The influence of neutralisation time lag on plant-available phosphorous in acid mine tailings

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"Nature is the source of all true knowledge. She has her own logic, her own laws, she has no effect without cause nor invention without necessity."

- Leonardo da Vinci

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"If the only prayer you ever say in your entire life is thank you, it will be enough."

- Meister Eckhart

ABSTRACT

The main goal of vegetation establishment on tailings storage facilities is to stabilise their slopes to improve the retention and infiltration of water, thereby reducing the effects of wind and water erosion. The neutralisation of acidic soils with agricultural lime is a common practice but with acidic mine tailings (e.g. gold and coal tailings), acid is generated by other sources. Therefore, the neutralisation incubation time of these tailings vary greatly from natural soils because the acidity is caused by geochemical oxidation processes in the tailings material. The weathering and oxidation of minerals present within the tailings, most frequently pyrite (FeS_2), produce sulphuric acid (H_2SO_4). These reactions may cause the tailings to have pH levels as low as 1.7. This extremely acidic environment accompanied by continuing oxidation reactions cause a major time lag in the neutralisation of the tailings material. Applying fertiliser directly after treating the material with the appropriate amount of lime, will have very little to no success as the optimum pH for these nutrients to be available for plant uptake is around 5.5 to 7.5, depending on the plant species. For example, preliminary studies have proven that gold tailings generally have a neutralisation incubation time of approximately six weeks, when the pH of the material increases from 3.0 to 6.0 over this period. This research focuses on the plant availability of phosphorus (P) in acid mine tailings. The aim of the study was to determine if a neutralisation incubation period of six weeks before fertiliser treatments would result in increased plant availability of P.

Two different analytical methods were used to monitor P in the growth mediums (i.e. Olsen and Bray-1). The final results obtained from the pot trials showed an increase in the plant availability of P when superphosphate was applied after the neutralisation incubation period, compared to when lime and fertiliser were applied at the same time. Better germination rates were also obtained from the growth mediums where the Olsen method extracted higher concentrations of P ($r + 0.789$; $p < 0.05$). Additionally, it was found that the use of the Bray-1 method to extract P delivered inaccurate results in heavy limed tailings materials.

Key terms: acidification, Bray-1, lime, mine rehabilitation, Olsen, oxidation, pH

OPSOMMING

Plantegroei word op die hellings van slikdamme gevestig om dit te stabiliseer en sodoende die materiaal se infiltrasie- en waterhouvermoë te verbeter, wat dan weer bydra tot die bekamping van wind- en watererosie. Dit is algemene praktyk om suur gronde met kalk te neutraliseer, maar wanneer dit by suur mynslikmateriaal (bv. goudslik) kom, word die sure deur ander bronne gegenereer. Dit is juis om hierdie rede dat die neutralisering van suur mynslik baie anders is as die neutralisering van natuurlike suur gronde. Die suur in sulfiedryke mynslik word geproduseer deur geochemiese oksidasiereaksies wat binne-in die materiaal plaasvind wanneer daar suurstof en vog teenwoordig is. Die verwering en oksidasie van minerale soos piriet (FeS_2) produseer swaelsuur (H_2SO_4), wat daartoe lei dat die mynslik 'n lae pH van tot 1.7 kan hê. Hierdie suur omgewing, tesame met aanhoudende oksidasiereaksies, veroorsaak dat die neutralisasie van suur mynslik baie langer neem. Om by hierdie lae pH-toestande die mynslik direk na kalkbehandeling met kunsmis te behandel, sal swak resultate tot gevolg hê aangesien die optimale pH vir hierdie nutriënte om beskikbaar te wees vir plantopname, ongeveer 5.5 tot 7.5 is, afhangend van die plantspesie. Vorige studies het reeds bewys dat goudslik 'n neutralisasie-inkubasietydperk van ongeveer ses weke het, waartydens die pH van 3.0 na 6.0 toeneem. Hierdie navorsingsprojek was gefokus op die plantbeskikbaarheid van fosfor (P) in suur mynslik. Die doel van hierdie studie was om vas te stel of 'n neutralisasie-inkubasietydperk van ses weke voor kunsmisbehandeling verbeterde plantbeskikbaarheid van P tot gevolg het.

Die Olsen- en Bray-1-metodes is gebruik om P-vlakke in die groeimediums te monitor. Die finale resultate na afloop van die potproewe het getoon dat P-vlakke wel hoër is wanneer superfosfaat toegedien is na die neutralisasie-inkubasietydperk, in vergelyking met wanneer kalk en superfosfaat gelyk toegedien is. Die groeimediums wat hoër P-vlakke getoon het (volgens die Olsen-metode), het ook beter plantegroei getoon ($r + 0.789$; $p < 0.05$). Daar is ook gevind dat die Bray-1-metode se resultate minder akkuraat is wanneer groeimediums met 'n groot hoeveelheid kalk behandel is.

Sleutelterme: Bray-1, kalk, mynrehabilitasie, oksidasie, Olsen, pH, versuring

LIST OF ABBREVIATIONS AND SYMBOLS

AEC	Anion Exchange Capacity
AMD	Acid Mine Drainage
Al	Aluminium
AP	Acid Potential
B	Boron
Ca	Calcium
Cd	Cadmium
CEC	Cation Exchange Capacity
CO_3	Carbonate
Cu	Copper
EC	Electrical Conductivity
EMP	Environmental Management Plan
Fe	Iron
H_2O	Dihydrogen monoxide (water)
HCl	Hydrogen chloride
K	Potassium
KCl	Potassium chloride
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
NAP/NAG	Net Acid Potential/Net Acid Generation
NH_4F	Ammonium fluoride
P	Phosphorus
Pb	Lead
PDI	Phosphorus desorption index
PO_4	Phosphate

PSD	Particle Size Distribution
S	Sulphur
SO_4	Sulphate
TSF	Tailings Storage Facility
U	Uranium
Zn	Zinc

GLOSSARY

Absorption	The uptake of substances (e.g. water, ions and nutrients) by the plant root as a result of diffusion along an activity gradient; the process where one substance is taken into and included within another substance.
Active acidity	The pool of soil or growth medium acidity characterised by the activity of H^+ ions present in the soil solution. This pool of acidity is measured through standard pH testing.
Adsorption	The accumulation of a chemical species at the surface of an existing solid.
Anion exchange capacity	The sum total of exchangeable anions (e.g. $H_2PO_4^-$, HPO_4^{2-}, Cl^-, NO_3^-, SO_4^{2-}, etc.) that a soil or other growth medium can adsorb.
Arenaceous	A material that consists of sand or sand-like particles.
Auriferous	Gold-bearing rocks or minerals.
Bituminous coal	Hard, brittle, carbon-rich coal with alternating shiny and dull layers. Also called “household coal”.
Breccia	A coarse-grained clastic sedimentary rock composed of angular fragments.
Cation exchange capacity	The sum total of exchangeable cations (e.g. Ca^{2+}, Mg^{2+}, K^+, Na^+, etc.) that a soil or other growth medium can adsorb. Measured in cmol(+)/kg.
Chert	A hard, extremely compact, dull to semi-vitreous chemical sedimentary rock, consisting predominantly of cryptocrystalline silica.
Conglomerate	A clastic sedimentary rock composed of rounded, waterworn pebbles, cemented in a matrix of sand, silt, clay, calcium carbonate, silica, iron oxide or mixtures of these.

Conjugate base	The substance formed when a weak (e.g. H_2O) or strong acid (e.g. H_2SO_4) loses a hydrogen ion (H^+). The conjugate base gains the H^+ lost by the acid.
Diffusion	The spreading or scattering of matter under the influence of an energy gradient, the energy being quantitatively expressed in terms of the chemical potential of the substance concerned, and approximated by concentration, vapour pressure or similar properties.
Dolomite	A chemical sedimentary rock with the chemical formula of $Ca,Mg(CO_3)_2$.
Ecosystem	A community of organisms and the environment which they live in, forming an interacting system.
Electrical conductivity	The capacity of a material to conduct electricity. It is reported in mS/m in soils and water, and is directly related to the amount of dissolved salts in solution.
Erodibility	The degree or capability of being eroded; susceptibility to erosion.
Exchangeable acidity	The titratable H^+ ions that can be replaced from the exchange complex by a neutral salt solution.
Fertiliser	Any organic or inorganic material of natural or synthetic origin that supplies one or more nutrient elements essential for plant growth and reproduction.
Fixation	The process or processes in a growth medium where certain chemical elements essential for plant growth are converted from an available to an unavailable form for plant uptake, e.g. phosphate fixation or potassium fixation.
Geochemical	All aspects of geology that involve chemical changes.
Grit	An accumulation of small hard particles of sand, earth, stone, etc.
Groundwater	The part of the subsurface water in the zone in which permeable rocks are saturated with water under pressure equal to or greater that atmospheric pressure.

Growth medium pH	The negative logarithm of the hydrogen ion (H^+) activity in a growth medium. It represents the degree of acidity or alkalinity of a growth medium, expressed in terms of the pH scale.
Heavy metal	Elements that form part of the transition elements on the periodic table, e.g. manganese, iron, cobalt, nickel, copper, zinc, silver, cadmium, tin, tantalum, platinum, gold, mercury, tellurium, lead, bismuth, etc.; those metals with densities of the pure metal >5 000 kg/m^3.
Latent acidity	See “potential acidity”.
Lime	A soil amendment consisting mainly of calcium carbonate but which may include magnesium carbonate and other materials used to neutralise soil acidity and to supply calcium and magnesium for plant growth.
Mineral	An inorganic substance with a specific chemical composition. Mixtures of mineral particles comprise the composition of rocks.
Mudstone	A blocky or massive, fine-grained sedimentary rock in which the proportions of clay and silt are approximately the same.
Ore body	Accumulation of minerals, dissimilar from the host rock, where the concentration of a metal is high enough to be worth commercial exploitation.
Oxidation	A chemical reaction where a compound or substance loses electrons and the positive valence is increased, e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^-$.
Particle size distribution	The percentage of particles, usually by mass, in each size fraction into which a dispersed sample of a soil, sediment or rock has been separated.
Photosynthesis	The process by which plants or other organisms that contain chlorophyll use light energy from the sun to convert water and carbon dioxide into life-supporting compounds, such as oxygen and glucose.

