risk index (PERI). This can be calculated from previous Colwell P and PBI analyses in standard farm soil tests. PERI provides a way of identifying where to carry out follow-up sampling to directly measure free-P (as $CaCl_2$-P) and target treatments at high P-loss areas of farms. Any new farm-scale soil sampling should consider analysis of $CaCl_2$-extractable P to directly determine free-P in topsoils with most commercial soil testing laboratories being able to accommodate this for minimal additional cost.

There was some surface transport of particulate IMG in the top-dress experiment, mostly in the first year after application, but there was no corresponding increase in particulate P transport. This risk was assessed under intense rainfall conditions as the worse-case scenario. In paddock situations, particulate transport can be mitigated by allowing buffer zones around drainage lines, applying IMG only where there is sufficient grass cover or by timing application to ensure greatest soil contact time before the winter runoff period.

Adding IMG to soils increases Mn and SO_4 in runoff and leachates but not to an extent that poses a risk to aquatic ecosystems. Surface application of IMG also greatly limits the leaching losses of Mn from IMG as compared with other experiments where IMG is mixed with soil (Degens et al. 2022). Aquatic risks associated with Mn are mitigated by the high concentrations of Ca also leaching or washing from the IMG in the soils. This beneficial effect of Ca is also likely to limit Mn effects on pasture plants in acidic sands, with minimal additional Mn uptake measured in plants at the highest rate of IMG application (60 t/ha). However, further work is required to investigate whether sufficient Ca leaches with Mn into the future to continue mitigating against Mn toxicity. This is more relevant for top-dressed IMG because in this case Mn initially leaches slower than Ca and the leaching of Ca may be exhausted sooner than for Mn.

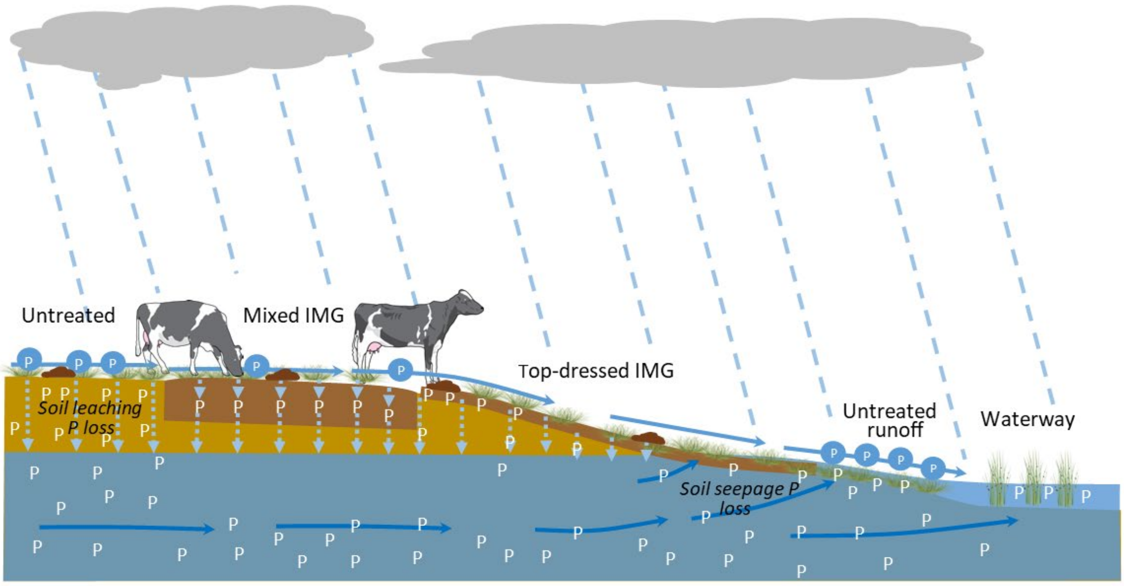


Figure 16: Conceptual model of P transport pathways and IMG's influence on these at the Mucca Dairy site

IMG treatment also increases SO_4^{2-} leaching but does not result in excessive uptake by plants. Increased leaching of Ca and SO_4 is expected to persist for more than five years, even at the lowest rate of IMG. The long-term trends and magnitudes of the leaching risks will be investigated in ongoing work.

IMG treatment of soils also slightly increased leaching of Co, Cd and Zn, but the hardness of the waters associated with co-leaching of Ca generally mitigated any potential aquatic risks. This assumes the extremely conservative scenario of undiluted discharge of leachate waters as groundwater to waterways. The increased Co in leachates most likely originated from the applied IMG whereas the Zn and Cd was mostly mobilised from the soils.

Other aspects of plant nutrition were not generally affected by IMG application, although the status of some major elements may need to be periodically checked. The high available Ca following IMG treatment may sometimes induce deficiencies in Mg or K in the first year or so, either by inhibiting plant uptake or accelerated leaching of these cations. Leaching of Mg was consistently increased with all rates of top-dressed IMG, whereas effects on the leaching of K were less consistent and smaller. The magnitude of these fluxes in the first year was within the bounds of what can be readily replaced with a single annual application of fertiliser containing K and Mg. Furthermore, this risk is expected to diminish rapidly over time as Ca leaching will decrease with the gypsum being washed out. Periodic soil (and occasional leaf tissue) analysis (for K and Mg) to monitor nutrient status will guide whether follow-up applications of K and Mg are necessary to avoid the risk of deficiencies developing.

Amending soils with IMG in the Peel region may not be cost-effective for farmers when considering the pure economics of on-farm P retention. However, when we look holistically, IMG is a cost-effective intervention when compared with alternative ways to remove P from downstream waterways. An initial cost-benefit analysis indicates that costs outweigh direct benefits to farmers by more than double when top-dressing with IMG at 20 t/ha. At present, the main on-farm benefit is the increased retention of P that would otherwise be sourced as fertiliser P, but this could extend to supply of S and improved pH in some soils. The value of other benefits may increase with time if there are improvements in soil organic C retention. The off-farm benefits of P retention may outweigh those on-farm, particularly in terms of the cost of removing P from water in drainage systems. IMG application costs to farms are largely determined by transportation but also depend on the sale price of IMG.

Further investigation into the effects of IMG on soil properties, plant uptake of nutrients, P loss and patterns of Mn, Co and SO_4 leaching will be carried out under the Healthy Estuaries WA program, alongside further trials in different soil and farm settings. These are aimed at building confidence among farmers and agronomists around the use of IMG as a soil amendment in pasture production systems.

