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Investigation of the Mineral-Based By-Product NUA as a Soil Amendment: Results from the Bullsbrook Turf Farm Trial Extension 2008-2009

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Cover Photograph:

Description: Turf regrowth in sites amended with the heavy minerals processing residue NUA (neutralised used acid), April 2010. Photographer: Laura Wendling © 2010 CSIRO

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EXECUTIVE SUMMARY

Between 2005 and 2008, CSIRO conducted a 1,357-day field trial comparing soils amended with neutralized used acid (NUA) to untreated (control) soils at the Bullsbrook Turf Farm, Western Australia. Results from this trial indicated that NUA was a promising material to reduce nutrient and trace element leaching and to increase solute retention within the sandy soils on the Swan Coastal Plain. Phosphate P (PO₄-P) and total nitrogen (TN) in leachates from NUA-amended turf sites were reduced by 97% and 82%, respectively, relative to control sites.

Given the promising results obtained during the original field trial, a trial extension was undertaken to further investigate the efficacy of NUA as a turf farm soil amendment under a modified fertilisation regime. The hypothesis tested was that P, N and micronutrients retained by NUA in the original trial would be bio-available and continue to sustain turf growth in the absence of additional fertiliser inputs. The trial extension design and major findings are outlined below.

Following the original Bullsbrook Turf Farm field trial, control and NUA-amended experimental sites were further subdivided, resulting in two control and two NUA-amended experimental sites. One each of the control and NUA-amended sites received normal fertiliser applications as determined by the turf farm manager for the duration of the trial extension, whereas the remaining control and NUA-amended sites did not receive any additional fertiliser.

The duration of the trial extension at the Bullsbrook site was 206 days or nearly seven months, bringing the cumulative monitoring of the Bullsbrook Turf Farm field trial site to 1,563 days, or approximately 4.3 years. The Bullsbrook trial extension was terminated after seven months when lysimeter data indicated that both of the unfertilised control and amended sites had inadvertently been fertilised with N and P (possibly due to application of a fertiliser or foliar sprays) on at least one occasion on or prior to day 1,563.

Due to persistently dry conditions over the summer of 2008/2009, difficulty was experienced in collection of three replicate lysimeter samples each from the control fertilised, control unfertilised, NUA-amended fertilised and control unfertilised sites. Little or, no lysimeter leachate (volume of leachate collected between each sampling period), was collected for much of the trial extension. Additionally, persistent dry conditions resulted in patchiness in turf (re)growth within amended, and to a greater extent, the control sites. Soil moisture contents were also extremely variable, and thus monitoring of soil moisture was abandoned early during the trial extension.

The greatest nutrient fluxes to the shallow groundwater during the Bullsbrook Turf Farm trial extension occurred within the control sites whether fertilised or unfertilised, with rates for both N and P species often substantially greater than occurred in the original trial. The NUA-amended sites, in contrast to the control sites, had the lowest nutrient flux from the fertilised site. The continuing low nutrient flux from the NUA-amended fertilised site indicates a continuing uptake of nutrients by the NUA-amended soils, even after more than three prior years under turf cultivation.

The total lysimeter leachate flux, although low compared to the original trial, was consistently greater in the control fertilised and control unfertilised sites relative to both NUA-amended sites. Average lysimeter leachate pH varied widely for the four treatment sites but displayed a similar range to the earlier long-term field trial. The amended unfertilised and amended fertilised sites had a pH of 7-8, while corresponding control unfertilised and control fertilised sites were typically 2-4 pH units lower.

The EC of lysimeter leachates for the control fertilised and amended fertilised sites were similar to the long-running average EC from the original Bullsbrook field trial while control unfertilised and amended unfertilised EC values were considerably lower. As within the original Bullsbrook field trial, average major ion concentrations in leachates followed EC with varying fidelity. In general Na, and to a lesser extent Cl, and total alkalinity, most closely resembled the temporal EC profile, with these three ions constituting the majority of the leachate anion composition.

Geochemical analyses of lysimeter leachates indicated that the majority of both amended fertilised and amended unfertilised lysimeter leachates had compositions reflecting locally-derived irrigation water and the Ca-SO₄-rich leachate composition of NUA. A few samples also resembled an average Perth rainwater composition indicating that it may have occasionally constituted the dominant lysimeter leachate. The majority of control fertilised site lysimeter leachate samples formed a mixing array reflecting the average irrigation water composition and that of both of the amended sites. This indicated that either some surface runoff or subsurface groundwater mixing between the two sites and/or the dissolution of gypsum or other Ca- and SO₄-bearing phases within fertilisers applied to the control fertilised site had occurred.

Average dissolved P concentrations in the Bullsbrook trial extension varied considerably between the four experimental sites. The dissolved P concentrations in the amended fertilised leachates was typically <0.2 mg/L, similar to that of the original field trial. Dissolved P concentrations in the control unfertilised and amended unfertilised leachates were generally <2 mg/L, and intermediate in concentration between the two fertilised sites. The control fertilised site had the highest single leachate P concentration of 68 mg/L, whereas the concentration in the corresponding amended fertilised site was only *ca.* 4 mg/L. Mean NH₃-N, NO₃-N and TKN concentrations were generally similar to the majority of the original Bullsbrook field trial for all four experimental sites.

Geochemical analyses, modelling and petrography identified two principal mechanisms for P uptake and retention by NUA-amended soil: surface adsorption or co-precipitation of P to form hydroxyapatite ($Ca_5(PO_4)_3OH$), and surface adsorption or co-precipitation onto the abundant Fe oxides/hydroxides which constituted a major mineralogical constituent of the NUA.

Based on an incorporation rate of 5% NUA in the NUA-amended soils, and a phosphorus retention index (PRI) of approximately 25, the PRI for the NUA alone was estimated to be 500. Long-term conditions, however, including the rate of irrigation, and hence gypsum dissolution, will strongly influence the ultimate PRI, and hence P uptake capacity.

Rates of turf regrowth at the Bullsbrook Turf Farm during the trial extension generally followed the trend: fertilised amended > unfertilised amended >> fertilised control > unfertilised control. This indicated that nutrients and trace elements accumulated from previous cultivation, or complimentary factors such as the increased water-holding capacity of the NUA-amended soils, and additional fertiliser applications had a substantial influence on turf regrowth. In contrast to the trend observed in rates of regrowth, there was little difference between the biomass of harvested turf sites except for the unfertilised control turf sites which had substantially less biomass. Turf height prior to harvest was substantially greater for both the fertilised amended and control sites relative to their unfertilised equivalents.

1. INTRODUCTION

Extremely promising results were achieved in terms of nutrient (both N and P species) and trace element retention and turf regrowth after harvest following incorporation of NUA (neutralised used acid) as an approximately 5% (w/w) blend to Swan Coastal Plain surface soils at the Bullsbrook Turf Farm during a trial between 2005 and 2008 (Douglas et al., 2010). At the recommendation of CSIRO, an extension of this original three year trial was commissioned by Iluka Resources, Ltd. The trial extension was undertaken to further investigate the efficacy of NUA as a potential turf farm soil amendment. This report constitutes a collation and synthesis of findings during this trial extension.

As a background to the report on this trial extension a summary of both the original Bullsbrook turf trial (Section 1.1) and the trial extension (Section 1.2), and an amended scope of work (Section 1.2.2) are presented below. The full report on the original trial is also available (Douglas et al., 2010).

1.1. Original (2005-2008) project motivation and background

Leaching of applied nutrients, particularly P, presents a major problem in the largely unretentive soils in coastal regions of South West Western Australia. In an attempt to redress this problem the application of a by-product generated from heavy mineral processing, NUA, is being trialled. This Fe-rich residue has a high P sorption capacity, and thus if incorporated into the upper layers of unretentive soils has the potential to ameliorate many of the problems of P leaching. Neutralised used acid is generated during the production of synthetic rutile from ilmenite where sulfuric acid is used to leach impurities from the reduced ilmenite. The spent acid is then neutralised with quicklime to form NUA. The main chemical reaction involved in the generation of NUA is:

 $2Fe^{3+} + 3SO_4^{2-} + 3CaO + 3H_2O \rightarrow 2FeOOH + 3CaSO_4.2H_2O$

which forms an intimate mixture of Fe-oxyhydroxides (and related Fe-minerals) and gypsum. A substantial quantity of Mn present within the system also precipitates upon neutralization, but at a lower pH than other minerals in the system. The synthetic rutile industry generates significant quantities of NUA which is normally disposed of in lined storage systems.

The high P sorption capacity of NUA may be useful in situations where fertilisers are used extensively on soils which are largely unretentive for P (e.g. Ellen Brook, Peel/Harvey catchments) to prevent or diminish the rate of nutrient export to adjacent waterways. Prior investigations **MERIWA** Projects M122, M208, M344 (e.g. M230 and www.doir.wa.gov.au/meriwa; Douglas et al., 2010) and other industry research have demonstrated that NUA has potential value as a soil conditioner and P sorbent. However, the stability of the nutrient (P) fixation over time and trace element mobility under varying soil conditions have not been addressed.

Three Western Australian synthetic rutile production sites are within catchments that experience eutrophication, giving rise to algal blooms and presenting subsequent public and environmental health risks. It is widely accepted that improved nutrient retention within the respective catchments both in the short- and long-term will lead to improved quality in the receiving waters.

Thus, based on existing information, and the prospect of this potential soil amendment being used on a broader scale, the continued evaluation of NUA is warranted.

1.1.1. Aim and Scope of Research - 2005-2008 turf farm trial

A research program was proposed by CSIRO in consultation with Iluka Resources, Ltd., in 2005 to investigate and quantify the mobility of trace elements and radionuclides, and nutrient retention characteristics of NUA when applied as a soil amendment beneath turf farms in South West Western Australia.

The primary goal of the initial study which was undertaken between 2005 and 2008 at the Bullsbrook Turf Farm (Douglas et al., 2010) was to investigate the extent of migration, if any, of a range of elements and radionuclides beneath growing turf. The primary goal also reflected the potential benefits of using NUA: namely, enhanced P retention at both the turf farm and properties where the turf is laid; greater moisture retention of the soil; trace element retention by the NUA; and enhanced turf productivity. This original trial of NUA at the Bullsbrook Turf Farm site ran for 1,357 days, equivalent to more than 45 months or approximately 3.7 years, from 1 January 2005 to 17 September 2008. This length of time was approximately seven months longer than the originally agreed-upon period. Further lysimeter sampling was also undertaken at low frequency in the intervening period. Further details of the 2005-2008 field trial are provided in Douglas et al. (2010).

1.1.2. Major outcomes - 2005-2008 turf farm trial

Major outcomes of the 2005-2008 period of Bullsbrook trial are outlined in Douglas et al. (2010). These promising results for NUA in terms of its ability to substantially reduce leaching of P (>97%), N (>82%) and a suite of trace elements to shallow groundwater in addition to its low toxicity and low radioactivity when applied as a soil amendment formed the foundation for the planning and execution of an extended field trial at the Bullsbrook Turf Farm trial site.

1.2. Aim and Scope of Research 2008-2009 turf farm trial extension

1.2.1. Original proposed scope of work 2008-2009 turf farm trial extension

At the end of the 1,357-day NUA trial there were two experimental turf sites (control and NUAamended) at the Bullsbrook Turf Farm as described in Douglas et al. (2010). These sites were further subdivided in half resulting in two control and two experimental sites for the trial extension (Figure 1).

One each of the control and NUA-amended sites received normal fertiliser applications as determined by the turf farm manager. The alternate control and NUA-amended sites did not receive any additional fertiliser for the duration of the trial (206 days). Water application was determined on an as required basis by the turf farm manager.

The preparation and monitoring of the control and NUA-amended sites were as follows:

- Installation of an additional four lysimeters so that three lysimeters were in each site (12 lysimeters in total).
- Analysis of pH, EC, major ions, AI, Fe, Mn and nutrients (P as PO₄-P, N as TKN, NO₃-N, NH₃-N and Si) and solute flux in lysimeter leachates.
- Determination of Phosphorus Retention Index (PRI) in soil profiles and analysis of total phosphorus, total nitrogen and total carbon in soil profiles from each site prior to and at the conclusion of each trial.
- Determination of leaf biomass and leaf nutrient chemistry in quadrants within each site at regular intervals using an adaption of a remote sensing technique.
- Determination of soil moisture profiles at regular intervals.

The experimental design and monitoring regime outlined above addressed the three areas of nutrient bioavailability, comparative growth rates and water retention and use as outlined in Section 1.1.

The duration of the proposed NUA Turf Trial Extension was six months in the first instance with a possible extension to 12 months upon review and agreement between Iluka Resources, CSIRO and Sports Turf Technology.

Figure 1. (a) Bullsbrook Turf Farm, and (b) detail of existing experimental site and proposed subdivision. Three lysimeters were placed within each experimental site.



