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Deniz Sara Arslan

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Declaration

I hereby declare that this thesis is the results of my own investigations, except where otherwise stated. All other sources are acknowledged by bibliographic references. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree unless, as agreed by the University, for approved dual awards.

Candidate: Deniz Sara Arslan

Signature:

Acknowledgements

Abstract

The over-application of mineral fertilisers has long been regarded as an unsustainable practice due to the various negative implications it has on terrestrial and aquatic habitats, the atmosphere and the soil itself. However, due to increasing population pressures and the undeniable need for intensive agriculture, the use of fertilisers is unlikely to diminish in the near future. It is for this reason that organo-mineral fertilisers have gained increasing attention for potentially being as efficient as mineral fertilisers with fewer associated risks. Whilst organo-mineral fertilisers have not been extensively studied in general, they have been studied even less in a non-agricultural setting, e.g. sports turf nutrition. Two organo-mineral specialty fertilisers (manure-based and plant-based) for professional sports turf were therefore tested alongside two mineral-based fertilisers (urea-based and ammonium-based) and a control. Three experiments were set up in a controlled greenhouse to replicate small-scale sports-turf environments, observing the agronomic efficiency as well as the impacts of the various fertilisers on soil characteristics, microbiology and environmental impacts such as leaching, ammonia and nitrous oxide emissions. Results demonstrated that soil biochemical properties did not extensively differ between treatments, except for pH where the organo-mineral fertilisers significantly increased soil pH. Microbial activity demonstrated an initial lag time in the mineral fertiliser treatments compared to the organo-mineral treatments and the control. Grass dry matter yield was significantly greater for all treatments in comparison to the unfertilised Control but did not significantly differ between the mineral and organo-mineral treatments. There was an indication of increased nitrogen content of the grass clippings from all fertiliser treatments compared with the control, but this was not significant. Leaching of nitrate and ammonium, as well as gaseous ammonia and nitrous oxide emissions were highest from the urea-based mineral fertiliser with lowest losses from the plant-based organo-mineral fertiliser (although omitted from the nitrous oxide experiment). The results provide evidence to support the efficient and sustainable use of organo-mineral fertilisers on professional sports-turf with future research being recommended to run agronomic experiments for longer and to incorporate a wider variety of mineral fertilisers, specifically slow-release varieties.

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1.0 Introduction to the study

The use of fertilisers is an inevitable consequence of our growing population pressures and undeniable need for intensive agriculture. The fertilisation requirements for agricultural crops can vary drastically depending on variables such as crop and soil type, age, usage, biology, weather patterns (Mark and Puri, 2013). With the hopes that precision agriculture (and land management) become more of a reality as time goes on, we currently rely on maximising nutrient use efficiency without being able to assess every type of soil ecosystem that fertilisers are applied to. The over-application of fertilisers, is an issue that comes with a variety of negative environmental impacts. The use of organo-mineral fertilisers (fertilisers that have a partial organic and partial mineral source) has shown to have promising results in terms of maintaining yield and production efficiency whilst reducing harmful side-effects. However, a large amount of studies undertaken on organo-mineral fertilisers use raw manure or plant matter that is supplemented by mineral fertilisers, resulting in skewed comparisons e.g. 300kg ha^{-1} of mineral fertiliser and 3t ha^{-1}, 5t ha^{-1}, 10t ha^{-1} or similar of organo-mineral fertilisers (e.g. Akanbi et al. 2006; Ibe et al., 2011). Whilst these types of studies are important and also provide encouraging results, it is equally important to undertake studies on organo-mineral fertilisers in a commercial fertiliser form (e.g. granular or liquid) to better understand their performance and consequential management. Furthermore, previous studies on organo-mineral fertilisers have focused more on crop production and agricultural soil dynamics with very few focusing on nutrient supply to non-agricultural ecosystems, e.g sports turf, and the potential negative environmental impacts such as nutrient leaching, volatilisation of ammonia or nitrous oxide emissions from such systems. This study aimed to better understand the nitrogen use efficiency of organo-mineral fertilisers as a commercial granular compound, when applied to professional sports turf environments. For this to take place, three experiments were undertaken. The first was a potted agronomic experiment that looked at the compared the effect of organo-mineral fertilisers with mineral fertilisers on a variety of soil chemical properties, microbial activity and leaching of nitrogen (N) as nitrate (NO_3^-) or ammonium (NH_4^+). The second experiment used a desktop-based flow-through system that was set up using acid traps to assess ammonia (NH_3) emissions. The third experiment looked at nitrous oxide (N_2O) emissions using an automated closed-chamber system.

1.1. Introduction to ecosystem services delivered by soil and turfgrass environments

Soil is arguably the most important resource on Earth as it encompasses and enables a wide range of other products and processes. While in its simplest form, soil is the combination of mineral material from physically weathered rocks and organic matter from the decomposition of plants and animals, the differences in composition ratios as well as age, anthropogenic and environmental influence affect the overall soil health and quality (Ashman and Puri, 2013). The benefits that humans can obtain from healthy soils are incredibly widespread with McBratney et al. (2014) arguing that the maintenance of soil security (and its ecosystem services) be given the same attention as food security, water security, energy security, climate stability, biodiversity and other ecosystem services (ES). Table 1.1 depicts some of the various types of ES delivered by soil as described by multiple sources. An economic estimate of the value of soil biodiversity for ES was estimated at 1.5 quadrillion USD (Pimentel et al. 1997) whereas Table 1.2 is a summary of various soil ES and their economic value as taken from Jónsson and Davíðsdóttir (2014). Nonetheless, these values can be criticised due to lacking ES and lacking data on ES but also due to many of the processes being life-enabling and potentially priceless.

Table 1.1: List of soil ES as described by Breure et al. (2012), Robinson et al. (2013), Adhikari and Hartemink (2016), Bavaye et al. (2016), Birgé et al. (2016) and Baer and Birgé (2018). Percentages correspond to amount of papers published on type of soil ecosystem service (between 1975-2014) (Adhikari and Hartemink, 2016).

Type of Ecosystem Service	Ecosystem Service
Provisioning (34%)	Agriculture (food, fuel, textiles, fibres, timber) through provision of topsoil, subsoil, peat, etc.
	Sand/Clay/Gravel/Coal minerals
	Turf/Sod
	Biomedical resources (including genetic diversity)
	Bioresources, soil stabilisers
	Decomposition and waste processing environment
Regulating (41%)	Cleaning, degrading, transforming
	Water (in/)filtration and purification (Hydrological regulation)
	Nutrient retention
	Carbon sequestration
	Soil organic matter dynamic and structure regulation
	Structural support buffering (shrink/swell)
	Climate regulation & Atmospheric gas regulation
	Hazard regulation
	Buffering of extreme temperatures
	Buffering floods and droughts
	Erosion control

Landslides/slumps
Liquifaction
Dust emissions
Biodiversity
Gene pool
Pollination and seed dispersal
Pest control and pathogen/disease regulation; human pathogens
and disease transmission + vector control

Cultural (8%)   Sports and recreational fields
Preservation of historical artifacts
Cooking
Burial grounds
Aesthetic landscapes
Spiritual

Supportive (14%)   Biodiversity
Bioturbation
Nutrient cycling

Table 1.2: Economic values for soil ecosystem services, displayed as international dollars through conversion of a local currency to USD and correcting to the purchasing power of USD (Jónsson and Davíðsdóttir, 2014).

Soil service category	Services/functions	Valuation method	International dollar (id$) 2012	id$ units
Support functions	Biodiversity pool	Various methods	2.1 trillion	id$/yr^{-1}
	Nutrient cycling	Replacement cost, market price, hedonic price	24–180	id$/ha^{-1}/yr^{-1}
	Soil formation	Market price	18–28	id$/ha^{-1}/yr^{-1}
	Water cycling	Market price	62–126	id$/ha^{-1}/yr^{-1}
Regulating services	Biological control of pests and diseases	Avoided cost, provision cost	59–268	id$/ha^{-1}/yr^{-1}
	Climate regulation	Choice experiments, market price, replacement cost	2–268	id$/ha^{-1}/yr^{-1}
	Hydrological control	Damage cost, hedonic cost, replacement cost, benefit transfer, defensive expenditure, provision cost, contingent valuation, choice modelling	30–1175	id$/ha^{-1}/yr^{-1}
	Recycling of wastes and detoxification	Provision cost	77–330	id$/ha^{-1}/yr^{-1}
	Filtering of nutrients and contaminants	Provision cost, defensive expenditure	544–6402	id$/ha^{-1}/yr^{-1}
Provisioning services	Biomass production	Market price, producers price	231–22,219	id$/ha^{-1}/yr^{-1}
	Clean water provision	Damage cost, net factor, hedonic cost	34–101	id$/ML
	Raw materials	Producers price	9–147	id$/t
	Physical environment	Defensive cost, replacement cost, provision cost	32–110	id$/ha^{-1}/yr^{-1}
Cultural services	Heritage	Net factor	ND	No data
	Recreation	Damage cost	571,720	id$/yr^{-1}
	Cognitive	No data	ND	No data

Turfgrass landscapes also provide important ES such as high quality aesthetic value which may simultaneously increase property value, an irreplaceable surface for recreational and sports activities in both a private and professional setting, the maintenance of air, soil and water quality and the reduction of glare, noise and visual pollution (Aldous, 2014; Monteiro, 2017). Larson et al. (2011) also state that the habitat that turf ecosystems provide for a variety of beneficial invertebrates contributes to pest suppression, the decomposition of clippings and that, nutrient cycling and good soil tilth. Furthermore, according to Monteiro (2017), compared to other types of vegetation cover, turf seemed to have a higher potential for reducing runoff, increasing infiltration, purifying water from sediment and pollutants, controlling erosion, improving soil quality and reducing fire hazards. It can be noted that lawns are often seen as

an "ecological disaster" due to the high amounts of soil additives applied to them (e.g. pesticides, fertilisers). However, this makes sustainable management even more important as Milesi et al. (2005) calculated that managed turfgrasses (i.e. golf courses, sports fields and home lawns) cover around 164,000km^2 of land in the USA which was three times larger than the area used for any irrigated crop at the time. The amount of land covered with managed turfgrass was only expected to increase.

Soil micro, meso and macro-organisms have been identified in playing a large role in enabling and increasing the efficiency of soil ES or influencing ecosystem stability through affecting plant diversity, productivity and reaction to environmental changes (Barrios, 2007; Blouin et al. 2013; Yang et al. 2018). Furthermore, Lehman et al. (2015) stress the importance of using soil biological services to mitigate soil degradation. Microorganisms in the soil promote soil aggregation through biomass and secretions while fungi, plant roots and macro invertebrates help aggregation through the production of glycoproteins, through rhizodeposition or by tunnelling and transforming organic residues, respectively. Furthermore, microorganisms play a large role in moderating the abundance, speciation and plant availability of nutrients in soil which is of particular importance when considering added nutrients or other chemical treatments into the soil. Bacteria, fungi and predatory insects can also be used as control agents for insect pests while invertebrates also control weed populations (Lehman et al. 2015). Finally, microorganisms can affect plant growth and vigour through a variety of ways. All these reasons and more are why Lehman et al. (2015) recommend understanding a soil's biological complexity to be able to manage the land appropriately through targeted biological changes.

Decomposing biological matter within the soil constitutes soil organic matter of which 50-58% of dry weight is soil organic carbon (SOC) (Johns, 2017). SOC has been correlated to soil biodiversity, food webs and some ES and is therefore often used as a proxy to determine soil health, especially as it is considered to play a large role in soil fertility and agricultural productivity, made evident through the conventional soil management practices that deplete SOC stocks by 0.2-1% annually, which in turn reduce the soil's ES deliverance capabilities in the long term (Brady et al. 2015). SOC can be increased through a variety of microbial processes, irrigation, the addition of manure, compost or fertiliser to the system, root exudates, root turnover and overall plant growth (Trost et al., 2013; Johns, 2017; Schipper et al. 2017). Paradelo et al. (2015) also find that liming soils increases SOC content in most cases – likely due to an increase in plant productivity through more favourable soil conditions. While grazing is seen as having a negative impact on SOC stocks, with Eze et al. (2018) measuring a

significant net decrease in SOC due to grazing (while lime and fertiliser additions increased SOC) and with Tessema et al. (2020) reporting that grazing management could increase SOC in East African grasslands, other large scale reviews report that external factors play a larger role. Abdalla et al. (2018) mention that the impact of grazing on SOC is climate dependant, furthermore supported by McSherry and Ritchie (2013) stating that six variables explain 85% of the variation in the effects of grazing on SOC (soil texture, precipitation, grass type, grazing intensity, study duration, sampling depth). However, mechanical processes including tillage but also extensive mowing negatively impact SOC, causing Zhang et al. (2013) to advise grassland managers to use appropriate mowing heights and frequencies on hay grasslands, among other recommendations.

Since nitrogen (N), phosphorus (P), and potassium (K) are largely considered limiting elements for plant growth, and therefore to an extent SOC, their addition can help to increase production although also dependent on environmental conditions, therefore needing more research – especially in combination with other nutrients (Gong et al. 2021). Whilst a review by Schipper et al. (2017) found that most studies on P fertiliser applications do not change SOC stocks, other long-term studies or large-scale reviews have determined that the input of N fertilisers seems to increase SOC stocks however when taking into account its production, transportation and application emissions, there is only a net gain in carbon sequestration in temperate cropping regions (Alvarez, 2005) causing Körschens (2002) to state that the only environmentally acceptable way to attain high yields would be to combine organic and mineral fertilisers. This is further supported by Liu et al. (2006) that find the highest SOC increases are with manure and mineral fertiliser application, as opposed to sole manure or mineral fertiliser application, also supported by Du et al. (2009) who find that the improvements by N and P fertiliser alone had a negligible effect on SOC stocks, unlike when crop residues were also added alongside fertiliser, further supported by Li et al. (2018) who report that all of the treatments that received organic manure had significantly higher SOC stocks compared to the others (standard mineral application, double mineral application, control). The limited research on the effect of fertilisers on turfgrass' SOC content has shown that while it does increase, it may be offset when considering the other emissions related to fertilisers, as mentioned previously (Qian et al. 2010). When including these into calculations, Townsend-Small and Czimczik (2010) calculate that mineral fertiliser usage on ornamental lawns may be slightly offset through carbon sequestration with low rates of fertiliser application whereas application on athletic fields is not offset due to the frequent surface restoration.

Franzluebbers and Haney (2006) originally recommended the following indicators to be used primarily in organic agricultural systems as determinants of soil health: SOC and N, inorganic N, extractable P, water-stable aggregation and stability, flush of CO_2 post wetting of soil, microbial substrate utilisation, and soil pH. However, with climate change, soil moisture may be an effective method of measuring stress in a natural resource system and should potentially also be considered (Mukherjee et al. 2018). Furthermore, Trivedi et al. (2016) argue that the bacterial communities in soil (with their abundance, richness and composition) are important drivers for ecosystem functions and their sensitivity to changes in land use management help them act as early indicators for soil quality, especially as these changes may precede detectable changes in soil physical or chemical properties. Similarly, an analysis by Bünemann et al. (2018) found that biological indicators are under-represented even though they show great potential and that the commonly used indicators are soil organic matter, soil pH, available P and water storage. Table 1.3 shows suggestions for appropriate indicators relative to focus of study (Raghavendra et al. 2020).

Table 1.3: Proposed measurable indicators of soil health relative to focus of study (taken from Raghavendra et al. 2020).

Soil health indicators	Rationale for selection
Bulk density	Plant root penetration, porosity, adjust analysis to volumetric basis
Soil aggregate stability	Soil structure, erosion resistance, crop emergence an early indicator of soil management effect
Water holding capacity/infiltration	Runoff, leaching, and erosion potential
pH	Nutrient availability, pesticide absorption and mobility, process models
EC (electric conductivity)	Defines crop growth, soil structure, water infiltration; presently lacking in most process models
CEC (cation exchange capacity)	CEC represents the total amount of exchangeable cations that soil can absorb
Soil organic carbon/organic matter	Defines soil fertility and soil structure, pesticide and water retention, and use in process models
Soil nutrients status	Availability of crops, leaching potential, mineralization/immobilization rates, process modeling, capacity to support plant growth, environmental quality indicator
Suspected pollutants	Plant quality, and human and animal health
Soil respiration	Biological activity, process modeling; estimate of biomass activity, early warning of management effect on organic matter
Enzymes (dehydrogenase, β-glucosidase, acid and alkaline phosphatase, microbial biomass, and soil respiration)	Electron transferences in the respiratory chain in living cells, C oxidation, organic phosphorus cycling, source and/or drain of C and nutrients, microbial mineralization of organic carbon
Mycorrhiza	Nutrient mobilization, soil aggregation
Trichoderma	Residue decomposition
Lipid profiling	Diversity and biomass
Earthworm	Indicate relative change in soil structure, nutrient recycling, regulate soil water, aeration, and provide drainage

1.2. Current and future trends in soil health and fertiliser use

While many benefits are shown to come from the maintenance of healthy soils, the unfortunate reality demonstrates that soil health is rapidly depleting around the world with 25% of land being highly degraded with an uncertain future due to many variables, some undetermined (Gomiero, 2016). Stringer (2012) summarises soil degradation into three main categories: erosion, chemical degradation and physical degradation. Table 1.4 gives more detail on each of these processes. Stringer (2012) also mentions the importance of soil biodiversity for the maintenance of all soil processes and states that warming climates significantly decrease

richness and diversity of these communities, affecting ecosystem functions. A further point of concern is the effect of microplastic pollution on soil properties and its biota which has limited research till date but hazardous potential (Zhu et al. 2019).

Table 1.4: Examples of processes resulting in soil degradation. Data taken from Stringer (2012).

Type of degradation	Examples
Erosion of fertile topsoil	Natural erosion on slopes through rainfall and surface runoff. Anthropogenic induced through clearing of vegetation (e.g. deforestation). Anthropogenic induced through post-harvest exposure of agricultural land. Climate change induced through increased rainfall or other weather patterns in certain locations.
Chemical degradation	Loss of nutrients and/or organic matter through intensive agriculture or lack of return of nutrients to soil either due to lack of access to appropriate fertilisers (i.e. poverty) or lack of incentive to maintain soil quality (i.e. lack of land ownership). Salinisation due to natural transportation of salts from saline deposits or groundwater to soil or due to improper irrigation by humans. Acidification through intensive agriculture or through local or diffuse pollution (e.g. SO_x and NO_x emissions from industry and transport causing soil acidification).
Physical degradation (affects e.g. soil water flows, gaseous exchange/diffusion, biota)	Compaction of soil through heavy machinery or increased grazing. Sealing of soil under impermeable material i.e. concrete, plastic, glass, metal. Water logging Subsidence

The lack of recognition in including soil as a vital resource plays a large part in the difficulties of reducing soil degradation (Koch et al. 2013). While not all degradation happens on agricultural soil, many mitigation efforts focus on agricultural management which Lal (2015) summarises into four categories: 1) retention of crop residue mulch, 2) incorporation of a cover crop in the rotation cycle, 3) use of integrated nutrient management involving combination of chemical and bio fertilisers, 4) elimination of soil mechanical disturbances.

An analysis of 77 countries and their fertiliser usage (against a variety of factors) from 1970-2011, established that a 1% increase in population pressure corresponds to a 0.118% increase in fertiliser use intensity (Xiang et al. 2020). This is somewhat supported through India's rapid increase in fertiliser consumption, jumping from 70,000 tonnes in 1950 to >20 million tonnes four decades later and only slowing due to supply-side constraints (Chand and Pandey, 2009). In 2030, nitrogen fertiliser consumption is expected to be between 18.76 and 23.45 Mt, depending on growth rates and pricing policies (Tewatia and Chand, 2017). In order to cope with the growing global population pressure, Kummu et al. (2012) suggest improving the food

supply chain. According to their findings, a quarter of global food crops for food supply are wasted and mitigating this could result in a decrease in fertiliser usage by a fifth (alongside a reduction in freshwater and cropland usage). Simultaneously, it seems that most "developed" countries use policies to reduce their fertiliser usage whereas most "developing" countries use policies to increase productivity (Xiang et al. 2012).