Key conclusions from this study are:

- IMG treatment of low PBI soils saturated with P on farms is recommended to reduce P in runoff and leaching.
- Top-dressing pastures with IMG at 20 tonnes/ha is sufficient for immediate effects on P loss.
- Based on the cost-benefit to the farmer, widespread adoption of this practice would need to be managed and supported.
- Treating pastures to retain P in soils is much cheaper than treating downstream waters to remove P.

Appendices

Appendix A — Rainfall simulator design and operation

Runoff simulations were carried out on 1 m x 1 m randomly selected quadrants in each plot with delivery of water as an even spray of droplets from a mounted frame.

A steel barrier (100 mm x 1.2 mm x 3,000 mm) was gently hammered into the ground around each quadrant, forming a 20 mm high edge with a 90 mm deep subsurface barrier. Runoff from the quadrants was captured in an aluminium sill and channel that discharged into a sealed collection bottle. The collection sill consisted of 10 x 10 mm angle mounted on a 90 mm deep x 2 mm thickness aluminium plate with a 20 x 20 mm channel. This was installed with the sill at ground level on the quadrant side and the channel cut below ground-level outside the quadrant. During each assay, the water collected in the bottle was continuously pumped into a 20 L collection bucket using a peristaltic pump. A shelter was situated over the sill channel to stop direct inflow of simulated rain.

Rain was simulated using an FL-10 wide angle Full-Jet nozzle (TeeJet Technologies UWA) mounted on a frame 1.1 m above the quadrant. This height was tested to ensure maximum evenness of water delivery to saturate the soils evenly, although is below the height needed for droplets to reach terminal velocity to simulate rainfall erosion (Humphry et al. 2002). Water was delivered from a 100 L tank using a 12 V Flow Jet high-flow triplex pressure pump operating at 1 to 2 bar.

Water was applied using the sprayer for 5 to 15 minutes to saturate the soils and generate surface runoff. Runoff was collected for a 30-minute period and subsampled for analysis.

Soils were sampled from each quadrant within several hours of completing each assay. Composite samples of the 0–2 cm layer were taken as 16 cores on a 20 cm grid. Samples of the 0–10 cm layer were taken as nine cores on a 25 cm grid.

The setup was sheltered from any wind during the rainfall simulation using plywood panels.