1.2.2. Amended scope of work 2008-9 turf farm trial extension

Although only funded for a six-month period, the trial extension at the Bullsbrook site ran for 206 days, or nearly seven months in total, to bring the cumulative monitoring of the Bullsbrook Turf Farm field trial site to 1,563 days, nearly 52 months or approximately 4.3 years. The Bullsbrook trial extension was terminated after seven months when lysimeter data indicated that the unfertilised control and amended sites had inadvertently been extensively fertilised with N and P (possibly as a result of application of complete turf fertiliser and/or foliar sprays) on one or more occasions on or prior to day 1,567. Data for the trial are only presented for days 1,307-1,451, which were considered to be the last reliable data collected. Nonetheless, three further months of lysimeter sampling were completed over the agreed period in addition to approximately eight extra months in the original 2005-2008 turf trial and between trial sampling. Thus, more than one year of additional lysimeter sampling was undertaken that has allowed the compilation of an approximately 4.3-year record of shallow groundwater response to turf growth on NUA-amended and control soils at Bullsbrook Turf Farm.

Considerable difficulty was experienced in regular collection of three lysimeter samples each from the control fertilised, control unfertilised, NUA-amended fertilised and control unfertilised sites over the summer of 2008/2009 in terms of inadequate sample volumes due to the persistent dry conditions, even with watering by the overhead sprinkler systems. This resulted in very low leachate volumes being recorded for the majority of the extension trial (see later). Nonetheless, only day 1,489 (29 January 2009) contained insufficient sample volume in either of the control or NUA-amended fertiliser sites for lysimeter sampling.

A legacy of the low leachate volumes was also an inherent patchiness in turf (re)growth within both amended and to a greater extent within the control sites. In addition, soil moisture contents appeared to be extremely variable and thus were abandoned early in the trial. However, the field trial was extended by approximately three additional months over the original six months with a greater focus on groundwater quality.

1.3. 2008-9 trial extension details and key dates

An extension of the field trial at Bullsbrook Turf Farm commenced in September 2008 with the final lysimeter sampling occurring in mid-April, 2009. The trial extension further subdivided the control and NUA-amended turf sites to investigate the performance of fertilised versus unfertilised turf. The hypothesis was that P, N and micronutrients retained in the NUA would be bioavailable and thus continue to sustain growth in the absence of additional fertiliser inputs.

The Bullsbrook component of the Iluka-NUA field trial was undertaken at Bullsbrook Turf Farm, owned by Mr John Maas of Cooper Rd. Bullsbrook, WA, 6084. This is the site where turf was cultivated on both NUA-amended and control soils.

The Bullsbrook site was of approximately 1 ha in size consisting of essentially flat aspect, rectangular 0.5 ha NUA-amended and control sites, respectively. The soils at the trial site are structure-less pale yellow to grey, medium to coarse sands. A full description of the chemistry and mineralogy of the sands is given in Douglas et al. (2010). Both the NUA-amended and control sites had a previous history of turf cultivation; however, no turf had been grown for at least the preceding five years before the original turf trial which commenced in 2005.

As previously stated, the Bullsbrook trial extension was terminated when lysimeter data indicated that the unfertilised control and amended sites had inadvertently been extensively fertilised with N and P (possibly as a result of application complete turf fertiliser and/or foliar sprays) on one or more occasions on or prior to day 1,563. Thus data reported herein for the Bullsbrook Turf Farm trial extension are inclusive of days 1,357-1,451, which was considered to be the last reliable day in which data collected.

The key dates and experimental parameters pertinent to the Bullsbrook Turf Farm trial extension which are reported in detail are given below:

Lysimeter sampling

- o 31 August 2008
- o 17 September 2008
- o 16 October 2008
- o 18 November 2008
- o 22 December 2008
- o 29 January 2009
- o 17 April 2009

Soil core sampling

- o 13 May 2009
- Turf sampling grass (nutrients)
 - o 17 April 2009
- Turf sampling (grass + roots)
 - o 25 November 2008
- Turf harvesting
 - o 4 December 2008
- Turf regrowth after harvesting
 - o 18 December 2008
 - o 22 February 2009
 - o 17 April 2009

2. METHODS

2.1. Lysimeter installation and sampling

Additional lysimeters were installed at the Bullsbrook trial site using methods previously described in Douglas et al. (2010).

The lysimeter catch vessel was composed of polyethylene and had a cone-shaped base with a plastic tube (10 mm diameter) exiting from the lowest point. The top of the lysimeter was buried to a depth of 15 cm below the soil surface at the interface of the NUA-amended soil and unamended lower soil. The vessel was prepared by placing a filter fabric over the opening in the base, and then packing the vessel with soil collected from the site. The lysimeter catch vessel was 24 cm in diameter (giving an overall catchment area of 0.0453 m²) and 10 cm deep. Four lysimeters were installed in both the control and NUA-amended sites. Leachate collected from the individual lysimeters was aggregated and total volumes recorded.

The tube from the base of the vessel was fitted into the lid of a sealed 10 L polyethylene jerry can installed below the vessel (gravity feed). Two 2 mm polyethylene tubes were also fitted into the lid of the jerry can, one extending to the base of the jerry can (suction tube) to recover the soil leachate, and the other terminating just inside the jerry can (breather tube). Any leachate that passed through the soil profile was stored in the jerry can until it was extracted, usually between monthly and bi-monthly intervals using a suction pump.

2.2. NUA incorporation

No new NUA was incorporated into the field site prior to or during the trial extension. Prior to the 2006-2008 trial, NUA was applied to the experimental site at the rate of 150 dry tonnes per ha (Douglas et al., 2010). The NUA was incorporated into the soil to a depth of approximately 10-15 cm using a rotary hoe with a roller mounted on the back to allow the depth of incorporation to be better controlled. During incorporation, most lumps within the NUA quickly dispersed during the mechanical phase or during initial post-application watering. Further homogenization of the NUA into the existing soil occurred during the incorporation of the grass runners.

2.3. Fertiliser type and incorporation

During the initial 2006-2008 trial, approximately 7 tonnes of Nitrophoska Blue, a pelletized fertiliser specifically formulated for the turf industry and imported from Germany was applied to the 1 ha trial site. The fertiliser was spread using a Marshall Multispreader. These machines use a belt feeder and spinners to evenly distribute the fertiliser. Given a P content of approximately 6.2% in the fertiliser, 434 kg of P was applied during the field trial. Fertiliser applied to the NUA-amended and control sites was supplied on an as required basis as determined by the owner and staff and Bullsbrook turf farms. Contrary to the recommendations of CSIRO and Sports Turf technology, single supplementary Fe-Mn and N (as urea) foliar sprays were also applied during the trial to both the NUA-amended and control sites.

During the 2008-9 trial extension fertiliser was only applied to the amended fertilised and control fertilised sites as per the trial design. No restrictions were placed on the amount or type of fertiliser applied, to conform as closely as possible to usual turf farm agricultural practices.

2.4. Grass establishment and harvesting

During the 2006-2008 trial, commercial soft leaf buffalo (Palmetto- *Stenotaphrum secundatum*) turf was established using a muck spreader to distribute runners. The runners were derived from shredded instant turf using an industry standard ratio of 1 m² of instant turf to 10 m² of site (NUA-amended or control) site. The runners were stolonised (incorporated) into the upper 50 mm of the NUA-amended or control soils using a rotary hoe fitted with a roller. Grass harvesting was undertaken using a tractor-mounted harvester. After harvesting, remnant grass strips were watered and fertilised to facilitate their growth and re-establishment over the NUA-amended and control sites.

Grass rolls of approximately 2.5 m in length and 0.4 m in width which also contained a few millimetres of the underlying NUA-amended or control soil were harvested three times during the initial 2006-2008 trial. During the 2008-2009 trial, turf was harvested from the control and experimental sites in the first week of December, 2008.

2.5. Irrigation

The trial site was watered with a new generation irrigation system commonly termed a "Floppy Sprinkler". These irrigation systems have a high uniformity of water coverage even in windy conditions while only having a low output of approximately 5 mm per hour. During the "grow in" phase of the turf under summer conditions, the system needs to run at least twice per day for about 45 minutes each time. This applies approximately 7.5 mm of irrigation per day and just over 50 mm per week. The irrigation water was sourced from an on-site bore which abstracted the water from the superficial aquifer using a submersible pump.

2.6. Soil sample collection

Soil depth profiles from 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-30 cm and 30-40 cm were collected from both the amended and the control sites from the four sites (control and amended fertilised and unfertilised) near the lysimeters. Soil samples were obtained using a 56 mm diameter soil corer with samples collected in clear polythene bags. Upon return to the laboratory, all samples were homogenised, dried at 105°C, and a sub-sample ground using a WC ring mill which was rinsed with clean river sand and compressed air to clean the mill between each sample.

2.7. Turf collection

Turf was collected from 0.5 x 1 metre sections marked out with spray paint. The turf was removed to a depth of approximately 20 cm to ensure the majority of root mass was also removed. Upon return to CSIRO laboratories the same day, soil was removed from the root mass using high pressure water hoses. The resultant turf leaf and root biomass was then dried at 80°C in a laboratory oven prior to weighing, and sampling and analysis of turf leaf chemistry.

2.8. Major and Trace Element Analysis

2.8.1. X-ray fluorescence (XRF) analysis - fusion

Soil samples were analysed by X-ray fluorescence (XRF) for major elements (expressed as weight percent oxides): SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, and trace elements (expressed as μ g/g): Ba, Ce, Cl, Cr, Co, Cu, Ga, La, Ni, Nb, Pb, Rb, S, Sr, V, Y, Zn, and Zr using fused glass discs, at CSIRO Land and Water Laboratories, Adelaide, Australia using the methods of Norrish and Chappell (1977). Approximately 1 g of each oven dried sample (105°C) was accurately weighed with 4 g of 12-22 lithium borate flux. The mixtures were fused at 1050°C in a Pt/Au crucible for 20 minutes then poured into a 32 mm Pt/Au mould heated to a similar temperature. The melt was cooled quickly over a compressed air stream and the resulting glass disks were analysed on a Philips PW1480 wavelength dispersive XRF system using a dual anode Sc/Mo tube and algorithms developed in the CSIRO Adelaide laboratory.

2.8.2. X-ray fluorescence (XRF) analysis – pressed powders

Soil samples were also analysed by XRF for major elements (expressed as weight percent element): Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, S, and trace elements (expressed as µg/g): Ag, As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, I, In, La, Mo, Ni, Nb, Nd, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Ta, Te, Th, TI, U, V, W, Y, Yb, Zn, and Zr using pressed powders. Approximately 4 g of each sample was accurately weighed with 1 g of Licowax binder. The mixtures were shaken vigorously for 30 seconds using a laboratory test tube shaker. The mixtures were pressed to 10 tonnes with a boric acid backing and the resulting pellets analysed on a Spectro X-Lab 2000 energy dispersive XRF system using a Pd X-ray tube and 5 secondary excitation targets.

2.8.3. Data set preparation

The final XRF data set consisted of the major elements expressed as weight percent oxides from the fusion analysis. Where common trace elements existed between the fusion and pressed powder analysis existed, their internal consistency was compared. The lowest detection limit of either the fusion or pressed powder technique was used in reporting data. Due to the use of the WC ring mill during sample preparation, W has been removed from the list of analytes while low (<10-20 μ g/g) Co concentrations as a trace element contaminant should be interpreted with caution.

2.9. Lysimeter leachate analysis

All lysimeter samples were filtered through a syringe-mounted 0.45 um cellulose nitrate filter prior to analysis. Samples for metals/metalloids analysis were acidified by adding 0.1 mL of Superpure HNO₃ to 100 mL lysimeter leachate in a plastic sample bottle. Anion samples were filled completely so that there was no headspace in the plastic bottle. All samples were stored in darkness at 4°C prior to analysis at Genalysis Laboratory Services Pty Ltd, Maddington, WA. All analytical methods based on APHA Standard Methods for the Examination of Water and

Wastewater are referenced to the 21st Edition (2005) except for NH_3 -N which is from the 18th Edition (1992).

2.9.1. Metal and metalloid analysis via ICP-OES and ICP-MS

Lysimeter leachates were analysed on a Perkin Elmer Elan 9000 ICP-MS or Optima 5300 ICP-OES using standard laboratory methods. These methods are described in APHA Standard Methods for the Examination of Water and Wastewater and are referenced to the 21st Edition (2005). Samples blanks, replicate samples and standard waters of a similar matrix type were included in each analytical run. A summary of the analytical suite, method and detection limit is given in Table 1.

2.9.2. Anions, pH, Electrical conductivity, Total Kjeldahl Nitrogen

A summary of analytical methods for anions, pH, EC total Kjeldahl N (TKN) and alkalinity, their APHA Method code (2005), detection limits and a brief description of the of analytical method for the Bullsbrook lysimeter leachates is given in Table 2.