In regards to agricultural grasslands, these make up around 25% of the global land surface area which makes them a key component of land management concerns, especially since grassland ecosystems play a large role in carbon storage and sequestration (Yang et al. 2017). Around two thirds of grasslands are used agriculturally and are commonly utilised to supply livestock feed (Ros et al. 2020). While the demand for meat and dairy is expected to double by 2050, the sustainable increase of productivity in grassland ecosystems is therefore vital (Ros et al. 2020). For intensively farmed temperate grasslands, the recommended rates of added N fertiliser are between 200-400 kg N/ha (Ghosh et al. 2017). Understandably, golf courses require a much lower N application as their primary use is to not supply high yields. N and P are largely the focus of fertiliser related research, although potassium (K) has been shown to be a limiting nutrient as well in up to 70% of studied terrestrial ecosystems (Sardans and Peñuelas, 2015). In urban turfgrass systems (including recreational lawns, parks, school grounds, athletic fields etc.) there is an increasing shift in reducing the amount of mineral fertilisers used. This is largely due to the high amount of emissions from applied fertilisers (N in particular) as well as concerns regarding leaching, runoff and its respective knock-on effects (see section 4) (Bartlett and James, 2011; Kong et al., 2014; Mathew et al., 2016).

Although the mineralisation of soil organic matter is the predominant source of N in extensive grassland systems, the increase in animal agriculture has encouraged the use of increasing amounts of N fertiliser, although unfortunately only 30% is recovered by plant protein and 70% is lost to the environment (Ghosh et al. 2017). Australia exemplifies this increased reliance as it has shifted from receiving its N in grasslands from almost entirely legumes to almost entirely fertilisers – a trend that will have to be reversed for sustainability concerns (Rawnsley et al. 2018).

Another concern with the increasing demand of fertiliser use on grasslands is the requirement of P – a finite and depleting mineral resource – which is expected to have to increase over four times to achieve an 80% increase in grass production to supply the projected demand for 2050 (Sattari et al. 2016). Globally, the most important P input for grassland systems is from manure but mineral fertilisers are also still used as inputs, with roughly 80% of P fertiliser inputs being used by Europe alone (see Table 1.5). Furthermore, historically there has been net depletion of P in grassland systems due to a lack of input from feed (from cropland systems), mineral fertiliser, manure or atmospheric deposition and an affluence of outputs through animal products, the transfer of manure to cropland systems and erosion (Sattari et al. 2016). 113Tg (113 million tonnes) were transferred from grassland systems to cropland systems for fertilisation between 1970-2005 (Asia being responsible for 44%; other regions ~10% each) (Sattari et al. 2016). However, in the UK, agricultural grasslands are the most prominent point of accumulation of P in the soil (Rothwell et al. 2022).

Table 1.5: Phosphorus budget in various grassland systems in 1970 and 2005 (Sattari et al. 2016).

Region	Area (10^6 ha)		Grass P uptake (kg ha^{-1})		Internal manure (kg P per ha)		External manure (kg P per ha)		Fertilizer P (kg P per ha)		Imported feed* (kg P per ha)		Exported manure to cropland* (kg P per ha)		Livestock products (kg P per ha)		Other use of manure (kg P per ha)		Erosion (kg P per ha)		Grassland P budget† (kg P per ha)	
	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005	1970	2005
Africa	882	904	1.9	3.1	1.6	2.6	0.0	0.0	0.1	0.1	0	0.1	0.3	0.5	0.0	0.1	0.0	0.0	0.1	0.2	−0.1	−0.4
Asia	874	971	5.1	6.4	1.8	2.1	0.1	0.2	0.1	0.1	0.2	0.7	1.2	1.8	0.1	0.4	2.2	2.5	0.2	0.2	−3.1	−3.7
East Europe	107	115	10.2	4.0	8.0	3.4	0.7	0.6	0.4	0.1	2.6	2.2	3.1	1.4	1.2	0.8	0.3	0.1	0.6	0.6	−1.3	0.2
Latin America	487	546	4.0	6.0	3.6	4.9	0.0	0.0	0.1	0.1	0.2	0.2	0.5	1	0.2	0.4	0.0	0.0	0.3	0.5	−0.5	−1.4
North America	263	256	5.1	4.1	4.5	3.4	0.4	0.5	0	0	1.2	1.9	1.2	1.7	0.5	0.7	0.1	0.2	0.3	0.4	−0.3	−0.4
Oceania	462	407	1.3	1.4	1.2	1.2	0.0	0.0	0.1	0.1	0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.1
West Europe	79	67	18	15.7	13.3	13.2	1.6	2.5	3.2	1.7	2.1	4	4.5	3.6	2.2	2.8	0.0	0.0	1.5	2.1	−1.1	−0.1
World	3,150	3,270	4.0	4.6	2.6	2.9	0.1	0.2	0.1	0.1	0.3	0.6	0.8	1.1	0.2	0.4	0.6	0.8	0.2	0.3	−1.1	−1.5
Intensive	560	537	13.2	16.1	7.6	8.8	0.6	1.1	0.6	0.4	1.9	3.5	4	5.8	1.0	1.6	2.4	3.4	0.7	1.0	−4.8	−6.6
Pastoral	2,590	2,730	2.0	2.4	1.5	1.7	0.1	0.2	0	0	0	0	0.1	0.2	0.1	0.1	0.2	0.3	0.1	0.2	−0.2	−1.4

Internal + external manure + fertilizer P are soil P inputs; grass P uptake is an output term in the soil P budget.
*Imported feed P represents the feed produced in croplands that is taken in by ruminants in the grassland system. Exported manure to cropland is the manure P produced by ruminants (intensive and pastoral) that is transferred to croplands.
†The grassland system P budget is computed as follows: external manure (applied manure from non-ruminants), fertilizer P, imported feed and atmospheric deposition (0.2 kg P per ha) are grassland P inputs; and export manure to cropland, livestock products' P, the other use of manure P and erosion are grassland P outputs. Weathering is an internal flow.

The agronomic efficiency of P to global average grassland yield is 32kg kg^{-1} (yield increases by 32kg per kg of applied P), but the agronomic efficiency decreases with higher P application rates (Ros et al. 2020.) Apart from the quantity of P already present in the soil prior to application, soil pH, soil organic matter content and soil clay content all had significant impacts on yield response to P fertiliser applications. A soil pH of 5-6 showed the highest yield response (of 60%) which is likely due to acidic soils limiting the availability of plant available P due to its binding with aluminium and iron hydroxides, while alkaline soils (> 7), increase the probability of P forming calcium-phosphate precipitates, which are poorly soluble and again decrease plant available P (Ros et al. 2020). The correlation between soil organic matter content and yield response to P showed that the agronomic efficiency of P was 9 times higher in soils with an organic matter content that was > 5% (compared to soils <2% organic matter content)

and is hypothesised to be due to the competition between P and organic matter on soil reactive surfaces as well as higher organic matter contents in soil improving soil structure, water holding capacity, aeration, infiltration and a reduced risk of soil erosion (Ros et al. 2020). Finally, a soil clay content of < 10% did not have a significant increase in grassland production post-fertilisation whereas soils with a clay content above 25% had a yield response of 75%. This is thought to be due to the retention of water and nutrients in the soil through an increased clay content (Ros et al. 2020). Furthermore, the inclusion of legumes (e.g. clover or alfalfa) in grassland ecosystems doubled the agronomic efficiency of P fertiliser applications (22kg kg^{-1} without legumes; 46 kg kg^{-1} with legumes), and is due to the higher requirement of P in legumes which is less accessible due to their thicker roots and shorter root hairs (Ros et al. 2020).

This research demonstrates that it is important to find a balance between mineral input and yield response, e.g. by including/increasing legume cover, managing livestock manure returns to grasslands, understanding soil properties prior to application.

1.3 Fertiliser Management on Sports-turf

In high end sports turf, the limited amount of soil and organic matter and high irrigation and drainage of the grounds (through sand-based substrate) not only increases the risk of fertiliser losses to the environment but also reduces the amount of ecosystem services made available from the soil environment (Barton and Colmer, 2006; Townsend-Small and Czimczek, 2011). Sports-turf management is very different to agricultural applications of fertilisers for a variety of reasons. Primarily, the desired outcome is not improved yield, it is improved aesthetic and playability, which in turn requires a frequent fertilisation management plan alongside other processes, for example irrigation, surface restoration, mowing at short heights and other chemical applications (Wilson, 2018; Riches et al., 2020). Nitrogen fertilisation is particularly important for colour, vigour, and rooting and is applied mainly as quick or slow-release inorganic nitrogen fertilisers but also organic N fertilisers (Zanelli et al., 2021). The use of organo-mineral fertilisers on professional sports-turf is not known. The frequent and intensive management of sports-turf is so prominent that a full life-cycle assessment found artificial turf to be more sustainable than regular turf for sportsgrounds when used at full capacity (Itten et al., 2021). Data from sports-turf is lacking throughout literature, specifically in regards to gaseous emissions, which may be due to the grounds needing to remain playable and not obstructed with equipment and/or not having large amounts of turf/soil cores extracted (Riches

et al., 2020. Nonetheless, Zanelli et al. (2021) observed that factors like soil temperature, moisture and grass types/combinations largely influence the success of different types of nitrogen fertiliser.

1.4 Organic, mineral and organo-mineral fertilisers

The addition of nutrients to high quality athletic fields is essential for the maintenance of a fair, aesthetic, and safe playing environment. The main nutrients of concern for appropriate turf management and their functions are outlined in Table 1.6. The wide variety of fertilisers ensure thatthe desired outcome is able to be targeted alongside the plant and soil requirements whilst considering environmental conditions. As mentioned previously, the different potential negative impacts that fertilisers can have on the environment should be mitigated where possible, causing the choice of appropriate fertilisation to become difficult as this will be specific to every site applied, taking into consideration soil type, age, topography, biology amongst others. For the purpose of this section, only fertiliser functions will be taken into consideration and none of the external costs or benefits a groundskeeper may encounter will be discussed i.e. variance of cost.

Table 1.6: Primary nutrients, their respective functions and tissue target range (in %) for sports turf (adapted from Cockerham et al. 2011).

Nutrient	Function	Tissue Target Range (%)
Nitrogen	Major component of plants, specifically chlorophyll	2.8-5.5
Phosphorus	Protein production Energy transfer (ATP) Root, rhizome, stolon and tiller development	0.3-0.6
Potassium	Metabolic processes/Water use	1.0-3.5

Simply put, an organic fertiliser must contain organic C and nutrients that are solely of biological origin whereas a mineral fertiliser alternatively contains nutrients in their mineral form and thus do not have to be carbon-based or biologically derived (EC Regulations, 2019). Needless to say, there are further criteria involved in classifying a fertiliser as organic, organo-mineral or inorganic however, when considering solid fertilisers, the main components are a minimum of 15% organic C by mass and a minimum of 1, 2, or 2.5%, by mass, of a nutrient (depending on which nutrient and whether or not it is the only primary nutrient) for organic fertilisers (EC Regulations, 2019). For solid inorganic fertilisers, the minimum threshold for

organic C is 1% by mass (that is not present in various forms e.g. urea, coating agents) with minimum nutrient thresholds for the primary nutrients falling at 1.5-10% depending on a variety of factors (variability due to nutrient type, combination and whether it is a straight or compound fertiliser) (see: PFC 1(C) of EC Regulations, 2019).

The fast-acting and dependable nature of mineral fertilisers has inevitably caused organic manures and other organic sources to be replaced – largely being upheld to this day (Tripathi et al., 2020). However, the supplementation of mineral nutrients to organic fertilisers allow less fertiliser to be added whilst increasing the predictability and reliability of the fertilisers (Smith et al., 2020). Commonly used mineral forms of N are urea (CH_4N_2O) and ammonium nitrate (NH_4NO_3) with urea currently accounting for 73.4% of global N fertiliser applications (Zhang et al., 2019). Both forms come with their own set of cons with urea being prone to the volatilisation of ammonia (NH_3) and ammonium nitrate being more susceptible to leaching and both being susceptible to nitrous oxide (N_2O) emissions, either directly or indirectly (Chambers and Dampney, 2009; Smith et al., 2012; Forrestal et al., 2016; Wang et al., 2019). Fortunately, the aforementioned negative impacts can be mitigated through the use of coatings and inhibitors although their efficiency is still debated (Chen et al., 2018; Chen et al., 2019; Folina et al., 2021; Woodward et al., 2021).

The use of organo-mineral fertilisers represents a promising solution to the issues regarding lack of nutrition and reliability from organic fertilisers and the potential for harmful impacts from mineral fertilisers. A major issue with the current understanding on the impacts of organo-mineral fertilisers is that the majority of studies use raw materials (e.g. manure, biochar etc.) as the organic component in their studies. This creates issues as the comparisons may be 300kg ha^{-1} of mineral fertiliser with e.g. 3, 5 or 10t ha^{-1} of organo-mineral fertiliser (e.g. Akanbi et al. 2006; Ibe et al., 2011). While these are important studies to understand more economic options for fertilisation that still provide high yield and nutritional quality of products (especially for low-income countries), they do not necessarily provide reliable information how the soil characteristics are affected by the various fertilisers. For example, by applying raw manure which has a moisture content of 6-90% and an organic matter content of 18-47% (Smith et al. 2020), the subsequent analyses of soil quality using either moisture or organic matter content of the soil can be very skewed. On the other hand, many studies that use processed organic compounds in their organo-mineral fertilisers do not state sufficient information regarding their fertiliser products i.e. NPK ratios, organic sources etc. A further issue consists of studies classing fertilisers as organo-mineral fertilisers when they do not fall in line with regulatory

definitions. According to the 2019 EU Regulations, the following is a simplified definition of what comprises an organo-mineral fertiliser.

Co-formulation of:

- One or more inorganic sources of N, P_2O_5, K_2O ($\geq$ 8% mass in solid fertilisers; $\geq$6% mass in liquid fertilisers)
- One or more materials containing carbon, and nutrients, of solely biological origin (with an organic carbon content of $\geq$7.5% mass in solid fertilisers; $\geq$3% mass in liquid fertilisers)

Nonetheless, there is substantial evidence that commercial organo-mineral fertilisers are still as efficient, if not more, as mineral fertilisers. Alane (2015) and De Mota et al. (2019) show that less organo-mineral fertiliser can be used to achieve a higher yield than mineral fertilisers when applying equivalent amounts. This efficiency is potentially dependent on the crop/plant that the fertiliser is applied to. For example, Deeks et al. (2013) found that the application of an organo-mineral fertiliser provided a lower yield than their mineral counterparts in wheat production but provided a higher yield in rapeseed and maize production. A common concern with the use of organo-mineral fertilisers is the accumulation of heavy metals in the soil due to the recycling of organic resources such as sewage sludge. However, this has been shown to not be the case in the limited research that has been conducted on this (Deeks et al., 2013; Vitale et al., 2017).

A study by Tejada et al. (2005) compared the efficiency of organo-mineral fertilisers where the organic and inorganic compounds were processed and applied as a singular granular compound or as a blend of the two. Over the course of repeated trials, they found that the singular combined granular compound was more efficient than the blend application, in the context of crop production.

1.5 Environmental concerns regarding N fertiliser use

Climate change and the increasing awareness regarding the need of sustainable practices by humans does not exclude turfgrasses. A lifecycle assessment on various types of sports turf in Zurich football fields which included their construction, renovation, operation and disposal costs revealed that the environmental impacts for the operation of natural and hybrid turf was significantly higher than artificial turf (at optimal capacity) due to the high production costs of

fertilisers as well as the resulting eutrophication effects (Itten et al. 2021). This emphasises the importance of efficient and optimised fertiliser management. Fertilisers have received increasing attention with improved knowledge on the impact mineral additives have on the naturally occurring nutrient cycles. Attention has focused more on N and P as the pollution of K does not seem to be harmful to surrounding ecosystems.

The reviewed N cycle by Stein and Klotz (2016) has clarified that there are five main processes that occur: ammonification, nitrification, denitrification, anammox and nitrite-nitrate interconversion (Table 1.7). Losses of N are often of primary concern not only due to the variety of ways it can be lost but also because nitrous oxide (N_2O) has a potent global warming potential of 296-310 times that of carbon dioxide (CO_2) whilst also potentially being the most ozone-depleting gas (Braun and Bremer, 2018b; US EPA, 2021). The denitrification process, which can result in the release of NO and N_2O is, like many other processes, impacted by soil and abiotic conditions as well as excess N in the soil (Frank and Guertal, 2013a). Bremer (2006) observed an increase of 63% of N_2O emissions when turf was fertilised with 250 kg ha^{-1} year^{-1} as opposed to 50 kg ha^{-1} year^{-1}. The use of coated urea, specifically polymer-coated urea, has been observed to reduce N_2O emissions due to the reduced availability of denitrifiable N at any given point (Frank and Guertal, 2013a; Braun and Bremer, 2018a). Slow-release fertilisers also seem to be beneficial regarding ammonia (NH_3) volatilisation, with only 2% of applied fertiliser being volatilised (sulphur coated urea, ureaformaldehyde, isobutylidene diurea compared with non treated urea (Frank and Guertal, 2013a)). Urea has furthermore been found to be a major source of NH_3 emissions from turfgrass ecosystems, with 40-60% volatilised when irrigation did not follow, as opposed to 1-2% volatilised when 5cm of irrigation water followed (Frank and Guertal, 2013a). Volatilisation of NH_3 is concerning due to its potential to return to ecosystems via N deposition (dissolved in rainwater and as dry deposition), and subsequent soil acidification and/or eutrophication (Cameron et al., 2014). Nonetheless, the concerns regarding microplastic pollution from polymer-coated fertilisers also need to be noted. While research is limited, especially for turfgrass, Katsumi et al. (2021) reported agricultural land in Japan to be a source of microplastic pollution to the surrounding coastal areas, especially during the irrigation season with 77-99% of microplastic pollution on beaches being from the fertiliser microcapsules. They suggest biodegradable coatings as an alternative.

Table 1.7: Basic nitrogen cycle processes with explanation (Stein and Klotz, 2016).

Process	Basic explanation
Ammonification	1. Through nitrogen fixation: conversion of atmospheric dinitrogen (N_2) into ammonia (NH_3) or ammonium (NH_4^+) by bacteria and archaea. Oxygen sensitive and energy intensive process. 2. Assimilatory/Dissimilatory nitrite (NO_2^-) reduction to NH_4^+ : anaerobic process performed by bacteria and fungi.
Nitrification	Aerobic process that, depending on micro-organism community present, can be through two step process: 1. Oxidation of ammonia (NH_3) to NO_2^-. 2. Oxidation of NO_2^- to nitrate (NO_3^-). (This process can also be reversed through anaerobic respiration labelled nitrite-nitrate interconversion.) Or through a direct process of oxidation from NH_3 to NO_3^-
Denitrification	Anaerobic respiration process resulting in the production of N_2 from various other forms. Depending on micro-organism, process may be direct from NO_2^- or NO_3^- into N_2, otherwise may be incomplete, resulting in formation of nitric oxide (NO) or nitrous oxide (N_2O).
Anammox	**An**aerobic **amm**onium **ox**idation by *Brocadiaceae* bacteria using NO_2^- and NH_4^+ to produce N_2 directly.
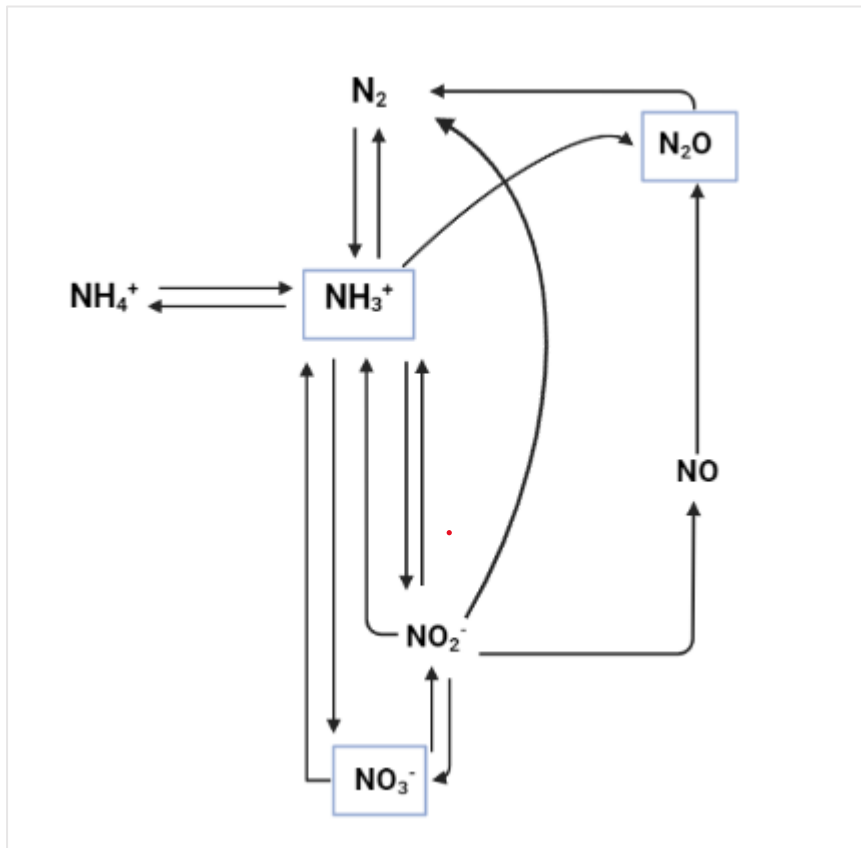
Figure 1.1: Simplified N cycle, complimentary to Table 1.7, highlighting different forms of N and the pathways focused on in this study.