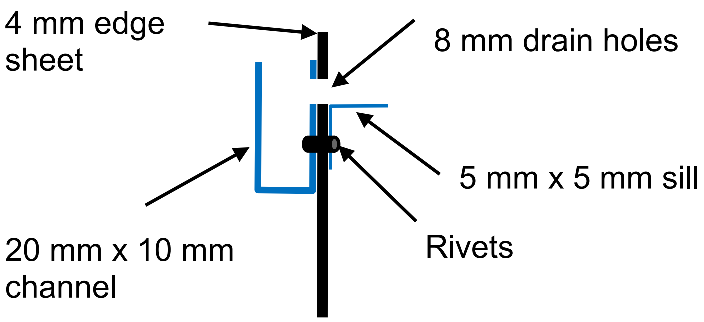


Figure A17: Collect channel design elements

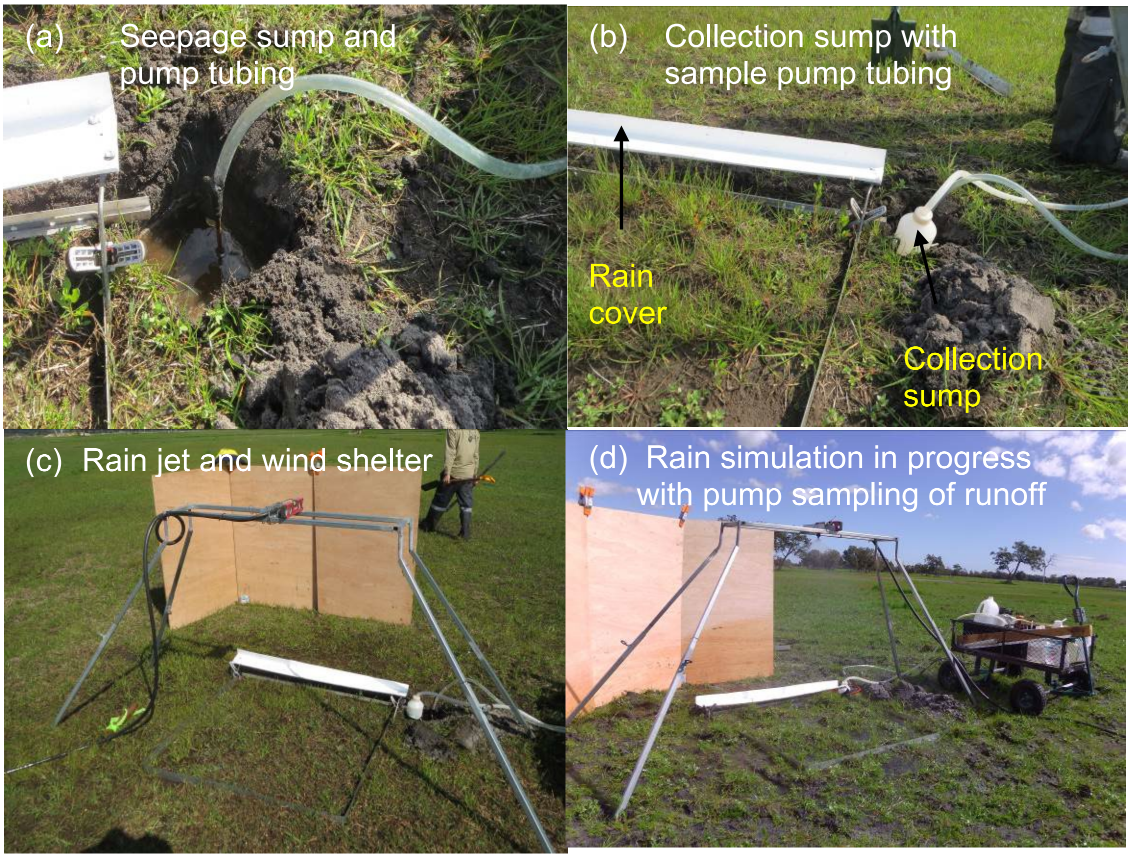


Figure A18: Assembly of small-quadrant simulated rainfall unit

Appendix B — Analysis specifications

Leachate water – analysis suite			
Property	**Method**	**Limit of resolution**	**Reference**
Physical properties	pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature, measured with a YSI probe	pH 0.01 EC 0.001 ms/cm DO 0.1% Temp 0.1°C	(APHA 1998)
Total P (TP)	Persulphate digestion and ascorbic acid colorimetric method (APHA method 4500-P, current)	0.005 mg/L	(APHA 1998)
Total N (TN)	Persulphate digestion and cadmium reduction method (APHA method 4500-N, current)	0.025 mg/L	(APHA 1998)
NH_3-N	Phenate colorimetric method (APHA method 4500-NH_3, current)	0.01 mg/L	(APHA 1998)
NO_x-N	Cadmium reduction and colorimetric method (APHA method 4500-NO_3-, current version)	0.01 mg/L	(APHA 1998)
Filterable reactive P (FRP = soluble P)	Ascorbic acid colorimetric method (APHA method 4500-P, current)	0.005 mg/L	(APHA 1998)
Dissolved organic N (DON)	By calculation from TN analysis on filtered sample	0.05 mg/L	(APHA 1998)
Total P – filtered (to calculated organic P)	Persulphate digestion and ascorbic acid colorimetric method (APHA method 4500-P, current)	0.005 mg/L	(APHA 1998)
Dissolved organic C (DOC)	APHA method 5310: inorganic carbon must be purged before analysis, hence volatile organic species will be lost. Report as non-purgeable organic carbon.	1 mg/L	(APHA 1998)
Anions (Cl, SO_4)	Ion chromatography or turbidimetric methods	Cl 1mg/L SO_4 1 mg/L	(APHA 1998)
Alkalinity	Titration	1 mg/L	(APHA 1998)

Leachate water – analysis suite			
Property	**Method**	**Limit of resolution**	**Reference**
Dissolved metals (Ca, Mg, Sr, Fe, Mn, K)	Digestion in nitric/hydrochloric mix with peroxide finish Analysis of digest by ICPAES – generally metals >1 mg/L Analysis of digest by ICPMS – metals <1 mg/L	Mg, Ca, K, Na – 1 mg/L	(APHA 1998)
Total metals (As, Ba, Bi, Co, Cr, Cd, Cu, Fe, Ga, Mn, Ni, Pb, Th, Ti, U, Zn)	Digestion in nitric/hydrochloric mix with peroxide finish. Analysis of digest by ICPMS – metals <1 mg/L (anhydride generation for As)	Fe, Mn, Ga, Sr, – 1 µg/L As, Ba, Bi, Cd, Cr, Co, Cu, Pb, Zn – 0.5 µg/L U, Th – 0.1 µg/L Bi, Cd – 0.05 µg/L	(APHA 1998)

* Note: Soluble P is determined as FRP

Soil sample – analysis suite			
Property	**Method**	**Limit of reporting**	**Reference**
pH	pH in 0.01 M $CaCl_2$ extract of air dried soil (<35ºC) with 1:5 soil:solution – method 4B41 pH in water with 1:5 soil:solution – method 4A1	Not applicable	(Rayment & Lyons 2011)
EC	ED in 1:5 deionised water extract of air dried soil with 1:5 soil:solution – method 3A1	0.01 dS/m	(Rayment & Lyons 2011)
PBI	Equilibration of air dried (<35ºC) soil with 100 mg/L P solution (1:10) with automated reactive P measurement – method 9I2a/b	1	(Rayment & Lyons 2011)
PRI	10 mg P/L solution in 0.02M KCl in a 1:20 soil:solution ratio with air dried (<35ºC) soil for 16 hours with analysis of P remaining in solution	Not applicable (units of mL/g)	(Rayment & Lyons 2011)
Colwell P (plant-available P)	0.5 M $NaHCO_3$ extraction (1:100) of air dried (<35ºC) soil with automated reactive P measurement – method 9B2	15 mg/kg	(Rayment & Lyons 2011)
$CaCl_2$-P	Method 9F2 – 0.01 M $CaCl_2$ extraction (1:5) with automated reactive P measurement	0.005 mg/kg	(Rayment & Lyons 2011)
KCl extractable S	Method 10D1 – 0.25 M KCl extraction (1:7) at 40ºC with SO4 measurement by ICPAES	0.5 mg/kg	(Rayment & Lyons 2011)
Colwell K	Method 18A1 – 0.5 M $NaHCO_3$ extraction (1:100) for 16 hours with automated reactive P measurement	1 mg/kg	(Rayment & Lyons 2011)
NH_4 and NO_3	Method 7C2b – 2M KCl extraction (1:10) at 25ºC for 1 hour with N measurement by automated colourimetric measurement	1 mg/kg	(Rayment & Lyons 2011)

Soil sample – analysis suite			
Property	**Method**	**Limit of reporting**	**Reference**
CEC with prewash	Method 15E1 – alcohol and glycerol prewash to remove soluble salts with 1 M NH_4Cl extraction (1:10) and cation determination by ICPMS	0.1 c $mole_c$/kg	(Rayment & Lyons 2011)
Total organic carbon	Combustion and infrared analysis, persulphate UV oxidation – method 6B3 OR Dichromate digestion and titration – method 6A1	0.05%	(Rayment & Lyons 2011)
Total P	Strong acid digestion (either Kjeldahl concentrated sulfuric or nitric) with analysis by ascorbic acid – method 9A3a	2 mg/kg	(Rayment & Lyons 2011)
Total S	High temperature combustion (by LECO or other analyser) of dried and finely ground soil – method 10A2	0.01 % (100 mg/kg)	(Rayment & Lyons 2011)
Total metals (Ca, Mn, Fe)	Strong acid digestion (aqua-regia – HNO_3 and HCl) of oven dried and finely ground soil with analysis of extracts by ICPMS (for high % elements) – method 17B1 (reverse Aqua regia) or method 17C1 (Aqua regia)	Ca, Fe – 50 mg/kg Mn – 5 mg/kg	(Rayment & Lyons 2011)
Total metals (Sr, Pb, Cd etc)	Strong acid digestion (aqua-regia – HNO_3 and HCl) of oven dried and finely ground soil with analysis of extracts by ICPAES (for lower % elements) – method 17B1 (reverse Aqua regia) or method 17C1 (Aqua regia)	Sr – 0.1 mg/kg Cd – 0.05 mg/kg	(Rayment & Lyons 2011)

Plant sample – analysis suite			
Property	**Method**	**Limit of reporting**	**Reference**
Total C, N	High temperature combustion (by LECO or other analyser)	0.01 %	(McQuaker et al. 1979)
Total P, K, S, Cu, Zn, Mg, Mn, Ca, Mn, Na, Fe, B	Digestion by H_2O_2 and nitric acid of dried ground samples with digestate analysed by ICP spectroscopy (ICPOES)	0.01 %	(McQuaker et al. 1979)
Total Cd, Mo, Co, Se, Pb, Cu, Ar, Ni, U, Th + other trace elements	Digestion by H_2O_2 and nitric acid of dried ground samples with digestate analysed by ICP-MS	0.01 mg/kg	(McQuaker et al. 1979)

Appendix C — Lysimeter design and sampling

Zero-tension lysimeters were used to collect water percolating from topsoils during winter and spring in two experiments. While this design can sometimes fail to capture all recharge, research shows that this does not influence the concentrations of leachates (Peters & Durner 2009). Furthermore, installation of the pan immediately beneath the soil surface with increased surface area can minimise these losses (Jemison & Fox 1992).