Element	Method	Detection	Units	Element	Method	Detection	Units
As	/MS	0.001	mg/L	Cu	/OES	0.1	mg/L
Ва	/MS	0.5	µg/L	Fe	/OES	0.1	mg/L
Cd	/MS	0.2	µg/L	К	/OES	1	mg/L
Со	/MS	0.001	mg/L	Mg	/OES	0.1	mg/L
La	/MS	0.02	µg/L	Mn	/OES	0.1	mg/L
Pb	/MS	0.005	mg/L	Na	/OES	1	mg/L
Rb	/MS	0.2	µg/L	Ni	/OES	0.1	mg/L
Se	/MS	0.005	mg/L	Р	/OES	1	mg/L
Sr	/MS	0.2	µg/L	S	/OES	1	mg/L
Th	/MS	0.05	µg/L	Sc	/OES	0.1	mg/L
U	/MS	0.05	µg/L	Si	/OES	0.5	mg/L
AI	/OES	0.1	mg/L	Ti	/OES	0.1	mg/L
В	/OES	0.1	mg/L	V	/OES	0.1	mg/L
Са	/OES	0.1	mg/L	Zn	/OES	0.1	mg/L
Cr	/OES	0.1	mg/L				

Table 1. Summary of metal/metalloid analytical suite for ICP-MS or ICP-OES analysis and detection limits for the lysimeter leachates.

Element	Method	Detection	Units	Method code APHA	Description
CI	/COL	5	mg/L	4500-CI E	colorimetric analysis: highly coloured ferric thiocyanate is formed in solution, the intensity is proportional to the chloride concentration
NH ₃ -N	/COL	0.5	mg/L	4500-NH3 C	colorimetric analysis: NH₃ measured by nesslerization by producing a yellow colour
NO ₃ -N	/COL	0.5	mg/L	4500-NO3 B and G	colorimetric analysis: UV screening followed by reduction of NO ₃ to NO ₂ and colorimetric determination of NO ₂ as a pink azo dye
PO ₄ -P	/COL	0.05	mg/L	4500-P E	colorimetric analysis: orthophosphate is reacted in acid solution to form a blue colour
EC	/METER	10	µS/cm	2510A	conductivity meter
рН	/METER	0.1	NONE	4500-H	pH meter
F	/SIE	0.1	mg/L	4500-F C	ion selective electrode measurement in a buffered solution
Acidity	/VOL	5	mg CaCO₃/L	2310B	titration with sodium hydroxide
CO ₃ ²⁻	/VOL	5	mg CaCO ₃ /L	2320B	titration with dilute hydrochloric acid and calculation of CO_3 , HCO_3 and OH
HCO3 ²⁻	/VOL	5	mg CaCO₃/L	2320B	as above
OH	/VOL	5	mg CaCO ₃ /L	2320B	as above
TKN	/VOL	0.2	mg/L	4500-N B	digestion of sample to convert all N to ammonia which is then distilled and titrated with acid

Table 2. Summary of analytical methods for anions, pH, EC total Kjeldahl nitrogen (TKN) and alkalinity, APHA Method code, detection limits and a brief description of the method of analysis for lysimeter leachates.

COL – colourimetric analysis SIE – Specific Ion Electrode METER – electronic meter used VOL – Volumetric titration

3. **RESULTS**

3.1. Lysimeter geochemistry – time series in control and NUAamended sites

Leachate data expressed as an average composition obtained from the four control or four experimental lysimeters are shown in Figure 2 and Figure 3. Also included are data from the original Bullsbrook field trial for reference. The leachate data have been grouped into three categories to aid interpretation:

- Physico-chemical parameters (pH, electrical conductivity EC), major cations and anions (Na, K, Ca, Mg, Cl, SO₄, total alkalinity), Si, Fe and Mn (Figure 2, Figure 3).
- Nutrients including PO₄-P, NH₃-N, NO₃-N, total inorganic nitrogen (TIN = NH₃-N + NO₃-N), and total Kjeldahl nitrogen (TKN = NH₃-N + organic N), and average lysimeter flux (Figure 5 Figure 10).
- Minor elements in alphabetical order: Al, As, B, Ba, Cd, Co, Cr, Cu, F, La, Ni, Pb, Rb, Sc, Se, Sr, Th, Ti, U, V, Zn (Figure 11 Figure 14).

Units for the majority of analytes are expressed as mg/L except for As, Ba, Cd, Co, La, Rb, Se, Sr, Th and U which are expressed in μ g/L. Detection limits vary for some elements due to the use of different analytical techniques and improvement in analysis during the course of the study.



Figure 2. Physico-chemical parameters (pH, electrical conductivity - EC) and major cations (Na, K, Ca, Mg) in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 3. Major anions (CI, SO₄, total alkalinity), Si, Fe and Mn in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

3.1.1. Physico-chemical parameters (pH, EC), major cations and anions (Na, K, Ca, Mg, Cl, SO₄, total alkalinity), Si, Fe and Mn

Average lysimeter pH varied widely for the four treatment sites and in a similar range to the earlier long-term field trial (Figure 2). The amended unfertilised and amended fertilised sites had pH between 7 and 8. In contrast, both the control unfertilised and control fertilised sites were typically 2-4 pH units lower with the control fertilised site having a final pH of 4.00. Similarly, low pH only occurred on two other occasions over the 1,451 days of the present and previous Bullsbrook Turf Farm trial.

The average EC of the soil leachates is shown in Figure 2. Initial EC for the control fertilised and amended fertilised sites was similar to the long-running average from the original Bullsbrook Turf Farm field trial while control unfertilised and amended unfertilised EC measurements were considerably lower. For the remainder of the trial, however, the EC generally remained below 0.5 mS/cm.

As identified in the original Bullsbrook Turf Farm field trial (Douglas et al., 2010), average major cation and anion concentrations in leachates (Na, K, Ca, Mg, Cl, SO₄, total alkalinity) followed EC with differing degrees of fidelity. In general Na, and to a lesser extent Cl and total alkalinity, most closely resembled the temporal EC profile (Figure 2, Figure 3), with these three major ions constituting the majority of leachate ions. Other ions such as K, Ca and SO₄ displayed a similar pattern in concentration, but of different relative concentrations compared to EC (Figure 2, Figure 3). Interestingly, Ca and SO₄ concentrations within the control fertilised site had a similar concentration profile to both NUA-amended sites during the trial extension period (Figure 2, Figure 3). Differences in average Ca and SO₄ concentrations in particular for the NUA-amended soil leachates compared to the control soil leachates were related to gypsum dissolution from the NUA and are discussed later.

Average Si concentrations in the original Bullsbrook Turf Farm field trial displayed an exponentiallike decay concentration profile with a similar average concentration in both the control and NUAamended soil leachates. In contrast, average Si concentrations in the control area, (Figure 3), during the trial extension were more erratic. Within the field trial extension, in general, both the control fertilised and control unfertilised average dissolved Si leachate concentrations were considerably higher than dissolved Si concentrations in both NUA-amended sites which rarely exceeded 2 mg/L.

Average dissolved Fe concentrations rarely exceeded 0.5 mg/L in both amended and the control fertilised site during the trial extension (Figure 3). In contrast, average Fe concentrations in the control unfertilised site were initially 2-4 times higher than the other three sites.

Average lysimeter concentrations of Mn were generally below 0.1 mg/L for both the NUAamended and the control unfertilised site (Figure 3). Later in the trial, however, average dissolved Mn concentrations in the control fertilised attained a maximum of *ca.* 0.75 mg/L, approximately 15 times that of the other three sites and temporally corresponding with the very low pH at this site.

3.1.2. Origin and variation in major cation (Na, K, Ca, Mg) and anion (Cl, SO₄, $HCO_3 + CO_3$, F) leachate geochemistry

A more detailed analysis of major cation (Na, K, Ca, Mg) and anion (Cl, $HCO_3 + CO_3$, SO_4 , F) concentrations was undertaken using a Piper diagram (Figure 4) incorporating data from both the original Bullsbrook Turf Farm field trial and both of the control and amended sites in the trial extension. The majority of major cation and anion compositional variation within all of the sites in both the original Bullsbrook Turf Farm field trial and the field trial extension was constrained within three mixing end members:

- rainwater with a composition similar to that of Perth rainwater;
- local irrigation water abstracted from shallow groundwater bores on site at Bullsbrook Turf Farm; and
- a leachate primarily derived from gypsum dissolution from the NUA which plots at, or in close proximity to, the 100% Ca and 100% SO₄ lower triangle apex respectively and 100% CI + F + SO₄ and Ca + Mg upper diamond apex of the Piper diagram (Figure 4).

The majority of both amended fertilised and amended unfertilised lysimeter leachates defined a linear mixing array between locally-derived irrigation water and the Ca-SO₄-rich leachate composition of NUA (Figure 4). A few samples also plotted near an average Perth rainwater composition indicating that ostensibly unattenuated rainwater may occasionally have formed the major lysimeter leachate solute composition, probably as a result of major local rainfall events.

The majority of control fertilised site lysimeter leachate samples formed a linear mixing array halfway between the average irrigation water composition and that of both of the amended sites (Figure 4). This may indicate either a degree of surface runoff or subsurface groundwater mixing between the two sites and/or the dissolution of gypsum or other Ca- and SO₄-bearing phases within fertilisers applied to the control fertilised site.

Comparison of the control fertilised to the control unfertilised site indicated that the application of fertiliser, which may contain ~5% Ca and ~7.8% SO₄ (recalculated from Table 5; Douglas et al., 2010), was the mostly likely source of Ca and SO₄ as described above. The control unfertilised site had lysimeter leachate chemistry most characteristic of irrigation-rainwater mixing with no apparent NUA component suggesting limited if any solute exchange. The leachate compositions also suggested an effective separation (no mixing) between both control and amended sites during the field trial extension.



Figure 4. Piper diagram of lysimeter leachates from original Bullsbrook trial and Bullsbrook trial extension. Also plotted are compositions of average groundwater (n = 3) used to irrigate the turf, and average Perth rainwater.

3.1.3. Nutrients and average lysimeter flux

Average lysimeter nutrient concentrations within the two NUA-amended and two control sites for PO_4 -P, NH₃-N, NO₃-N, TIN and TKN are shown in Figure 5 - Figure 9. Due to the large range of lysimeter leachate concentrations recorded over the original trial and trial extension the information is depicted on two scales.

Average dissolved P concentrations in the Bullsbrook Turf Farm trial extension varied considerably between the four sites (Figure 5). Control fertilised areas reached the highest concentrations of 68 mg/L whereas in the amended fertilised site the corresponding concentration was only approximately 4 mg/L or 6% of the control fertilised area were typically <0.2 mg/L, similar to those of the original field trial. Average dissolved P concentrations in the control unfertilised and amended unfertilised sites were generally <2 mg/L and intermediate in concentration between the two fertilised sites.



Figure 5. Mean PO_4 -P concentrations in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Average inorganic NH₃-N and NO₃-N, and hence, total inorganic nitrogen (TIN = NH₃-N + NO₃-N) concentrations were generally similar in range to the majority of the original Bullsbrook Turf Farm field trial for all four Bullsbrook trial extension sites (Figure 6 - Figure 8). A large increase in average inorganic N concentrations of NH₃-N and NO₃-N to approximately 65 mg/L and 288 mg/L, respectively, occurred, however, within the control fertilised site corresponding with the large increase in average PO₄-P concentration. The resultant TIN concentration during this large increase in average dissolved N and N concentrations exceeded 350 mg/L.



Figure 6. Mean NH_3 -N concentrations in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 7. Mean NO_3 -N concentrations in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 8. Mean total inorganic nitrogen (TIN) concentrations in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Average total dissolved total Kjeldahl nitrogen (TKN) concentrations were similar in both the original Bullsbrook Turf Farm trial and for the majority of time in the trial extension for all four sites (Figure 9). As documented in average dissolved PO_4 -P, NH_3 -N, NO_3 -N and TIN concentrations (Figure 5 - Figure 8), however, there was a correspondingly large increase in TKN.



Figure 9. Mean total Kjeldahl nitrogen (TKN) concentrations in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

The total lysimeter flux (litres of leachate collected between each sampling period, (Figure 10) was consistently higher in the control fertilised and control unfertilised areas relative to both NUA-amended sites throughout the Bullsbrook Turf Farm trial extension with a similar range of fluxes to that of the original Bullsbrook trial. Lysimeter fluxes were also much higher (~4-5 times) at the commencement of the field trial extension. The leachate flux to the control fertilised and control unfertilised site lysimeters was typically 1.5 - 5 times that of the fertilised and unfertilised NUA-amended sites.