N also has the potential to be lost via surface runoff, although within the turf sector research is more focused on runoff of P. Nonetheless, some reports indicate that the concentrations of N in runoff are high enough for eutrophication, with concentrations in the watercourse only needing to be as low as 1mg N L^{-1} (Frank and Guertal, 2013a). Due to associated health risks from drinking water contaminated with NO_3, maximum contaminant limits have been set for leaching of NO_3 into groundwater: 10mg L^{-1} of NO_3-N or 50mg L^{-1} NO_3 (US Environmental Protection Agency (2011); EU Groundwater Directive (2006). Besides eutrophication, the health risks of NO_3 contamination have been linked to methaemoglobinaemia in babies and cancer and heart disease (Cameron et al., 2014). Of the studies that have observed NO_3^- leaching from turf, the majority declare to find leaching rates to be under the maximum contaminant limit with one study finding 3.6% of groundwater samples near golf courses to have NO_3^- concentrations above the limit, which the authors attribute to the land previously being used agriculturally (Cohen et al., 1999; Frank and Guertal, 2013a). According to Quiroga-Garza et al. (2001), fertiliser treatments comprised of urea and sulphur-coated urea that was tested on bermudagrass, caused leaching of NO_3-N 10-19 times higher than the permitted 10mg L^{-1} (US EPA, 2011), when the photoperiod was under 12 hours. Here too, the use of slow-release fertilisers on turf has the potential to reduce NO_3^- leaching and the subsequent negative impact of fertilisers on the environment (Frank and Guertal, 2013a).

Both runoff and leaching of P sources are also a large concern as this may lead to eutrophication of water bodies (Frank and Guertal, 2013b). Since the application of sedimentary P rock to agricultural fields has been long ongoing (alongside the deforestation and burning of trees and human waste), only estimations can be made regarding the pre-anthropogenically altered P cycle, causing Filippelli (2008) to state that current P levels in the oceans are twice as high as they were before human input. Filippelli (2002) explains that historically apatite minerals were the significant weathering source for P, where P was removed either through the organic acids released by plant roots, or the reduced rhizosphere pH via CO_2 release through respiration near roots hairs, or by degradation processes of organic matter. This study also concludes that in order for P in organic matter to become available for plant uptake, the enzyme phosphatase must be used which plants, soil microbes and the symbiotic fungi *mycorrhizae* produce. The limit for elemental P in water is set at 0.1µg L^{-1} (US Environmental Protection Agency, 1976) with experiments measuring runoff from turfgrass unfortunately often finding this threshold to be exceeded, while some studies also observe significant decreases in P lost via runoff when irrigation was only applied after 24 hours or longer (Frank and Guertal, 2013b). Similarly, there

has been some research regarding leaching of P in turf and sandy soil environments. Both N and P have the potential to be primarily immobilised and then mineralised over longer time scales – causing accumulative leaching potential over time to be concerning.Ericskson et al. (2005) observed leaching of K on a mixed species turf and a St. Augustine grass-based turf totalling to 55 and 44% of total applied K, respectively. The leaching of K is not regarded as a concern for the environment but more of a concern regarding turf quality therefore causing frequent fertilisation to be common (Frank and Guertal, 2013b).

The effect that fertilisers have on soil health and quality is another issue to be considered as soil and land degradation is of international concern (Pravalie et al. 2021). A long-term study by Meng et al. (2005) which observed the effects of various organic, mineral and organo-mineral treatments on sandy loam soil over 13 years found that the addition of organic manure significantly increased soil organic C and N contents compared to mineral inputs where treatments that did not receive mineral P had significantly lower SOC stocks and these treatments had soil organic N levels even lower than the control plots. As mentioned in section 1, the importance of SOC on soil health should be considered and appropriate nutrient management is therefore crucial. Many of the processes mentioned regarding nutrient loss to the environment are heavily influenced by abiotic conditions like temperature, wind speed, precipitation (or irrigation) as well as the use of recycled water potentially increasing nutrient load into the soil (Cockerham, 2011; Frank and Guertal, 2013a; Frank and Guertal, 2013b). Finally, understanding soil qualities and their relationship to various minerals is necessary to understand fertiliser choices and dynamics.

Overall, this review highlights the diversity of different organo mineral fertilisers, and the many knowledge gaps surrounding the environmental fate of organo-mineral fertilisers. For example, their effect on soil characteristics and the soil microbial community, how they impact fertilisation dynamics (e.g. rate, frequency), and how their application can affect the environment. It is especially of interest, to compare them and their effects to those of various mineral fertilisers that are commonly used.

1.6 Aims and Objectives

Due to the aforementioned gaps in knowledge and with the context of organo-mineral fertilisers on turf-based sportsgrounds highly lacking in research, it was important to conduct this study

to gain a better overall understanding of the performance and efficiency of organo-mineral fertilisers. The main aims constituted to gain a better understanding of how organo-mineral fertilisers compared to mineral fertilisers in regards to their effect on soil health, the soil microbiology and the environment. Three experiments were therefore undertaken. The first was a potted agronomic experiment that observed various soil properties (pH, EC, moisture and organic matter content), soil microbial activity, and the leaching of nitrogen (N) as nitrate (NO_3^-) or ammonium (NH_4^+). The second experiment used a desktop-based flow-through system that was set up using acid traps to assess ammonia (NH_3) emissions. The third experiment looked at nitrous oxide (N_2O) emissions using an automated closed-chamber system. These hoped to fulfil our objectives and research questions comprised of:

Are commercial organo-mineral fertilisers as efficient as mineral fertilisers?

To what extent do organo-mineral fertilisers impact soil health?

Are organo-mineral fertilisers beneficial for the soil microbiome (as compared to mineral fertilisers)?

Do organo-mineral fertilisers reduce the risk of nutrient leaching?

How do organo-mineral fertilisers compare to other mineral fertilisers regarding gaseous emissions of NH_3^+ and N_2O?

2.0 Agronomic Experiment

2.1 Introduction

Fertilisers are vital to optimise plant production, however, they are often applied inappropriately in turfgrass systems. A wide range of factors are affected by the application of fertilisers, both in the short and long term. For example, the use of reduced forms of N has been shown to promote soil acidification which in turn may cause deficiencies in various nutrients (P and K and micronutrients) but also increases the potential for N_2O losses (Tripathi et al., 2020). Interestingly, the application of organo-mineral fertilisers has been shown to increase soil pH which could prove to be a beneficial alternative to liming (Ayeni et al., 2012; Ayeni and Ezeh, 2017) although this is also not consistently the case (Deeks et al., 2013).

Organo-mineral fertilisers have also been shown to alleviate salinisation of soils (Rady, 2012; Semida et al. 2013) – a mechanism that is considered one of the most critical limiting factors in agricultural soils. Inappropriate irrigation practices often contribute to promoting soil salinity due to a net accumulation of mineral salts at the soil surface. Similarly, the excessive application of N fertilisers with a low recovery rate of the soil has also been shown to induce salinisation (Rady et al., 2013; Han et al., 2015; Shrivastava and Kumar, 2015). Excess salinity affects plants during all stages of development via ion toxicity, nutrient deficiencies, osmotic and oxidative stress and the limitation of water uptake but may also adversely affects the soil microbiome which may indirectly affect plant growth (Shrivastava and Kumar, 2015). However, the application of organo-mineral fertilisers has shown to be successful in alleviating these impacts (Rady, 2012; Semida and Abd El-Mageed, 2014; Meena et al., 2015). This positive effect has been attributed to the increase in organic C and therefore water holding capacity of the soil. Babalola et al. (2007) also found the application of organo-mineral fertilisers to improve the infiltration rate of water. Furthermore, Rady (2012) considers the potential of calcium inhibition of Na uptake as being a benefit of adding Ca-rich fertiliser.

Soil organic matter is generally considered to be the most important indicator of soil health as it has a direct effect on the soil's physical, chemical and biological properties (Tripathi et al., 2020). Although it is widely accepted that the addition of N fertiliser may increase soil organic matter (SOM) due to the increase of plant matter (rooting, decay of biomass etc.) it is also possible that the application increases decomposer microbe activity which may consequently increase organic matter decomposition promoting its loss (Singh, 2018). A meta-analysis on long-term fertilised cropping systems found that there was a 12.8% increase in SOM content

with mineral fertiliser applications, compared to the untreated controls (Geisseler and Scow, 2014). The increase in SOM is also attributed to increasing the microbial biomass by 15.1% in the fertilised plots.

A healthy soil microbiome is crucial for the maintenance of healthy soils, as well as the supply of nutrients to plants, decomposition of organic matter, biocontrol of pathogens or toxins etc (Tripathi et al., 2020). While multiple biotic and abiotic factors can affect this ecosystem, the application of mineral fertilisers has been shown to reduce fungal/bacterial biomass ratios in the soil while organic fertilisation has the opposite effect (Tripathi et al., 2020). The impact of pH on microbial biomass seems to be quite stark, as a meta-analysis demonstrated there to be a decrease in microbial biomass in soils with a pH < 5 whilst increasing by an average of 48% in soils with a pH of 7 (Geisseler and Scow, 2014). The type of N source did not affect microbial biomass.

As N is generally considered to be the most important nutrient added to turfgrass systems, assessing fertiliser N use efficiency is also important, especially when considering that inappropriate application can have a negative impact on long-term soil health and quality. Some studies have demonstrated an increased availability of primary nutrients after the application of organo-mineral fertilisers (Tejada et al., 2005; Ojeniyi et al., 2009; Ayeni et al., 2012; Ayeni and Ezeh, 2017). However, although there may be an increased bioavailability of nutrients, yield is only sometimes reported as being higher in the organo-mineral fertiliser treatments with there generally being no significant difference in yield between mineral and organo-mineral treatments (Etukudo et al., 2015; Ciesielczuk et al., 2019; Bai et al., 2022). Deeks et al. (2013) demonstrated that the efficiency of organo-minerals on crop yield may be crop-specific as they found wheat to have a significantly higher yield when fertilised by mineral fertilisers. Within professional sports-turf management, root establishment is also of key importance. Organo-mineral fertilisers are argued to improve rooting in comparison to their mineral counterparts (Paré et al., 2009; Moita-Nassy et al., 2020). Kania et al. (2007) found surface application of organo-mineral fertiliser to pre-existing lawns to induce new lateral root growth as well as promoting a dense root hair coverage. This increase in rooting is attributed to increased organic-matter input (Chivenge et al., 2011).

Large amounts of fertiliser N are lost to the environment via NO_3^- leaching, NH_3 volatilisation and N_2O production. There is evidence that NO_3^- leaching is higher in commercial mineral fertilisers than in organo-mineral fertilisers (Richards et al., 1993; Florio et al. 2015). However,

Richards et al. (1993) also found N uptake to be lower from organo-mineral fertilisers supplemented with urea or ammonium nitrate when compared to a commercial ammonium nitrate fertiliser by an average of 9.1%. This is countered by Florio et al. (2015) who found that there was a higher uptake of N from the organo-mineral fertiliser treatments by *Lolium perenne* (by 17.9%) than the mineral-based counterparts. This was ascribed to the increased bioavailability of N from organo-mineral fertilisers as well as the slower release of N which better matched plant demand. A similar explanation was given by Cheng et al. (2010) when observing increased rooting, in tall fescue grass, from organic fertilisers as opposed to chemical fertilisers.

Based on evidence from previous studies, the hypotheses of the following study are as follows:

H1 = Soil pH will decrease over time with mineral fertiliser application whereas they will increase with organo-mineral application.

H2 = Soil electrical conductivity (EC) will increase over time with fertiliser application with mineral fertiliser treatments causing higher salinity than organo-mineral fertiliser treatments.

H3 = Soil moisture and organic matter content will increase over time with fertiliser application with organo-mineral fertiliser treatments providing higher organic matter content and subsequently a higher moisture content than the mineral fertiliser treatments.

H4 = Microbial activity will increase over time with fertiliser applications with organo-mineral fertiliser treatments having a higher rate of microbial activity.

H5 = There will be significant differences between the different soil layers (topsoil and underlying sand) amongst all observations.

H6 = Yield of grass clippings will be higher due to fertilisation with there being no significant difference between mineral and organo-mineral fertiliser treatments.

H7 = The C and N content in the grass clippings will be higher in fertilised treatments with a higher N uptake by the organo-mineral fertilisers than the mineral fertiliser applications.

H8 = There will be an increase in rooting over time   in the organo-mineral treatments due to their slower release of nutrients as compared to mineral fertilisers.

H9 = There will be significantly higher N leaching in treatments with fertiliser applications with mineral fertiliser treatments having a higher amount of N lost through leaching than organo-mineral fertiliser treatments.

2.2 Methods

2.2.1 Experimental Setup

The aim was to simulate an athletic turf environment using replicated plant pots in a greenhouse. The organo-mineral specialty fertilisers are specific to high-sand and a perennial ryegrass dominated sward. Two litre pots were filled with 1.75 kg of acid washed silica sand and topped with a commercial turf roll (2 cm thick) comprised of 25% *Lolium perenne*, 40% *Festuca rubra rubra,* and 35% *Festuca rubra litoralis* (chosen due to *Lolium perenne* being commonly used on sportsgrounds). Pots were watered with 100 ml of deionised water three times per week (Monday, Tuesday, Wednesday). Thursdays they were not watered as Fridays they were saturated in order to obtain leachate (see below). They were not watered on the weekends. They were left to establish for two weeks prior to fertilisation.

The 16-3-6 mineral and organo-mineral treatments were fertilised at the recommended 40 g/m^2 (as is the recommended rate by ICL Ltd.) corresponding to 0.71 g of fertiliser per 15 cm diameter pot. The 14-3-6 treatment was applied to contain equal amounts of N as the 16-3-6 organo-mineral and mineral lab-made blend, resulting in 0.81 g to be applied per 15 cm diameter pot. This equates to an equivalent total N application rate of 400 kg ha^{-1}. The lab-made 16-3-6 mineral fertiliser blend was made using urea, diammonium phosphate, and potassium chloride, chosen as the minerals in the organic portion of the 16-3-6 organo-mineral fertilisers were urea, diammonium phosphate and potassium chloride (Table 2.1).

There were 12 replicates per treatment as half the replicates were destructively sampled after four weeks, whilst the rest were maintained for another four weeks before harvesting. The pots were divided into three different soil layers when obtaining samples: topsoil layer (0-2 cm), middle sand layer (2-7 cm) and the bottom sand layer (7-13 cm).

Table 2.1: Summary of applied treatments and their compositions.

Name	Fertiliser Type	NPK Ratios	Components
OM Golf (ICL)	Organo-mineral	16-3-6	Organic component comprised of plant waste (including potassium rich vinasse) and urea and diammonium phosphate as primary mineral NP sources.
OM Kruimel (ICL)	Organo-mineral	16-3-6	Organic component comprised of poultry litter and urea, diammonium phosphate and potassium chloride as primary mineral NPK sources.
Lab 16-3-6	Mineral	16-3-6	Lab made blend of urea, diammonium phosphate and potassium chloride.
Market 14-3-6 (Velvit)	Mineral	14-3-6	Commercially bought fertiliser containing ammonium, phosphorus pentoxide and potassium oxide.

2.2.2 Data Collection

Soil/sand layers were analysed for their pH and EC values, nitrate and ammonium levels, soil moisture, organic matter contents on weeks 4 and 8. The soil pH and EC values were measured using standard electrodes on a 1:2.5 (w/v) ratio of soil/sand to distilled water. Using potassium sulphate extractions (ratio 1:5 w/v of substrate to K_2SO_4), NH_4^+ and NO_3^- concentrations were measured using colorimetry (Mulvaney, 1996; Miranda et al., 2001). Soil moisture content was measured by drying samples (105°C, 24 h) whilst organic matter content was quantified by loss-on-ignition (450°C, 16 h).

To determine the effect of fertiliser type on microbial activity within the soil/sand layers, a ^{14}C-glucose experiment was undertaken where 5 g (±0.5 g) of soil/sand of each layer was taken at four an eight weeks following fertiliser applications and 1 ml of ^{14}C-glucose added to induce microbial activity. 1 M NaOH traps were added to the vessels to capture any $^{14}CO_2$ emitted. The NaOH traps were changed after 1, 3, 6, 24, 48, 72 and 96 hours after addition of ^{14}C-glucose and incubated at room temperature for the duration of the experiment. Scintillation liquid was added to the NaOH traps after recovery and their ^{14}C content evaluated using a liquid scintillation counter (Wallac 1409).

Grass clippings were taken once a week and their fresh and dry weight determined after oven drying (80°C, 24 h). Clippings were then finely ground using a ball mill before being analysed

for organic carbon and nitrogen content using a Truspec CN analyser (LECO Instruments). Grass roots were carefully removed from the soil at the end of the experiment, washed, dried at 80°C and then weighed.

Leachate was collected once a week and analysed for NO_3^- and NH_4^+ using colorimetry (Mulvaney, 1996; Miranda et al., 2001). Leachate was obtained by adding 200 – 250 ml until the pots were saturated and leachate was obtained in saucers placed underneath the pots. the amount of water added varied from week to week due to environmental fluxes in temperature, humidity etc. Leachate volume was not determined.

2.2.3 Statistical analyses

All data was analysed using IBM SPSS Statistics 27. To analyse differences between weeks four and eight, a paired samples t-test was used. When testing for differences between treatments with the weekly measurements over the course of eight weeks, a repeated measures ANOVA was used. When analysing differences between soil layers or treatments, a one-way ANOVA and potentially subsequently a post-hoc Tukey's test was used when assumptions of homogeneity and normality were met (Levene's Test) otherwise a Welch Test and Games-Howell post-hoc were used.