Plant nutrients	The elements or groups of elements taken in by a plant that are essential to its growth and used in elaboration of its food and tissues.
Potential acidity	The pool of soil or growth medium acidity primarily associated with tailings or soil in a semi-stabilised geochemical equilibrium where the material still contains pyrite (FeS_2) or jarosite in a reduced or unoxidised state (Fe^{2+}).
Precipitation	A chemical reaction where substances accumulate to form a new solid phase.
Quartzite	A metamorphic rock derived from sandstone, composed essentially of quartz.
Rehabilitation	The action of repairing damaged ecosystems to the best functioning state as determined by the biological, geological and chemical potential of the landscape conditions.
Residual acidity	The pool of soil or growth medium acidity commonly associated with non-exchangeable H^+ and Al^{3+} ions bound to organic matter and clay particles in a growth medium.
Sandstone	A well-sorted sedimentary rock, consisting mainly of quartz grains, often accompanied by feldspar, mica and other minerals.
Sedimentary rock	A rock formed from materials deposited from suspension or precipitated from solution and usually, but not necessarily, consolidated.
Senescence	The condition or process of deterioration with age.
Shale	A fine-grained sedimentary rock formed by the consolidation of clay, silt or mud and characterised by a finely stratified structure that is approximately parallel to the bedding which is commonly most conspicuous on weathered surfaces.
Siltstone	A fine-grained clastic sedimentary rock composed predominantly of silt-sized particles.

Soil	The unconsolidated mineral and organic material on the immediate surface of the earth that serves as a natural medium for plant growth.
Soil solution	The aqueous liquid phase of a growth medium and its solutes in equilibrium with the solid phase.
Stromatolite	A carbonate-rich rock that formed due to the accumulation of $CaCO_3$ crystals on algal or bacterial communities.
Tailings	A combination of fine-grained waste material and processing fluids that remain after the extraction of economic minerals from natural resources.
Tailings storage facility	A designated area or facility used to store and confine tailings.
Toxicity	The injurious or lethal effect of a substance (element or compound) on plants or other organisms.

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PROJECT CONCEPTUALISATION

1.1 Introduction

It is common practice in the agricultural industry to use lime in the neutralisation of acidic soils. Lime, more specifically dolomitic lime, is also used in the rehabilitation of acidic mine tailings (e.g. gold and coal tailings) to neutralise the acidity of the material for vegetation establishment on tailings storage facilities (TSFs). The degree of acidity in some of these tailings materials, which have been measured to be as low as 1.7 (Van Deventer, 2015), is much more severe than for naturally acidic soils where fulvic, humic and citric acids are the key culprits. Therefore, it is a much more challenging task to neutralise acidic tailings materials than acidic soils. This is due to the main source of acidity in mine tailings being the chemical weathering and oxidation of sulphide-bearing minerals, most often pyrite (FeS_2), that produces sulphuric acid (H_2SO_4) as explained by Khozhina and Sherriff (2006).

Sulphuric acid is much stronger than the acids present in natural soils. Therefore, a higher amount of lime is needed to increase the pH of the tailings to a level where the nutrients applied as fertilisers are available for plant uptake. The neutralisation reaction brought on by the addition of lime also takes much longer in acidic tailings when compared to natural soils, depending on the initial pH of the tailings, oxidation potential, particle size distribution and pyrite content.

The pH of a growth medium plays a vital role in the availability of plant nutrients, proving that the extremely low pH value of some tailings is one of the major problems that is experienced during vegetation establishment on TSFs (Beegle, 2001; Van der Nest, 1991). Soil pH – a measure of the acidity or alkalinity of a soil – is the most commonly measured and reported soil property. Several problems associated with the rehabilitation of mine tailings can be defined and predicted by determining the pH of the growth medium. The reason for this, according to Singer and Munns (1992), is that soil pH influences most solid-liquid interactions within the soil system. Kohizma and Sheriff (2006) and Ssenku *et al*. (2014) state that poor germination and seedling survival rates are attributed to the tailings having such low pH values, high salinity, low organic carbon and heavy metals being available at very high concentrations in addition to low levels of available phosphorus and nitrogen.

The availability of phosphorus (P) in acidic mine tailings is the main focus of this project for the reason that this primary plant nutrient is most available for plant use at a pH value of between 6.5 and 7 (Beegle, 2001). The remaining two primary plant nutrients, potassium (K) and nitrogen (N), already increase in plant availability at pH values of between 4.5 and 5.5. Therefore, if the pH of the growth medium reaches the level for the availability of P, with regard to pH, it is safe to accept

that the other primary nutrients will also be available for plant uptake. It is known that acidic, sulphate-rich mine tailings exhibit a pH far lower than what is needed for P to be available for plant uptake. This is caused by continuous oxidation of sulphide minerals and because phosphorus tends to react with aluminium and iron oxides at pH values lower than 6.5 to form less soluble compounds, rendering it unavailable for plant use (Johnston *et al*., 1991).

Applications of fertiliser directly after lime treatment are common in the rehabilitation of acidic mine tailings. Although this may not present any problems for natural soils with higher pH readings and a less hostile geochemical environment than tailings, the same cannot be said for mine tailings material with a much greater acidification potential. This is attributed to the neutralisation reaction brought on by the lime that may take several weeks to raise the pH of the material to a more desired level. The application of fertiliser directly after the material has been treated with lime will lead to the indefinite fixation of essential plant nutrients (e.g. N, P and K). At pH levels lower than 4, P will be rendered permanently unavailable for plant uptake as the pH for the optimal availability of P is between 5.5 and 7.5 (Beegle, 2001).

A neutralisation incubation pilot study paved the way for the main research project. In this pilot study, 13 different acidic mine tailings material were treated with dolomitic lime to determine the approximate time for neutralisation. These results were then used in the tailings material selection process for the main research project.

For the main study, four different types of acidic mine tailings with a diverse spectrum of lime requirements have undergone a further investigation into the neutralisation incubation time lag of acidic mine tailings with regard to the availability of phosphorus. The materials include three different types of gold mine tailings, one fine coal discard tailings material and a naturally acidic soil that has served as the control medium for the study.

The project was, therefore, aimed at the improvement of mine rehabilitation practices by determining the optimum neutralisation time of various acidic mine tailings to ensure increased plant availability of phosphorus.

1.2 Background

1.2.1 Rehabilitation of TSFs

Modern civilisation is highly dependent on features such as aeroplanes, ceramics, construction materials, metals, paint, computers, and so forth, which are all manufactured from products extracted from the earth by the mining industry (Kossoff *et al*., *2014*). South Africa has been the largest gold producer in the world since the commencement of its gold-mining activities over a century ago. This has resulted in the construction of many tailings storage facilities (TSFs) all

over the country where substantial volumes of tailings are deposited (Rösner & Van Schalkwyk, 2000).

In combination with tailings, large amounts of heavy metals, along with sulphide minerals (e.g. pyrite), are contained within TSFs. During the process of gold extraction, an alkaline solution, for example, quicklime (CaO), is added to attain a pH of 10.3. This pH is most suitable for cyanidation since it ensures that free cyanide ions that are essential for the electrochemical reaction of gold dissolution are not lost as free cyanide gas. This means that tailings are initially deposited onto the TSF in an alkaline state. It is only after the lime has reacted with the free cyanide ions and/or leached out and the sulphide-rich material is exposed to moisture and oxygen, that the sulphides are converted to sulphuric acid. This is a major environmental threat because the sulphuric acid produced through oxidation can now seep into the surrounding environment and mobilise heavy metals also present in the tailings (Changul *et al*., 2010; Ritcey, 2005).

TSFs pose a great environmental and social hazard in the form of dust, soil contamination and surface and groundwater contamination (Van Deventer *et al*., 2009). Tailings display many physiochemical characteristics that have deteriorating effects when they are released into the environment. Some of these characteristics are, among many others, very low pH conditions, high electrical conductivities (above 400 mS/m), high concentrations of heavy metals, low cation exchange capacities, and so forth. These physiochemical characteristics will persist for many years in an environment polluted with tailings material, threatening the existence of many intolerable plant communities as well as the establishment of pioneer plant species in bare areas. Areas too hostile for plant inhabitancy due to these extreme physiochemical conditions are much more susceptible to severe water and wind erosion, leading to the contamination of nearby soils and water bodies (Ssenku *et al*., 2014; Van Deventer, 2015). According to Ritcey (2005), Rösner and Van Schalkwyk (2000) and Van Deventer *et al*. (2009), other environmental and social impacts of TSFs, especially those containing sulphide minerals, are as follows:

- Uncovered TSFs generate large quantities of dust that contribute significantly to air and water pollution. The health of nearby communities may be affected negatively as the PM10 24-hour fallout criteria of 75 $\mu g/m^{-3}$ is frequently surpassed.
- Acid mine drainage (AMD) seepage containing high concentrations of heavy metals and other chemicals pollute nearby surface and underground water bodies.
- Nearby dams and streams are contaminated as a result of surface runoff from TSFs.
- In some cases, the deteriorating effect of TSFs may reach areas very far from the facility itself. For example, when the upper catchment of a stream or river is exposed to AMD, the contaminated water is transported and spread throughout the whole catchment. This may lead to the contamination of wetlands and riparian areas, as well the death of a wide range of plant and animal species. Farms along an AMD polluted catchment may also be

affected in the sense that the water is used for irrigation purposes – irrigating soils with this water will have detrimental effects on the quality of soils (e.g. salination, acidification, etc.) and produce.

- Research conducted on gold TSFs showed that due to significant concentrations of radionuclides, high levels of radiation are experienced on and around gold TSFs (even after rehabilitation), which may have damaging health effects in the case of prolonged exposure.
- TSFs have a very low aesthetical value due to their unnatural and uninviting appearance, giving the mining industry an unpleasant reputation.

The practice of rehabilitating TSFs attempts to repair a degraded environment to a state where ecosystem functions are stable. Rehabilitation practices will not return the area to its pre-existing levels of structure, function and composition but rather yield a self-sustaining ecosystem of the area (Haagner, 2008; Muller, 2014). According to Schoenberger (2016), "the most critical arena for reducing the likelihood of mining-related environmental disasters lies in the handling of tailings". Establishing surface stability to prevent erosion by way of wind and water is the main objective in the rehabilitation of TSFs. Establishing vegetation covers, also known as phytostabilisation, on TSFs is a cost-effective and ecologically responsible method used to stabilise the outer surfaces of the TSFs. A vegetation cover aids in reducing the quantity of tailings material or silt transported to the surrounding environment by means of wind and/or water (Van Deventer *et al*., 2007).

Successful establishment of a vegetation cover may further improve the physical, chemical, biological and aesthetical conditions of the tailings material as a growth medium (Schimmer *et al*., 2015). This may encourage the establishment of a self-sustaining vegetation cover in due course, for research has found that tailings material could be colonised by plant communities, starting with pioneer species that have entered the environment by means of wind or water (Ssenku *et al*., 2014; Van Deventer, 2015). However, Ssenku *et al*. (2014) state that this may be a very slow process with low species diversity for a prolonged period. Hattingh and Van Deventer (2004) also found that proper monitoring and maintenance programmes for at least five years following initial vegetation establishment were essential to achieving a sustainable vegetation cover of TSFs.