Total lysimeter fluxes for the control fertilised and control unfertilised areas were 6.8 ± 2.3 L, ($\mu \pm 1\sigma$) L and 9.1 ± 2.7 L, respectively. This contrasts with the total lysimeter flux for the amended fertilised and amended unfertilised areas of 2.4 ± 0.8 L and 6.3 ± 1.9 L, respectively. Interestingly, the majority of the amended unfertilised area flux (~73%) occurred on the first sampling occasion of the Bullsbrook Turf Farm trial extension. If this anomalous flux is omitted, the total flux based on the average of the other fluxes would be approximately 2.4 ± 0.3 L, a total flux identical to that of the amended fertilised area.

In the original Bullsbrook Turf Farm field trial, total lysimeter fluxes in the control area were approximately 1.8 times that of the amended fluxes. For the Bullsbrook trial extension, assuming a similar flux in both the amended fertilised and amended unfertilised areas of 2.4 L, the ratio relative to the corresponding control area was ~2.7 and 3.8 or ~2.7 and ~1.4, respectively (if the higher flux for the amended unfertilised area is used – see above).



Figure 10. Mean lysimeter flux from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

3.1.4. Minor elements: Al, As, B, Ba, Cd, Co, Cr, Cu, F, La, Ni, Pb, Rb, Sc, Se, Sr, Th, Ti, U, V, Zn

As outlined in the report on the original Bullsbrook field trial (Douglas et al., 2010), average concentrations of a number of minor elements, in particular Cd, Co, Cu, La, Ni, Pb, Sc, Ti and V

were frequently close to or below analytical detection limits in the lysimeter leachate (Figure 11 - Figure 14). In addition, some of these elements with low concentrations had varying analytical detection limits during the course of the field trial which may have obscured primary trends in the data. Nonetheless, temporal trends for the abovementioned elements were often similar with isolated spikes in concentration frequently replicated between control and NUA-amended leachates. Importantly, detection limits (which sometimes varied between analyses) for elements such as Cd, which is known for its toxicity to biota, were extremely low (0.01 μ g/L).

Average solute leachate concentrations for control fertilised, control unfertilised, amended fertilised and amended unfertilised areas are given in Table 3. Average solute concentrations for the control fertilised and control unfertilised areas are a compilation of data from both the original Bullsbrook trial and extension (n = 42). Control unfertilised and amended unfertilised are a compilation of data from the Bullsbrook trial extension only (n = 5).

In general, average leachate solute concentrations were similar in both the original Bullsbrook Turf Farm trial and that of the trial extension, however, some variation exists and this is documented below.

Average leachate trace element concentrations in the Bullsbrook Turf Farm trial extension can be broadly categorised into five broad groups:

- Elements either uniformly low or similar in concentration to the original Bullsbrook trial leachates: Cd, Cr, La, Ni, Pb, Sc, Se, Sr, U, V and Zn.
- Elements similar in both original Bullsbrook trial and trial extension: Cd, Cr, La, Ni, Pb, Sc, U, V, and Zn.
- Elements enriched in control fertilised and/or control unfertilised leachates: AI, B, Rb, and Ti.
- Elements enriched in amended fertilised or amended unfertilised leachates: Co, and Cu.
- Elements increasing in concentration in all four areas: F.



Figure 11. Minor elements AI, As, B, Ba, Cd, and Co in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 12. Minor elements Cr, Cu, F, La, Ni and Pb in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 13. Minor elements Rb, Sc, Se, Sr, Th, and Ti in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.


Figure 14. Minor elements U, V and Zn in lysimeter leachates from fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Analyta	Unito	Control	Control	Amended	Amended
Analyte			0 19	rentilised	Onertinsed
AI	mg/∟	0.36	2.10	0.20	0.05
AS	µg/L	2.9	1.80	1.2	0.01
B	mg/L	0.14	0.06	0.12	0.07
Ва	µg/L	59	0.25	73	0.25
Ca	mg/L	148	39	644	528
Ca	µg/L	0.3	0.06	0.4	0.09
CI	mg/L	368	124	438	160
Co	µg/L	0.8	0.38	2.0	0.53
Cr	µg/L	35	4	20	3
Cu	µg/L	791	380	1975	534
EC	mS/cm	1.26	0.05	2.86	0.53
F	mg/L	0.51	1.15	0.77	1.06
Fe	mg/L	0.33	0.64	0.27	0.05
HCO ₃	mg/L CaCO₃	22	30	75	70
K	mg/L	90	49	73	19
Mg	mg/L	32	6	58	9
Na	mg/L	150	47	185	42
N-NH ₃	mg/L	8.0	0.79	1.1	0.18
N-NO ₃	mg/L	29.2	1.96	8.2	1.32
TIN	mg/L	37.2	2.75	8.9	1.50
TKN	mg/L	33.0	6.66	4.4	2.46
рН	-	6.04	5.56	7.37	6.96
P-PO ₄	mg/L	8.7	1.00	0.3	0.05
La	µg/L	2.6	0.4	1.2	0.3
Mn	mg/L	0.08	0.04	0.06	0.01
Ni	µg/L	30	3	28	5
Pb	µg/L	2.0	0.6	1.9	0.3
Rb	µg/L	35	13	27	7
Sc	µg/L	14	2	17	2
Se	µg/L	1.0	0.5	1.4	0.5
Si	mg/L	2.8	2.8	1.7	1.7
S-SO ₄	mg/L	279	78	1561	1081
Sr	μg/L	865	217	4161	1887
Ti	μg/L	19	54	17	2
V	μg/L	17	3	18	2
Zn	μg/L	89	125	121	110
Th	μg/L	0.21	0.25	0.20	0.10
U	μg/L	0.10	0.07	0.13	0.08

Table 3. Summary of average solute leachate concentrations for control fertilised, control unfertilised, amended fertilised and amended unfertilised areas.

3.2. Lysimeter geochemistry – estimated flux to groundwater for control fertilised and unfertilised and NUA-amended fertilised and unfertilised sites

3.2.1. Nutrient flux to groundwater

An estimated flux rate to the groundwater for various solutes was calculated for the control fertilised and unfertilised and NUA-amended fertilised and unfertilised sites based on lysimeter geochemistry and leachate flux (Figure 15). A summary of nutrient fluxes (PO_4 -P, NH₃-N, NO₃-N, TIN and TKN) for the present study extension and that of the original Bullsbrook Turf Farm field trial are given in Figure 15 and Table 4.



Figure 15. Summary of nutrient fluxes (PO₄-P, NH₃-N, NO₃-N, TIN and TKN) for the present study extension and that of the original Bullsbrook Turf Farm field trial.

Table 4. Summary of nutrient fluxes (PO₄-P, NH₃-N, NO₃-N, TIN and TKN) for the present study extension and that of the original Bullsbrook Turf Farm field trial.

Analyte	N-NH₃	TKN	TIN	N-NO ₃	P-PO ₄
Control Fertilised Extn	20.4	33.7	141.5	121.1	82.4
Control Unfertilised Extn	5.9	6.9	22.7	16.8	42.1
Amended Fertilised Extn	0.1	0.2	5.6	5.5	6.5
Amended Unfertilised Extn	4.1	4.6	15.6	11.6	29.8
Control Original Trial	17.1	19.5	64.6	47.5	26.6
Amended Original Trial	3	3.4	31.4	28.4	0.7

In general, the highest nutrient fluxes occurred within the control sites with the highest rate of nutrient loss in the control fertilised site with $P-PO_4$ and TIN fluxes exceeding 80 and 140 kg/ha/yr, respectively (Figure 15, Table 4). These fluxes for $P-PO_4$ and TIN were over twice the long-term average flux for the control (fertilised) site in the original Bullsbrook Turf farm field trial.

In general, the lowest nutrient fluxes occurred either in the amended fertilised site in the trial extension or in the amended (fertilised) area of the original trial. The amended unfertilised site in the trial extension had a higher nutrient flux, and in particular for P-PO₄, than might be reasonably expected; however, as outlined in Section 3.1.3, this increased flux was primarily due to an anomalously high leachate volume collected on one occasion which accounted for ~73% of the total volume. If the leachate nutrient flux is recalculated using the remaining fluxes used to estimate an average, then the amended unfertilised area has the lowest nutrient flux of any area in either the original Bullsbrook Turf Farm trial or the trial extension.

3.2.2. Flux of all elements to groundwater

In a broader context, fluxes for all major and trace elements to shallow groundwater from the control fertilised and unfertilised and NUA-amended fertilised and unfertilised sites were also examined. These were ranked in the order of increasing element flux in the control unfertilised relative to the amended unfertilised soil leachates (Figure 16).

The largest element fluxes from the control unfertilised site relative to the amended unfertilised site occurred for the analytes Al, Ti, P-PO₄, Fe, N-NH₃, Mn and As with a range of other analytes also having larger element fluxes (Figure 16). Conversely, alkali and alkaline earth cations such as Ca, Mg, Na and Sr and the major anions SO_4^{2-} and CO_3^{2-} , and HCO_3^{-} (total alkalinity) were enriched in the amended unfertilised leachate.

The largest element fluxes from the control fertilised site relative to the amended fertilised site occurred for the analytes P-PO₄, the N species TKN and TIN, As, La, Cr and Al (Figure 16). In a similar trend to the unfertilised sites, alkali and alkaline earth cations such as Ca, Mg, Na and Sr and the major anions SO_4^{2-} and CO_3^{2-} , and HCO_3^{-} (total alkalinity) were enriched in the amended fertilised leachate.

Thus, overall there were similar trends, albeit different levels of enrichment or depletion, in leachate composition irrespective of whether fertiliser continued to be applied or was withheld as part of the trial extension. Most notable, however, was the increased flux of N and P species leached in the fertilised sites (Figure 15, Figure 16, Table 4).



Figure 16. Lysimeter geochemistry – ratio of control unfertilised to amended unfertilised fluxes and control fertilised to amended fertilised fluxes. Analytes are ranked according to an increasing ratio of the control unfertilised to amended unfertilised fluxes.

3.3. Saturation of Specific Mineral Species in Bullsbrook Lysimeter Leachates

3.3.1. Geochemical modelling of lysimeter leachates - a background

Geochemical modelling of the Bullsbrook Turf Farm lysimeter leachates from control and NUA amended sites was undertaken using PHREEQC for Windows V1.5.10 (Parkhurst, 1995). The PHREEQC calculations involved calculation of the saturation index (SI) of selected mineral phases, in particular, those of Al and Fe minerals. Both Al and Fe minerals were modelled as it is likely that minerals formed from these two elements will also strongly influence the speciation of the majority of other major and trace elements in the lysimeter leachates both temporally and over a wide range of pH.

The saturation index (SI) for a given mineral is defined as:

SI =
$$\log IAP/K_{sp}$$

where IAP = ion activity product of the chemical species involved in the reaction, and

 K_{sp} = the solubility product for the designated mineral

The SI gives an estimation of the degree of over- (SI > 0), under- (SI < 0) or equilibrium (SI = 0) saturation of a particular mineral phase for the prevailing leachate chemistry. In practice, an SI within \pm 0.5 of 0 can be assumed to be in equilibrium with the solution. The SI is commonly plotted as a function of solution pH, to examine the effect of pH on mineral equilibria and hence, saturation/solubility, or time, to examine temporal variation.

Plots of saturation indices and pH for the Bullsbrook Turf Farm lysimeters are shown in Figure 17 - Figure 34. Minerals modelled were those likely to be influential in regulating the Fe, Al, Mn Si and major ion chemistry of the lysimeter leachates during the original trial and the trial extension.

3.3.2. Mineral Saturation Indices

Results of the SI modelling for Fe-bearing minerals in Bullsbrook Turf Farm lysimeter leachates are presented in Figure 17 - Figure 19. As identified in earlier modelling of a range of minerals in lysimeter leachates (Douglas et al., 2010), the degree of over- or undersaturation of all Fe minerals was strongly related to pH. In general, there was an increasing degree of oversaturation with increasing pH. Goethite generally displayed a temporal trend of oversaturation (positive SI) for all but the control fertilised site where there were four instances of undersaturation (Figure 17). In general, both the NUA-amended and control leachates, irrespective of fertilisation status in the trial extension displayed a similar degree of saturation over time. Ferrihydrite ($Fe(OH)_3$) displayed a similar temporal trend to goethite; however, all sites varied from over- to undersaturation (Figure 18). Sodium jarosite ($NaFe_3(SO_4)_2(OH)_6$) was generally undersaturated irrespective of site, particularly during the trial extension (Figure 19).