N uptake by the plants from the fertiliser treatments was calculated as the difference between the grams of N in the grass clippings (calculated by knowing % of N by mass) of the various treatments (NT) and the Control (NC) (assuming that there would have been a similar N content in the absence of the fertilisers through supplementation of N in the soil). These values were then divided by the total N applied and multiplied by 100 to produce percentages (see below).

$$N\ uptake = \frac{NT - NC}{N\ applied} \times 100$$

2.3 Results

2.3.1 Substrate analyses

The soil and sand layers were analysed for their pH, EC, moisture, organic matter, nitrate and ammonium contents. The differences between treatments, layers, and time are depicted in Table 2.2. There were no obvious patterns for any of the variables when observing differences between treatments but it is clear that there are more differences between treatments after 8 weeks post fertiliser application. With regards to soil depth, significant differences were mainly found between the top layer (soil) and the middle and bottom layers (sand) for pH, EC and organic matter content. For moisture, there were no significant differences between layers except for the Control at Week 4. At Week 8, there were no significant differences between the layers for moisture content. There were no significant differences between the middle and bottom sand layers in any observation. For time, there were more significant differences in pH and organic matter content as opposed to EC and moisture content. However, the organic matter content measurements in the middle and bottom layer for the commercial mineral fertiliser Market 14-3-6 (Velvit Ltd.) in week 4 are unusually high and hence can be considered invalid.

Table 2.2: Differences in pH, EC, soil moisture and organic matter content over time and between layers and treatments. Significant results ($p \leq 0.05$) are displayed as * for time (e.g. for pH, the top layer of the Control is significantly different between weeks 4 and 8), as a lower-case letter for differences between layers within the same treatment (e.g. for pH, the top layer of the Control is significantly different to its middle and bottom layer at 4 weeks), and capital letters for differences between treatments (e.g. for pH, the middle layer of the Control is significantly different to the middle layer of OM Kruimel at 4 weeks).

Treatment	Layer	pH 4 weeks		pH 8 weeks		EC (μS cm⁻¹) 4 weeks		EC (μS cm⁻¹) 8 weeks		Moisture (%) 4 weeks		Moisture (%) 8 weeks		Organic Matter (%) 4 weeks		Organic Matter (%) 8 weeks	
Control	Top	5.91	*ab	6.69	*	68.17	*ab	39.68	A*ab	5.28	*ab	11.43	AD*	0.80	*ab	1.37	A*ab
	Middle	6.48	A*a	7.03	AD*	16.22	a	16.48	a	1.57	A*a	3.54	EFG*	0.08	Aa	0.13	a
	Bottom	6.68	C*b	7.04	GK*	15.41	b	14.88	Cb	2.30	*b	3.90	*	0.06	Eb	0.11	Gb
Lab 16-3-6	Top	5.72	*cd	6.55	*ab	45.98	Acd	44.73	Bcd	6.33		8.89	B	0.71	cd	1.37	cd
	Middle	6.57	c	6.99	BEa	9.90	*c	13.32	*c	4.58	A*	2.57	E*	0.13	Bc	0.09	Cc
	Bottom	6.69	*d	7.10	HL*b	9.52	d	10.85	Cd	5.73		2.94		0.11	F*d	0.07	EF*d
Market 14-3-6	Top	5.22		7.06		94.18	Aef	67.95	e	7.10		9.06	C	0.82	*	1.31	B*ef
	Middle	5.82		7.09	CF	18.29	e	12.62	e	6.70		3.21	H	0.58	ABCD	0.18	CDe
	Bottom	5.54	B*	7.00	IM*	20.90	f	12.78		7.28		3.57		0.62	EFGH	0.18	EGHf
OM Golf	Top	5.87	*e	6.78	*cd	59.38	gh	51.75	fg	5.22		7.44	D	0.67	*ef	1.04	*gh
	Middle	6.42	*	7.49	ABC*c	12.31	g	14.32	f	4.05		2.47	F	0.10	Ce	0.17	g
	Bottom	6.75	B*e	7.33	GHIJ*d	15.45	h	11.89	g	5.93		3.49		0.09	Gf	0.14	FIh
OM Kruimel	Top	5.71	*fg	6.86	*ef	55.77	ij	85.87	Abhi	5.25		5.74	ABC	0.76	gh	0.83	ABij
	Middle	6.26	A*f	7.44	DEF*e	14.19	*i	15.80	*h	4.98		1.86	GH	0.10	Dg	0.08	Di
	Bottom	6.32	C*g	7.68	JKLM*f	10.88	j	12.78	i	6.39		2.23		0.09	Hh	0.07	HIj

2.3.2 Microbial analyses

Overall, the standard errors for the ^{14}C-glucose results were very small, however, the results themselves were similar too, hence there were fee major differences between treatments. Based on the total amount of CO_2 emitted, there were no significant treatments between treatments in the top or bottom layers but in the middle layer the lab-made blend 16-3-6 had significantly more microbial activity than all other treatments (Control: p=0.004; Market 14-3-6: p=<0.001; OM Golf: p=0.006; OM Kruimel: p=0.047). There was also a significant difference between the commercial mineral fertiliser Market 14-3-6 and the manure-based organo-mineral fertiliser OM Kruimel (ICL Ltd.) (p=0.002). After 8 weeks, the top layer of the plant-based organo-mineral fertiliser had significantly higher activity rates than the lab-made blend 16-3-6 (p=0.007) and the commercial mineral Market 14-3-6 (Velvit Ltd.) (p=0.015). In the middle layer, the commercial mineral Market 14-3-6 performed the worst but was only significantly different to the plant-based organo-mineral fertiliser OM Golf (ICL Ltd.) (p=0.002). However, what can be observed is that in week 8, there was a lag time for the mineral fertilisers for the bacterial activity to reach the same rates of activity as the control and the organo-mineral fertilisers.

When comparing cumulative CO_2 emissions between layers and treatments in week 4 and 8, there were only significant differences (p=≤0.05) in the top layer of the lab-made blend 16-3-6, the commercial mineral Market 14-3-6 (Velvit Ltd.) and the plant-based organo-mineral OM Golf (ICL Ltd.) and in the middle layer of the lab-made blend 16-3-6.

When comparing the various layers to each other, there were no consistent differences in microbial activity between the top (soil) layer and the middle and bottom (sand) layers (Figure 2.1).
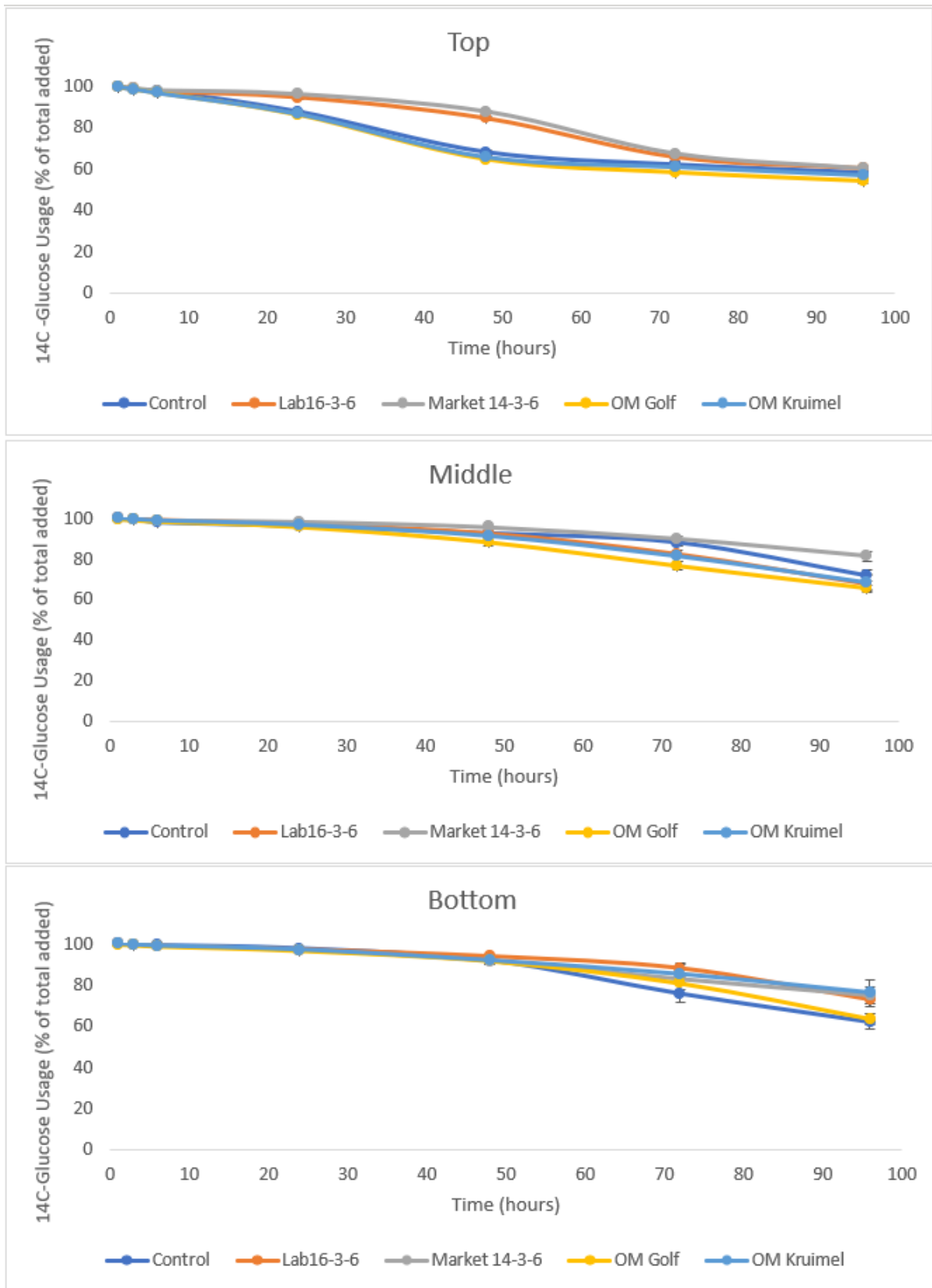
Figure 2.1: The activity rate of the microbial community (at different layers, eight weeks after fertiliser application) through utilisation of ^{14}C-Glucose as a percentage of total added. Values are means ± SEM (n=6).

2.3.4 Grass clippings and root analyses

Overall, the Control had a higher initial harvest of grass, however, the clippings did not increase in weight as much as the clippings from the fertiliser treatments. The final cumulative weights at week 8 were compared using a Welch Test and Games-Howell post-hoc which determined that only the Control was significantly different (lower) to all other treatments ($p=\leq0.001$) (Figure 2.2). The manure-based organo-mineral fertiliser OM Kruimel (ICL Ltd.) also had a higher initial harvest of grass but did not increase at a rate significantly different to the other treatments.

Repeated measures ANOVA did not find a difference in C content over time in the clippings but did find a significant difference in N content ($p=<0.043$) (Figure 2.3). Overall, variability between samples was quite high hence when comparing treatments at singular time points, there were no significant differences within weeks 1-5. At week 6, the control was significantly different to Lab 16-3-6 ($p=0.027$), Market 14-3-6 (Velvit Ltd.) ($p=0.010$), and OM Golf (ICL Ltd.) ($p=0.038$). In week 7, the control was significantly different to all other treatments: Lab 16-3-6 ($p=<0.001$), Market 14-3-6 (Velvit Ltd.) ($p=<0.001$), OM Golf (ICL Ltd.) (0.005) and OM Kruimel (ICL Ltd.) ($p=0.006$). At week 8 the variability increased again and the control was only significantly different to the manure-based OM Kruimel (ICL Ltd.) ($p=0.031$).

The uptake of N in the clippings, demonstrated that the Control had the lowest overall N content at 0.06%, followed by the plant-based organo-mineral fertiliser OM Golf (ICL Ltd.) at 0.11%, the manure-based organo-mineral fertiliser OM Kruimel (ICL Ltd.) at 0.12%, the lab-made blend 16-3-6 at 0.13%, and finally the commercial mineral fertiliser Market 14-3-6 (Velvit Ltd.) at 0.23% (Figure 2.4).

Root weights showed no significant treatment differences after 4 or 8 weeks growth after fertilisation. The only significant difference between treatments was between the lab made blend 16-3-6 and the Control after eight weeks (difference of 6.9 g; $p=0.031$) (Figure 2.5).
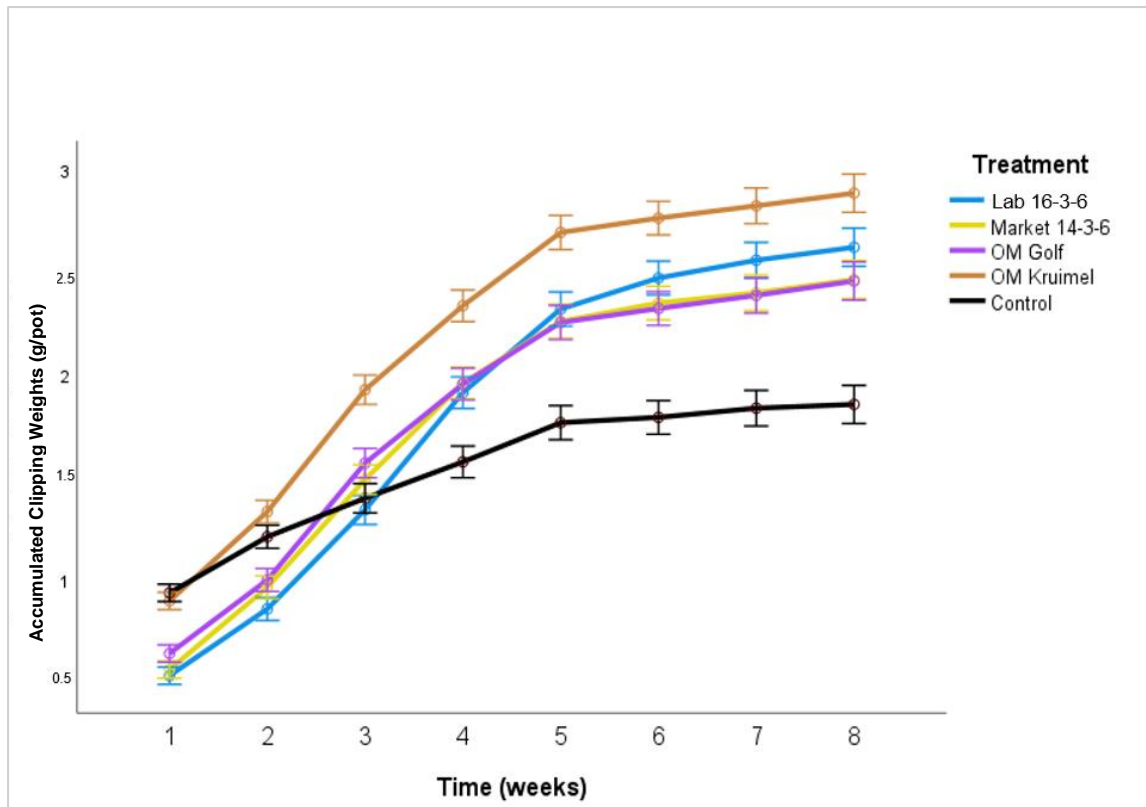
Figure 2.2: Cumulative clipping weights for the different treatments over eight weeks. Mean ± SEM (*n=12 until week four; n=6 thereafter*).
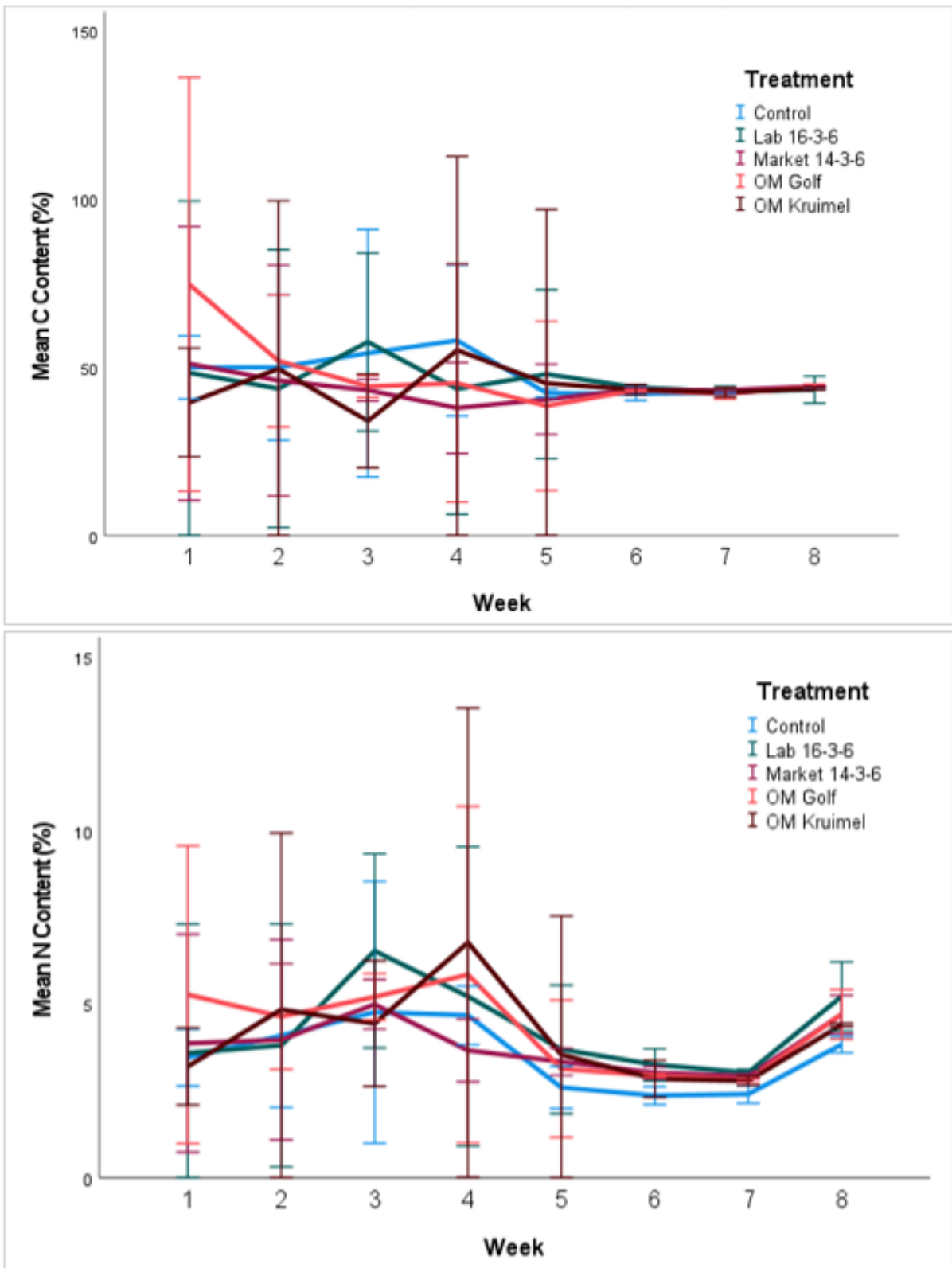
Figure 2.3: Foliar carbon (top) and nitrogen (bottom) contents of the clippings of the various treatments over time. Error bars display 95% CI. (*n=3*)
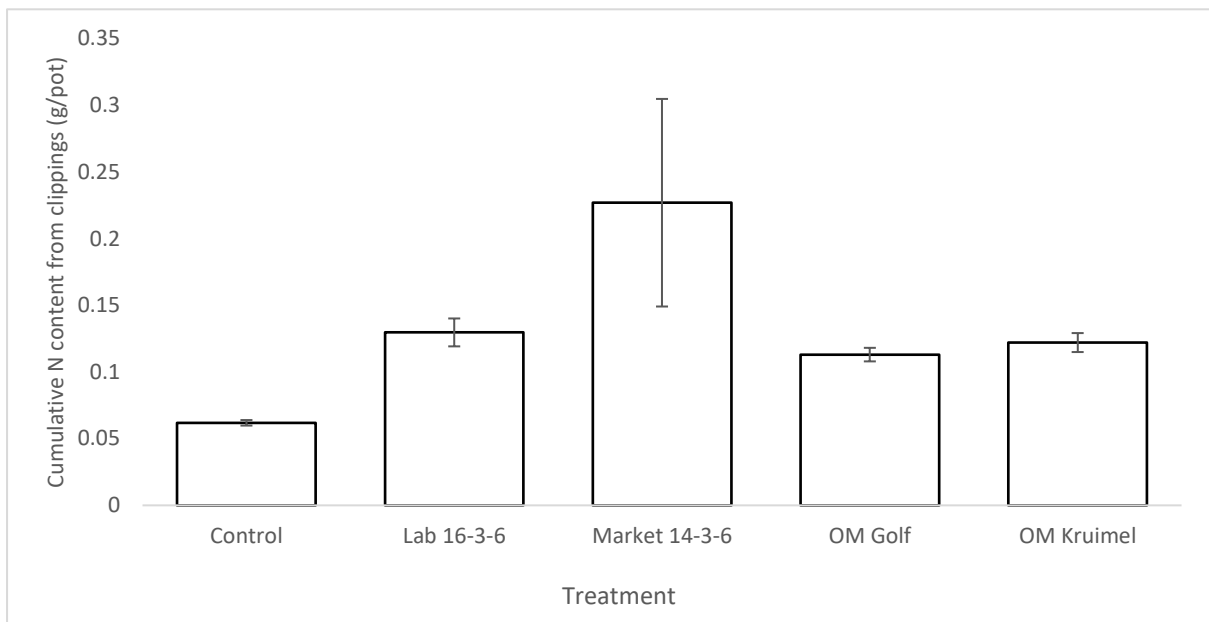
Figure 2.4: Cumulative nitrogen uptake (g) in clippings between the various treatments. Error bars ±SEM
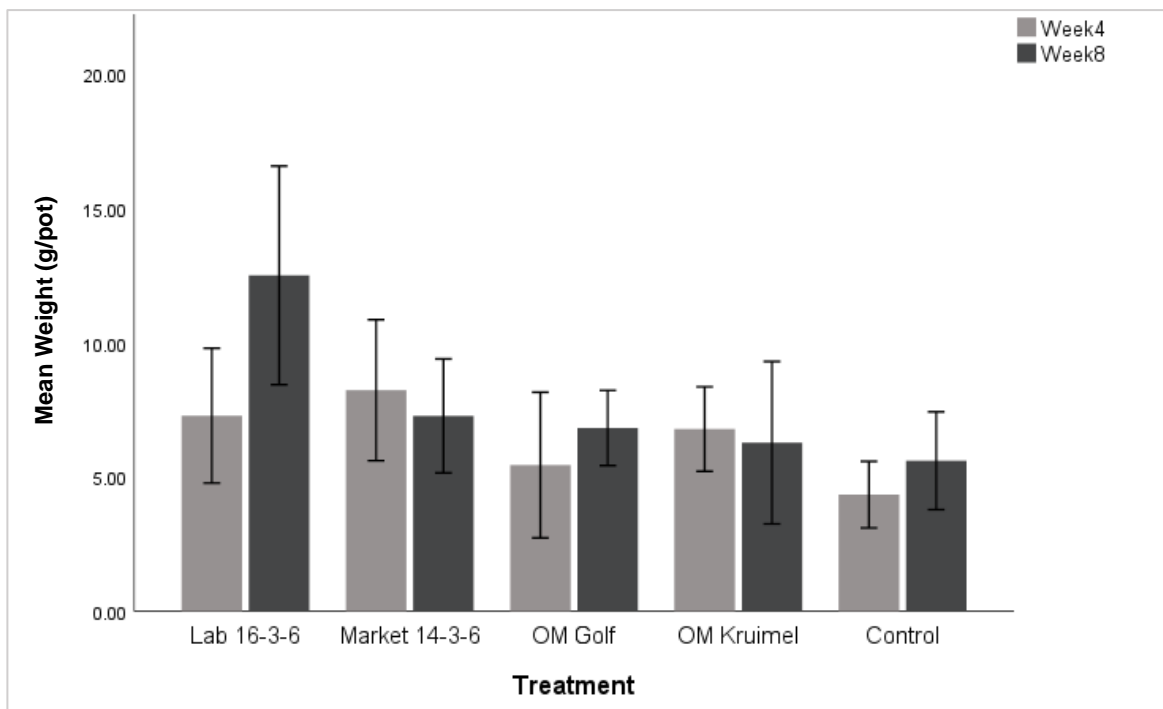
Figure 2.5: Root weights of various treatments after four weeks and eight weeks of fertiliser application. Error bars display 95% CI (*n=6*).