1.2.2 South African legislation with regard to mine rehabilitation and TSFs

Several examples of abandoned mining sites are present in South Africa on the coal fields of Mpumalanga and KwaZulu-Natal, as well as the Witwatersrand. As a result, mining activities are frowned upon for they are seen as the main destroyers of the natural environment (Marais, 2013). Prior to the advent of the Minerals Act, which was publicised in 1991, mining houses gave no thought to protecting the environment. Previously mined areas and tailings storage facilities (TSF)

were often left unrehabilitated prior to mining companies being liquidated or leaving the country (Swart, 2003). Ever since, much progress has been made with regard to environmental legislation and, as stated by Haagner (2008), South Africa now has some of the broadest and most progressive environmental regulations in the world. As stated by the Bill of Rights of the Constitution of the Republic of South Africa (Act 108 of 1996), citizens have the right:

(a) to an environment that is not harmful to their health or wellbeing; and
(b) to have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that –
    (i) prevent pollution and ecological degradation;
    (ii) promote conservation; and
    (iii) secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development.

The abovementioned act gave way to many more environmental acts. The National Environmental Management Act (NEMA) (Act 107 of 1998) enforces the "duty of care and remediation of environmental damage" principles. Section 28 of this act ensures that responsible parties in the pollution or degradation of the environment must take reasonable measures to prevent such pollution or degradation from occurring, continuing or recurring. It is also stated that where harm to the environment is authorised by law or cannot be reasonably avoided or stopped, pollution or degradation to the environment must be reduced and remedied (South Africa, 1998a). The Act also ensures that before operation permits are granted, all potential environmental impacts thereof have been considered and that mitigation and/or preventative measures have been initiated (Haagner, 2008).

The Mineral and Petroleum Resources Development Act (MPRDA) (Act 28 of 2002) clearly stipulates that the holder of the mining or prospecting right remains responsible for any environmental liability, pollution or ecological degradation, and the management thereof, until the Minister has issued a closure certificate to the holder concerned. The MPRDA also states that the environment affected by the prospecting or mining operations must be, as far as reasonably practicable, rehabilitated to its natural or predetermined state or to a land use which meets the generally accepted principle of sustainable development. Furthermore, Section 38 of the MPRDA as well as Section 34 of the NEMA ensures that the directors of a firm or members of a close corporation are equally responsible for any environmental damage, pollution or degradation caused by the firm or close corporation which they represent or represented (Marais, 2013; South Africa, 1998a; South Africa, 2002).

The submission and official approval of an Environmental Management Programme or Environmental Management Plan (EMP), based on an environmental impact assessment (EIA), is one of the most important requirements with regard to the environment and its rehabilitation (Swart, 2003).

The MPRDA clearly states that any mining rights applicant must conduct an EIA and submit an EMP according to the regulations set out in Section 39 of the MPRDA within 180 days of the date on which he or she is notified by the Regional Manager to do so (South Africa, 2002).

The following are additional South African legislative acts that influence mine rehabilitation and closure, and hold the polluter accountable for any environmental damage:

- The National Environmental Management: Biodiversity Act (NEMBA) (Act 10 of 2004) addresses species and organisms posing potential threats to biodiversity. The NEMBA entails that alien and invasive species must be managed and controlled to prevent or minimise any harm to the environment and to biodiversity (South Africa, 2004).

- Section 20 and 21 of the Environment Conservation Act (ECA) (Act 73 of 1989) addresses the operation, control and management of waste and also provides for the identification of activities which may have negative or damaging effects on the environment (South Africa, 1989).

- Section 19 of the National Water Act (Act 36 of 1998) deals with preventing and relieving the effect of pollution. The Act provides for the responsibility to protect water resources through a wide range of regulations, which include pollution prevention, water reuse or reclamation, water treatment and water discharge (Swart, 2003). The Act explains that where a situation exists that causes pollution of a water source, the owner of the land must take all reasonable measures to prevent it from occurring, continuing or recurring. Section 151 (South Africa, 1998b) discusses penalties for failing to comply with these regulations.

- Alongside the National Water Act, the Conservation of Agricultural Resources Act (CARA) (Act 43 of 1983) also requires that no polluted water may flow from mining areas into rivers or underground aquifers (Haagner, 2008). The CARA upholds the preservation of natural soil, water resources and natural vegetation. The CARA also entails the control of weeds and invader plants, as well as the restoration of eroded or disturbed land (South Africa, 1983).

- The legal obligations enclosed in Part IV of the Atmospheric Pollution Prevention Act (Act 45 of 1965) address steps to be taken in the control and prevention of dust pollution (South

Africa, 1965). Broader regulations with regard to dust pollution were publicised in 2004 in the National Environmental Management: Air Quality Act (Act 39 of 2004).

- Several mine tailings are associated with radioactive elements (e.g. uranium) as a result of pyrite oxidation and chemical leachates (Swart, 2003). Section 46 of the Nuclear Energy Act (1999) addresses the disposal of radioactive waste. The Act states that "no person may, without the written permission of the Minister, discard radioactive waste in any manner or cause it to be discarded" (South Africa, 1999).

- The Mine Health and Safety Act (Act 29 of 1996) provides protection for the health and safety of employees or any other individuals on mining sites. The Act assigns a responsibility to the mine manager to identify and mitigate health and safety hazards. The mitigation must be done by (1) eliminating the risk, (2) controlling the risk at the source or (3) minimising the risk. In the case where the risk remains, a programme must be set in place to monitor the risk at all times (Hattingh & Van Deventer, 2004; South Africa, 1996).

1.3 Project motivation and significance

The fixation or retention of soluble phosphorus (P), when applied to tailings (pH 2.7) in the form of superphosphate (8.3), was proven through a pilot study conducted at the beginning of 2016. For this pilot study, the tailings material (New Machavie tailings – NMC2) was simultaneously treated with dolomitic lime and fertiliser. The changes in pH(H_2O) and plant-available phosphorus levels (with the use of the P Bray-1 analyses) were monitored over a period of ten days. Data for this pilot study can be seen in Appendix E.

The results obtained from the study are illustrated in Figure 1 where it is shown that the pH(H_2O) of the material has increased from 2.7 to 4.1 over the ten-day period. The total amount of available phosphorus in the tailings increased drastically from 9.2 mg/kg to 15.7 mg/kg one day after the treatments but decreased again to 10.5 mg/kg ten days after the treatments.

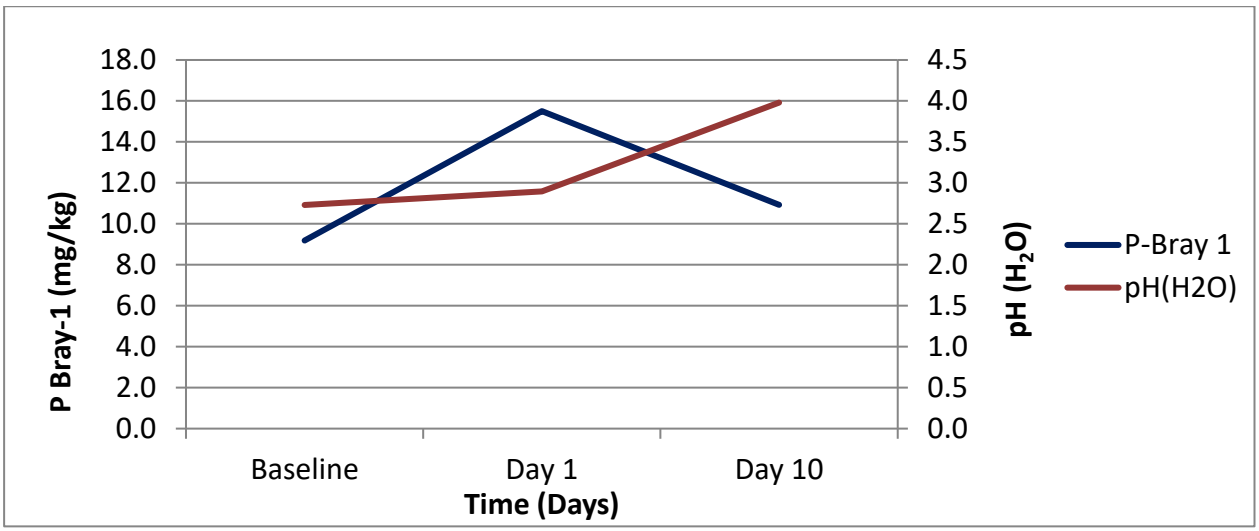


Figure 1: The change in pH(H_2O) versus the change in P availability over a period of ten days after being treated with lime and fertiliser simultaneously.

Therefore, approximately 70% of the fertiliser applied, was rendered permanently unavailable for plant use after ten days as a consequence of P fixation. With a less than 50% success rate when applying lime and fertiliser at the same time, a change in this practice must be considered. In light of the results presented in Figure 1, the research focused on improving P availability in acidic tailings by allowing a neutralisation incubation period between lime and fertiliser treatments. The incubation period allows a longer period of time for the lime to react and raise the pH of the material to a level where less phosphorus would be lost to fixation as a result of an extremely acidic environment.

The research shows excellent commercial value since South Africa's rehabilitation industry spends millions of Rands on lime and fertiliser annually, with low efficiency, as proven by the pilot study discussed above. The mine rehabilitation industry could save significant expenditure by considering the time lag of the neutralisation of acidic mine tailings. By allowing the neutralisation reaction to take its course to raise the pH of the acidic tailings material to a more desired level before fertiliser applications, more of the nutrients would be available for plant use. Consequently, less fertiliser would be needed in future for re-applications.

1.4 Hypothesis

The literature states that phosphorus (P), an essential plant nutrient, is optimally available for plant use at pH levels between 5.5 and 7.5 (Desta, 2015; Johnston & Steën, 2000). At pH levels lower than four, which is the case for most acidic tailings materials, P is almost entirely unavailable for plant uptake. This is due to rapid transformation processes such as the precipitation and adsorption of P with aluminium and iron oxides (Beegle, 2001; Poozesh *et al*., 2010; Van der Nest, 1991; Van Deventer & Hattingh, 2008)

The acidity of sulphide-bearing tailings is much more severe than with naturally acidic soils (Thomas & Hargrove, 1984; Van Deventer, 2015); therefore, a larger amount of lime, accompanied by a longer period for neutralisation to take place, is essential before applying fertiliser to the growth medium (tailings).

The main hypothesis of the research was that plant-available P measurements in highly limed acidic tailings will vary when a neutralisation incubation period of six weeks is implemented before fertiliser applications, compared to the common practice where lime and fertiliser are applied at the same time, with no neutralisation incubation time between the applications.

Due to the research project consisting of more than one aim and research question, several sub-hypotheses were formulated as listed below:

1. If the acidic growth mediums deal with a great variation in pH values, owing to different pools of acidity and ongoing acidification reactions that take place within the tailings (Hattingh, 2005; Van Deventer & Hattingh, 2008), it is hypothesised that the time lag in neutralisation of different acidic tailings will vary.

2. Different pools of acidity (Brady & Weil, 2008; Van Deventer, 2015) and ongoing acidification (Hattingh, 2005; Van Deventer & Hattingh, 2008) as a result of constant oxidation reactions may affect the interpretation of pH values. It is therefore hypothesised that different procedures of measuring pH could produce different values.