Each lysimeter was a shallow circular PVC collection pan with a conical base draining via plastic tubing to a 20 L polycarbonate drum beneath the pan (Figure A19). The drums were fitted with sampling tubes (held in the base of the drums with a Teflon coated weight) and an air return tube, that allowed air to exit as water entered the inlet tube. Collection and air return tubes (4 mm ID black polythene) were used for faster sample pumping.

Previous research suggests that lysimeters are prone to lateral losses of unsaturated flows but that side walls can minimise this effect (Gee et al. 2002). For annual leachate volumes of >100 mm/yr, side walls of at least 5 cm on the collection pan can reduce losses to <10% (Gee et al. 2002). For the top-dress experiment, 31.5-cm-diameter pans with a 5 cm side wall were used creating a catch area of 779 cm^2. Each collection pan was filled with medium-grained washed white sand to facilitate free drainage of water from the soil to the drain tube. A fine nylon mesh was used to stop the sand washing into the tubing.

Each lysimeter was installed by digging a ~0.6 m pit with an adjacent bench of ~0.4 m with the pans installed beneath undisturbed soil. The top of each pan was specifically set below the soil layer of interest and seated on bricks with soil firmly packed around these to prevent settling. Once the pan was in place, the collection drum was seated in a deeper hole offset from the pan to ensure water would flow freely into the drum from the pan. The drum was set at an angle with the sampling tubes (weighed down with a Teflon-coated sleeve) placed inside at the lowest corner of the drum. Soil was placed back around the drum (in the same layers as the surrounding profile) and compacted.

The sample and air tubes were fed to the surface, housed in 90 mm diameter PVC tubes and protected from cattle or machine damage using a cast steel well cover (265 mm OD FB series). To prevent insect contamination, the air tubes were capped with aquarium bubbler stones and the sample tubes were capped with coarse syringe filters.

Leachate collected in the drums was pumped using a hand-vacuum extraction pump (6.5 L Alemlube pump) every four to five weeks depending on rainfall. The first part of each sample was used to rinse the pump with all volume collected and measured to the nearest 50 mL. The collection pump was rinsed with deionised water between each sampling.

Leachate volume is measured as mL and recorded as millimetres leachate (on an area basis) using the conversion * 0.0128 (being volume/31.5).

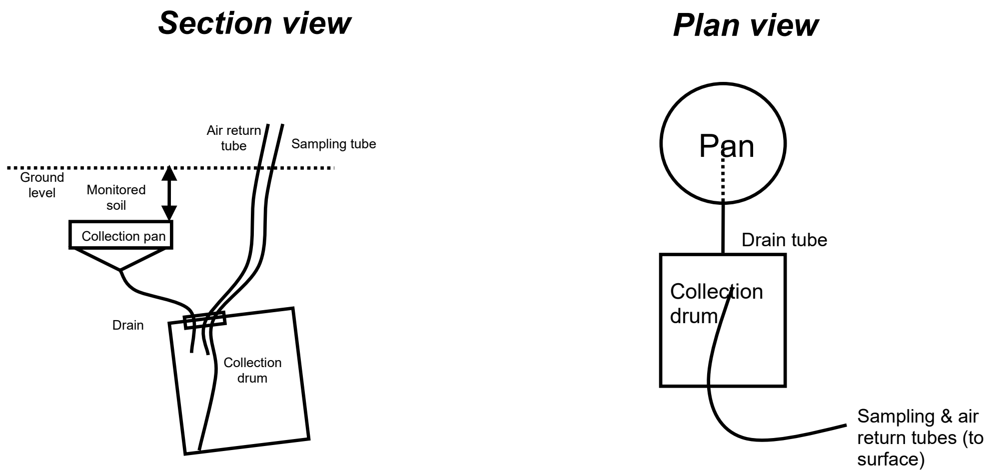


Figure A19: Lysimeter design and installation plan

Appendix D — Stability of nutrient fractions in lysimeter samples

The stability of nutrients in leachates collected by the lysimeters was investigated to determine whether there was significant change in totals or fractions with storage. Lysimeter leachates were collected at semi-regular intervals, with sample waters remaining in the drums for up to four weeks before collection.

The effect of longer residence times was tested by storage and repeat analysis of randomly selected samples for up to 18 weeks. Excess water from sampling of five lysimeters was collected, transferred to archive 1 L containers, then stored in the field under conditions to replicate the lysimeter drums (in a tub beneath the soil surface) and sampled at varying intervals for up to 18 weeks. The storage conditions were intended to replicate the same soil temperatures and darkness to which the leachate samples in the lysimeter drums were subject.

TP and soluble P gradually increased on average 0.06 mg/L with storage times up to 12 weeks (Figure A20). Microbial activity in the stored samples would be expected to decrease TP, particularly with biofilm growth inside the bottles that would not be retrieved during sampling. The increase in TP in most samples is attributed to a sub-sampling error (with fine colloidal particulates in the samples) rather than any increase in P with the absence of an external source. Gradual increases in soluble P may reflect mineralisation of organic fine particulate P or organic P from heterotrophic microbial activity in the samples. The mineralisation of P from organic forms is likely to vary depending on the amounts of available P relative to P in the organic matter on which the microbes are growing.

In contrast with P, total N consistently decreased in the stored samples by average of 2 mg/L (Figure A20). Changes in the concentrations in most samples were gradual over the storage time, rather than being confined to the first few weeks or increasing with time. Most of the decrease in TN is primarily reflected in declining DON (Figure A20) and particulate N. There were inconsistent variations in inorganic N (NH_4 and NOx) despite large differences in the initial concentrations (Figure A20). As with P, this was most likely due to heterotrophic microbial growth on organic C in the samples. Microbial growth on particulate and dissolved organic N contributed to increased adhesion of this to the walls of the sample containers, removing this from the bulk samples. Loss of N as denitrification was unlikely with the initial DO of the collected samples being > 5.5 mg/L. Similarly, loss of NH_4 as NH_3 gas was unlikely because sample pH values were < 6.5, which is well below pH > 8 where this is likely to occur (because NH_3 makes up more than 10% of this form of N in solution).