2.3.5 Leachate Analyses

Using a repeated one-way ANOVA to analyse how the different treatments performed in regards to leaching events demonstrated that overall the lab-made blend 16-3-6 performed the worst. When analysing NO_3^- concentrations over time, the lab-made blend did not leach the most in week one but was the only treatment that increased in NO_3^- concentrations in week 2. The lab-made blend 16-3-6 was significantly higher in overall NO_3^- concentration than all other treatments except for the manure-based organo-mineral fertiliser OM Kruimel (ICL Ltd.) (with significance values being p=0.004 for the Control, p=0.004 for the commercial mineral Market 14-3-6 fertiliser (Velvit Ltd.) and p=0.009 for the plant-based organo-mineral fertiliser OM Golf) (Figure 2.6). However, when looking at individual time points (week 1 and 2), the manure-based organo-mineral fertiliser OM Kruimel was still leaching significantly less than the lab-made blend 16-3-6. From the treatments (excluding control), the commercial mineral Market 14-3-6 performed the best being the only treatment that was not significantly different to the Control over the length of the project (with significance values being p=0.004 for the lab-made blend 16-3-6, p=0.005 for the plant-based organo-mineral fertiliser OM Golf, p=0.023 for the manure-based organo-mineral fertiliser OM Kruimel). Regarding NH_4^+ leaching from the various treatments, both mineral fertilisers performed significantly worse than the organo-mineral fertilisers. The lab-made blend had the highest concentrations overall with a significance value of p=<0.001 for all other treatments and the Control. Similarly, the commercial mineral Market 14-3-6 fertiliser was significantly different to all treatments and the Control at a significance level of p=<0.001, except for the manure-based organo-mineral fertiliser where p=0.049. These results indicate that between the two organo-mineral fertilisers, the plant-based OM Golf had less NO_3^- and NH_4^+ lost from the system via leaching.
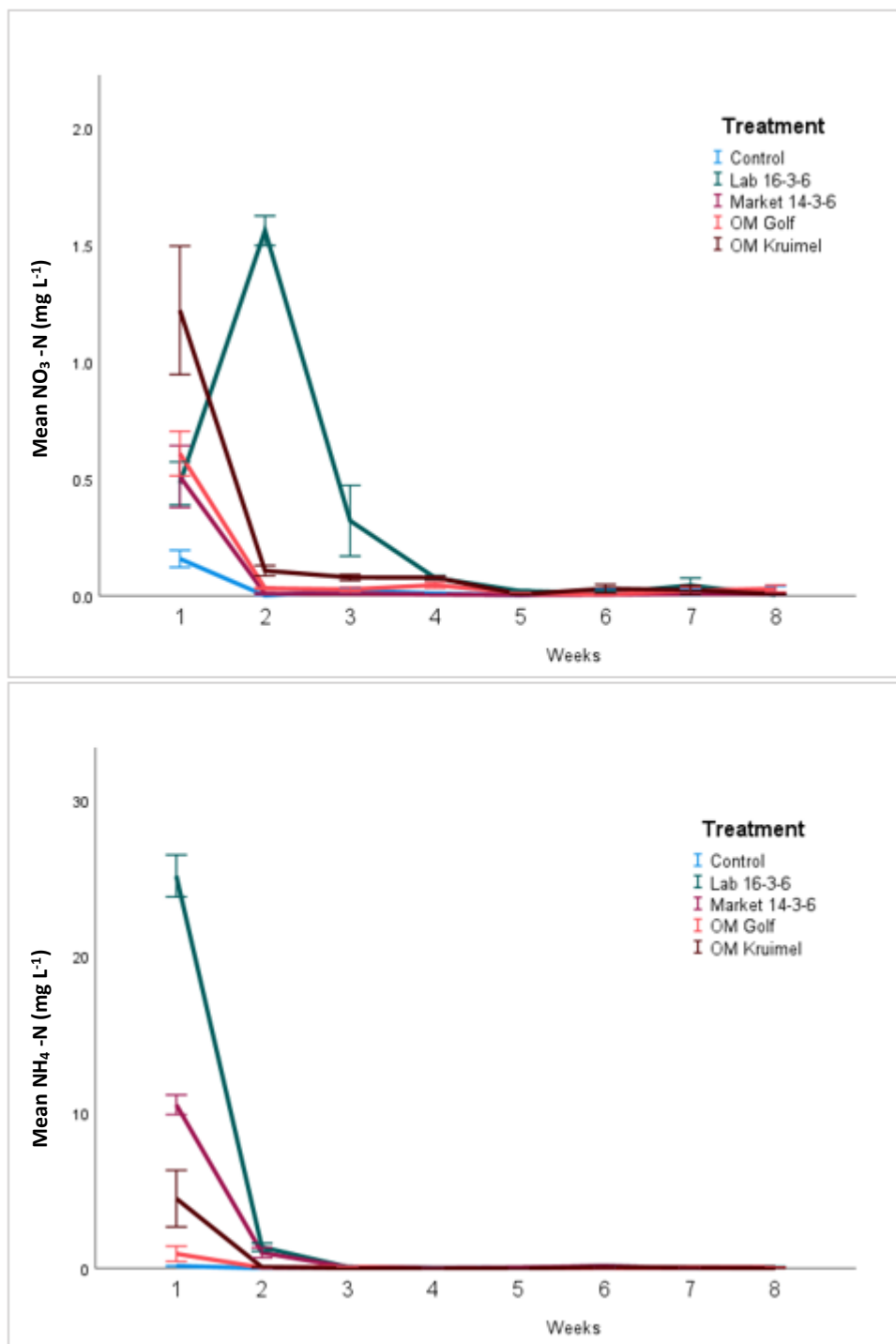
Figure 2.6: Concentrations of NO_3-N (top) and NH_4-N (bottom) leached from various fertiliser treatments and control over the span of eight weeks. Values are means $\pm$ SEM ($n = 6$)

2.4 Discussion

Over time, soils are expected to acidify, become more saline, lose their capacity to retain water and lose organic matter in response to the repeated use of mineral fertilisers (Shrivastava and Kumar, 2015; Tripathi et al., 2020;). Our study did not find the soils/sands to decrease in pH over time, instead they seemed to neutralise. As there were no baseline measurements for the various treatments (at week 0), it could have been argued that the soils decreased in pH in the four weeks post-fertilisation but increased again within the four weeks following that. Nonetheless, the Control follows the same pattern and therefore it is unlikely that the change in pH was due to the addition of fertilisers. Another explanation is that the excessive leaching events may have successfully removed nutrients present that were having an effect on pH and thus causing the soils/sands to become more neutral. Potentially, there were also carbonates in the sand that buffered the pH effect. The first hypothesis stating that the soil pH will decrease over time with the mineral fertilisers whilst increasing with organo-mineral application is therefore partially rejected as the values did not significantly decrease for the mineral fertiliser applications but did significantly increase for the organo-mineral treatments (in all soil layers). The change observed in the Control was also significant between all layers. Whilst the mineral fertilisers also increased in pH overall, it can be noted that the lab-made blend 16-3-6 (urea-based) fertiliser only had a significant change in the top and bottom layer whilst the commercial Market 14-3-6 (Velvit Ltd.) fertiliser (ammonium-based) only had a significant change in the bottom layer. This may be as ammonium-based fertilisers are known to have a higher potential to acidify soils, due to the release of H^+ during the conversion from ammonium to nitrate (Smiley and Cook, 1973).

For EC and soil moisture content, measurements did not consistently increase or decrease over time and most measurements were not significant over time, resulting in the rejection of our second hypothesis (H2) that the soil EC will increase over time with fertiliser application with the mineral fertiliser treatment causing a higher increase in salinity than the organo-mineral fertiliser treatments. However, the EC of the top layer (soil) compared to the bottom layers (sand) were generally significantly higher. This is to be expected due to sand having a low cation exchange capacity allowing nutrients to leach from the soil. The top layer of the Control significantly decreased in salinity over time (and this can be observed in most other treatments as well albeit statistically insignificant) which could be due to plentiful irrigation, therefore preventing an accumulation of minerals.

For soil moisture content, there was a significant difference in moisture content between the top (soil) layer and the bottom (sand) layers, which became much larger after eight weeks. Given that the purpose of the high sand content in professional sports turf environments is to facilitate drainage and maintain an even and playable field, it would be interesting to observe whether the soil layer does increase in moisture content outside of a greenhouse environment, as the Control would suggest.

At four weeks post-fertiliser application, the results for the organic matter content of the soil were significantly different between the top (soil) and middle and bottom (sand) layers for all treatments except for the commercial mineral 14-3-6 fertiliser (Velvit Ltd.). This must have been down to an error as the values suggest the sand layers to have a comparable amount of organic matter in them as is in the soil which is unlikely – especially considering that the layers were significantly different to each other eight weeks post-fertilisation which would require an unrealistic turnover of biomass. These results, as well as the significant results should therefore be considered with caution. However, there seems to be an increase in organic matter content overall in the top layers of the various treatments over time. As the Control found this increase to be significant and a clear difference between treatments is lacking, it is likely that this can be attributed to the general growth and turnover of biomass as opposed to any organic matter added to system. Nonetheless, it could be possible that over an extended period of time, the addition of organic matter to the system may have a significant impact which would be expected (Diacono and Montemurro, 2011; Antille and Godwin, 2014) Due to the lacking statistically significant results in our observations regarding soil moisture and organic matter content, H3 (stating that these will increase over time with the organo-mineral treatments providing a higher organic matter and subsequently a higher moisture content) has to be rejected.

Due to the impact soil pH has on microbial biomass, we could have expected our microbial data to reflect our pH data as pH was higher in week 8. The microbial activity measured did not have any significant differences between the time points in the Control which would suggest that the significant differences observed in the top layer of the lab-made blend 16-3-6, the commercial mineral fertiliser 14-3-6 (Velvit Ltd.) and the plant-based organo-mineral fertiliser (ICL Ltd.) are subject to the applied treatments. Interestingly, there was an overall increase in microbial activity in week 8 for the lab-made mineral fertiliser blend 16-3-6 although this (together with the other mineral fertiliser: Market 14-3-6) initially had a slower rate of activity than the organo-mineral fertilisers and the Control. Whilst the research on the

effect of organo-mineral fertilisers on the microbial community is limited, the higher rate of microbial activity, biomass or diversity in soils supplied with organic fertilisers in comparison to mineral fertilisers has been observed in multiple studies and meta-analyses (Goyal et al., 1992; Lori et al., 2017; Ren et al., 2018; Bebber and Richards, 2022). A meta-analysis by Kallenbach and Grandy (2011) that observed the effect of manure-based organic amendments on the microbial biomass of carbon and nitrogen found rapid restoration of the microbial community. Furthermore, they found that the composition and application rates of the amendments were the strongest regulators of microbial carbon, with cattle-manure performing the best from the various manure-types. In this case, there were no consistent differences in microbial activity between treatments, and thus the hypothesis (H4) has to be rejected although an extended observation period may be needed to assess the impacts of fertiliser type on soil microbial activity. Further analysis of the microbial community itself may also prove useful.

We were able to accept our sixth hypothesis, stating that grass clipping weights will be higher due to fertilisation but without significant differences between fertiliser treatments. The clipping weights demonstrated that the Control did not produce as much biomass as the fertilised treatments. While there were no significant differences between fertiliser treatments for the final cumulative weights, it shows that the organo-mineral fertilisers are as efficient as mineral fertilisers regarding yield. This is widely accepted throughout literature with Luo et al. (2018) finding an average increase of 27% higher yield through the use of organic amendments as opposed to mineral fertilisers (in an agricultural setting). Furthermore, Hijbeek et al. (2017) found in their meta-analysis regarding organic additives on yield that for sandy soils (alongside other specific cases) the addition of an organic input significantly increased attainable yield. When looking closer at the C and N contents of the clippings, there were no significant differences for C and none for weeks 1-5 regarding N. During weeks 6 and 7, when variability between samples was the lowest, it was evident that the Control had a lower N content in the clippings compared to the other treatments. The high variability in the first five weeks for both C and N could hint at the results being limited by the low sample replication (n=3 due to resource constraints) and higher sample sizes would be recommended. Only the commercial mineral fertiliser 14-3-6 (Velvit Ltd.) fell within the target N tissue range described by Cockerham et al. (2011) but due to the high variability may not hold true for future assessments. Nonetheless, without an overall consistent difference in treatments, we have to fully reject H7. Regarding root biomass, it is expected that all fertiliser treatments increase plant growth and therefore stimulate root growth as well. It is therefore unexpected for the rooting of the lab-

made blend to be significantly higher after eight weeks. A possible explanation for this is that due to increased leaching potential etc. of the urea in this treatment, nutrients accumulated closer to the bottom of the pot, incentivising root growth after the previous measurements at four weeks. Nonetheless, H8 had to be rejected.

When observing leaching potential of N over time, there were significant differences amongst the various treatments but overall the threshold of 10mg of NO_3-N per litre was not exceeded. After two weeks, the majority of nitrification subsided, reflecting in the decreased concentrations of leached NO_3^- and NH_4^+. This is comparable with Kania et al. (2007) who observed similar results. However, regarding the leaching of inorganic N from golf courses, results vary markedly with leaching representing between <1% to 35% of applied N (Bock and Easton, 2020). The results demonstrate that the organo-mineral fertilisers have the potential to leach less than both mineral fertilisers in regards to $NO_3^=$ which is supported by Richards et al. (1993) and Florio et al. (2015). This allows us to accept our final hypothesis but only in regards to leaching of NO_3^-. The low leaching rates of NH_4^+ from the commercial mineral fertiliser comparison (Market 14-3-6, Velvit Ltd.) is unexpected. Interestingly, Tejada et al. (2005) found inorganic N losses to be reduced by 16% when using an organo-mineral fertiliser as opposed to an organic and inorganic blend. This potentially provides scope for future research on appropriate organo-mineral fertilisation.

2.5 Conclusion

Overall, the results from this experiment were quite varied with most hypotheses being partially or fully rejected. Some notable results from this experiment (which were generally significant although not amongst every case) include the increase in pH over time within the organo-mineral treatments, an increase over time of organic matter content between all treatments (attributed to general biomass turnover), a lag-time in microbial activity within the mineral fertiliser treatments after eight weeks, and a higher concentration of NO_3^- in leached samples from both mineral fertilisers. The organo-mineral fertilisers did not significantly differ from the mineral fertilisers in terms of N uptake or root growth. This experiment took place over the span of two months with only a single fertiliser application. Therefore, it is recommended that future studies run experiments for longer time periods and potentially more fertilisation events (comparable to reality) in order to provide more conclusive results.

3.0 Ammonia Volatilisation Experiment

3.1 Introduction

Although various protocols and legislative frameworks have been established in an effort to reduce ammonia (NH_3) emissions (e.g. Gothenburg Protocol, UNECE Framework Code for Good Agricultural Practice for Reducing Ammonia Emissions, UK Clean Air Strategy 2019), evaluation and mitigation strategies seem to be concentrated around high-income countries, notably the EU (Zhang et al. 2020), with trends nonetheless still demonstrating an increase in atmospheric NH_3 in these areas (Warner et al. 2017). This is concerning considering the various impacts NH_3 volatilisation and consequently, terrestrial deposition has on the environment and public health (Behera et al. 2013). Atmospheric NH_3 is the only primary alkaline gas which plays a large part in regulating the acidity of suspended particulate matter, cloud water and precipitation (Behera et al. 2013), imbalances in this can cause a reduction in air quality and increase soil acidification rates while extensive N returned to the terrestrial environment can also cause eutrophication of water bodies (Ti et al. 2019). Ultimately, excessive NH_3 can contribute to biodiversity loss, negatively impact human health and contribute to climate change (Ti et al. 2018). Brink and Grinsven (2011) estimated the annual health cost of NH_3 emissions within the European Union to be between US\$18 - 140 billion.