3. It is hypothesised that real-time germination of seedlings and growth performances will vary between a scenario where a neutralisation time lag is implemented before fertiliser applications and a scenario where no neutralisation time lag is implemented due to a difference in P availability (Brady & Weil, 2008; Desta, 2015; Johnston & Steën, 2000).

1.5 Aim and objectives

The main aim of the study was to determine the ideal period before fertiliser applications to ensure increased plant-available P levels.

Detailed neutralisation and P availability pot trials were conducted on four different tailings (three gold and one coal tailings) as well as a naturally acidic soil that served as the control medium throughout the study to achieve the following objectives:

- Evaluate the change in pH of the growth mediums that have been treated with dolomitic lime. The data will be used to identify a neutralisation incubation time for improved P

availability that can be used over a wide range of sulphide-rich acidic tailings materials (Phase 1).

- Compare three different procedures of measuring pH on the different growth mediums (acidic tailings and a naturally acidic soil), namely a leaching procedure, a conventional procedure and an incubation procedure (shaking the soil solution for 24 hours at 120 rpm).
- Determine if P availability is improved after allowing a neutralisation incubation period before fertiliser applications, compared to a scenario where lime and fertiliser are applied simultaneously (Phase 2).
- Evaluate the effect of high lime applications on the reliability of the Bray-1 method in determining plant-available P in acidic growth mediums.
- Determine if the seedling survival rate and growth performance are improved when fertiliser is applied after a neutralisation incubation period (Phase 3).

1.6 Research questions

Three research questions were formulated according to the hypotheses and the aims and objectives listed above. These research questions will be answered in the concluding chapter of this document (Chapter 5):

Research question 1:

What is the most suitable time lag for the neutralisation of acidic mine tailings to improve the plant availability of P?

Research question 2:

What is the most suitable procedure to measure pH in highly limed tailings over time for these specific neutralisation time lag reactions?

Research question 3:

What is the influence of a neutralisation time lag on the plant availability of P, germination and growth performance of vegetation in acidic mine tailings?

1.6.1 Scope of work

The research project commenced in 2016 when two pilot studies were conducted (1) to investigate the significance of the research and (2) to identify the growth media that would be used in the more detailed pot trials. The significance of the research, as previously discussed, was examined by treating an acidic tailings material (pH 2.7) with lime and fertiliser simultaneously

to determine the amount of P lost through fixation or retention transformations as a result of the material still being too acidic.

Thirteen different tailings material, including a control medium, were collected and used in a seven-week neutralisation incubation trial study where the pH(H_2O) of the material was monitored weekly. The goal of this trial study was to identify four tailings material that would be used in more detailed fertiliser pot trials. Tailings with varying lime requirements, geologic occurrence and results for the neutralisation incubation pot trial were identified. Three different gold tailings (Crown, NM700 and NMC1) and one coal tailings were identified to be used in the fertiliser pot trial.

A fertiliser pot trial, which commenced in March of 2017, was conducted on the growth mediums identified during the neutralisation pot trial along with a sandy, acidic soil that served as the control medium throughout the study. The study was divided into two groups, namely Group A and Group B. Group A was treated with lime and fertiliser all at once, whereas Group B was initially treated with lime only. The fertiliser for Group B was applied after a neutralisation incubation period of six weeks.

A supplementary pot trial, identical to the trial that had commenced in March of 2017, was conducted to determine the effect of high concentrations of calcium (Ca) as a result of high lime applications on the suitability of the P Bray-1 method. This pot trial was also used to compare different procedures of measuring pH on the growth mediums. The procedures that were used included a leaching procedure, the conventional procedure and a procedure where the soil solution is shaken for 24 hours at 120 rpm.

An additional experiment was conducted on the two groups where seedling survival rates were compared between the two scenarios.

All the pot trials were conducted in Potchefstroom at the nursery for Research on Soil Science and Mine Rehabilitation on the property of the North-West University.

1.6.2 Delineations and limitations

Pot trials were conducted throughout the study as opposed to field studies in order to obtain analogous environmental conditions for all the growth media throughout the study as the material had originated from different locations. Nevertheless, the pot trials provided valuable insights into the importance and dynamics of a neutralisation incubation period between lime and fertiliser ameliorants.

Funding was a severe limitation throughout the study and a factor that also contributed to the use of pot trials rather than field studies. Limited funds also resulted in phosphorus being the only plant nutrient studied and P analyses only being conducted three times for every scenario and not weekly as desired.

It is important to take into consideration that geochemical oxidation and weathering within tailings are ongoing processes and that the pH and other chemical parameters of a TSF is ever-changing, even after several ameliorations. It is an unnatural ecosystem caused by anthropogenic activities that would need human interference for many years to obtain a sustainable vegetation cover. Therefore, it must never be expected to behave the same as a natural ecosystem with natural soils, fauna, flora and microbial communities.

1.7 Chapter overview

The aim of Chapter 1 is to inform the reader on the importance of this research project, to list the aims and objectives and to provide the hypotheses of the study. This chapter also contains the scope of work, as well as the delineations and limitations experienced throughout the research period.

Chapter 2 serves the goal of providing a theoretical background on the topics that this research project relates to (e.g. pH, pyrite oxidation, neutralisation of acidic growth mediums, the chemistry of phosphorus in growth mediums, etc.).

All of the methodologies followed during the pot trials as well as the materials used throughout the project, are described in Chapter 3.

The results obtained from the various pot trials conducted throughout the research period are discussed and compared to other literature or previous studies in Chapter 4.

Conclusions are made in Chapter 5, followed by recommendations for future studies in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The aim of this chapter is to provide the reader with detailed background knowledge on all major factors regarding this research study. It is constructed to begin with the most basic information, namely defining tailings, describing their physical and chemical properties and explaining how this material can serve as a growth medium for plants. It also comprises in-depth discussions on growth medium pH, soil acidity and the pools of acidity in soils and tailings materials. These subjects are followed by detailed descriptions of pyrite oxidation, neutralisation of acidic growth mediums and the reaction of phosphorus (P) in soil and other growth mediums.

2.2 Tailings

Vast quantities of rock are displaced, crushed and processed during the mining and recovery of minerals. At the end of the process, the greater part of the fine material (tailings), along with process waste, are transported to a mining disposal area (Ritcey, 2015), most commonly known as “tailings storage facilities” (TSFs). Tailings can be defined as “mixtures of crushed rock and processing fluids from mills, washing plants or concentrators that remain after the extraction of economic metals, minerals, mineral fuels or coal from the mine resource” (Kossoff *et al*., 2014).

TSFs, also known as “tailings dams”, are, unlike water retention dams, composed of mine waste that is simply stacked or dumped mechanically by means of hydraulic disposal equipment in stages in correlation to the generation of mine waste (Schoenberger, 2016; Van Deventer *et al*., 2009). The construction of these long, steeply sloped TSFs entails the hydraulic deposition of fine tailings together with waste water or processing fluids in the form of slurry, which has an average wet density of 1.2 $g.cm^{-3}$ (Van Deventer *et al*., 2009), where it dries out over time (Haagner, 2008).

2.2.1 Physical and chemical properties of tailings

Individual particles of tailings typically have an angular shape. The grain size and, consequently, the textural classification of different types of tailings may vary largely as it is essentially influenced by the mining method, the geology of the ore and the metallurgical practices during the metal recovery process. Despite this, most tailings are free of gravel (<2 mm) and clay particles (<0.002 mm) (Kossoff *et al*., 2014).

The chemical properties of tailings depend largely on the mineralogy of the ore body and the host rock (Kossoff *et al*., 2014; Van Deventer & Hattingh, 2008). For example, the host rocks in the Bushveld Igneous Complex are pyroxenite, norite and anorthosite. These rocks mainly comprise amphibole, plagioclase and olivine, which are all very alkaline (pH 10-11) when milled during ore-processing processes. Their alkalinity is owed to hydrolysis (Eq. 1) and oxidation (Eq. 2) of the minerals during weathering (Van Deventer & Hattingh, 2008):

$$Ca_2Al_2Si_2O_8 + 9HO \rightarrow Ca(OH)_2 + Al_2Si_2O_5(OH)_4 \quad \text{(Eq. 1)}$$

$$4CaFeSi_2O_6 + O_2 + 4H_2CO_3 + 6H_2O \rightarrow 4FeOOH + 8H_2SiO_3 + 4CaCO_3 \quad \text{(Eq. 2)}$$

In Equation 1, it is evident that through the hydrolysis of $Ca_2Al_2Si_2O_8$ (plagioclase), a base and $Al_2Si_2O_5(OH)_4$ (clay mineral) are formed. The cations released during hydrolysis are mainly Ca^{2+}, Mg^{2+}, K^+ and Na^+, which are all vital plant nutrients. During the oxidation of $CaFeSi_2O_6$ (amphibole) (Eq. 2), $CaCO_3$ (lime), FeOOH and H_2SiO_3 are formed. This proves that these tailings do not acidify as a result of weathering. In the ideal climate zone where decomposition is dominant as a weathering process (Weinert N-value <5), these tailings may weather to a clayey texture after long enough time has passed (Van Deventer & Hattingh, 2008).

Tailings originating from the Witwatersrand Supergroup differ greatly from those originating from the Bushveld Igneous Complex. The gold-bearing ore from the Witwatersrand Supergroup is comprised of 70% to 90% SiO_2 (quartz), accompanied by small amounts of FeS_2 (pyrite) and other minerals such as K, Na and Ca feldspars, sericite, chlorite, calcite and dolomite. Other minerals may also be present, depending on the mineralogy of the original ore body (Bezuidenhout & Rousseau, 2006; Kossoff *et al*., 2014; Van Deventer & Hattingh, 2008).

The key minerals present in tailings that originate from the Witwatersrand Supergroup are quartz, mica and chlorite, accompanied by pyrophyllite and traces of potassium(K)-feldspar. Pyrite and jarosite exist in small concentrations that range from 2 wt % to <0.5 wt % in these tailings (Hansen, 2015; Yibas *et al*., 2010). Yibas *et al*. (2010) also found that the concentration of pyrite increased with depth. Because jarosite is a secondary mineral that forms after the oxidation of pyrite, the concentration of this mineral also increases with depth to the point where the environment is still favourable for oxidation to take place.

Fresh, unoxidised tailings are alkaline (pH 8-9) when first deposited onto a TSF; however, the tailings acidify to a great extent as soon as it comes into contact with moisture and oxygen due to the oxidation of FeS_2 (pyrite), according to Equation 3 (Van der Nest, 1991; Van Deventer & Hattingh, 2008) below. A more detailed discussion of pyrite oxidation can be found in Section 2.5.

$4FeS_2 + 15O_2 + 10H_2O \rightarrow 4FeOOH + 8H_2SO_4$ (Eq. 3)

From Equation 3 it is evident that secondary oxidised minerals, such as goethite, form as a result of pyrite oxidation. Other minerals may also form, depending on the mineralogy of the ore body, pH, climate and redox state. Examples of these minerals are $CaSO_4 \cdot SO_4$ (gypsum), $PbSO_4$ (anglesite), $Al_2Si_2O_5(OH)_4$ (kaolinite) and $KFe_3(SO_4)_2(OH)_6$ (jarosite) (Kossoff *et al*., 2014).