These results indicate that nutrient concentrations are likely to change gradually in lysimeter drums but the average magnitude of this is limited for sampling intervals of less than four weeks and influences N more than P.

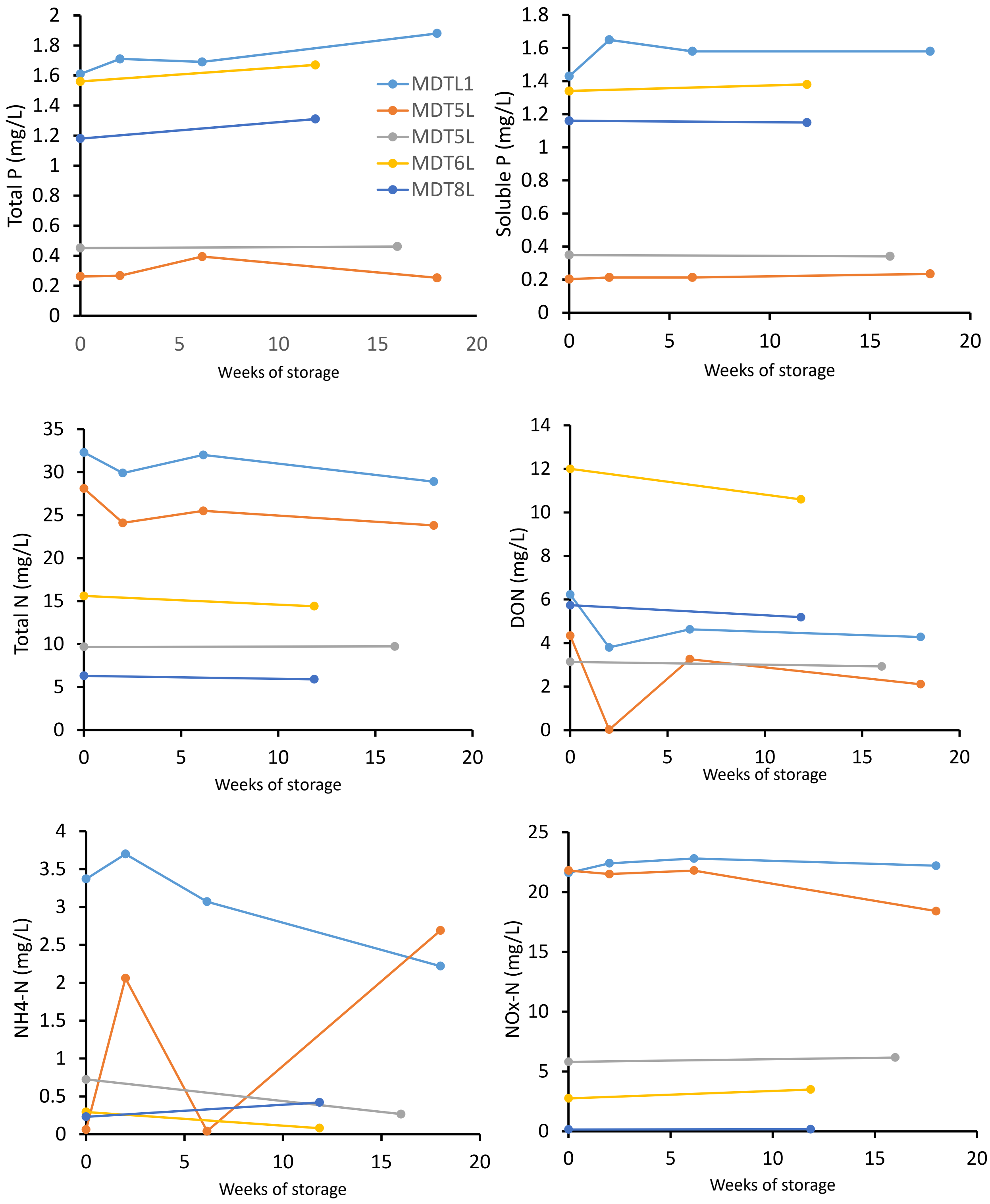


Figure A20: Trends in total and forms of N and P in soil leachate samples with storage under field conditions.

Appendix E — Element and bulk property analysis of Iron Man Gypsum

Table A20: Major element analysis (corrected to 39% moisture content) and major properties of IMG used in this experiment with summary analysis of collated independent samples from multiple bulk analyses and published sources

Element[1]/ property	Mucca Dairy Bulk IMG[2]	Average	Minimum	Maximum	Number samples/ reports[3]	Analysis methods
Ca	10.1	11.3	9.3	13.0	8	XRF, Digestion & ICPMS
Fe	7.5	10.0	7.0	14.1	8	XRF, Digestion & ICPMS
S	9.1	9.1	8.0	10.2	8	XRF, Digestion & ICPMS
Mn	1.9	2.0	1.5	2.4	8	XRF, Digestion & ICPMS
Mg	0.5	0.6	0.5	0.8	8	XRF, Digestion & ICPMS
Ti	0.1	0.4	0.1	1.3	8	XRF, Digestion & ICPMS
pH	8.1	8.1	7.7	8.4	6	1:5 in 0.01M $CaCl_2$
Neutralising value (bulk)[4]	4.8	4.8	3.5	7.0	5	HCl digestion
PBI	840	879	828	970	3	PBI-Colwell correction
PRI	>1000	>1000	>1000	>1000	3	

[1] Element contents are % by weight corrected to median moisture content of 39% for received bulk samples.

[2] Composite sample of 20 cores taken from bulk IMG delivered to experiment site.

[3] Combined published and DWER analysis data. Published data from Degens and Shackleton (2016), Douglas et al. (2012), Sharma et al. (2018) and Wendling et al. (2012). DWER analysis data from four truckload batches used for field experiments over four years.

[4] Bulk neutralising value (as % equivalent $CaCO_3$) based on analysis of an unsieved whole sample. A particle size weighted neutralising value is less than this with >47% of dry sieved IMG being >1 mm.