However, the loss of NH_3 via volatilisation is not only a threat to people's health and the environment but also a major cause of fertiliser use inefficiency. Using the IPCC estimate, for volatilisation, of 10%, there were an estimated 11.2 – 15.7 million tonnes of fertiliser-N lost globally in 2014 due to volatilisation (Pan et al. 2016). This value can also be countered by Sutton et al. (2013) who calculated that up to 65 million tonnes of N volatilised in 2008 (which also included non-fertiliser sources). With climate change and increased anthropogenic activity, they state that this value could increase to 132 million tonnes in 2100. According to Misselbrook and Gilhespy (2021), the total NH_3 emissions for the UK in 2019 were 238.8kt. The agricultural sector is responsible for around 80 – 90% of global NH_3 emissions (82% in the UK; Guthrie et al. 2018) of which animal agriculture is responsible for 34.1% - 42.3% while the application of mineral fertilisers contributes 31.8% – 46.5% (Behera et al. 2013). The production of NH_3 takes place during the ammonification part of the soil nitrogen cycle as ammonium (NH_4^+) is produced. NH_4 can subsequently be converted to NH_3 and is more likely with favourable conditions: high urease enzyme activity and increased soil pH, soil

temperature, soil water content, and wind speed (Knight et al. 2007; Mariano et al. 2019). For urea, the general ammonification reaction takes place as follows (Stefanakis et al. 2014):

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$
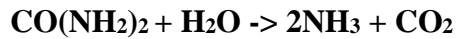
In a meta-analysis conducted by Pan et al. (2016), it was found that up to 64% of globally applied N (from urea) was lost as NH_3, with an average value of 18%. They found that this could be mitigated by using fertilisers without a urea base, the deep placement of fertilisers, irrigation after application and mixing with amendments. Conversely, their findings show that split application did not affect NH_3 loss but the use of nitrification inhibitors increased volatilisation by 38%. This is further supported by Lam et al. (2016) that found that nitrification inhibitors reduced N_2O emissions but increase NH_3 emissions by 3-65% in all observations: ammonium- and urea-based fertilisers and animal waste. However, while a meta-analysis by Wu et al. (2021) further identified nitrification inhibitors to cause an average increase in NH_3 volatilisation of 35.7% across studies, they mention that this was not the case with ammonium-based fertilisers and that manure fertilisers had less of an impact on NH_3 volatilisation than urea fertilisers (attributed to two main processes: the increased NH_4^+ in the soil due to the inhibition of conversion to NO_2^- and the increase of soil pH due to the application of nitrification inhibitors). Other studies suggest the abatement of N_2O emissions using nitrification inhibitors do not increase in NH_3 losses, which may also be attributed to soil conditions and the type of nitrogen inhibitors used (Kim et al., 2012; Misselbrook et al., 2014; Recio et al., 2018; Yao et al. 2020; Cui et al. 2021).

While there are not many studies that have observed the effect of volatilisation from organo-mineral fertilisers, they may still have the potential for lower NH_3 emissions than mineral fertilizer alone due to mixed N sources (especially when considering nitrate sources) whilst also potentially having an increased nitrogen use efficiency due to their organic components. A meta-analysis by Xia et al. (2017) also demonstrated that substituting synthetic fertiliser with organic manure significantly decreased NH_3 losses at spreading by 26.8% although this could not be repeated in the experiments of Zhang et al. (2019) who suggest that efficacy may be dependent on the type of manure, liquid and solid fractions, microbial activity levels and the ratio of manure substituted. Organic fertilisers have been shown to have a lower ammonia emission factor than mineral fertilisers but can, however, vary largely between the various types of organic sources. For example, Zandvakili et al. (2019) found cow manure and compost to have the lowest amount of NH_3 emissions, compared to other organic sources with blood

emitting the most – similar findings were supported by Erwiha et al. (2020). However, caution needs to be taken when utilising these values as NH_3 losses can be present from organic sources prior to application as a fertiliser (e.g. during storage) (Behera et al. 2013; UNECE 2014).

With organo-mineral fertilisers increasing in popularity, it is important to try to benchmark their environmental and agronomic effects alongside other fertiliser types. Therefore, in this study the NH_3 emissions of two conventional types of organo-mineral fertilisers (with mineral compound being urea-based) were compared to two types of mineral fertilisers – one with a urea base and the other with an ammonium base. We hypothesised that the organo-mineral fertilisers would result in lower NH_3 emissions than the urea-based mineral fertilizer, with the ammonium-based fertilizer (the reference treatment) generating the lowest NH_3 emission.

3.2 Methods

3.2.1 Experimental Setup

Following a similar design to Misselbrook et al. (2005), a flow-through NH_3 emission measurement system was set up using a pump to pull air through 12 chambers containing soil cores with applications of respective replicated treatments. Cores were created using 9cm diameter PVC pipe cut into 13cm lengths, taping mesh to the bottom, filling with ~11cm sand and then placing a 9cm diameter disc of grass turf (2 cm thick) on top. The turf used comprised of 40% *Festuca rubra rubra,* 35% *Festuca rubra litoralis* and 25% *Lolium perenne.* This was chosen due to the provision of *Lolium perenne* – commonly used on sportsgrounds. The chambers had transparent lids with suba seals to allow photosynthesis and watering via a syringe, respectively.

Four fertiliser treatments were applied: Plant waste-based organo-mineral 16-3-6 fertiliser (ICL Fertiliser Ltd.), poultry litter-based organo-mineral 16-3-6 fertiliser (ICL Fertiliser Ltd.), a laboratory-made 16-3-6 mineral fertiliser using the main mineral components found in the organo-mineral treatments, and commercial 14-3-6 mineral fertiliser (Velvit Ltd.) (see Table 2.1, previous chapter). Cores were left to establish for two weeks before commencing the experiment and were watered twice a week with 50ml deionised water. Cores were watered with 50ml after applying fertiliser treatments and once again (50ml) after ten days via injection through suba seal. A control (no amendment) treatment was omitted as volatilisation was not expected, however a commercial 14-3-6 mineral fertiliser treatment was included as a reference

because it is ammonium-based, and a typical composition of a large proportion of fertilisers used in the UK (Wray, 2016). 16-3-6 fertilisers were applied at a rate of 40g m^2 (equivalent of 64kg N ha^{-1}, as standard recommendation from ICL for one-time fertilisation on sports fields) and the equalised amount of N was applied for the 14-3-6 fertiliser, totalling to 45.7g m^2 (equivalent to 76kg N ha^{-1}).

In order to capture any NH_3-N volatilised, a 200ml 0.0125M phosphoric acid trap was placed after the chambers containing the amended soil cores (Figure 3.1). Incoming air was purified of any NH_3-N already present by being passed through another 200ml 0.0125M phosphoric acid trap and then subsequently cleaned of potentially harmful acid vapours by passing through a 200ml distilled water trap before reaching each chamber containing the amended grass (see Figure 3.1). The flow rate of air was maintained at 3.5 litres per hour using individual flow meters for each chamber.

Acid traps were changed and aliquots were taken from the final acid traps (between chamber and pump, Figure 3.1) after 1, 3 and 6 hours on the first day and then every 24 hours thereafter for 16 days. Aliquots from the acid traps were analysed for NH_4-N using colorimetry (Mulvaney, 1996). The total NH_4-N (equal to the total NH_3-N emitted) in each trap was calculated by multiplying the NH_4-N concentration by the final volume of the acid in the trap.
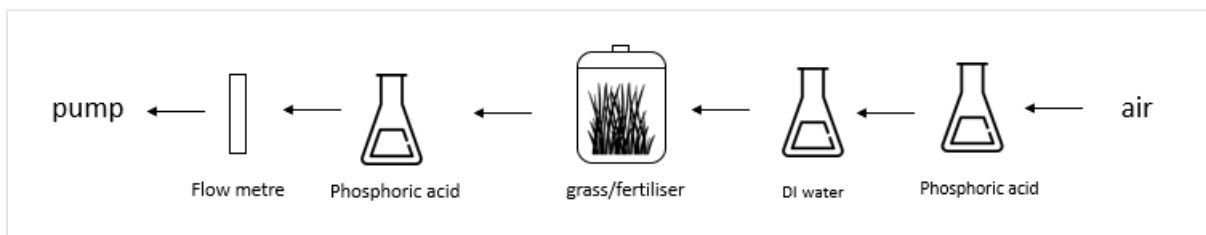
Figure 3.1: Simplified schematic of experimental design.

3.2.2 Recovery Test

Prior to running the experiment, recovery tests were undertaken to establish efficiency of the system to trap NH_3, particularly as a distilled water trap had now been added to the system (previous experiments using the system had not used a water trap). This was done by adding a petri dish base with 20ml ammonium sulphate (0.5g l^{-1} N), and initiating a reaction (NH_4^+ to NH_3) by adding 1ml of 1M sodium carbonate via injection through the suba seal to the

ammonium sulphate, and running the system for 2 hours without the distilled water trap, and halting the reaction by adding 1ml of 1M sulphuric acid to the petri dish. During this time the system was run at 3.5 l min^{-1} and the NH_3 was trapped in the phosphoric acid trap. This was then repeated with the addition of the distilled water trap. Samples were taken from the last phosphoric acid traps (between chamber and pump, Figure 3.1) and the total NH_3-N emitted and trapped was compared with the ammonium sulphate-N added to determine the recovery of NH_3 from the chambers with and without the water trap.

3.2.3 Statistical Analysis

Statistical analyses were performed on IBM SPSS Statistics 27. A one-way repeated measures ANOVA was run to determine significant differences between treatments and volatilisation over time with a post-hoc Tukey test used to specify differences. To determine differences at specific time points (peak concentrations and final cumulative measurements) a one-way ANOVA and post-hoc Tukey's were used. Bonferroni corrections were continuously made. Analyses were run using mg of NH_3 lost per m^2 per hour and a significance value of $p < 0.05$.

3.3 Results

The average temperature for the duration of the experiment was $18.7°C \pm 2.5°C$. Initially, there seems to have been NH_3 volatilisation present at hours 1, 3, and 6 which quickly declined before increasing again before peaking at around 48 hours for all treatments (Figure 3.2). By 144 hours (day 6), volatilisation had ceased. The lab-made mineral blend had the highest overall NH_3-N emission factor of 30.7% (cumulative 1967mg NH_3 volatilised per m^2). Following this were the organo-mineral fertilisers OM Kruimel (ICL) (poultry-manure based) with 12.1% (772mg $NH_3 \text{ m}^{2-1}$), then OM Golf (ICL) (plant-based) with 8.9% (567mg $NH_3 \text{ m}^{2-1}$) and finally the mineral market comparison 14-3-6 (Velvit) with 4.3% (274mg $NH_3 \text{ m}^{2-1}$) (Figure 3.3).

Overall, the one-way repeated measures ANOVA demonstrated that there was a significant difference between treatments which the post-hoc Tukey's test determined to be between the lab-made mineral blend 16-3-6 and all other treatments only. When comparing concentrations at specific time points during peaks (24, 48, 72, 96, 120, 144 hours) this was again confirmed as only the lab-made blend was significantly different (greater) to all other treatments

(p=<0.001 for all treatments at 48 hours). At 96 hours, the lab-made blend was only significantly different to the mineral market comparison 14-3-6 (Velvit) (p=0.017) and the OM Golf organo-mineral 16-3-6 fertiliser (ICL) (p=0.025). There were no significant differences between treatments at 24, 120 or 144 hours.

A one-way ANOVA on the final accumulated emission values, demonstrated that the lab-made blend resulted in significantly greater NH_3 emissions compared with all other treatments. The difference in emissions between the lab-made mineral blend 16-3-6 and the mineral market comparison 14-3-6 (Velvit) was the highest and most statistically significant as p=<0.001. Between the lab-made blend and the organo-minerals p=0.001 for OM Golf (ICL) and p=0.002 for OM Kruimel (ICL).
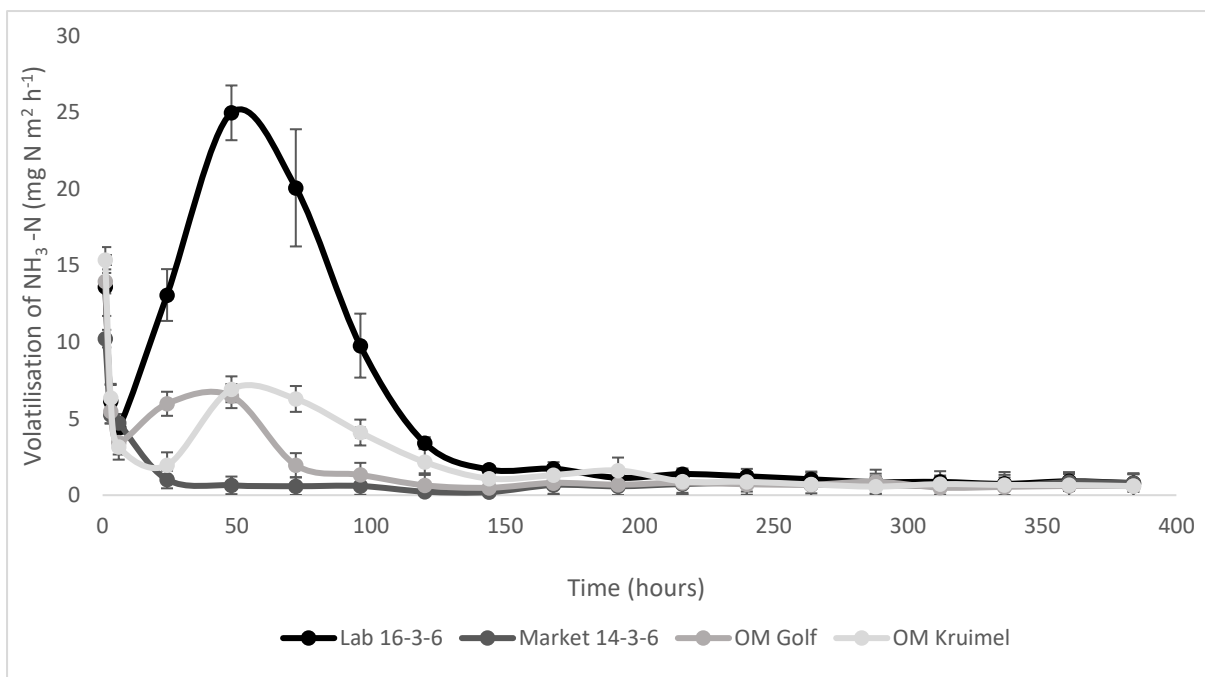
Figure 3.2: Average daily fluxes of NH_3 volatilisation across various treatments. Values represent means ± 1 SEM. (*n=3*).
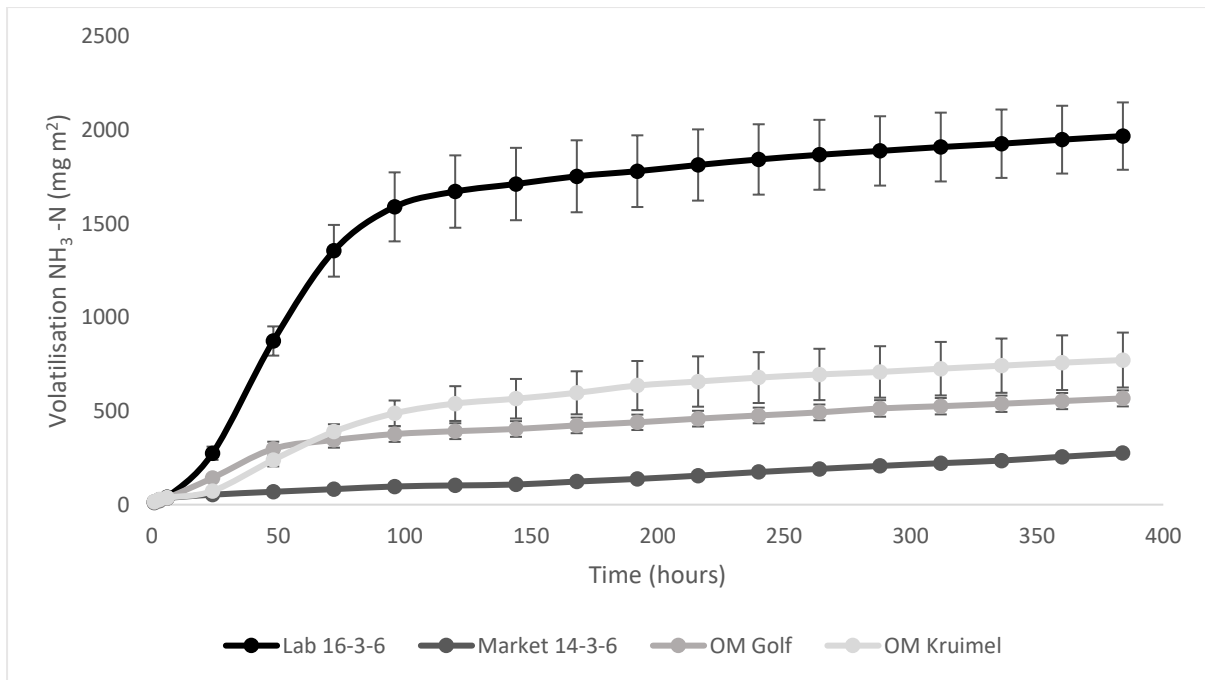
Figure 3.3: Cumulative volatilisation of NH_3 across various treatments. Values represent means $\pm$ SEM. (*n=3*).

3.4 Discussion

Whilst it seems like an initial volatilisation reaction was taking place within the first hour of the experiment, this is unlikely as a time delay must take place to allow the primary enzymatic hydrolysis (via urease) to occur (Mariano et al. 2019). A possible explanation for the apparent high rates of NH_3 emissions measured within the first few hours is that NH_3 was present at high concentrations within the greenhouse (e.g. due to other experiments being fertilised) and that the air within the chambers was contaminated before it was possible to have the filtered air pumped into the system. Either way the results up to hour 6 are considered anomalous and we suggest that the volatilisation data prior to hour 6 should not be (and were not) included in subsequent data analysis.

Overall, we were able to partially accept our initial hypothesis in that the organo-mineral fertilisers generated significantly less ammonia than the urea-based lab mix. However, whilst the ammonium-based fertiliser produced the least ammonia, this was only significantly different to the lab-made 16-3-6 comparison. The lab-made 16-3-6 blend containing urea produced the most NH_3 emissions with an emission factor of 30.7%. Although this is comparable to other studies, it should be noted that conditions can heavily impact the amount

of volatilisation from urea, potentially causing it to be half or twice as high as our observation. This is corroborated by Chambers and Dampney (2009), who observed an averaged emission factor of 27% from 15 grassland experiments, where individual studies showed a range of 10-58% for granular urea-based fertilisers. However, when compared to the organo-mineral fertilisers used in this study, it was clear that the organo-mineral fertilisers performed much better in regard to NH_3 volatilisation as these only had emission factors of 12.1% (OM Kruimel; ICL) and 8.9% (OM Golf; ICL). The emission factors of the organo-mineral products may have been significantly lower than that of the lab-made mineral fertiliser but were still higher than other organic fertilisers within literature e.g. 4.68% for a microalgae biofilm (Siquiera Castro et al. 2017), 3.17% - 6.11% for poultry litter (Akiyama et al. 2004), 3.7% - 4.1% from a straw-rich pig manure (Szanto et al., 2007). This is to be expected though as the both organo-mineral fertilisers still contained a mineral urea-based N source. The commercial ammonium-based 14-3-6 mineral fertiliser had an emission factor of 4.3% but was not statistically different to the organo-mineral treatments. This could suggest that the organo-mineral treatments are as effective as ammonium-based fertilisers when trying to reduce NH_3 emissions. However, that would need to be observed in a variety of conditions in order to hold true e.g. varying soil conditions, abiotic conditions, field trials etc. Furthermore, having a treatment that contains a urease inhibitor would be of interesting, partially as the application of untreated urea should not necessarily be a practice anymore, but also as studies observing the efficiency of urease inhibitors e.g. N-(n-butyl) thiophosphoric triamide, on NH_3 emissions show a reduction of roughly 52 or 53%, (Silva et al. 2017; Cantarella et al. 2018) which is comparable to the organo-mineral fertilisers in this study.