Pyrite is also present in significant quantities in coal tailings. Other minerals, such as chalcopyrite, sphalerite, galena and pyrrhotite, are also present in measurable quantities (Kossoff *et al*., 2014).

2.2.2 Tailings as a growth medium for vegetation establishment

The attainment of a self-sustaining plant community that is dynamic and has the ability to change and adapt as the rehabilitated site ages and matures, is the main objective with regard to the establishment of vegetation on TSFs (Van Deventer & Hattingh, 2008). For tailings material to serve as a growth medium for vegetation, one must understand the functions a growth medium has to fulfil to sustain plant growth.

Hattingh and Van Deventer (2001) define the function of a soil with respect to crop production. Nonetheless, this definition can be used for any substrate that serves as a medium for plant growth. Hattingh and Van Deventer (2001) state that the function of a growth medium is directly related to its effectiveness in providing essential plant nutrients, a growth substrate and an environment that supports photosynthesis. The function of a growth medium can be subdivided into several components, as presented in Table 1.

Table 1: The main functional components of a growth medium to support plant growth (Hattingh & Van Deventer, 2001).

Functional component	Description of the functional characteristics or processes
Medium for plant growth	Suitable medium for seed germination, root development and root growth. Absence of adverse chemical conditions within the growth medium (e.g. acidity, salinity, sodicity, etc.). The ability to supply balanced quantities of essential plant nutrients. Suitable medium for the survival of microbial communities that are vital for processes such as nutrient cycling and decomposition. The ability to promote root growth and development.
Water regulation	The ability to receive, store and release moisture for plant use. The ability to sufficiently retain water to buffer and reduce the effects of drought. The ability to have properties that allow for sufficient water infiltration and water storage to reduce runoff.
Gas regulation	The ability to accept, hold and release gasses. The ability to support and allow adequate air movement within the growth medium and air exchange with the atmosphere.
Energy regulation	The capacity to recycle energy-rich organic matter.
Buffer or filter	The capacity to sufficiently accept, hold and release plant nutrients. The ability to sequester energy compounds and/or bio-toxic elements. The ability to detoxify substances harmful to plants.

Establishing a vegetation cover on a TSF, also known as phytostabilisation, will improve the surface stability of the facility and, through this, prevent wind and water erosion – the main objective in the rehabilitation of TSFs (Van Deventer *et al*., 2007). Therefore, the deposition of wind- and water-transported tailings material or silt onto adjacent land is minimalised by the establishment of vegetation on the bare areas of the facility (Hattingh, 2005). Van Deventer (2008) summarises the functionality and benefits of vegetation covers on TSFs as follows:

- A vegetation cover reduces and, in some cases, totally suppresses dust pollution.
- It reduces the degree of water runoff from steep slopes.
- It improves the stability of soil aggregates.

- In areas of excessive water-ponding (e.g. toe paddocks and solution trenches), plant species, for example, reeds (phragmites) and certain grass species, may be planted since they utilise a large amount of water to survive.
- Plant species with deep root systems have the ability to cycle nutrients from inside the growth medium (tailings) to the surface (by way of leaves that fall to the surface). Through this, younger plants with shallower root systems have a nutrient-enriched growth medium.
- Some plant species have the ability to absorb harmful or toxic elements (e.g. U, Pd, Cd, etc.) from the growth medium. The plants store these elements in their wood cells with no risk to the environment.
- Certain fast-growing woody plant species (e.g. eucalyptus trees) can be utilised as building material or firewood.
- As soon as a vegetation cover is established on a TSF, an ecological cycle starts to form where the vegetation can support bird and insect species and sometimes even small animals.
- The presence of a vegetation cover aids in the survival of several microbial communities. These microbial communities are essential as they increase aggregate formation and the concentration of a number of organic substances and enzymes by means of digestive processes.
- A vegetation cover, especially bigger and higher plant species (e.g. eucalyptus trees) can act as windbreaks during windy weather conditions.
- Last, but certainly not the least, a vegetation cover improves the aesthetic value of a TSF.

It is clear that the establishment of vegetation on TSFs has numerous benefits towards the facility itself and the surrounding land. For tailings material to serve as a medium for plant growth, it must have the ability to physically and chemically function as a medium for plant growth. Hossner and Hons (1992) state that the site or area must be evaluated thoroughly to identify any adverse characteristics of the tailings material to serve as a growth medium before the TSF is prepared for the establishment of vegetation.

One should always bear in mind that natural soils and tailings material differ significantly and one should, therefore, never expect tailings to behave identically to soil as a medium for plant growth. As stated by Haagner (2008), tailings material is very “alien a growth medium”, emphasising the fact that soil and tailings material as growth mediums should be treated differently. There are several potential limitations to vegetation establishment on tailings material, which include severe acidity, high salinity and high concentrations of heavy metals as well as high concentrations of Al and Fe (Akcil & Koldas, 2006; Hossner & Hons, 1992; Lee & Kim, 2008).

Improving the physiochemical conditions of the tailings material to serve as a growth medium for plants is the first and most important stage in the revegetation of TSFs. Comprehensive background research, coupled with chemical, physical and biological assays of the growth medium, will determine the method of amelioration as well as the composition of the plant species introduced into the area. The results from these studies are then used to develop a plan to improve the extreme physiochemical conditions of tailings and reduce the differences between tailings and natural soils as growth mediums (Khozhina & Sherriff, 2006; Ssenku *et al*., 2014). The process of selecting the appropriate plant species that will be established on the TSF is also of great importance and based on years of experimental research. The criteria based on which the selection of plant species used for vegetation establishment is done, are as follows, as described by Hossner and Hons (1992):

- physical and chemical properties of the tailings material
- climatic characteristics and geographic location of the TSF
- elevation
- seeding season
- compatibility with other plant species
- topographic exposure (e.g. slope angle and slope length)
- land use objectives

According to Madejon *et al*. (as cited in Mingorance *et al*., 2016), plant species used for vegetation establishment on TSFs are identified through careful consideration of their ability to survive, reproduce and restore or "regenerate" under the occasionally hostile physiochemical conditions in tailings material. Caravaca *et al*. and Mendez and Maier (as cited in Mingorance *et al*., 2016) list the following characteristics that make these species ideal for this purpose:

- easy to establish
- fast-growing
- drought-resistant
- able to grow in nutrient deficient growth mediums
- tolerant to acidity
- have dense canopies and root systems

For vegetation establishment on TSFs, grass species are considered a "nurse crop". In addition to rapid growth, grasses help decrease and control erosion with their fibrous root systems, stabilise the slopes of the TSFs, decrease moisture loss from the growth medium due to evaporation and aid in soil formation or "paedogenesis" through the production of organic matter (Conesa *et al*.; Hao *et al*.; Wang *et al*.; Yuanyuan *et al*.) (as cited in Mingorance *et al*., 2016).

In summary, the process of establishing a vegetation cover on an acidic TSF entails the following, as described by Kozhina and Sherriff (2006):

- A neutralising substance (e.g. dolomitic lime) is worked into the material to improve pH conditions.
- Inorganic fertilisers and/or organic materials (e.g. topsoil or organic waste material) are worked into the tailings to improve the nutrient status, organic carbon content, texture, cation exchange capacity (CEC) and water-holding capacity of the material.
- Finally, seed mixtures, developed through years of experimental research, are introduced to the growth medium.

The establishment of vegetation covers on TSFs is a complex and multidisciplinary field. There are many physical, chemical and biological factors of the TSF itself, as well as the material it consists of, that play crucial roles in determining the method of rehabilitation (e.g. amelioration methods and plant species composition). Some of the factors are as follows (Van Deventer, 2015):

- slope length and angle of the TSF
- erodibility of the material (this is determined by soil structure, particle size distribution, the shape of the particles, organic carbon content, permeability, physical and chemical dispersivity, swelling and the ability of the material to form dust when exposed to strong winds)
- paedogenic processes present (mineral weathering, nutrient recycling, increase in CEC and organic carbon content in the upper layers of the TSF, and horizon differentiation)
- overall quality of the tailings as a growth medium in terms of the ability of the material to function as a soil
- mineralogy of the tailings
- electrical conductivity (EC) of the material, which is directly related to its salt content
- pH(H_2O) and pH(KCl) that will influence the plant availability of nutrients and metals (e.g. aluminium) as well as the tempo of sulphide oxidation

In conclusion, proper monitoring and maintenance of a vegetated TSF is crucial for the sustainability and success of the project. This must be practised for at least five years following initial vegetation establishment (Van Deventer & Hattingh, 2004).

2.3 Growth medium pH

The pH of a growth medium, conveyed as $-\log[H^+]$, is a measure of the activity or concentration of the hydrogen (H^+) ions in the soil solution (Brady & Weil, 2008; Sparks, 2003). Renowned as the “master variable of soils” (Sparks, 2003), pH is one of the most important and commonly measured soil properties (Kalra, 1995; Winegardner, 1995). The reason for this is that most soil-

liquid interactions within a soil system are influenced by soil pH (Singer & Munns, 1992). As described by Sparks (2003), soils that have a pH of <7 are considered acidic and soils with a pH of >7 are alkaline. Soils with a pH of 7 are defined as neutral (Jones, 2012; Sparks, 2003). Table 2 describes pH values with regard to the degree of acidity or alkalinity of a soil as given by Winegardner (1995).

Table 2: Descriptions for various degrees of soil acidity and alkalinity (Winegardner, 1995).

Acid description	pH
Extremely acidic	<4.5
Very strong	4.5 – 5.5
Medium acidic	5.6 – 6.0
Slightly acidic	6.1 – 6.5
Neutral	6.6 – 7.3
Mildly alkaline	7.4 – 7.8
Medium alkaline	7.9 – 8.4
Strongly alkaline	8.5 – 9.0
Very alkaline	>9.1

As seen in Table 2, the degree of acidity for sulphide-rich tailings material mostly falls in the category of extremely acidic (pH <4.5). The production of acid mine drainage (AMD) is a direct result of the oxidation and chemical weathering of sulphide minerals present within these tailings that could cause the material to have pH values as low as 1.7 (Van Deventer, 2015). These low pH values are the result of the presence of free acids (e.g. H_2SO_4) in the tailings material (Thomas & Hargrove, 1984). Refer to Section 2.5 for a more detailed discussion on the reactions that cause the high degree of acidity in tailings.

Growth medium pH plays a substantial role in the availability of plant nutrients. Hossner and Hons (1992) and Viljoen (2013) explain that the pH of a growth medium directly influences conditions that favour the availability and phytotoxicity of plant nutrients and other elements (e.g. Fe, S, B, Cu, Mo, Zn, etc.). Very low pH conditions in a growth medium may lead to Al^{3+} toxicity (as well as toxic levels of other metal ions) and deficiencies in certain essential elements or nutrients, particularly Ca, Mg, P and Mo (Foy, 1984).