Table A21: Minor element analysis (as ppm corrected to 39% moisture content) of IMG used in this experiment with summary analysis of collated independent samples from multiple bulk analyses and published sources

Element[1]	Mucca Dairy Bulk IMG[2]	Average	Minimum	Maximum	Number samples/ reports[3]	Analysis methods
Ag	<2	< 2	< 2	< 2	2	XRF
As	5.3	5.8	3.6	7.2	9	XRF, Digestion & ICPMS
B	NA[4]	11.5	–	–	1	Digest
Ba	15	26	14	47	9	XRF, Digestion & ICPMS
Bi	<0.1	1.7	< 0.1	5.0	6	XRF, Digestion & ICPMS
Br	<0.1	1.5	< 1	8.6	3	XRF
Cd	0.07	0.5	< 0.04	0.7	7	XRF, Digestion & ICPMS
Ce	NA	103	68	116	4	XRF
Co	216	156	112	262	9	XRF, Digestion & ICPMS
Cr	56	67	56	87	9	XRF, Digestion & ICPMS
Cs	NA	4.0	< 1	9.3	4	XRF
Cu	15	19	14	32	9	XRF, Digestion & ICPMS
Ga	14	15	12	19	8	XRF, Digestion & ICPMS
Ge	NA	< 1	–	–	2	XRF
Hf	NA	< 7	–	–	2	XRF
I	NA	< 7	–	–	2	XRF
K	NA	551	420	775	4	XRF
La	NA	34	24	45	5	XRF, Digestion & ICPMS
Mo	NA	1.8	<0.5	1.4	3	XRF, Digestion & ICPMS
Na	NA	1140	539	2210	4	XRF
Nb	NA	19	12	38	4	XRF
Nd	NA	34	24	52	3	XRF
Ni	59	47	34	65	9	XRF, Digestion & ICPMS
P	NA	976	270	3700	4	XRF
Pb	34	25	5.7	58	9	XRF, Digestion & ICPMS
Rb	NA	7	7	7	2	XRF

Element[1]	Mucca Dairy Bulk IMG[2]	Average	Minimum	Maximum	Number samples/ reports[3]	Analysis methods
Sb	NA	8	2.9	11	3	XRF, Digestion & ICPMS
Sc	NA	< 4	< 4	< 4	2	XRF
Se	0.2	0.9	< 0.2	3.6	7	XRF, Digestion & ICPMS
Sm	NA	< 10	< 10	16	2	XRF
Sn	NA	2.6	< 0.5	5.0	3	XRF, Digestion & ICPMS
Sr	701	644	521	754	8	XRF, Digestion & ICPMS
Ta	NA	< 6	< 6	< 6	2	XRF
Te	NA	< 6	< 6	< 6	2	XRF
Th	79	84	70	110	2	XRF
Tl	NA	7.1	5.7	8.6	2	XRF
U	3.7	7.8	3.7	11.5	8	XRF, Digestion & ICPMS
V	NA	58	36	75	3	XRF, Digestion & ICPMS
Y	NA	13	12	14	2	XRF
Yb	NA	< 9	< 9	< 9	2	XRF
Zn	26	29	20	49	9	XRF, Digestion & ICPMS
Zr	NA	36	11	106	4	XRF

[1] Element contents are % by weight corrected to median moisture content of 39% for received bulk samples.

[2] Composite sample of 20 cores taken from bulk IMG delivered to experiment site.

[3] Combined published and DWER analysis data. Published data from Degens and Shackleton (2016), Douglas et al. (2012), Sharma et al. (2018) and Wendling et al. (2012). DWER analysis data from four truckload batches used for field experiments over four years.

[4] NA = not analysed.

Appendix F — Plant tissue analysis

Table A22: Summary nutrient and element concentrations in Balansa clover tops (early Oct. 2018)

Treatment	N	P	K	S	Ca	Mg	Cu	Zn	Mn	Fe	Co	Mo
	%						mg/kg					
No IMG (untilled)	4.0a[1]	0.50a	2.8a	0.36a	1.7a	0.29a	6.2a	45a	42a	96a	0.12a	1.1a
No IMG (tilled)	3.8a	0.44a	2.2a	0.39a	1.5a	0.30a	5.8a	48a	42a	97a	0.12a	0.8a
20t/ha	3.8a	0.43a	2.9a	0.43a	1.6a	0.30a	6.5a	44a	56a	104a	0.21b	0.9a
60t/ha	3.4a	0.38a	2.5a	0.56b	1.8a	0.32a	6.2a	46a	137b	117a	0.42c	1.0a
Adequate range[2]	2.2–3.0	0.3–0.5	2.0–4.0	0.22–0.51	1.0–2.0	0.25–0.7	5–30	25–70	60–498	50–60	NA	0.5–1.0
Toxic range[2]	>5	NA	NA	NA	NA	NA	NA	NA	>1330	NA	NA	NA

[1] Average values (of three replicates) followed by the same letters are not statistically different (P>0.05).

[2] Adequate and toxic concentration range of whole plant tops at flowering for *Trifolium balansae* (now *Trifolium michelianum*) for K, S and Mn; all other values estimated from *Trifolium subterraneum* or *Trifolium repens* (Reuter & Robinson 1997).

Table A23: Summary nutrient and element concentrations in Abundant ryegrass tops (mid-Oct 2018)

Treatment	N	P	K	S	Ca	Mg	Cu	Zn	Mn	Fe	Co	Mo
	%						mg/kg					
No IMG (untilled)	3.8a[1]	0.48a	3.13a	0.37a	0.42a	0.19a	8.0a	47a	42a	71a	0.05a	2.1a
No IMG (tilled)	3.6a	0.45a	3.15a	0.39a	0.39a	0.19a	7.4a	43a	42a	76a	0.05a	2.2a
20t/ha	3.5a	0.46a	3.23a	0.41ab	0.40a	0.17a	7.8a	39a	82b	78a	0.17b	1.8a
60t/ha	3.9a	0.39a	3.23a	0.44b	0.43a	0.18a	7.8a	39a	120c	82a	0.23b	1.5a
Adequate range[2]	3.0–4.2	0.35–0.5	2.0–3.2	0.24–0.41	0.25–0.3	0.16–0.5	6–15	25–150	25–250	50–60	NA	0.15–0.5
Toxic range[2]	NA	NA	NA	NA	NA	NA	NA	>400	>1330	NA	NA	>60

[1] Average values (of three replicates) followed by the same letters are not statistically different ($P>0.05$)

[2] Adequate and toxic concentration range of whole plant tops for *Lolium multiflorum* (Italian ryegrass) for Mn, K, Cu and Zn (Reuter & Robinson 1997; McDonnell et al. 2018); all other values estimated from *Lolium perenne* (perennial ryegrass) (Reuter & Robinson 1997; Rosas et al. 2007). NA = not known.