Figure 17. Variation in the saturation index of goethite (FeOOH) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 18. Variation in the saturation index of ferrihydrite $(Fe(OH)_3)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 19. Variation in the saturation index of Na-jarosite $(NaFe_3(SO_4)_2(OH)_6)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Previous modelling of the SI for AI-bearing minerals (Douglas et al., 2010) indicated that these minerals had a convex saturation pattern with maxima in estimated SI generally occurring between pH 5.5 and 6.5. During the trial extension both the amended fertilised and amended unfertilised sites were consistently oversaturated with respect to gibbsite (AI(OH)₃) and the clay mineral kaolinite (Al₂Si₂O₅(OH)₄) which displayed markedly similar patterns of saturation. In contrast, both control sites varied between moderate over- and undersaturation (Figure 20, Figure 21). Amorphous silica (SiO_{2(am)}) was consistently undersaturated irrespective of site through the entire Bullsbrook Turf Farm trial extension (Figure 22). Alunite (KAl₃(SO₄)₂(OH)₆) and basaluminite (Al₄SO₄(OH)₁₀.5H₂O) varied from over- to undersaturation for all sites during the trial extension while jurbanite (AlOHSO₄) was consistently undersaturated.



Figure 20. Variation in the saturation index of gibbsite $(AI(OH)_3)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 21. Variation in the saturation index of kaolinite $(Al_2Si_2O_5(OH)_4)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 22. Variation in the saturation index of amorphous silica $(SiO_{2(am)})$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 23. Variation in the saturation index of alunite $(KAI_3(SO_4)_2(OH)_6)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 24. Variation in the saturation index of basaluminite $(Al_4SO_4(OH)_{10} \cdot 5H_2O)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 25. Variation in the saturation index of jurbanite (AIOHSO₄) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Consistent with the original Bullsbrook Turf Farm trial, gypsum (CaSO₄·2H₂O) and anhydrite (CaSO₄) remained at or close to equilibrium with solution (± 0.5 SI) for the NUA-amended soil leachates for the majority of the trial extension whether fertilised or unfertilised (Figure 26, Figure

27). Control fertilised sites were either near to saturation or strongly undersaturated while and unfertilised sites were always undersaturated.



Figure 26. Variation in the saturation index of gypsum (CaSO₄·2H₂O) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 27. Variation in the saturation index of anhydrite (CaSO₄) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

Of the other Ca-bearing minerals, both calcite and dolomite were at or near saturation for the trial extension for both amended sites while both control sites were below saturation (Figure 28, Figure 29). Fluorite (CaF₂) displayed an increasing temporal trend in terms of saturation within the original trial into the trial extension for the amended fertilised and amended unfertilised sites (Figure 30). Both control sites were strongly undersaturated with respect to fluorite. Hydroxyapatite (Ca₅(PO₄)₃OH) was predominantly oversaturated for leachates within both amended sites, mostly undersaturated for the control fertilised site and always undersaturated for the control unfertilised site (Figure 31).



Figure 28. Variation in the saturation index of calcite $(CaCO_3)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 29. Variation in the saturation index of dolomite ((Ca,Mg)CO₃) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 30. Variation in the saturation index of fluorite (CaF_2) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 31. Variation in the saturation index of hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

The Mn minerals rhodochrosite ($MnCO_3$), pyrolusite (MnO_2) and manganite (MnOOH) all remained undersaturated throughout the original Bullsbrook trial and trial extension (Figure 32 - Figure 34). In general, the amended fertilised and amended unfertilised showed the least degree of undersaturation throughout both trial periods.



Figure 32. Variation in the saturation index of rhodochrosite (MnCO₃) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 33. Variation in the saturation index of pyrolusite (MnO_2) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.



Figure 34. Variation in the saturation index of manganite (MnOOH) as a function of time in fertilised and unfertilised control and NUA-amended sites throughout the original Bullsbrook Turf Farm field trial and the trial extension.

3.4. Major and trace element geochemistry

3.4.1. Bullsbrook Turf Farm Soil and NUA

A summary of the average major and trace element geochemistry of the pre-amended, control, and post NUA-amended soils, NUA, the Post Archean Australian Shale (PAAS) (Taylor and McLennan, 1985), and fertiliser prior to the trial extension are given in Table 5. This table and following description of pre-amended, control, and post NUA-amended soils, NUA, the PAAS has been reproduced from Douglas et al. (2010) for the purposes of providing a necessary background to the following sections.

Both the pre-amended soil (prior to amendment with NUA) and the control soil had a very similar composition with SiO₂ >98%, indicative of the high quartz content of the soil (Bassendean Sand). Apart from a small amount of Al₂O₃ (0.11–0.17%) and Fe₂O₃ (0.39–0.42%), other major element concentrations were low. Similarly, trace elements were generally impoverished in the pre-amended and control soils, with the only trace element enrichments of note being Cr, Zr and the light rare earth elements (LREEs - La, Ce, Pr). Total N in Bullsbrook Turf Farm soils was low (0.02 – 0.03%).

The geochemistry of the NUA was dominated by the presence of five major elements (expressed as oxides): Fe₂O₃, CaO, SO₃ and to a lesser extent TiO₂ and SiO₂ (Table 5). Collectively these five oxides constituted over 87.6% of the mass of the NUA. Trace elements that displayed some enrichment (\geq 2 times) in the NUA, particularly when compared to the pre-amended and control soils included V, Ni, Cu, Zn, Ga, As, Se, Sr, Y, Nb, Ce, Tl, Pb, Bi and Th. Elements in the NUA depleted relative to the pre-amended and control soils included Cr, Mo, Sn, Ba and Nd. A small uncertainty exists in the robustness of the analysis of Co, Zr and the LREE, particularly in the NUA sample potentially due to matrix effects in the XRF analysis. Total N in NUA was low (0.03%).

The PAAS is commonly used as an estimate of the average major and trace element geochemistry of the continental crust. In comparison to the PAAS, the pre-amended/control soils were highly enriched in SiO_2 and largely impoverished in all other major and trace elements (Table 5). In contrast, the NUA-amended soils, which displayed a hybrid composition of the control/pre-amended soils and the NUA in the proportion of approximately 90-95%:5-10% by mass, respectively, had a major and trace element composition more similar to that of the PAAS.

The geochemical analysis of the Nitrophoska Blue fertiliser indicated it was principally composed of K_2O , P_2O_5 , CaO, SO₃, Cl, Fe₂O₃ and TN. These components constituted over 78% of the mass of the fertiliser. Trace element enrichments were common in the fertiliser relative to both the NUA and the pre-amended and control soils. Enrichments of note were Cu, Zn, Br, Cd, I and U.

Element	Pre-amended	Control	NUA-amended	PAAS	NUA	Fertiliser
SiO ₂	98.21	98.13	82.13 62.80		3.64	0.64
Al ₂ O ₃	0.11	0.17	1.30 18.90		0.38	0.28
Fe ₂ O ₃	0.39	0.42	4.18	7.22	19.30	3.11
MgO	0.00	0.00	0.18	2.20	1.33	0.30
CaO	0.07	0.06	3.22	1.30	21.41	7.01
Na₂O	0.00	0.00	0.01	1.20	0.41	1.21
K ₂ O	0.00	0.00	0.03	3.70	0.13	17.89
P ₂ O ₅	0.07	0.08	0.45	0.16	1.17	14.19
MnO	0.00	0.00	0.03	0.11	3.23	0.04
TiO ₂	0.00	0.00	0.60	1.00	1.50	0.04
SO ₃	0.02	0.02	2.43	n/a	30.46	19.60
CI	0.00	0.00	0.04	n/a	0.20	5.30
TN	0.03	0.02	0.03	n/a	<0.02	10.66
TOTAL	98.90	98.92	94.61	98.59	83.16	80.26
V	9	9	27	150	71	48
Cr	287	287	158	110	80	83
Co	< 2.0	< 2.0	16	23	172	< 2.0
Ni	16	15	19	55	90	4
Cu	3	2	14	50	44	56
Zn	3	3	13	85	30	232
Ga	1	1	4	20	26	0
Ge	< 0.4	< 0.4	< 0.4	n/a	< 0.4	0.5
As	< 0.4	< 0.4	0.4	n/a	10	< 0.4
Se	1	2	2	n/a	5.4	2
Br	2	2	- 7	n/a	<2	_ 247
Rb	2	3	5	160	6	28
Sr	7	9	133	200	725	115
Y	5	6	13	27	19	34
Zr	72	69	263	210	16	20
Nb	8	10	17	19	17	6
Мо	14	17	8	1	3	14
Ag	0.3	0.3	0.3	n/a	0.3	0.4
Cd	0.5	0.6	0.4	n/a	<0.1	1.4
Sn	2	2	1	4	3	1
Sb	< 0.8	< 0.8	< 0.8	n/a	0.4	2
Те	n/a	n/a	n/a	n/a	<0.1	n/a
I	1	1	1	n/a	1	4
Cs	3	5	2	15	1	1
Ва	21	24	13	650	38	18
La	30	34	26	38	35	11
Ce	39	41	54	80	95	14
Yb	1	1	1	2.8	1	1
Hf	0	1	8	5	1	4
Hg	1	2	1	n/a	<0.01	1
TI	3	3	4 n/		0.07	4
Pb	3	5	13		21	9
Bi	1	3	5	0.25	0.03	1
Th	7	9	34	14	112	15
U	< 0.9	< 0.9	< 0.9	3	6	19

Table 5. Major (%) and trace (μ g/g) element geochemistry of pre-amended, control and post NUA-amended soils, Post Archean Australian Shale (PAAS), NUA and fertiliser.

3.4.2. Soils from Bullsbrook Turf Farm Trial Extension

Soil cores were collected in May 2009, 286 days after initiation of the Bullsbrook Turf Farm trial extension. Soil depth profiles from 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-30 cm and 30-40 cm were collected from both the amended and the control sites from the four sites (control and amended fertilised and unfertilised) near the lysimeters. Mean major and trace element composition data from the upper depth interval (0-15 cm) from four sites corresponding to the depth of incorporation (*ca.* 15 cm) of NUA are presented in Table 6 and Figure 35-Figure 38.

The major compositional discontinuity occurring due to the incorporation of NUA into the upper 15 cm of the Bullsbrook soil profile was apparent for a range of major and trace elements. Both the amended fertilised and unfertilised sites exhibited significantly greater Ca, S, Fe, Mn, Mg and P concentrations in the top 15 cm of soil than occurred in the control sites (fertilised and unfertilised, Table 6). The NUA-amended sites also displayed slightly elevated concentrations of Sr in surface (0-15 cm) soils as compared to control sites.

Importantly, the concentration of P retained in the upper 15 cm of the soil profile in the NUAamended sites (Figure 37) was approximately three times that of either of the control fertilised or control unfertilised sites. Soil P concentrations below 15 cm were similarly low (~0.01%) for all four sites irrespective of the presence of NUA in the upper profile or changes in the fertilisation history experienced in the trial extension.