The results presented here may also be indicative of the type of organic material used in the organo-mineral compounds as the plant-based OM Golf (ICL) performed slightly better, i.e. reduced NH_3 emissions (albeit statistically insignificant) compared with its poultry-litter counterpart. More research into the various types of organic material and therefore organo-mineral fertilisers is clearly needed. A study by Erwiha et al. (2020) which studied different organic sources and application methods concluded that there were significant differences between fertilisers, with blood meal and feather meal producing the highest NH_3 emissions. This is likely attributed to the variation in N concentration and N forms between the different organic sources (Zandvakili et al. 2019). Erwiha et al. (2020) also found solid organic fertilisers to produce higher amounts of NH_3 compared to liquid organic fertilisers which can also be recalled when further studying different types of organo-mineral fertilisers in the future. Tejada

et al. (2005) also demonstrate that organo-mineral fertilisers produced as combined granules, performed better than blends of organic and mineral fertilisers (regarding NH_4^+ and NO_3^- leaching). This could also be taken into account for further research and may also have been a point of weakness in our comparisons as the lab-made blend contained urea that was not in a combined granular compound with DAP and KCl, unlike the organo-mineral fertilisers, thus potentially making the urea more susceptible to reacting.

3.5 Conclusions

Overall, we have been able to partially accept our hypothesis as organo-mineral fertilisers emitted significantly less NH_3 than a urea-based mineral counterpart but not significantly more than the ammonium-based mineral comparison. Our findings would suggest that urea-containing organo-mineral fertilisers are a better alternative than urea-based mineral fertilisers when it comes to reducing emissions from NH_3 volatilisation, potentially to a lower urea supply. However, it is recommended that future studies assess this with varying abiotic conditions as well as during field trials. Further research can also focus on different organic sources within organo-mineral fertilisers and their subsequent emissions as well as the type of organo-mineral fertiliser applied e.g. granular blends, granular compounds, liquid fertilisers. Similarly, evaluating their use in different soils and sward heights would also be beneficial. Comparing the efficiency between urease inhibitors and organo-mineral fertilisers would also be interesting. Finally, given that organic substances like manure may volatilise ammonia prior to fertiliser application, it is important to consider the full life-cycles in future assessments.

4.0 Nitrous Oxide Emissions Experiment

4.1 Introduction

With nitrous oxide (N_2O) having a global warming potential 298 times that of carbon dioxide (over a 100-year period) and being an extensively harmful gas to the ozone layer, it is a crucial emission to manage in the various industries it is produced in – notably agriculture (IPCC, 2007; UNEP, 2013). Using an average "business as usual" projection, it is estimated that N_2O emissions will increase by roughly 83% between the years 2005 and 2050 (UNEP Drawing Down N_2O Synthesis Report, 2013). From anthropogenic sources, N_2O emissions are largely emitted in the agricultural sector, where the associated emissions from fertilisers, manure, urine, and crop residue use are compartmentalised into direct emissions (microbially generated, on site, post-application) and indirect emissions (often off site from leachate or volatilised ammonia) (Rees et al., 2013). Although the default IPCC estimate N_2O emissions to account for around 1% of applied N (1.0% for synthetic fertilisers and 0.8% for manure but rounded to 1% to account for uncertainties), Shcherbak et al. (2014) consider this value to be too conservative for high N-applications as they observed exponential growth as opposed to linear, for example causing an underestimation of emissions by 20% or 50% for crops overfertilised by an N-input of 300kg or 500kg ha^{-1}, respectively. This is also demonstrated in the UK (Cardenas et al. 2010; Thorman et al., 2020). The IPCC value may also overestimate emissions in other sites. The issue is further amplified by the maintenance of the 1% estimate, regardless of differences relating to biotic and abiotic factors known to control N_2O production, e.g. climate, temperature, water and oxygen content of substrate, substrate type and availability, pH, organic carbon and nitrogen content and ratio (Signor et al. 2013; Tian et al. 2020) as well as the fertiliser applied and their differences e.g. including N-source, coatings, usage of nitrification inhibitors, application rate (Bell et al. 2015; Harty et al. 2016). This has increasingly led to countries adopting their own specified emission factors that take more localised variables into account (e.g. climate, soil, N_2O sources) to provide more effective mitigation strategies (e.g. for the UK - Bell et al., 2015; Chadwick et al., 2018; Cardenas et al., 2019; Thorman et al., 2020).

While most studies on N_2O emissions from fertilisation focus on crop production, Braun and Bremer (2018a) compiled studies looking at N_2O emissions from fertilised turfgrass and compared N-sources to emission factors. They found various studies observing uncoated and untreated urea to have an emission factor ranging from 0.66-2.9%, and ammonium-based

fertilisers (ammonium-nitrate, ammonium-sulphate, ammonium-phosphate) to range from 0.6-1.2%. This would suggest that overall ammonium-based fertilisers have a lower emission factor than urea in a turf-based context. In literature, the general consensus is that ammonium-based fertilisers are less efficient than urea-based fertilisers in regards to nitrous oxide emissions (Venterea et al. 2005; Signor et al. 2013; Fernández et al. 2014; Harty et al. 2016). However, Smith et al. (2012) find that if the lower N_2O emissions from urea (as compared to ammonium nitrate and calcium ammonium nitrate) are adjusted to include subsequent emissions produced by higher ammonia emissions, there is little difference between N-sources. Although nitrification inhibitors and controlled-release fertilisers have shown to reduce N_2O emissions (Akiyama et al. 2010; Qiao et al. 2015), Riches et al. (2020) found evidence that these did not reduce N_2O during short-term observations when compared to urea on sports turf. They also found N_2O to be higher on sports turf than adjacent non-sports turf which would support the theory of exponential growth in emissions due to over fertilisation. A further study by Braun and Bremer (2018b) found evidence that poly-coated urea would perform better than uncoated urea in turfgrass environments. While there do not seem to be any studies that have observed the effects of manure application to N_2O emissions from turfgrass, it is widely accepted that manure applications significantly increase N_2O emissions due to the favourable conditions created for denitrification (Zhou et al. 2017; Thorman et al., 2020; Shakoor et al. 2021a; Shakoor et al. 2021b).

There is limited knowledge regarding N_2O emissions in turfgrass environments, especially in sports-turf environments which is further exacerbated due to the limited knowledge regarding the nitrogen use efficiency of organo-mineral fertilisers. Vitale et al. (2017) found evidence to suggest that organo-mineral fertilisers are a better alternative to mineral fertilisers when observing N_2O emissions as they provided higher yield in tomato plants with lower emissions compared to an ammonium-nitrate fertiliser (although the treatment using nitrification inhibitors provided the lowest emissions but also a lower yield). Alternatively, a long-term study by Meng et al. (2005) found a mixture of manure and NPK fertiliser to produce statistically insignificantly higher N_2O emissions than mineral fertiliser treatments but argue this to still be a better option when considering alternative impacts like soil health and crop yield. These gaps in knowledge provided an opportunity to study both how a urea-based and ammonium-based mineral fertiliser compare to each other in a turf environment, as well as the observing N_2O emissions from organo-mineral fertilisers generally. Three fertilisers were therefore compared: lab-made 16-3-6 urea blend, commercial 14-3-6 ammonium-based

fertiliser, organo-mineral 16-3-6 fertiliser (urea-based mineral component). With the limited information available, we hypothesised that the urea-blend would result in higher N_2O emissions than the ammonium-based fertiliser, with the organo-mineral fertiliser having the lowest emissions overall.

4.2 Methods

4.2.1 Experimental Setup

To act as replicates of sports-field samples, 12 large plastic boxes (78cm x 56cm x 43cm) were used and set up to simulate a replicated small-scale sports turf system. Holes (4 per box, 1cm diameter) were melted into the bottom of each box for drainage. The boxes contained a 10cm base layer of gravel to improve drainage and avoid sand loss through the drainage holes. Above that, acid washed silica sand was applied before adding a 2-3cm layer of pre-grown turf at the very top (comprised of 40% *Festuca rubra rubra,* 35% *Festuca rubra litoralis* and 25% *Lolium perenne*, chosen due to *Lolium perenne* being commonly used for sportsgrounds) (Figure 4.1). Samples were set up in a temperature controlled greenhouse (18.9 ± 1.7) with additional full-spectrum lighting and maintained by watering with 3l of water once a week.

Two mineral fertilisers and one organo-mineral fertiliser were applied: 16-3-6 laboratory-made blend using urea, DAP, and KCl; 14-3-6 market comparison using ammonium, P_4O_{10}, and K_2O (Velvit Ltd.); 16-3-6 organo-mineral comparison with poultry litter organic component and a urea, DAP, and KCl mineral component (ICL Ltd.). Individual fertiliser treatments were randomly allocated to a chamber applied using a random number generator. Fertiliser was applied by hand to the area within each chamber, at an equivalent rate of 64kg N ha^{-1} (equivalent to ICL Ltd. Recommended rate of 40g of fertiliser per m^2). Measurements of N_2O were made for four weeks after fertiliser application and watering took place once a week using 2l of deionised water within the chamber area and 1l of water for the remaining surface area of each box.

The N_2O emissions were measured using an automated chamber system (Marsden et al. 2018; Recio et al., 2019). Stainless-steel chamber bases (dimensions of 50cm x 50cm x 10cm) were inserted into the turf/sand within each of the sample boxes and their respective chambers (50cm x 50cm x 15cm) clamped in place on top (Figure 4.2). Chamber opening and closing was controlled via pneumatic actuators. During chamber closure, gas samples were transferred to

an Isotopic N_2O Analyser (Model: 914-0027, Los Gatos Research, Mountain View, California) via 1/4" Teflon tubing. The Isotopic N_2O Analyser (LGR) is capable of measuring N_2O isotopomers, but for this experiment the instrument was used for measuring N_2O concentrations only.

Baseline measurements were taken for one week before applying treatments to ensure that the system was working properly but also to act as a reference (control) for N_2O emissions of the samples themselves. A control was omitted due to interest in focusing on the comparisons between fertiliser treatments and due to replication limitations of the system. The automated measurement system is only able to link to 12 automated chambers, and previous trials have shown that four replicates should be the minimum for this system due to the variability of N_2O production and emission, hence this experiment included 3 treatments with 4 replicates of each.

Sampling took place by closing one chamber in sequence for 30 minutes and gas samples being taken every 5 seconds to measure the change in N_2O concentration within the headspace of the chambers. After every four chambers, a reference calibration was taken for ten minutes using ambient air. The LGR analyser was calibrated once per week using N_2O using a 1500 ppb N_2O calibration standard. The 30 minute chamber closure time and reference as sampling protocol allowed one cycle of sampling of all 12 chambers to take 6.5 hours, meaning that 3-4 fluxes could be measured per chamber per 24-hour day. Due to the cyclical sampling process, although 8 chambers would have 4 fluxes per day (and 4 chambers would have 3 fluxes), whichever 8 chambers are measured four times would change on a daily basis.
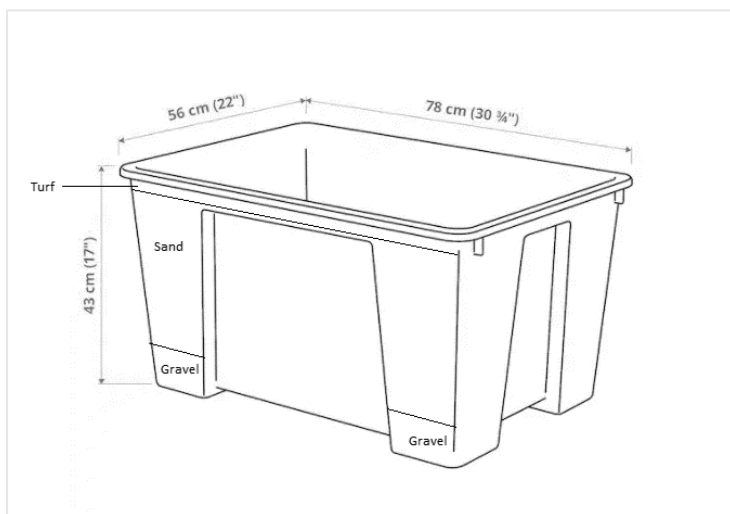
Figure 4.1: Schematic representation of the boxes used in this experiment.
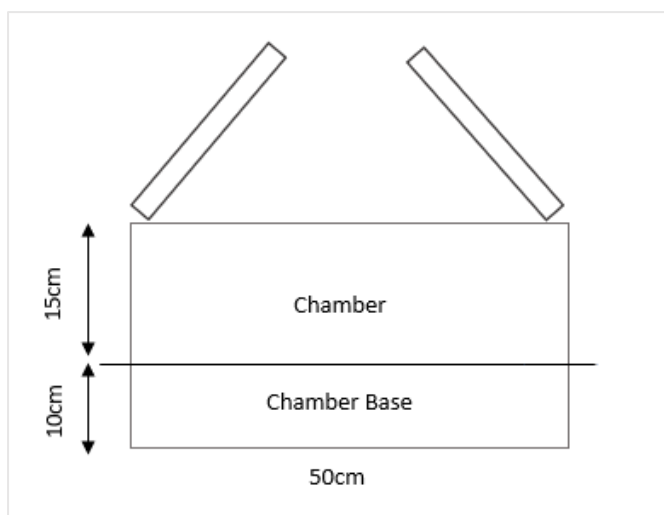
Figure 4.2: Schematic of an N_2O emission chamber used in this experiment.

4.2.2 Data processing and statistical analyses

Data was processed using RStudio version 4.1.2, statistical analyses were processed using IBM SPSS Statistics 27. Due to the high volume of data collected, daily flux measurements had to be summarised from the concentration values. This was done by determining the difference in N_2O concentration within the chambers between the start of the chamber closure and the end. The first minute of chamber closure was discarded to avoid potential carry-over from the previous chamber, and the measurements with a slope of N_2O concentration over time with an r^2 value < 0.8 were discarded. Trapezoidal integration was used to calculate emissions in between measured fluxes and therefore determine cumulative emissions. Significant differences in cumulative N_2O fluxes between treatments were determined using a Welch Test for the baseline measurements and a one-way ANOVA and post-hoc Tukey for the post-fertilisation measurements.

Emission factors per treatment were calculated by subtracting cumulative baseline emissions ($\sum BE$), scaled up to the total number of days the experiment was run for post-fertilisation, from the total emissions per treatment ($\sum TE$) during the measurement period and then divided by amount of N applied before multiplying by 100 to produce percentages, see below. (Due to a fault in chamber 5's tubing during the baseline measurements, an average of other baseline measurements was used instead.)

$$EF = \frac{\sum TE - \sum BE}{applied\ N} \times 100$$

4.3 Results

Initially, what can be observed is that there is a sharp increase in N_2O emissions after fertiliser application (Fig. 4.3; 4.4). Differences between treatments can be observed as the commercial mineral fertiliser Market 14-3-6 (Velvit Ltd.) does not increase as sharply as the other two treatments, thus not necessarily providing a clear peak. Both other treatments had a much clearer peak with the lab-made blend 16-3-6 having a higher increase in N_2O emissions and also a slower fall than the manure-based organo-mineral treatment OM Kruimel (ICL Ltd.). It seems that chambers 10, 11, and 12 had the highest variability between fluxes which could be answerable by these replicates being closer to the greenhouse entrance and thus being more susceptible to changes in temperature, air flow, and physical activity (Figure 4.3; 4.4).

Overall, the urea-based Lab 16-3-6 blend produced the highest amount of cumulative N_2O emissions, with the manure-based organo-mineral 16-3-6 fertiliser (ICL Ltd.) being the second highest and the commercial ammonium-based Market 14-3-6 mineral fertiliser (Velvit Ltd.) producing the least (Figure 4.5). These differences were determined to be significant. There was a significant difference in cumulative N_2O emission between Lab 16-3-6 and Market 14-3-6 ($p=0.044$). The lab-made blend 16-3-6 also produced significantly higher emissions than OM Kruimel, the organo-mineral fertiliser ($p=0.005$). The commercial Market 14-3-6 ammonium-based mineral fertiliser generated significantly less (cumulative) N_2O than the manure-based organo-mineral 16-3-6 fertiliser ($p<0.001$). Cumulative baseline measurements showed there to be no significant difference between respective chamber combinations prior to fertilisation (Welch Test).