Table A24: Summary nutrient and element concentrations in Abundant ryegrass tops (mid-Oct 2019)

Soil-hydrology zone and treatment		N	P	K	S	Ca	Mg	Cu	Zn	Mn	Fe	Co	Mo
		%						mg/kg					
Wet depressions	No IMG (untilled)	4.2a	0.60cd	4.40bc	0.42a	0.39ab	0.18a	9.4a	42a	48a	87a	0.04a	1.97
	No IMG (tilled)	4.0a	0.61d	4.68c	0.47a	0.31a	0.19a	8.8a	36a	58ab	89a	0.03a	2.24
	20t/ha	4.1a	0.60cd	4.43bc	0.45a	0.41abc	0.18a	8.3a	34a	88bc	101a	0.13b	1.15
	60t/ha	3.4a	0.43b	4.21a	0.41a	0.42abc	0.14a	6.4a	27a	111c	81a	0.18c	0.87
Dry rises	No IMG (untilled)	4.0a	0.51bc	3.35ab	0.41a	0.50bc	0.19a	9.3a	45a	59ab	89a	0.04a	1.39
	No IMG (tilled)	3.7a	0.58cd	3.66abc	0.43a	0.48a	0.18a	8.1a	39a	64ab	83a	0.03a	1.70
	20t/ha	4.0a	0.46b	3.77a	0.44a	0.50bc	0.18a	8.2a	38a	89bc	97a	0.11b	0.81
	60t/ha	3.6a	0.34a	3.13a	0.50a	0.59c	0.15a	7.9a	34a	115c	88a	0.13b	0.86
Adequate range[2]		3.0–4.2	0.35–0.5	2.0–3.2	0.24–0.41	0.25–0.3	0.16–0.5	6–15	25–150	25–250	50–60	NA	0.15–0.5
Toxic range[2]		NA	NA	NA	NA	NA	NA	NA	>400	>1330	NA	NA	>60

[1] Average values (of three replicates) followed by the same letters are not statistically different (P>0.05).

[2] Adequate and toxic concentration range as per Table A23.

Appendix G — Temporal patterns of nutrients in leachates from the Mucca Dairy top-dress experiment

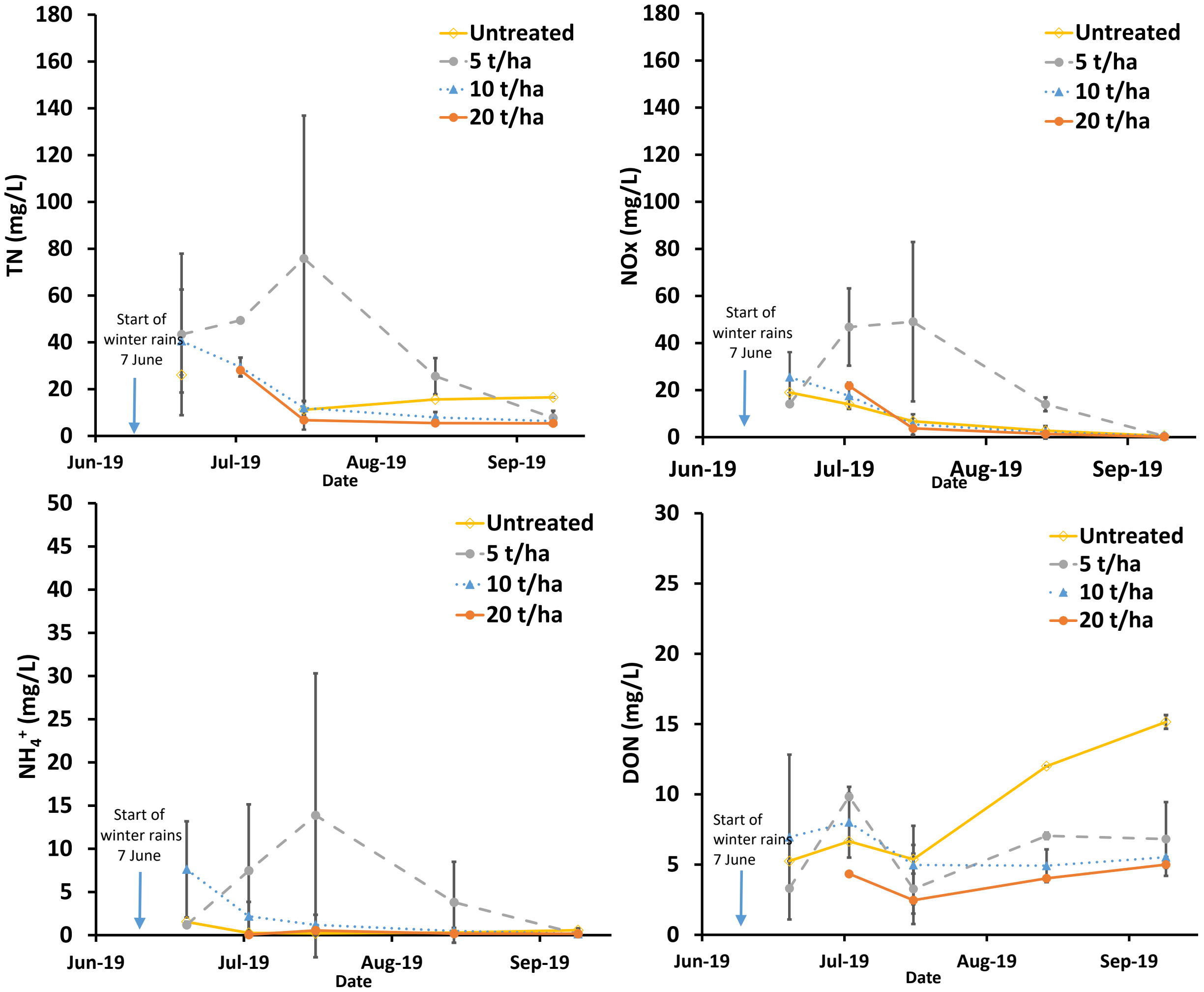


Figure A21: Total nitrogen (TN) and the dissolved N fractions – nitrate and nitrite (NO_x), ammonia (NH_4^+) and dissolved organic N (DON) in leachates from soils with different rates of top-dressed IMG (error bars represent standard deviation of two field replicates)

Appendix H — Concentrations of selected elements leached from soils in the Mucca Dairy top-dress experiment

Table A25: Summary pH, Cl, K and Mg concentrations (mean ± standard deviation) in soil leachates

Treatment	pH		Cl (mg/L)		K (mg/L)		Mg (mg/L)	
Untreated	5.81	±0.61	27	±18	9	±8 a*	4	±2 a
5 t/ha	4.76	±0.70	108	±172	18	±13 a	41	±24 b
10 t/ha	5.12	±0.62	23	±24	9	±11 a	35	±23 b
20 t/ha	5.49	±0.59	11	±15	15	±13 a	44	±13 b