Element soli Fertilised Unfertilised Fertilised Pertilised Unfertilised SiO ₂ 0.00 1.50 0.05 0.05 98.83 98.46 97.52 TiO ₂ 0.00 1.50 0.05 0.05 0.07 0.09 Al _Q O ₁ 0.11 0.38 0.11 0.11 0.14 0.41 Fe _Q O ₂ 0.33 10.00 0.044 0.044 0.044 0.011 0.011 0.011 0.011 0.011 0.011 0.022 0.022 SO, 0.002 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.042 0.022 SO, 0.022 0.046 0.001 0.011 0.011 0.011 0.011 0.022 SO, 0.022 SO, SO 0.03 0.3 <3 <3 <3 <3 SG SO SO <th></th> <th>Turf Farm</th> <th>NUA</th> <th>Control</th> <th>Control</th> <th>Amended</th> <th>Amended</th>		Turf Farm	NUA	Control	Control	Amended	Amended	
SiO ₂ 98.21 3.64 98.91 98.83 98.46 97.52 TIO ₇ 0.00 1.50 0.05 0.07 0.09 Al ₂ O ₁ 0.11 0.38 0.11 0.11 0.14 0.41 Fe ₂ O ₃ 0.39 19.30 0.04 0.04 0.34 0.25 MnO 0.00 3.23 0.00 0.00 0.05 0.02 MgO 0.00 1.33 0.00 0.01 0.01 0.01 CaO 0.07 2.1.41 0.02 0.03 0.04 0.06 Na ₂ O 0.00 0.13 0.01 0.01 0.01 0.02 SO ₂ 0.07 1.17 0.01 0.01 0.01 0.02 SO ₃ 0.02 30.46 0.00 0.01 0.01 0.01 Ci 0.00 0.2 c4 c4 c4 c4 Ag 0.3 0.3 c3 c3 c3 c3	Element	soil		Fertilised	Unfertilised	Fertilised	Unfertilised	
TiO ₂ 0.00 1.50 0.05 0.05 0.07 0.09 ALO3 0.11 0.11 0.14 0.44 0.44 Fe ₂ O ₃ 0.39 19.30 0.04 0.04 0.34 0.25 MnO 0.00 3.23 0.00 0.01 0.01 0.01 CaO 0.07 21.41 0.02 0.03 0.04 0.04 0.04 0.04 Na ₂ O 0.00 0.13 0.01 0.01 0.01 0.02 SO ₂ 0.07 1.17 0.01 0.01 0.01 0.01 Cl 0.00 0.23 0.346 0.00 0.01 0.01 0.01 Cl 0.00 0.23 0.3 -3 -3 -3 -3 SO ₂ 0.07 1.17 0.01 0.01 0.01 0.01 Cl 0.00 0.23 0.3 -3 -3 -3 -3 Bi 1 0.03	SiO ₂	98.21	3.64	98.91	98.83	98.46	97.52	
AlçO ₂ 0.11 0.38 0.11 0.11 0.14 0.44 0.44 FeQO ₂ 0.39 19.30 0.04 0.04 0.34 0.25 MnO 0.00 3.23 0.00 0.00 0.05 0.02 MgO 0.00 1.33 0.00 0.01 0.01 0.01 0.01 CaO 0.07 2.1.41 0.02 0.03 0.04 0.06 Na_O 0.00 0.41 0.04 0.04 0.04 0.04 0.04 KgO 0.00 0.11 0.01 0.01 0.01 0.02 0.02 Po_s 0.07 1.17 0.01 0.01 0.01 0.01 0.01 Cl 0.02 30.46 0.00 0.01 0.01 0.01 0.01 Cl 0.02 30.43 <3	TiO₂	0.00	1.50	0.05	0.05	0.07	0.09	
Fe ₂ O ₅ 0.39 19.30 0.04 0.04 0.34 0.25 MnO 0.00 3.23 0.00 0.00 0.05 0.02 MgO 0.00 1.33 0.00 0.01 0.01 0.01 CaO 0.07 21.41 0.02 0.03 0.04 0.06 Na ₂ O 0.00 0.41 0.04 0.04 0.04 0.04 0.04 Va 0.00 0.41 0.04 0.04 0.04 0.04 0.04 P ₂ O ₅ 0.07 1.17 0.01 0.01 0.01 0.01 Cl 0.00 0.20 :4 :4 :4 :4 Ag 0.3 :3 :3 :3 :3 :3 :3 Bi 1 0.03 :2 :2 :2 :2 :2 Br 2 :2 :2 :2 :2 :2 :2 :2 Cl 0.03 <	Al ₂ O ₃	0.11	0.38	0.11	0.11	0.14	0.41	
MnO 0.00 3.23 0.00 0.00 0.05 0.02 MgO 0.00 1.33 0.00 0.01 0.01 0.01 CaO 0.07 21.41 0.02 0.03 0.04 0.04 NgO 0.00 0.41 0.04 0.04 0.04 0.04 NgO 0.00 0.13 0.01 0.01 0.02 0.02 SO, 0.02 30.46 0.00 0.01 0.01 0.01 CI 0.00 0.22 < <th><4</th> <4	<4	Fe ₂ O ₃	0.39	19.30	0.04	0.04	0.34	0.25
MgO 0.00 1.33 0.00 0.01 0.01 0.01 CaO 0.07 21.41 0.02 0.03 0.04 0.06 Na ₂ O 0.00 0.41 0.04 0.04 0.04 0.04 KO 0.00 0.13 0.01 0.01 0.01 0.02 SO ₃ 0.02 30.46 0.00 0.01 0.01 0.01 CI 0.00 0.20 -4 -4 -4 -4 Ag 0.3 0.3 <3	MnO	0.00	3.23	0.00	0.00	0.05	0.02	
Ca0 0.07 21.41 0.02 0.03 0.04 0.06 Na ₂ O 0.00 0.41 0.04 0.04 0.04 0.04 K ₂ O 0.00 0.13 0.01 0.01 0.01 0.02 0.02 SO ₅ 0.02 30.46 0.00 0.01 0.01 0.01 0.01 Cl 0.00 0.20 -4 -4 -4 -4 Ag 0.3 0.3 <3	MgO	0.00	1.33	0.00	0.01	0.01	0.01	
Na ₂ O 0.00 0.41 0.04 0.04 0.04 0.04 K ₂ O 0.00 0.13 0.01 0.01 0.01 0.02 P ₂ O ₅ 0.07 1.17 0.01 0.01 0.01 0.02 SO ₅ 0.02 30.46 0.00 0.01 0.01 0.01 CI 0.00 0.20 <4	CaO	0.07	21.41	0.02	0.03	0.04	0.06	
	Na₂O	0.00	0.41	0.04	0.04	0.04	0.04	
P20s 0.07 1.17 0.01 0.01 0.02 0.02 S03 0.02 30.46 0.00 0.01 0.01 0.01 C1 0.00 0.20 <4	K₂O	0.00	0.13	0.01	0.01	0.01	0.02	
SO ₁ 0.02 30.46 0.00 0.01 0.01 0.01 0.01 Cl 0.00 0.20 -4 -4 -4 -4 -4 Ag 0.3 0.3 -3 -3 -5 -5 -53 As <0.4	P ₂ O ₅	0.07	1.17	0.01	0.01	0.02	0.02	
Cl 0.00 0.20 <4	SO3	0.02	30.46	0.00	0.01	0.01	0.01	
Ag 0.3 0.3 <3	CI	0.00	0.20	<4	<4	<4	<4	
As 3.7 2 3.3 3.7 Ba 21 38 <9	Ag	0.3	0.3	<3	<3	<3	<3	
Ba 21 38 <9	As	<0.4	10	3.7	2	3.3	3.7	
Bi 1 0.03 <2	Ва	21	38	<9	<9	<9	<9	
Br 2 <2	Bi	1	0.03	<2	<2	<2	<2	
Cd 0.5 <0.1	Br	2	<2	<1	<1	1.0	1.5	
Ce 39 95 <13	Cd	0.5	<0.1	<3	<3	<3	<3	
Co < 2.0	Ce	39	95	<13	<13	<13	<13	
Cr 287 80 5.7 5.7 8.0 9.7 Cs 3 1 <7	Co	< 2.0	172	136.0	152.7	130.3	111.3	
Cs 3 1 <7	Cr	287	80	5.7	5.7	8.0	9.7	
Cu 3 44 <1	Cs	3	1	<7	<7	<7	<7	
Ga 1 26 1.0 1.0 1.0 2.0 Ge <0.4	Cu	3	44	<1	<1	1.0	2.0	
Ge <0.4	Ga	1	26	1.0	1.0	1.0	2.0	
Hf 0 1 <6	Ge	<0.4	<0.4	<1	2.0	1.0	2.0	
Hg 1 <0.01	Hf	0	1	<6	<6	<6	<6	
I 1 1 <6	Hg	1	<0.01	<14	<14	<14	<14	
La 30 35 <11	I	1	1	<6	<6	<6	<6	
Mn <6	La	30	35	<11	<11	<11	<11	
Mo 14 3 <1	Mn	<6	3230	10.0	6.0	433	183	
Nb 8 17 2.0 1.7 2.0 2.3 Nd n/a n/a <7	Мо	14	3	<1	<1	<1	<1	
Nd n/a n/a <7	Nb	8	17	2.0	1.7	2.0	2.3	
Ni 16 90 <1	Nd	n/a	n/a	<7	<7	<7	<7	
Pb 3 21 <2	Ni	16	90	<1	<1	<1	<1	
Rb 2 6 <2	Pb	3	21	<2	<2	<2	<2	
Sb <0.8	Rb	2	6	<2	<2	<2	<2	
Sc n/a n/a <3	Sb	<0.8	0.4	<6	<6	<6	<6	
Se 1 5.4 <1	Sc	n/a	n/a	<3	<3	<3	<3	
Sm n/a n/a 11.0 <8	Se	1	5.4	<1	<1	<1	<1	
Sn 2 3 <2	Sm	n/a	n/a	11.0	<8	9.0	<8	
Sr 7 725 1.3 2.0 3.3 3.3 Ta n/a n/a 1.3 2.0 3.3 3.3 Ta n/a n/a <5	Sn	2	3	<2	<2	<2	<2	
Ia n/a n/a <5	Sr	1	725	1.3	2.0	3.3	3.3	
Te n/a <0.1	Ta Ta	n/a	n/a	<5 45	<5 45	<5	<5	
III/II2 <3 <3 3.0 3.0 TI3 0.07 3.7 4.3 3.0 3.5 U <0.9 6 <2 <2 <2 <2 V971 <4 <4 7.0 <4 Y519 <1 <1 1.0 <1 Yb11 10.3 10.0 12.0 10.5	10 Th	n/a	<u.1< th=""><th><5</th><th>< 5</th><th><5 2 0</th><th><0</th></u.1<>	<5	< 5	<5 2 0	<0	
II5 0.07 3.7 4.3 3.0 3.5 U <0.9 6 <2 <2 <2 <2 V971 <4 <4 7.0 <4 Y519 <1 <1 1.0 <1 Yb11 10.3 10.0 12.0 10.5	וח די	(112	< j 0 7	< 3	3.U 2.0	3.U 2.E	
U <0.9	11	3	0.07	3.1	4.3	3.0	3.5	
V 9 71 <4	U	<0.9	0 74	<2	<2	<z 7 0</z 	<2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	v	9	(°1 10	<4	<4	1.0	<4	
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7 2 202 20 40	1 D 7 n		20	10.3	10.0	12.0	10.5	
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Table 6. Major (%) and trace (mg/kg) element geochemistry of pre-amended Bullsbrook Turf Farm soil, NUA, and the top 0-15 cm of soils from control and amended fertilised and unfertilised sites.



Figure 35. Depth profiles of trace elements As, Co, Cr, Mn and Nb in control and amended, fertilised and unfertilised experimental sites as determined in May 2009. Where measured concentration was less than the limit of detection (LOD), values were assumed to be equal to half the LOD for graphing purposes.



Figure 36. Depth profiles of trace elements Sm, Sr, Tl, Yb and Zr in control and amended, fertilised and unfertilised experimental sites as determined in May 2009. Where measured concentration was less than the limit of detection (LOD), values were assumed to be equal to half the LOD for graphing purposes.



Figure 37. Depth profiles of major elements Si, Ti, Al, Fe, Mn and Mg (as oxides) in control and amended, fertilised and unfertilised experimental sites as determined in May 2009. Where measured concentration was less than the limit of detection (LOD), values were assumed to be equal to half the LOD for graphing purposes.



Figure 38. Depth profiles of major elements Ca, Na, K, P and S (as oxides) in control and amended, fertilised and unfertilised experimental sites as determined in May 2009. Where measured concentration was less than the limit of detection (LOD), values were assumed to be equal to half the LOD for graphing purposes.

3.5. Trial extension soil –Measurement of Phosphorus Retention Index (PRI), Total Nitrogen (TN) and Total Organic Carbon (TOC) in Control and NUA-Amended soils

The continuation of the field trial at the Bullsbrook site allowed sufficient time to obtain an estimate of the phosphorus retention Index (PRI) and TN profiles in control and NUA-amended soils. The control soil and the NUA-amended soil immediately prior to amendment had a similar PRI profile with depth. Surface soils to a depth of 5 cm had a PRI of 4-5 while deeper soils to 45 cm depth had a PRI typically of 1-2. Immediately after amendment with NUA, the NUA amended soil had a nominal PRI of ~25 at 5 cm depth and ~6 at 15 cm depth, while three years later the PRI had declined to ~13 and ~2 at 5 and 15 cm, respectively. Below 15 cm depth (the depth of NUA incorporation) the PRI was similar in both NUA-amended and control soils.

Total nitrogen concentration displayed a complex profile in Bullsbrook soils with a similar pattern for both pre-amended soils, control soils and NUA-amended soils immediately after NUA incorporation. After a sufficient time interval, however, TN within the upper 5 cm of the NUA-amended soils was approximately twice that of all other soils and five times that of soils at 45 cm depth.

Total organic carbon (TOC) was not measured in depth profiles, with only samples from the upper 15 cm (the depth of NUA incorporation) collected. Within the control soils TOC concentration was $0.22 \pm 0.10\%$. In comparison, TOC concentration in NUA-amended soils was $0.31 \pm 0.03\%$, representing an average increase in TOC retention of ~41%.



Figure 39. Variation of Phosphorus Retention Index (PRI) with depth for NUA-amended and control soils.



Figure 40. Variation of total nitrogen (TN) with depth for NUA-amended and control soils.

3.6. Trial Extension Turf – Regrowth Post Harvesting

3.6.1. Turf Harvesting 25 November 2008

Triplicate sections of turf were harvested from each control and amended fertilised and unfertilised experimental sites, respectively, in November 2008 (Figure 41, Figure 42). The turf sections were washed thoroughly to remove adhered soil from grass roots prior to drying and weighing of turf (see Section 3.7.1).



Figure 41. Harvesting and washing sections of turf, Bullsbrook Turf Farm, 25 November 2008.

There was little visible difference between sections of turf removed from each established experimental (control or amended, fertilised or unfertilised) site, either in terms of leaf appearance (Figure 42) or appearance of turf roots (Figure 43). Soils underlying amended areas appeared marginally darker than those in control areas due to NUA content (Figure 42).