The influence of pH on the availability of plant nutrients is illustrated in Figure 2. The degrees of plant availability for plant nutrients and elements are illustrated by the width of the lines in Figure 2. Wider lines illustrate higher plant availability and vice versa.

Aluminium (Al) toxicity accompanied by suboptimal nutrient availability, especially phosphorus (P), in acidic growth mediums has a limiting effect on plant growth on South African TSFs

(Poozesh *et al*., 2010; Van Deventer, 2015). The most significant culprits of growth medium acidity in soils are hydrogen (H) and aluminium (Al). Al is very important, especially in growth mediums with extremely low pH values (<4). At these low pH values, as illustrated in Figure 2, Al and Fe can be toxic to plants because they are more soluble and therefore more plant-available in extremely acidic conditions. With an increase in pH, the solubility and plant availability of these elements will decrease (Hossner & Hons, 1992; Myburgh, 2015; Sparks, 2003).

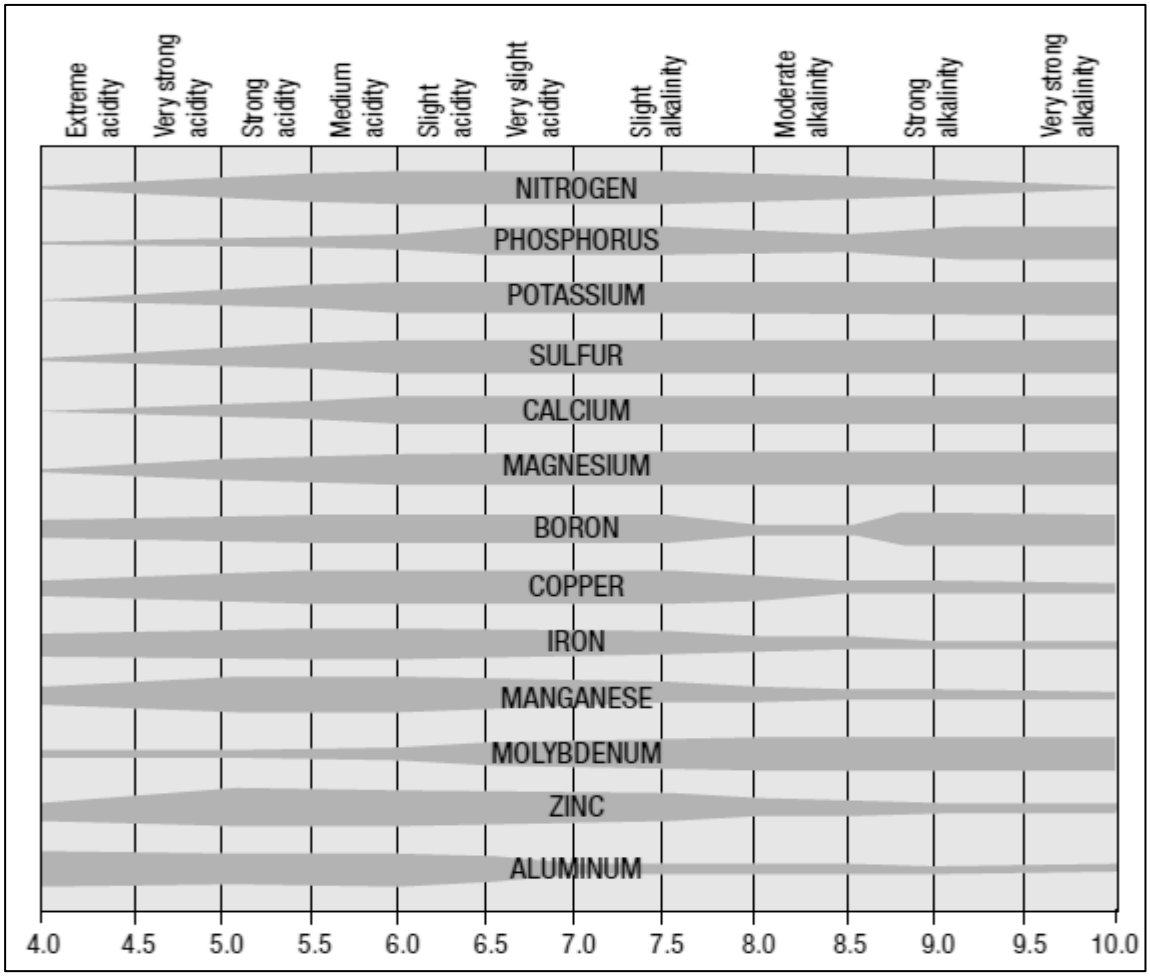


Figure 2: The influence of pH on the availability of plant nutrients and other elements (Beegle, 2001).

The focus of the research was on the availability of phosphorus (P) in acid mine tailings. As evident in Figure 2, P is optimally available for plant use at pH values of between 6.5 and 7.5. The plant availability of P starts to decrease at a pH of <6.5, and is least available at a pH of <4.0 (Beegle, 2001). To keep acidic tailings material at a pH of 6.5 or higher is merely impossible. This is due to the presence of sulphide minerals (e.g. FeS_2) within the material and the ongoing oxidation thereof. If there are unoxidised sulphide minerals present in the tailings material, re-acidification of the material will take place as soon as it comes into contact with moisture and oxygen. With sulphide-rich tailings, it is, therefore, more realistic to aim at keeping the pH of the material between 5 and 6, which is in accordance with Hazelton and Murphy (2007), who state that P availability is reduced at a pH(H_2O) of <5.0 and >8.5.

2.4 Soil acidity

Soil acidity is controlled by the composition of a soil along with ion exchange and hydrolysis reactions that take place between various soil components (Thomas & Hargrove, 1984). Nutrient availability and plant growth are directly affected by soil acidity through acidic reactions in the solution phase of the growth medium. Toxic concentrations of Al are present at pH levels <5.5, increasing as the pH of the growth medium decreases. Literature also states that along with toxic concentrations of Al^{3+}, soil acidity decreases base saturation as well as plant-available levels of P and other plant nutrients (Adams; Robinson; Schroder *et al*.) (as cited in Baquy *et al*., 2017).

Singer and Munns (1992) explain that soil acidity is mainly caused by continued periodic leaching and the addition of substances that have the ability to release H^+ ions (acids), lowering the pH of the soil or growth medium. The degree of soil acidity is very much dependent on the strength of the acids present in the soil solution, which is determined by its ability to ionise (release H^+ ions) when dissolved in water. H_2SO_4 (sulphuric acid), which forms as a result of the oxidation of FeS_2 (pyrite), is an example of a very strong acid. Carbonic acid (H_2CO_3) is an example of a weak acid as it slowly releases H^+ ions when dissolved in water (Snyder, n.d.). Figure 3 contains a simplified explanation by Singer and Munns (1992) on how the presence of acids, cation exchange and leaching leads to soil acidity.

In Figure 3, hydrogen ions (H^+) adsorb onto negatively charged exchange sites of soil particles as the concentration of acids (e.g. H_2SO_4) increase. This occurs through the exchange of H^+ with other metal cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+). Ionisation takes place in the presence of water, displacing the ions (cations and anions) of the acid. Vigorous leaching of soils or tailings with very low water-holding capacities removes anions of ionised acids together with displaced cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) that would, under normal circumstances, compete with H^+ ions for a place on the exchange sites of the soil particle. Over the course of time, the soil solution and the exchange complex of the soil become more acidic (Singer & Munns, 1992).

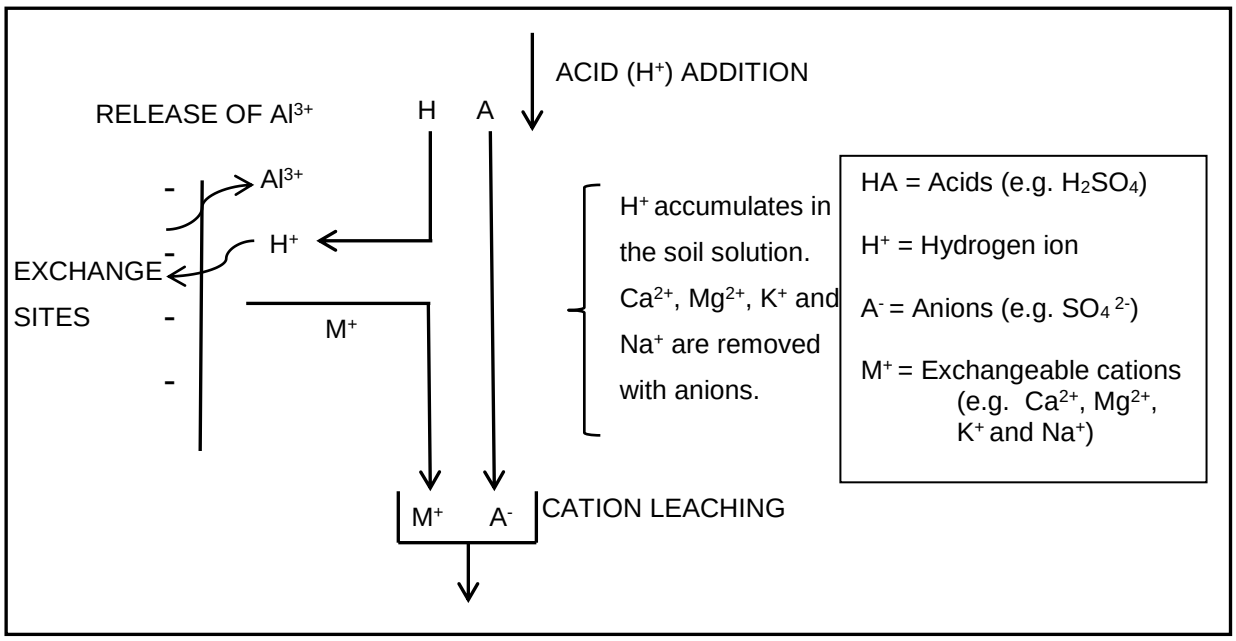


Figure 3: The role of acid addition, cation exchange and leaching in soil acidity (Singer & Munns, 1992).

The acidity in tailings material is mainly caused by the oxidation of sulphide-bearing minerals (e.g. pyrite, arsenopyrite, chalcopyrite, etc.), which may lead to pH values as low as 1.7 (Hossner & Hons, 1992; Sparks, 2003; Van Deventer, 2015). (Refer to Section 2.5 for a detailed discussion of the generation of acidity in tailings material.)