* Means followed by the same letter are not significantly different ($P<0.05$)

Table A26: Summary average volume-weighted Mn, SO_4 and hardness concentrations (mean ± standard deviation) in soil leachates

Treatment	Total Mn (as mg/L)		SO_4 (as mg/L)		Hardness (as mg $CaCO_3$/L)	
Untreated	0.07	±0.05	17	±6	91	±26
5 t/ha	1.37	±1.45	493	±121	597	±164
10 t/ha	1.07	±0.24	797	±201	885	±223
20 t/ha	1.57	±0.54	1310	±36	1614	±117

Appendix I — Correlations of leachate element, pH and DOC concentrations

Table A27: Matrix of correlation coefficients (r) for pH, leachate element and DOC concentrations

	DOC	*Cl*	*Ca (sol)*[1]	*Mg*[1] *(sol)*	*Fe (sol)*	*As (tot)*	*Cd (tot)*	*Cr (tot)*	*Co (tot)*	*Cu (tot)*	*Fe (tot)*	*Pb (tot)*	*Mn (tot)*	*Ni (tot)*	*Th (tot)*	*U (tot)*	*Zn (tot)*	*pH*	*SO_4*
DOC	1.00																		
Cl	0.21	1.00																	
Ca (sol)	-0.51*	0.09	1.00																
Mg (sol)	-0.19	0.58	0.75	1.00															
Fe (sol)	0.87	0.08	-0.59	-0.42	1.00														
As (tot)	0.31	0.21	0.37	0.47	0.14	1.00													
Cd (tot)	-0.14	0.76	0.49	0.75	-0.27	0.07	1.00												
Cr (tot)	0.76	0.22	-0.29	-0.10	0.76	0.20	-0.05	1.00											
Co (tot)	-0.20	0.37	0.58	0.67	-0.29	0.20	0.72	-0.12	1.00										
Cu (tot)	0.89	-0.02	-0.51	-0.34	0.74	0.31	-0.30	0.51	-0.28	1.00									
Fe (tot)	0.87	0.06	-0.59	-0.41	1.00	0.16	-0.28	0.78	-0.27	0.75	1.00								
Pb (tot)	0.39	0.26	-0.35	-0.05	0.34	-0.26	0.18	0.43	0.06	0.16	0.34	1.00							
Mn (tot)	-0.11	0.69	0.59	0.85	-0.26	0.35	0.80	0.11	0.69	-0.32	-0.24	0.12	1.00						
Ni (tot)	0.68	0.59	-0.01	0.38	0.52	0.28	0.50	0.54	0.44	0.47	0.52	0.39	0.38	1.00					
Th (tot)	0.75	0.48	-0.37	0.02	0.78	0.24	0.13	0.79	0.03	0.46	0.78	0.50	0.19	0.66	1.00				
U (tot)	0.94	0.03	-0.62	-0.42	0.93	0.15	-0.31	0.78	-0.33	0.86	0.93	0.38	-0.29	0.53	0.70	1.00			
Zn (tot)	-0.47	0.16	0.85	0.67	-0.58	0.17	0.65	-0.37	0.73	-0.42	-0.58	-0.21	0.62	0.10	-0.39	-0.60	1.00		
pH	-0.17	-0.43	-0.05	-0.29	-0.13	0.01	-0.47	-0.52	-0.33	0.15	-0.15	-0.39	-0.51	-0.35	-0.52	-0.14	0.00	1.00	
SO_4	-0.52	0.11	0.99	0.80	-0.63	0.40	0.49	-0.31	0.58	-0.54	-0.62	-0.34	0.61	-0.01	-0.37	-0.64	0.81	-0.07	1.00

[1] Sol = soluble element concentration, Tot = total element concentration.

[2] Note: Some elements such as soluble K, Mn and Sr and total Ba, Bi and Ti were not included for brevity.

* r >0.5 or <-0.5 are highlighted. All values >0.38 or <-0.38 are significant at P <0.05.

Shortened forms

ANOVA	Analysis of variance
$CaCl_2$-P	Calcium chloride extractable phosphorus
CEC	Cation exchange capacity
FRP	Filterable reactive phosphorus
IMG	Iron Man Gypsum
meq	Milli-equivalent
PBI	Phosphorus buffering index
PERI	Phosphorus environmental risk index
PRI	Phosphorus retention index
TN	Total nitrogen
TP	Total phosphorus
XRF	X-ray fluorescence

Glossary

ANOVA	Analysis of variance, being a statistical approach to partitioning variation due to different causes (factors) and testing whether these are by chance.
$CaCl_2$-P	Measurement of P in free-P in soils (generally ortho-phosphate P), obtained using a weak salt extract (0.01 M $CaCl_2$). This is also an indicator of soil-water P.
Cation exchange capacity	Cation exchange capacity, being a measure of the amounts of common positive ions (usually calcium, sodium, potassium and magnesium) that a soil can hold on clays, organic matter and iron oxides.
Colwell P	Measurement of plant-available P obtained by extraction with a bicarbonate solution.
Flux	Mass movement (as leachates in this report) per unit area per unit time (generally kg/ha/yr in this report).
FRP	Filterable reactive P which is the concentration of ortho-phosphate measured after filtering through a 0.45 um membrane. This is an indicator of phosphate-P concentration.
Iron Man Gypsum	The product name for a material rich in gypsum and iron oxide which is a secondary product of titanium refining at Iluka's plant in Capel.
meq	Milli-equivalent being the equivalent moles of positive or negative charge
Soluble P	Plain language term for phosphorus technically known as filterable reactive phosphorus (FRP). This is phosphorus determined as the reactive phosphorus (orthophosphate-P) in water after filtering through a 0.45 μm filter membrane.
Phosphorus buffering index	A measure of the inherent P-adsorption capacity of soils, prior to any fertiliser P application.
pH_{CaCl2}	Soil pH measured in a solution of 0.01M$CaCl_2$ extracted from soil.
Phosphorus environmental risk index	An indicator of potential risk of soil P loss (under leaching or runoff conditions) derived as Colwell P/PBI.
Phosphorus retention index	A measure of the capacity of soil to adsorb further P reflecting the residual P-adsorption capacity of soils. Values < 0 indicate no capacity to retain P, values > 0 indicate capacity to retain P.

Total nitrogen	The mass concentration of all forms of elemental N (organic and inorganic) in soil or water.
Total phosphorus	The mass concentration of all forms of elemental P (organic and inorganic) in soil or water.

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