The emission factors for the respective treatments were calculated as follow: the lab-made urea-based blend 16-3-6 had an emission factor of 0.97%, the commercial ammonium-based mineral fertiliser 14-3-6 had an emission factor of 0.33%, and the manure-based organo-mineral 16-3-6 fertiliser had an emission factor of 0.56%. It should be noted that these are partial emission factors due to the short-term nature of the experiment.
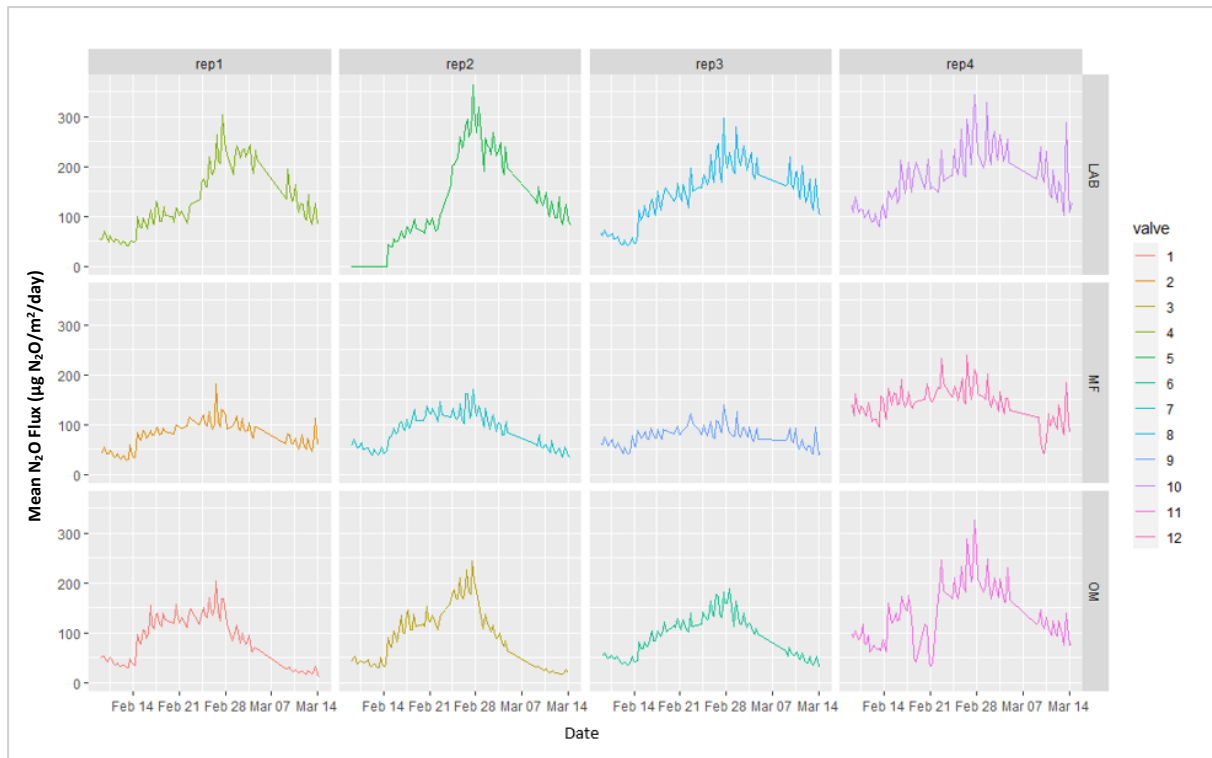
Figure 4.3: Individual chamber flux measurements. Fertilisation took place on Feb 14. Data was omitted between March 4-7 due to technical issues. Chamber 5 had faulty tubing that was replaced prior to fertilisation. Chamber 10 had faulty measurements between Feb 17-21 with unknown cause. LAB = Lab 16-3-6, MF = Market 14-3-6, OM = OM Kruimel.
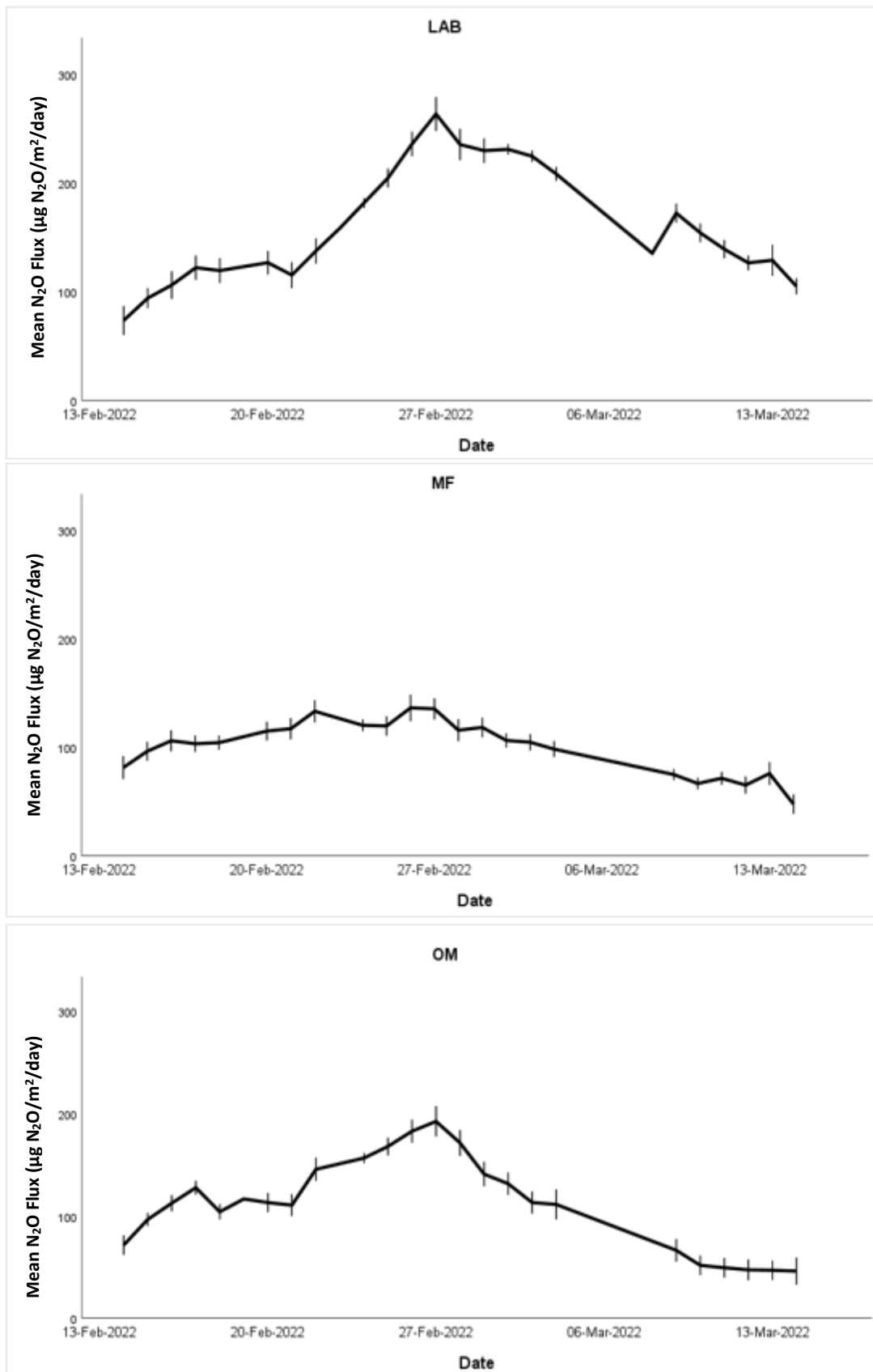
Figure 4.4: Mean daily N_2O flux measurements for each treatment post-fertilisation. Data was omitted between March 4-7 due to technical issues. LAB = Lab 16-3-6; MF = Market 14-3-6; OM = OM Kruimel. ±SEM
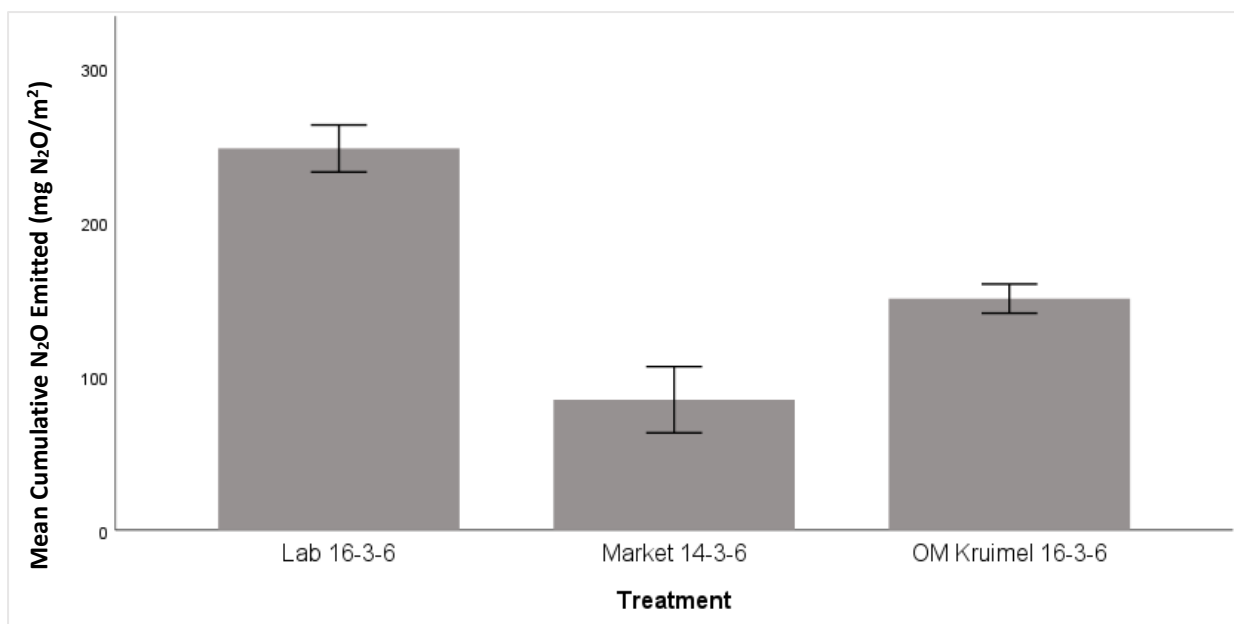
Figure 4.5: Mean cumulative N_2O emissions for the various treatments. ± SEM

4.4 Discussion

In our study, we found the Lab-16-3-6 urea-based blend to produce the highest amount of emissions with an emission factor of 0.97% - very much in line with the IPCC 1% estimate and somewhat in line with the UK specific emission factors at 0.5-0.7% for grasslands and 0.4-1.4% for arable fields (Thorman et al. 2020). The other two treatments were far lower at 0.33% for the ammonium-based mineral Market 14-3-6 (Velvit Ltd.) and 0.56% for the manure-based organo-mineral 16-3-6 fertiliser (ICL Ltd.). This partially fulfils our hypothesis in that the urea-based blend did emit the most N_2O but the organo-mineral fertiliser did not produce the lowest overall.

The low-rates for the ammonium-based fertiliser (Velvit Ltd.) are surprising as Thorman et al. 2020 measured emission factors from all recorded ammonium-nitrate and calcium ammonium-nitrate applications to be at 0.7-1.3%. The low rates in the ammonium-based Market 14-3-6 fertiliser (Velvit Ltd.) and the manure-based organo-mineral 16-3-6 fertiliser (ICL Ltd.) can somewhat be explained by the sampled areas previously not having been fertilised as well as the overall very low rate of fertilisation of 6.4g of N m^{2-1} (64kg per hectare) or which agrees with the concept of under-fertilisation causing emission values to fall under the linear increase according to the IPCC 1% (Shcherbak et al. 2014). There is also evidence to suggest that chambers that are larger than $0.2m^2$ (45x45cm) determine significantly lower emission factors

than smaller chambers (due to the headspace volume) (Shcherbak et al. 2014) which could have contributed as the chambers used were $0.25m^2$. However, these reasons would not explain the high/seemingly accurate emissions calculated for the lab-made 16-3-6 urea-based blend. This could be because by the urea prill was not part of a compound granule, and was hence more readily available for abiotic and biotic processes. A meta-analysis by Dutt and Tanwar (2020) found urea-based fertilisers to produce higher N_2O emissions than non-urea-based fertilisers from turf.

Assuming that these emission factors are all accurate and reflect true emissions, it is clear over this 4 week period, that the urea only treatment was the most unsustainable form of N to use in regards to N_2O emissions from sports-turf. According to this study, the use of a manure-based organo-mineral fertiliser results in similar N_2O emissions as an ammonium-based fertiliser. However, this study did not include a plant-based organo-mineral fertiliser which may prove to have significantly lower N_2O emissions compared to both the ammonium-based 14-3-6 commercial fertiliser and the manure-based 16-3-6 organo-mineral. This would corroborate conclusion by Charles et al. (2017), who describe manures to be in the medium-risk group regarding N_2O emission factors while composts and crop residues were in the low-risk group (however, compost/crop residues plus fertilisers moved them to the medium-risk group). A study by Thorman et al. (2020) observing a variety of manures, application methods, and sites found poultry manure to have a significantly higher emission factor than other manures during an autumn application (EF = 1.52%) as well as when applied on sandy loam (EF = 1.8%). As our experimental design contained a high sand content, this may also help explain our results alongside the consideration of further added urea to the poultry manure based organo-mineral fertiliser.

In this regard, considering that the organo-mineral fertiliser tested contained manure and the N source that provided the highest N_2O emissions in this study (urea), it performed well overall. This may potentially be due to urea being rapidly hydrolysed to ammonium and thus readily available for nitrification and subsequent denitrification to take place whereas the organo-mineral may have either acted as a protective layer reducing exposure of the urea (as suggested by Tejada et al., 2005, regarding leaching) or by having a mix of N sources – some that are partially readily hydrolysed and some that first need to undergo mineralisation. When further considering effects of NH_3 emissions on the total N_2O produced (refer to previous chapter), the lab-made blend 16-3-6 further demonstrates to be the most inefficient whilst the commercial mineral fertiliser Market 14-3-6 (Velvit Ltd.) is the most efficient.

A general benefit of adding organo-mineral fertilisers as opposed to regular mineral fertilisers is the addition of C to the system (Das et al. 2019) which in theory could fully or partially offset the negative impact of the emitted N_2O. Nonetheless, there is evidence to suggest that the addition of C may in fact increase N_2O emissions by increasing denitrification (especially in wet conditions) (Thorman et al. 2020) and furthermore a global meta-analysis by Zhou et al. (2017) find that the addition of carbon to agricultural soils does not offset N_2O emissions via carbon sequestration. Townsend-Small (2010) showed similar results when considering organic carbon sequestration in athletic fields but justify this to be due to the lack of sequestration possible as frequent surface restoration prevents the long-term accumulation of organic carbon. This would suggest that even an organo-mineral fertiliser would not provide many benefits in terms of carbon sequestration in sports-turf environments.

While this study serves as a good basis for future research regarding organo-mineral fertilisers, it was limited due to time constraints and the cumulative emissions calculated may still vary over the longer term. Data observing soil characteristics should also be observed as these have been shown to have a large impact. Further research should also consider looking at a variety of organo-mineral fertilisers and it would additionally be interesting to see how organo-mineral fertilisers compare to the application of fertilisers containing nitrification inhibitors. Higher replications and/or repetitions of trials using varying application rates would also be recommended due to the high variability amongst chambers and the difficulty in maintaining consistent technical efficiency.

4.5 Conclusion

Overall, the hypothesis that the urea-blend would result in higher N_2O emissions than the ammonium-based fertiliser, with the organo-mineral fertiliser having the lowest emissions overall could be partially accepted as the urea-based Lab 16-3-6 produced the highest amount of emissions. However, this hypothesis had to be partially rejected because the organo-mineral fertiliser 16-3-6 (ICL Ltd.) did not emit the least N_2O from the three treatments. This may be due to using a manure-based organo-mineral fertiliser and there could be potential for fully accepting our hypothesis if a plant-based organo-mineral fertiliser was used as manure tends to have higher emissions generally. The results from this experiment are limited as results would have ideally been calculated once the N_2O emissions had returned back to a background levels but due to time constraints this was not possible. It is therefore conceivable that

emissions may be different over the longer term. While the high emissions from the urea-based fertiliser are in line with other literature regarding N_2O emissions from turf, more research is needed in this field, as well as concerning organo-mineral fertilisers specifically in turf environments. While further research should incorporate a variety of organo-mineral fertilisers, using a variety of mineral fertilisers e.g. with the use of nitrification inhibitors would be interesting as well.

5.0 Synthesis of the Study

This project was undertaken to better understand the efficiency and potential benefits of organo-mineral fertilisers in sports turf environments. Table 5.1 summarises the statistically significant outcomes of the various studies. For the agronomic observations, the final measurements after eight weeks (and only using the top layer of soil as a reference) were used. For continuous observations e.g. leaching, gaseous emissions, the overall difference between treatments was used. The arrows are used in cases of significant differences between treatments, with an upwards pointing arrow being used for cases where treatments provided a more favourable result and with a downwards arrow demonstrating a less favourable result. Double arrows are used in cases where a treatment performed significantly better than some treatments and significantly worse than others.

When considering the agronomic experiment, it was clear to see that in the short time frame with only a single application, the organo-mineral fertilisers did not seem to be extensively different to the mineral fertilisers in terms of soil characteristics, microbial activity, clipping yield, clipping nutritional content or rooting, demonstrating that organo-mineral fertilisers are potentially an appropriate alternative to mineral fertilisers. Some observations seemed to foreshadow organo-mineral fertilisers as being a better option (e.g. as microbial activity in the mineral treatments experienced an initial time lag) while others seemed them to not be (e.g. soil moisture, organic matter content). In some cases, such as organic matter content, microbial activity, NO_3 and NH_4 leaching, the plant-based organo-mineral fertiliser (OM Golf 16-3-6; ICL Ltd.) performed better than the manure-based organo-mineral fertiliser (OM Kruimel 16-3-6; ICL Ltd.). Throughout the experiments, this was often a recurring pattern although not necessarily statistically significant. Regarding N_2O emissions, given the evidence previously stated, it could be expected that the plant-based organo-mineral product (OM Golf 16-3-6) would also perform better than the manure-based OM Kruimel 16-3-6.

When observing nutrient concentrations in leached water, the organo-mineral fertilisers performed better than the mineral fertilisers in regards to NO_3^- concentration and better than the urea-based mineral fertiliser in regards to NH_4^+ concentration. Regarding the volatilisation of NH_3, the organo-mineral fertilisers also proved to be more efficient than the urea-based mineral fertiliser (comparable to urease inhibitor treated fertilisers) whilst the ammonium-based mineral fertiliser had the lowest NH_3 volatilised, as expected. This was also reflected in

the final study that compared the two mineral fertilisers with the manure-based organo-mineral fertiliser on the basis of N_2O emitted.

Given the nature of organo-mineral fertilisers and their nitrogen sources, it would be expected that they would act similar to slow-release fertilisers as the organic matter aids in the retention of nutrients in the soil. The organic nitrogen fraction must first be converted to nitrite, then nitrate, while the mineral urea fraction primarily undergoes ammonification. Over the course of this study, the ammonium-based mineral fertiliser consistently performed better than expected and generally reflected in literature which may be dependant on the specific fertiliser composition as ammonium is readily available for plant uptake. Nonetheless, the organo-mineral fertilisers consistently performed as good as or better than the urea-based fertiliser although also containing urea as their mineral fraction and hence should be considered to used in its place.

Table 5.1 Summary of the various significant differences between treatments for each observation.

Variables	Fertiliser	Rating
pH	Control	
	Lab made blend 16-3-6	
	Mineral comparison 14-3-6	
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	
EC ($\mu S\ cm^{-1}$)	Control	↓
	Lab made blend 16-3-6	
	Mineral comparison 14-3-6	
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	↑
Soil moisture (%)	Control	↑
	Lab made blend 16-3-6	↑
	Mineral comparison 14-3-6	↑
	Plant-based OM Golf 16-3-6	↓
	Manure-based OM Kruimel 16-3-6	↓
Organic matter content (%)	Control	↑
	Lab made blend 16-3-6	
	Mineral comparison 14-3-6	↑
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	↓
Microbial Activity (% used)	Control	
	Lab made blend 16-3-6	↓

	Mineral comparison 14-3-6	↓
	Plant-based OM Golf 16-3-6	↑
	Manure-based OM Kruimel 16-3-6	
Clipping weight (g)	Control	↓
	Lab made blend 16-3-6	↑
	Mineral comparison 14-3-6	↑
	Plant-based OM Golf 16-3-6	↑
	Manure-based OM Kruimel 16-3-6	↑
Clipping C content	Control	
	Lab made blend 16-3-6	
	Mineral comparison 14-3-6	
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	
Clipping N content	Control	↓
	Lab made blend 16-3-6	
	Mineral comparison 14-3-6	
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	↑
Rooting	Control	↓
	Lab made blend 16-3-6	↑
	Mineral comparison 14-3-6	
	Plant-based OM Golf 16-3-6	
	Manure-based OM Kruimel 16-3-6	
NO_3 leaching	Control	↑
	Lab made blend 16-3-6	↓
	Mineral comparison 14-3-6	↑
	Plant-based OM Golf 16-3-6	↑
	Manure-based OM Kruimel 16-3-6	
NH_4 leaching	Control	↑
	Lab made blend 16-3-6	↓
	Mineral comparison 14-3-6	↓
	Plant-based OM Golf 16-3-6	↑
	Manure-based OM Kruimel 16-3-6	↓↑
NH_3 emissions	Lab made blend 16-3-6	↓
	Mineral comparison 14-3-6	↑
	Plant-based OM Golf 16-3-6	↑
	Manure-based OM Kruimel 16-3-6	↑
N_2O emissions	Lab made blend 16-3-6	↓
	Mineral comparison 14-3-6	↑
	Manure-based OM Kruimel 16-3-6	↑↓

In conclusion, while these results may have been attributed to the short time scale of the experiment, it demonstrates that the organo-mineral fertilisers used are not an inappropriate alternative to the conventional mineral fertilisers due to their consistently comparable performance. This study has successfully improved available knowledge relating to the turf

management using organo-mineral fertilisers and in general on commercial organo-mineral fertilisers as well (e.g. not a combination of raw manure and mineral fertilisers). A variety of approaches were used that have not been used in combination with organo-mineral fertilisers previously (e.g. Chapter 3, Chapter 4), thus adding to the importance of the completed study.

5.1 Limitations of the Research

These studies were limited by a variety of factors. Firstly, comparable mineral treatments were limited to a lab-made blend and an uncertain ammonium-based commercial fertiliser which may have not necessarily been reflective of the variety of fertilisers used – especially considering slow-release fertilisers or nitrification inhibitors. Secondly, experimental circumstances encompassing longer time frames, repeated applications, varying application and irrigation rates, as well as field trials would have been preferred. Some aspects of the supply of materials were affected due to political circumstances (Covid-19 and Brexit) which should ideally not be the case.

5.2 Recommendations and Prioritisation for Future Research

Whilst this study has provided a knowledgeable basis on a large variety of factors relating to soil health and fertiliser use efficiency, more research is needed on commercial organo-mineral fertilisers in general but especially in the turf industry. Priority lies with the comparison of a wider variety of mineral fertilisers, especially slow-release varieties. As this study determined potential for there to be significant benefits to soil and microbial ecosystems, longer time-scales and frequent applications should definitely be considered. As with all research, field observations as opposed to controlled environments are necessary for a more holistic understanding of these and similar products.

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