High concentrations of Al^{3+} in the soil solution are experienced in tailings and other growth mediums at pH levels <5.5 (Beegle, 2001). Dold (2014), Gunsinger *et al*. (2006) as well as Nengovhela *et al*. (2006) report that in tailings material, Al is liberated through the dissolution of aluminosilicate minerals within the oxidation zone of the TSF. As the concentration of Al^{3+} ions in solution increases, Al^{3+} ions displace H^+ ions and other exchangeable cations (e.g. Na^+, K^+, Mg^{2+} and Ca^{2+}) on the exchange complex. Aluminium toxicity occurs where more than 15 to 20% of the exchange complex of the growth medium is occupied by Al^{3+} ions. Aluminum toxicity can cause stunted plant roots, limited plant growth and impaired microbial activity (Foy, 1984).

2.5 Pools of acidity in soils and tailings material

Three major pools of acidity exist in soils and tailings material, namely *active acidity* (intensity), *exchangeable acidity*, also known as salt-replaceable acidity, and *residual acidity* (refer to Figure 4). These three types of acidities account for the *total acidity* of a soil (Brady & Weil, 2008; Winegardner, 1995). An equally important pool of acidity that also exists in sulphide-rich tailings material is *potential or latent acidity* (Brady & Weil, 2008; Van Deventer, 2015).

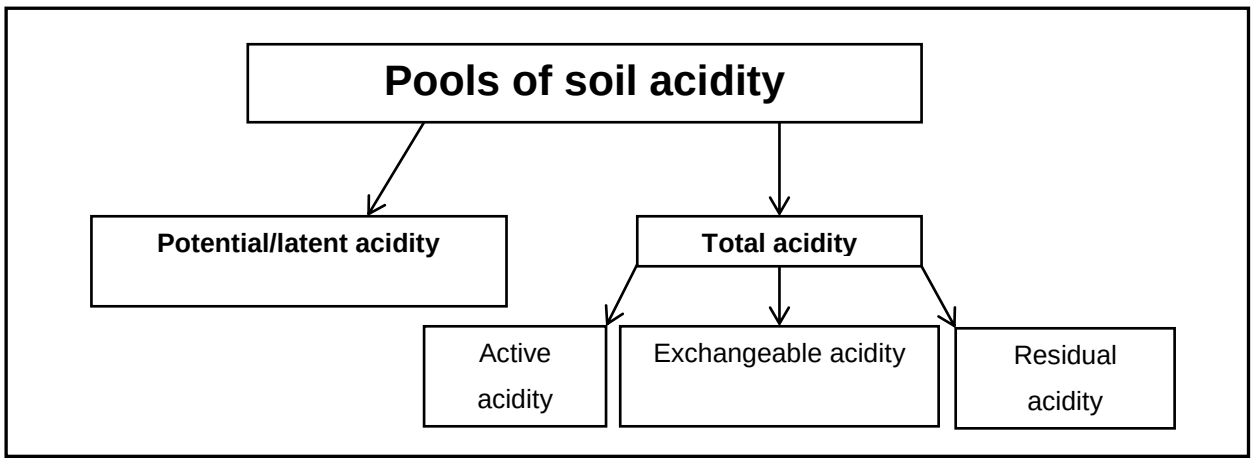


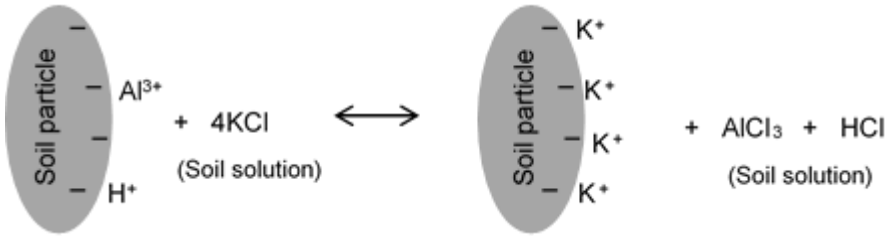
Figure 4: The pools of soil acidity (Bloem, 2015).

2.5.1 Active acidity

This pool of acidity (measured through standard pH testing) is characterised by the activity of the H^+ ions in the soil solution. The active acidity of a growth medium plays a key role in soil quality as it controls the solubility of numerous substances. This is despite the fact that it is much smaller than the exchangeable and residual pools of acidity. Active acidity can be increased through the hydrolysis of Al^{3+} ions as a result of a very acidic soil solution (Brady & Weil, 2008; Winegardner, 1995).

2.5.2 Exchangeable acidity

The fraction of the total acidity of a soil that can be detached from cation exchange sites through equilibrium reactions with unbuffered, neutral salts such as KCl, $CaCl_2$ or NaCl is known as exchangeable acidity. The exchangeable pool of acidity (measured by means of the pH(KCl) technique) presents high concentrations of exchangeable Al^{3+} and H^+ ions in the soil solution of very acidic soils (Brady & Weil, 2008; Thomas & Hargrove, 1984; Winegardner, 1995). According to Baquy *et al*. (2017), the main source of exchangeable acidity in acidic growth mediums is exchangeable Al^{3+} cations. Exchangeable acidity is presented through electro-statically bound Al^{3+} cations (also called "exchangeable Al") on colloid surfaces with pH-dependent negative charges (Abreu *et al*., 2003). Equation 4 demonstrates exchangeable acidity. Present in highly acidic soils, Al^{3+} has a high tendency to hydrolyse, splitting H_2O molecules into H^+ and OH^- ions, which increases the active acidity (Brady & Weil, 2008).



(Eq. 4)

2.5.3 Residual acidity

Also termed “non-exchangeable acidity”, this pool is associated with the amount of covalently bound H^+ cations on the individual particles or colloids as well as monomers and polymers of Al in the growth medium (Kinjo; Nachtigall & Vahl; Raij *et al.*; Raij *et al*.; Thomas & Hargrove) (as cited in Abreu *et al*., 2003).

The residual pool of acidity, which cannot be measured with the pH(KCl) or salt-replaceable technique, is related to non-exchangeable H^+ and Al^{3+} ions bound to organic matter and clay particles. With an increase in pH, the bound H^+ ions dissociate and the bound Al^{3+} ions are released into the soil solution and precipitate as amorphous $Al(OH)_3$. Residual acidity can be neutralised by incorporating alkaline materials into the soil, for example, $Ca,Mg(CO_3)_2$ (dolomitic limestone) (Brady & Weil, 2008).

2.5.4 Potential or latent acidity

This pool of acidity is primarily associated with tailings or soil in a semi-stabilised geochemical equilibrium where the material still contains pyrite (FeS_2) or jarosite in a reduced state or unoxidised state (Fe^{2+}). For example, when exposed to oxygen and moisture, pyrite oxidises (Fe^{3+}), releasing sulphuric acid (H_2SO_4) into the soil solution (Van Deventer, 2015). This pool of acidity also includes future oxidation and hydrolysis of minerals such as jarosite and schwertmannite that are formed as a result of the oxidation of $Fe(SO_4)$, as discussed in Section 2.6.

2.6 The oxidation of pyrite (FeS_2)

The high degree of acidity found in sulphide-rich mine tailings is the result of the chemical weathering and oxidation of pyrite (FeS_2) – a sulphide mineral (Van der Nest, 1991). As explained by Bell *et al*. (2001), the oxidation reaction produces sulphuric acid (H_2SO_4) in conjunction with ferrous and ferric sulphates, as well as ferric hydroxide. This brings about acidification of the material, altering the availability of plant nutrients and toxic elements (Al, Mn and heavy metals) (Envirogreen, 2004).

Pyrite is the most dominant sulphide mineral found within the mining residues or tailings material of South African gold and coal mines. Pyrite oxidation is associated with the formation acid mine drainage (AMD) along with the dissolution and precipitation of minerals and metals (Dold, 2014; Jackson & Parbhakar-Fox, 2016). The formation of AMD can only take place when acid is generated at a more rapid rate than it can be neutralised by any alkaline material present in the tailings (Nengovhela *et al*., 2006). Low pH values, ranging from 2 to 4, high electrical conductivity

(EC), high concentrations of heavy metals and high concentrations of Al, Fe and Mn are characteristic of AMD discharges (Akcil & Koldas, 2006; Lee & Kim, 2008).

Three primary components are essential for the oxidation of pyrite to take place, namely the sulphide mineral itself (pyrite), oxygen and moisture (Bejan & Bruce, 2015; Durand, 2012). The primary factors that regulate the rate of acid generation from sulphide oxidation (Akcil & Koldas, 2006; Nengovhela *et al*., 2006; Ritcey, 2005) are as follows:

- pH
- Temperature
- Oxygen content of the water phase
- Oxygen content of the gas phase, if less than 100% saturated
- Degree of water saturation
- Surface area of the exposed metal sulphides
- Chemical activity of Fe^{3+}
- Bacterial activity
- Chemical activation energy required to initiate the acid-generating reaction
- The degree of neutralisation through carbonate-rich minerals

Pyrite oxidation is a complex process that involves biochemical as well as geochemical mechanisms, hydrolysis and the formation of complex ions (Van der Nest, 1991; Van Deventer, Hattingh & Bloem, 2007). In order to properly understand the oxidation of pyrite and the formation of AMD, one must understand these chemical interactions as well as the sequences in which the reactions take place (Dold, 2014).

Equation 5 represents the nett reaction for the oxidation of pyrite. In this reaction, pyrite reacts with water and oxygen. The result is an insoluble iron hydroxide (ferric hydroxide), an amorphous iron hydroxide that forms when Fe^{3+} ions precipitate, and sulphuric acid (Van der Nest, 1991).

$$FeS_2\ (s) + 15/4O_2\ (aq) + 7/2H_2O\ (l) \rightarrow Fe(OH)_3\ (s) + 2H_2SO_4\ (aq) \qquad \text{(Eq. 5)}$$

The oxidation of pyrite takes place in a series of chemical reactions, where Equation 5 illustrates only the oxidation and hydrolysis of FeS_2. For every mole of pyrite present in the material, iron (Fe) loses 1 electron, sulphur (S) loses 14 electrons and oxygen gains 7.5 electrons. Also, one mole of iron is hydrolysed and precipitated for every mole of FeS_2 present in the material (Van der Nest, 1991). Through this, it is obvious that pyrite oxidation does not take place in a single chemical reaction. For every kilogram of FeS_2 present in the TSF, 1.63 kg of H_2SO_4 will be produced as a result of oxidation, based on the relative molecular weights shown in Equation 5, not taking into account any buffering or neutralisation actions (Ritcey, 2005).