Figure 42. Areas of turf before (top) and after removal (bottom) from: a) control fertilised; b) amended fertilised; c) control unfertilised; and d) amended unfertilised sites.



Figure 43. Roots of removed sections of turf from: a) control fertilised; b) amended fertilised; c) control unfertilised; and d) amended unfertilised sites.

3.6.2. Turf Regrowth 18 December 2008

Assessment of turf regrowth approximately two weeks after harvesting did not show substantial differences between control and amended treated and untreated areas (Figure 44). In all areas, turf regrowth from remnant strips was minimal.



Figure 44. Turf regrowth as of 18 December 2008 in: a) control fertilised; b) amended fertilised; c) control unfertilised; and d) amended unfertilised sites.

3.6.3. Turf Regrowth 22 February 2009

Assessment of turf regrowth approximately 10 weeks following turf harvest clearly showed enhanced tillering (strip re-growth) of turf from remnant strips in amended fertilised and unfertilised sites as compared to untreated control sites (Figure 43). The fertilised amended site had from ~50-90% coverage of the harvested area while the unfertilised amended site had ~20-40% coverage although patterns of re-growth were more irregular in form and patchy. In contrast, control fertilised and control unfertilised re-growth varied from ~10-30% with the majority of the growth confined to the remnant strip with little tillering.



Figure 43. Turf regrowth as of 22 February 2009 in: a) control fertilised; b) amended fertilised; c) control unfertilised; and d) amended unfertilised sites.

3.6.4. Turf Regrowth 17 April 2009

Approximately 18 weeks after turf harvest, both fertilised control and unfertilised control sites exhibited a greater degree of patchiness in turf regrowth than fertilised and unfertilised amended sites, respectively (Figure 45). Invasive weed growth was also more noticeable on the control sites. Although not readily apparent from the photographs in Figure 44, both the fertilised and unfertilised amended sites also had a generally healthier and greener appearance while grass within both control sites frequently displayed signs of yellowing.



Figure 45. Turf regrowth as of 17 April 2009 in: a) control fertilised; b) amended fertilised; c) control unfertilised; and d) amended unfertilised sites.

3.7. Trial Extension Turf –Biomass and Leaf Nutrient Chemistry

3.7.1. Turf biomass

There was no significant difference between the biomass of harvested turf sections from amended and control fertilised sites, or between amended and control unfertilised sites, respectively (Figure 46). Turf from both the control and NUA-amended sites exhibited a greater mean mass per unit area than turf from non-fertilised sites; however, only the unfertilised control turf sites had a mass per unit area that was significantly (i.e., more than one standard deviation from the mean) less than the mass per unit area of turf sections from other sites.



Figure 46. Mean mass of turf sections (in kg/m²) removed from control and amended, fertilised and unfertilised experimental sites at Bullsbrook Turf Farm, November 2008.

Similar to turf mass per unit area, there was no significant difference between the mean turf height or leaf mass from amended and control fertilised sites, or between amended and control unfertilised sites, respectively (Figure 47). Turf from both the control and NUA-amended sites exhibited a greater mean turf height and leaf mass than that from unfertilised sites; both the control unfertilised and amended unfertilised turf exhibited significantly (i.e., more than one standard deviation from the mean) shorter turf height and lesser leaf mass per unit area than the fertilised sites (Figure 47).



Figure 47. Mean turf height (solid bars) and mean leaf mass of turf clippings from 10 cm² area (patterned bars) in control and amended, fertilised and unfertilised experimental sites at Bullsbrook Turf Farm, April 2009.

3.7.2. Leaf Nutrient Chemistry

Chemical analyses of turf leaves collected in November 2008 indicated that there was no significant difference in N content of turf leaves between control or amended fertilised sites, or between control or amended unfertilised sites; however, turf leaves from both of the fertilised sites contained significantly greater N than turf leaves from unfertilised areas (Figure 48). The P content of turf leaves collected in November 2008 from control fertilised sites was significantly greater than the P content of turf leaves from amended fertilised, control unfertilised, and amended unfertilised sites (Figure 48). Trends in N and P content of turf leaves collected from control and amended, fertilised and unfertilised sites in April 2009 were similar to those observed in November 2008 (Figure 49).



Figure 48. Mean leaf nitrogen content (solid bars) and mean leaf phosphorus content (patterned bars) of turf clippings in control and amended, fertilised and unfertilised experimental sites at Bullsbrook Turf Farm, November 2008.



Figure 49. Mean leaf nitrogen content (solid bars) and mean leaf phosphorus content (patterned bars) of turf clippings in control and amended, fertilised and unfertilised experimental sites at Bullsbrook Turf Farm, April 2009.

3.8. Morphology of NUA amended soil

Optical (petrographic) microscopic analysis was used to investigate the morphology of NUAamended soil from the Bullsbrook trial site (Figure 50). Given the non-cohesive nature of the soils, epoxy resin was used to stabilise the constituents prior to mounting and polishing to produce the thin sections which form the basis of each image. Three components dominated the observed morphology of the soil. The first was large sub-rounded gypsum particles which appeared as light grey to brown speckled nuclei in plane polarised light and as the brightest greybrown images under crossed polarised light. The second major component was solid, dark brown sub-rounded to rounded particles in both plane and crossed polarised light which were the most abundant component. Given the dominance of quartz sand as identified by XRD and XRF analysis (Douglas et al., 2010) it is likely that these components are quartz sands coated in Fehydr(oxide)s derived from the NUA, as unamended soils do not contain sufficient Fe to form these pervasive coatings. The final component was the presence of small, discrete Fe-hydr(oxide)s present within the resin groundmass, interstitial to the larger gypsum and quartz grains. Also notable was the presence of a ubiquitous Fe-hydr(oxide) rind enveloping individual gypsum and possibly quartz grains. A minor component identified in XRD was muscovite that occurred as a small pleochroic, brightly coloured irregular lath best observed in the mid-left of the lower left (cross polarised) image (Figure 50).



Figure 50. Optical (petrographic) microscope images of an NUA-amended soil from Bullsbrook in plane-polarised light (upper images) and crossed polarised light (lower images). Individual images are at 5x magnification. The field of view is ~10 mm across.
4. **DISCUSSION**

4.1. Control and NUA-amended soil leachate nutrient geochemistry – effects of changed fertiliser practice

Research conducted during the initial Bullsbrook Turf Farm trial documented major changes in the composition of solute and in particular nutrients (N and P species) due to the incorporation of NUA at the rate of 150 t/ha into the upper 15 cm (equating to ~5% by mass) of the Bullsbrook soil profile (Douglas et al., 2010).

As summarised in Table 4 and Figure 15, the highest nutrient fluxes to the shallow groundwater continued to emanate from the control sites whether fertilised or unfertilised although the rates were often substantially higher when compared to the original trial. This may reflect both the antecedent fertiliser practices prior to the commencement of the trial, fertiliser practices during the trial and also potentially a progressive depletion of any remaining nutrient uptake capacity.

The NUA-amended sites, somewhat in contrast to the control sites, had the lowest nutrient flux from the fertilised site; however, the flux in the unfertilised site was largely influenced by one sample which constituted ~73% of the total volume and may have reflected site specific watering and hence infiltration. The continuing low flux from the amended fertilised site, however, attests to the continuing uptake capacity of the NUA amended soils even after more than three years under turf cultivation and harvesting.

4.2. Mechanisms of P retention by NUA-amended soils

Over three years of sampling, geochemical analysis and modelling and petrography have facilitated some insights into the mechanism of retention of nutrients, and in particular P in the NUA-amended soils at the Bullsbrook Turf Farm. Two principal mechanisms for P uptake and retention by NUA-amended soil were identified.

The first evidence of one of the key mechanisms in the retention of soluble P released from fertilisers was the continual release of Ca and SO₄ due to gypsum dissolution (Figure 2, Figure 3). In addition, geochemical modelling revealed that gypsum dissolution was an equilibriumdriven process such that solute Ca and SO₄ concentrations consistently remained in equilibrium with the solid phase via dissolution (Figure 26) irrespective of the prevailing fertiliser practice. The pattern of dissolution was also revealed in major cation and anion analysis in a Piper diagram (Figure 4) where groundwater compositions were principally constrained between an irrigation water (local groundwater used within the overhead sprinkler system) and Ca-SO₄ (gypsum) source derived from NUA dissolution with an occasional contribution from rainwater infiltration as might be reasonably expected at this site.

A direct consequence of gypsum dissolution and additional alkalinity contributions from irrigation water and/ or residual lime or carbonate from the NUA was the saturation or near saturation of a number of Ca-bearing minerals, in particular calcite, dolomite, fluorite and hydroxyapatite, in the NUA-amended soils over the majority of the initial and subsequent field trial extension. Control soils were generally moderately to highly undersaturated. Whereas both of the carbonate minerals, calcite and dolomite are known to bind P by surface adsorption or co-precipitation, it is the presence of hydroxyapatite ($Ca_5(PO_4)_3OH$) that implies this was one of the major mechanisms of P removal and retention within the NUA-amended soils as evidenced by the higher residual P concentrations within the upper soils layers after over three years of cultivation (Table 6, Figure 38).

A second key mechanism in the retention of P within the NUA-amended soils was undoubtedly due to surface adsorption and/or co-precipitation onto the abundant Fe-hydr(oxide)s which were a major mineralogical constituent of the NUA. Consistent patterns of oversaturation were apparent for both goethite (Figure 17) and ferrihydrite (Figure 18) in NUA-amended soils. A number of Albearing minerals were also oversaturated including gibbsite (Figure 20), alunite (Figure 23) and basaluminite (Figure 24), but this theoretical oversaturation occured in both the NUA-amended and control soils, the latter having little P-uptake capacity. Thus, the implication is that while theoretically oversaturated, these mineral phases may either not occur or may occur in such small amounts relative to ferrihydrite (or hydroxyapatite described above) as to not significantly influence P-uptake capacity.

Preliminary petrographic analysis of NUA-amended soils using optical microscopy also provided an initial insight into the distribution of gypsum and Fe-(hydr)oxides and the potential influence that this may have on reactivity in terms of both dissolution of gypsum and P-uptake. The ubiquitous coating of quartz grains already within the Bullsbrook soil, the formation of rinds around gypsum from the NUA, and an apparent paucity of Fe-(hydr)oxides within the groundmass suggested that sometime after application there was a migration of these Fe-(hydr)oxide minerals to coat existing substrates (Figure 50). If these coatings are sufficiently pervasive, they may not only influence the surface area and potentially reaction kinetics of the substrates in terms of gypsum dissolution or P-uptake, but may also constitute an evolving substrate over time that may ultimately influence subsequent P-bioavailability. Further detailed analysis involving electron microscopy and/or microprobe analysis is required to further resolve the relationship between the Fe-(hydr)oxide minerals and P-uptake and the possible presence of secondary phases such as hydroxyapatite.

Importantly, an estimated P uptake capacity (as a PRI) has been determined for NUA-amended soils from the Bullsbrook Turf Farm. Although an estimate of P-uptake, and hence a PRI has been previously attempted on virgin NUA these measurements were compromised by the dynamic nature of dissolution of gypsum to reach equilibrium with solution (a function of the experimental solid-solution ratio and experimental duration), the concurrent presence of abundant Fe-(hydr)oxides as adsorbent substrates and the potential role of Ca in assisting surface complexation and the precipitation of secondary minerals including carbonates, but most importantly, hydroxyapatite.

Based on an estimated incorporation rate of 5% NUA (w/w) in the NUA-amended soils, and a PRI of approximately 25, an initial PRI of the NUA can be estimated at 500. Previous analysis of PRI by Gilkes et al. (1994) suggested a PRI of >1000. As documented above, however, given the dynamic nature of gypsum dissolution, the presence of abundant Fe-(hydr)oxides and the formation of a suite of secondary minerals or surface complexes this is at best an estimate. If considered over the life of an NUA application it could be considered that for the gypsum component alone, dissolution of this mineral over time due to rainfall infiltration or active irrigation would lead to the formation of a groundwater solute in near continuous equilibrium with its parent mineral. In considering the formation of hydroxyapatite alone, the dissolved P concentration due to fertiliser application and dissolution would then give rise to a range of mineral saturation states; however, as observed in this study, for the majority of the initial trial and subsequent trial extension, irrespective of fertilisation status hydroxyapatite remained at or over saturation. Thus, by this measure a PRI for NUA would be many times that estimated here, in addition to additional uptake capacity from Fe-(hydr)oxides such as goethite and ferrihydrite.

4.3. Mechanisms of N retention by NUA-amended soils

Attribution of direct mechanisms for N retention or cycling within NUA-amended soils relative to the control soils at the Bullsbrook Turf Farm site is more problematic than for that of P. Previous investigations in laboratory trials (Hamon and McLaughlin, 2002) have also noted an apparent uptake of N and in particular NH₃-N, although exact uptake mechanisms have not been determined. In addition, the initial Bullsbrook Turf Farm trial also documented substantially reduced N leaching to the shallow groundwater (Douglas et al., 2010). It is possible that reductions in N leached to groundwater under NUA-amended soils may reflect one or more of increased plant uptake and/or transformations in N species leading to nitrification-denitrification and net system loss.

4.4. Implications of modified fertiliser application to NUA-amended soils in turf farms

Modification of the fertilisation regime on both control and NUA-amended soils during the trial extension was used to investigate the potential benefit of NUA in terms of bioavailable nutrients and trace elements stored within the NUA-amended soils during the initial trial and possible agronomic and environmental benefits due to the potential for reduced fertiliser use. The main parameters used to make a preliminary assessment of the effect of a modified fertiliser practice were rates of turf regrowth after harvest, turf biomass including turf height, and leaf nutrient chemistry.

Rates of turf regrowth at the Bullsbrook Turf Farm during the trial extension generally followed the trend:

fertilised amended > unfertilised amended >> fertilised control > unfertilised control

This trend suggests that nutrients and trace elements accumulated from previous cultivation, or complimentary factors such as the increased water-holding capacity of the NUA-amended soils, had a substantial influence on turf regrowth. Importantly, however, the rate of re-growth of turf on the fertilised control site did not exceed of the rate of turf re-growth on the unfertilised amended site suggesting a strong residual effect of NUA amendment in the absence of additional fertilisation. Thus, a potential exists in NUA-amended soils with a prior history of cultivation and fertilisation at current industry-wide rates for an on-going reduced fertiliser rate to still achieve rates of re-growth superior to existing control (unamended) soils.

In contrast to the trend observed in rates of regrowth, in terms of turf biomass there was no significant difference between the biomass of harvested turf sections from amended and control fertilised sites, or between amended and control unfertilised sites, although only the unfertilised control turf sections had a mass per unit area that was significantly less than other sites. Images of root density (Figure 43) also seem to confirm this observation. Thus, while actual turf biomass and root density may be similarly increased fecundity post-harvest is afforded by NUA-amendment.

Turf height on established turf prior to harvest was substantially greater for both the fertilised amended and fertilised control sites relative to their unfertilised equivalents. These differences, however, may reflect the application of foliar fertilisers that may contain both nutrients and/or trace elements and hence may correct potential macro- or micro-nutrient imbalances and potentially increase growth rates once applied. This latter point may also be reflected in leaf nutrient measurements collected on two occasions where N and in one case, P for the fertilised control was substantially greater in the fertilised sites.

5. CONCLUSIONS

South west Western Australia currently faces a significant challenge with regard to water resources. This area, while experiencing Australia's highest rates of climate change, rapid population growth and associated development, has also seen a substantial decrease in winter rainfall since 1975 (Swan River Trust, 2007). This reduction in rainfall has led to an increase in competition for water resources between the growing urban population and requirements for environmental flow. The safeguarding of existing water resources and investigation of alternatives to potable water supplies are critical to ensure long-term sustainability of water resources in south west Western Australia.

A major problem in the largely unretentive coastal soils of south west Western Australia is leaching of applied nutrients, particularly P. Off-site transport of nutrients is not only costly in terms of increased fertilizer requirements to maintain agricultural productivity, but is detrimental to adjoining or regional and coastal aquatic ecosystems. The presence of excess bioavailable nutrients is a major factor leading to the eutrophication of natural waters and the consequent degradation in water quality as documented in a range of south west Western Australian estuaries.

Following the original 1357-day field trial, an additional 206 day trial extension was used to further investigate the efficacy of NUA as a turf farm soil amendment under a modified fertilisation regime. The hypothesis tested was that P, N and micronutrients retained in the NUA in the original trial would be bioavailable and thus continue to sustain growth in the absence of additional fertiliser inputs. Accordingly, control and NUA-amended experimental sites were further subdivided, resulting in two control and two NUA-amended experimental sites. One each of the control and NUA-amended sites received normal fertiliser applications as determined by the turf farm manager for the duration of the trial extension, whereas the remaining control and NUA-amended sites did not receive any additional fertiliser.

Dry conditions over the summer of 2008/9 resulted in low and inconsistent lysimeter leachate volumes and corresponding patchiness in turf (re)growth within amended, and to a greater extent, the control sites. In addition, soil moisture contents were also extremely variable and thus were abandoned early during the trial extension.

The highest nutrient fluxes to the shallow groundwater during the Bullsbrook Turf Farm trial extension occurred within the control sites whether fertilised or unfertilised, with flux rates for both N and P species often substantially higher than the original trial. The NUA-amended sites, in contrast to the control sites, had the lowest nutrient flux from the fertilised site. The continuing low nutrient flux from the NUA-amended fertilised site suggests a continuing uptake of the NUA-amended soils, even after over three years under turf cultivation.

The total lysimeter flux (litres of leachate collected between each sampling period), although low compared to the original trial, was consistently higher in the control fertilised and control unfertilised areas relative to both NUA-amended sites. Average lysimeter leachate pH varied widely for the four treatment sites with a similar range to the earlier long-term field trial. The amended unfertilised and amended fertilised sites had a pH of 7-8, while corresponding control unfertilised and control fertilised sites were typically 2 to 4 pH units lower. The EC of lysimeter leachates for the control fertilised and amended fertilised sites were similar to the long-running average EC from the original Bullsbrook field trial, while control unfertilised and amended unfertilised EC measurements were considerably lower. Major ion chemistry of the lysimeter leachates followed EC with differing degrees of fidelity.

Geochemical analyses of lysimeter leachates indicated that the majority of both amended fertilised and amended unfertilised lysimeter leachates had compositions between locally-derived irrigation water and the Ca-SO₄-rich leachate composition of NUA. A few samples also resembled an average Perth rainwater composition indicating that it may have occasionally constituted the major lysimeter leachate. The majority of control fertilised site lysimeter leachate samples had compositions halfway between the average irrigation water composition and that of both of the amended sites. This indicated either some surface runoff or subsurface groundwater mixing between the two sites and/or the dissolution of gypsum or other Ca- and SO₄-bearing phases within fertilisers applied to the control fertilised site.

Average dissolved P concentrations in the Bullsbrook Turf Farm trial extension varied considerably between the four experimental sites. The dissolved P concentration in the amended fertilised area was typically <0.2 mg/L, similar to that of the original field trial. Dissolved P concentrations in the control unfertilised and amended unfertilised sites were generally <2 mg/L, and intermediate in concentration between the two fertilised sites. The control fertilised site reached the highest leachate concentration of 68 mg/L P, whereas in the corresponding amended fertilised site the concentration was only *ca.* 4 mg/L. Mean NH₃-N, NO₃-N and TKN concentrations were generally similar in range to the majority of the original Bullsbrook Turf Farm field trial for all four sites.

Geochemical analyses, modelling and petrography identified two principal mechanisms for P uptake and retention by NUA-amended soil. These mechanisms included surface adsorption or co-precipitation of P to form hydroxyapatite ($Ca_5(PO_4)_3OH$), and surface adsorption and/or co-precipitation onto the abundant Fe oxides/hydroxides present within NUA.

Based on an incorporation rate of 5% (w/w) NUA in the NUA-amended soils, and a phosphorus retention index (PRI) of approximately 25, a PRI of the NUA alone of 500 was estimated. Long-term conditions, however, including the rate of gypsum dissolution will strongly influence the ultimate P uptake capacity.

Rates of turf regrowth at the Bullsbrook Turf Farm during the trial extension generally followed the trend: fertilised amended > unfertilised amended >> fertilised control > unfertilised control. This suggested that nutrients and trace elements accumulated from previous cultivation, or complimentary factors such as the increased water-holding capacity of the NUA-amended soils, and additional fertiliser applications had a substantial influence on turf regrowth. In contrast to the trend observed in rates of regrowth, there was little difference between the biomass of harvested turf sections except for the unfertilised control turf sites which had substantially less biomass than other sites. Turf height prior to harvest was substantially greater for both the fertilised amended and control sites relative to their unfertilised equivalents.

Use of soil amendment materials such as NUA, with the capacity to absorb excess nutrients and reduce nutrient loads to local water bodies, has the potential to improve or protect the ecological integrity of freshwater systems impacted by catchment fertilizer loss. The Bullsbrook Turf Farm field trial and trial extension have demonstrated that in addition to significant reduction in off-site nutrient transport resulting from soil amendment with NUA, a suite of trace elements including Cd, As and Cr were retained to varying extents within the soil profile. The substantial reduction in leachate volume resulting from soil amendment with NUA also indicated that the potential may exist for a reduction in irrigation requirements due to the greater water holding capacity of NUA-amended soil. Preliminary testing of soil profiles late in the trial at Bullsbrook also revealed substantially higher retention of carbon in the NUA-amended soil (0.33% C) relative to control soils (0.22%). Successful turf regrowth in NUA-amended soil following the discontinuation of fertilizer application showed that a further potential benefit of NUA use as a soil amendment may

lie in the reduced use of fertilizer, particularly as both P and N were effectively retained and continued to be bioavailable within the amended soil profile.

The results of the Bullsbrook Turf Farm field trial suggest substantial potential for additional uses for NUA, including as a soil amendment for unretentive soils elsewhere on Swan coastal Plain, or for the reduction of nutrient leaching under new urban and peri-urban developments (e.g. new housing estates). Comprehensive physico-chemical characterisation in addition to field trial results indicate that NUA may possess further utility in the sub-catchment to catchment scale interception of nutrients within constructed wetlands or other nutrient filtration systems.

GLOSSARY

Alumina:	Al ₂ O ₃
Alunite:	$KAI_3(SO_4)_2(OH)_6$
Anhydrite:	CaSO ₄
Basaluminite:	$AI_4SO_4(OH)_{10} \cdot 5H_2O$
Calcite:	CaCO ₃
Ca-montmorillonite:	Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Denitrification:	Chemical reduction of oxidised nitrogen species (NO _x -N)
DOC:	dissolved organic carbon
Dolomite:	CaMgCO ₃
EC:	electrical conductivity
Eutrophication:	a process by which nutrient input from such sources as sewage effluent or leachate from fertilized fields causes a water body to become over-rich in organic and mineral nutrients, so that algae and cyanobacteria grow rapidly and deplete the oxygen supply
Ferrihydrite:	Fe(OH) ₃
Fluorite:	CaF ₂
Gibbsite:	Al(OH) ₃
Goethite:	α-FeOOH
Gypsum:	CaSO ₄ ·2H ₂ O
Hematite:	α -Fe ₂ O ₃
HF:	Hydrofluoric acid
HNO ₃ :	Nitric acid
Hydroxyapatite:	Ca ₅ (PO ₄) ₃ OH
IAP:	ion activity product
ICP-OES:	inductively-coupled plasma spectroscopy-optical emission spectrometry
Illite:	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂
Ilmenite:	FeTiO ₃
Jurbanite:	AIOHSO ₄
K-jarosite:	$KFe_3(SO_4)_2(OH)_6$
Kaolinite:	Al ₂ Si ₂ O ₅ (OH) ₄
Lime:	Ca(OH) ₂
LREE:	light rare earth elements (La, Ce and Pr)
Lysimeter:	a subsurface reservoir used to capture soil leachates
Manganite:	MnOOH
Magnetite:	Fe ₃ O ₄

Na-jarosite:	$NaFe_3(SO_4)_2(OH)_6$
NH ₃ -N:	ammonia nitrogen
Nitrification:	chemical oxidation of reduced nitrogen species (NH ₃ -N)
Nitrophoska Blue:	a pelletised fertilizer specifically formulated for the turf industry
NO _x -N:	nitrate (NO ₃) + nitrite (NO ₂)
NUA:	neutralised used acid, a by-product of heavy minerals processing
PO ₄ -P:	phosphate phosphorus
PRI:	phosphorus retention index
Pyrolusite:	MnO ₂
Pyroxene:	(Ca,Na)(Mg,Fe,Al,Ti)((Si,Al) ₂ O ₆)
Quartz:	SiO ₂
Quicklime:	CaO
Rhodochrosite:	MnCO ₃
Rutile:	TiO ₂
Schwertmannite:	Fe ₈ O ₈ (OH) ₆ SO ₄
SI:	saturation index
SRP:	soluble reactive phosphorus
Sulfuric acid:	H ₂ SO ₄
TEM:	transmission electron microscopy
TIN:	total inorganic nitrogen; TIN=NH ₃ -N + NO ₃ -N
TKN:	total Kjeldahl nitrogen; TKN=NH ₃ -N + organic N
TN:	total nitrogen, sum of all nitrogen species
TOC:	total organic carbon
TP:	total phosphorus, sum of all phosphorus species
Urea:	$(NH_2)_2CO$; an organic compound with two amine (- NH_2) groups joined by a carbonyl (- CO)
XRD:	X-ray diffraction
XRF:	X-ray fluorescence

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