Studies done by numerous scientists have gained valuable information on the chemical reactions that take place during the oxidation of FeS_2. The oxidation of pyrite, and consequently the formation of AMD, can be described by the following reactions (Ackil & Koldas, 2006; Ochieng *et al*., 2009; Van der Nest, 1991; Ritcey, 2005):

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \text{(Eq. 6)}$$

Equation 6, a rapidly occurring reaction which takes place at pH ≥ 4.5, illustrates the oxidation of FeS_2 in the presence of oxygen and water to dissolved iron, sulphate and hydrogen. An increase in the amount of total dissolved solids and acidity of the medium is the result of the increased dissolved Fe^{2+}, SO_4^{2-} and H^+ in the soil solution. The abovementioned equation is directly influenced by temperature, oxygen concentration, pH of the solution in contact with the pyrite particles, and the degree to which the material is saturated with water. A large amount of the Fe^{2+} (ferrous iron) produced in Equation 6 is then further oxidised to Fe^{3+} (ferric iron), according to the following reaction:

$$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad \text{(Eq. 7)}$$

The reaction illustrated in Equation 7 is catalysed by iron-oxidising bacteria, more specifically *Thiobacillus ferrooxidans*, which occur typically within the pH range of ≥ 2.5 and ≤ 4.5. It has been proven that *T. ferrooxidans* thrive at pH values below 4 (Nicholson *et al*., 1988). According to Bezuidenhout and Rousseau (2006), *T. ferrooxidans* do not play a significant role in sulphide oxidation under O_2 concentrations lower than 8%.

Fe^{3+} then precipitates as an insoluble $Fe(OH)_3$ (ferric hydroxide), known as “yellow boy”, at pH values between 2.3 and 3.5, leaving some Fe^{3+} ions behind in solution accompanied by a decrease in pH, according to Equation 8:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad \text{(Eq. 8)}$$

The remaining Fe^{3+} in solution that did not precipitate, as illustrated by Equation 8, may oxidise additional pyrite. The oxidation of FeS_2 by Fe^{3+} takes place more rapidly than by oxygen at pH values of <3.0. The solubility of Fe^{3+} increases at pH values <4.5 and starts to act as an oxidant. Fe^{3+} becomes the most important oxidant at pH values of <3.0. Fe^{3+} oxidises pyrite according to the reaction illustrated in Equation 9.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \text{(Eq. 9)}$$

Acid-producing reactions that form iron (Fe^{3+}), which ultimately precipitates as $Fe(OH)_3$, can be illustrated in Equation 10 (a combination of Eqs. 6-9):

$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$ (Eq. 10)

The oxidation of additional FeS_2 by stable Fe^{3+} can be represented by the following nett reaction (Eq. 11):

$FeS_2 + 15/8O_2 + 13/2Fe^{3+} + 14/7H_2O \rightarrow 15/2Fe^{2+} + 2SO_4^{2-} + 17/2H^+$ (Eq. 11)

The movement of air (oxygen) and water are the two main processes affecting pyrite oxidation and the movement of AMD. The chemical composition of the pore water of the tailings is influenced by several geochemical processes along the flow path. For example, the rate of pyrite oxidation is restricted by the transport of air through the material. In turn, this has a direct influence on the rate at which AMD processes take place within the TSF and, hence, influences the chemical composition of the pore water (Bezuidenhout & Rousseau, 2006; James, 1997).

The movement of water through the pores of the tailings (pore water) determines the moisture content of the tailings material at any point in time and space. This movement of pore water is determined by various factors, including deposit type, climate, material properties as well as the water management plan. The moisture content of the tailings material determines the fraction of air-filled pore space available for air movement and, henceforth, the rate at which the oxidation reactions take place (Bezuidenhout & Rousseau, 2006).

As explained by Yibas *et al*. (2010), there are three mechanisms responsible for O_2 transportation in a TSF: (1) transport with water (H_2O) containing oxygen; (2) air convection through the upper layer of the TSF; and (3) transportation of oxygen through the pore spaces within the tailings (in the gaseous and aqueous phases) by way of diffusion. The last mechanism, diffusion, is the dominant mechanism or process that governs the movement or transportation of O_2 through tailings material (James, 1997; Yibas *et al*., 2010). The concentration gradient between the tailings surface and the matrix, caused by pyrite oxidation, drives the diffusion process. Attributable to oxygen (O_2) transport limitations caused by diffusion, the concentration of O_2 becomes progressively lower with an increase in depth. For this reason, pyrite oxidation usually takes place just a few metres below the surface of the TSF (Bezuidenhout & Rousseau, 2006).

2.6.1 Environmental impacts of acid mine drainage (AMD) in South Africa

"AMD is the number one environmental problem facing the mining industry" (Usher *et al*., 2003:32) – this is the one concern agreed upon between the industry, labour, government and environmentalists. As previously discussed, AMD is formed when sulphide minerals in tailings are oxidised once exposed to oxygen and moisture (Akcil & Koldas, 2006; Nengovhela *et al*., 2006). Usher *et al*. (2003) summarise the complexity and seriousness of AMD in the following four points: AMD devastates aquatic biota, is practically impossible to reverse with the use of

existing methods, costs millions to treat and can continue for hundreds of years, and is very complex to treat and control.

Figure 5: A photograph of AMD seepage at a gold TSF in South Africa. Photograph taken by Daniell (2016), with permission.

Figure 5 is a photograph of an eighty-year-old Black Reef gold TSF (Van Deventer, 2017) in the North-West Province, South Africa. These tailings contain high concentrations of pyrite and has a pH of approximately 3.0. Here, AMD seepage can migrate into soils of surrounding farms, underground water bodies and the Wonderfontein Spruit. Over and above the high degree of acidity in AMD discharges, sulphates, toxic concentrations of trace elements (e.g. Al, Cr, Co, Cu, Fe, Mn, Ni and Zn) and radionuclides are present in streams, rivers and other areas impacted by AMD (Akcil & Koldas, 2006; Aucamp, 2000; Hansen, 2015; Rösner & Van Schalkwyk, 2000). These toxic trace elements, which are sometimes referred to as “heavy metals”, find their way into the environment through the acidic conditions created as a result of the oxidation of sulphide minerals (e.g. FeS_2). The high degree of acidity remobilises toxic trace elements where they migrate into surrounding soils, groundwater sources, rivers and other surface water bodies (Rösner & Van Schalkwyk, 2000). According to Stevenson (as cited in Usher *et al*., 2003), remobilised toxic trace elements kill biota through preventing the production of energy by way of binding with functional enzyme groups (mercaptan) and other proteins.

Van Deventer *et al*. (2008) state that there are three stages in which contamination from mining activities occur, namely sources, pathways and receptors. *Sources* are “contaminating substances with the potential to cause harm”; *pathways* are the “routes by which receptors could be exposed to, or affected by the contaminating substances”; and *receptors* are “entities that are

adversely affected by the contaminating substances" as defined by Hattingh (2003). Examples of various sources, pathways and receptors with regard to environmental impacts from AMD are listed in Figure 6.

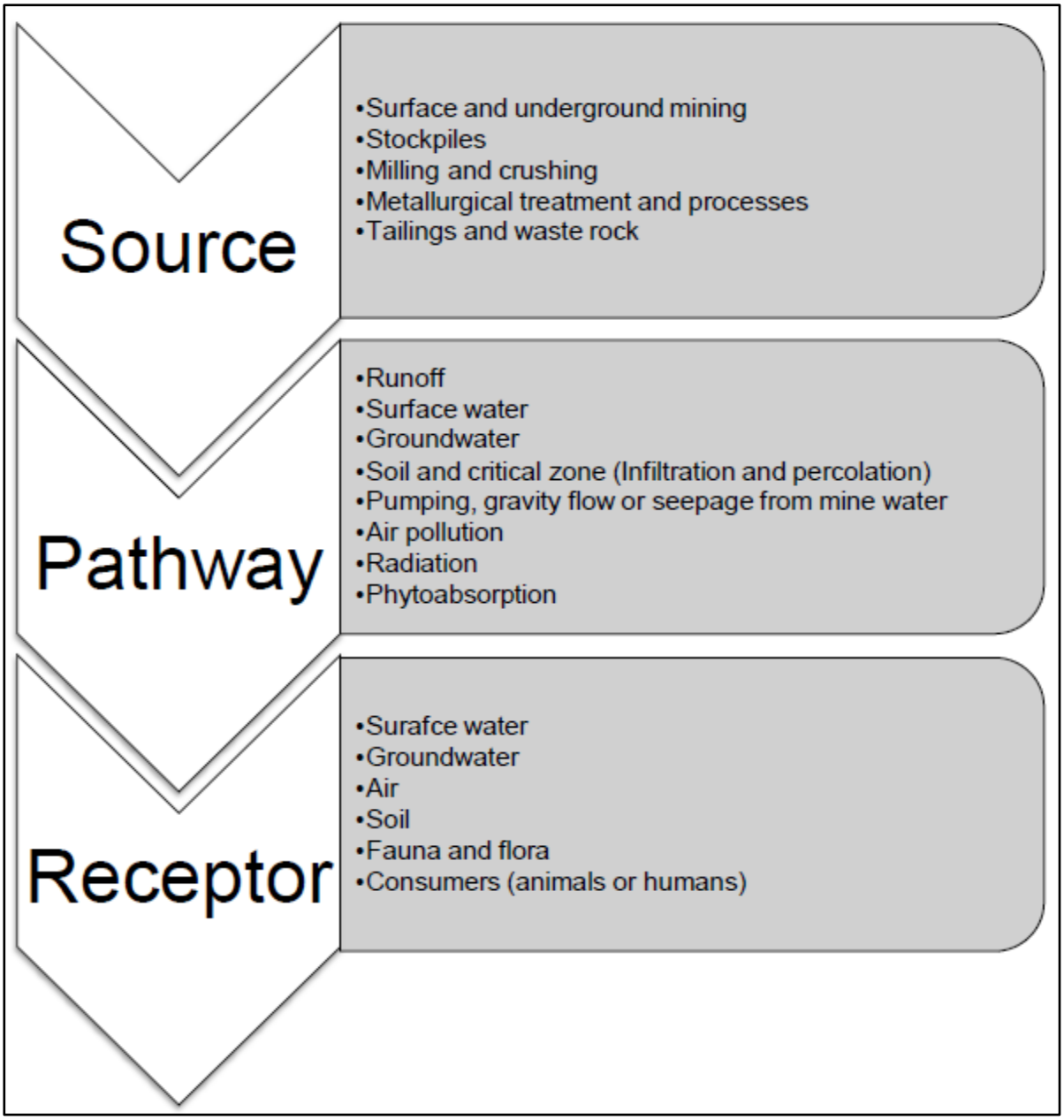


Figure 6: The three stages of environmental impacts brought on by acid mine drainage (adapted from Bezuidenhout & Rosseau, 2006; Van Deventer *et al*., 2009; Van Deventer, 2015).

2.7 Neutralisation of acidic growth mediums with lime

Acidic growth mediums are neutralised through the incorporation of alkaline materials consisting of Ca and Mg compounds that hold the ability to neutralise acidity. These alkaline materials, known as "agricultural liming materials", provide conjugate bases of weak acids. This means that the anions of the conjugate bases (e.g. CO_3^-) can react with H^+ ions to form weak acids (e.g. H_2CO_3). Examples of agricultural liming materials include hydrated lime, quicklime, marlstone,

limestone (calcitic or dolomitic), shells, and so forth, with limestone being the most commonly used liming material (Barber, 1984; Brady & Weil, 2008; Singer & Munns, 1992).

Dolomitic limestone is used when the magnesium (Mg) levels of the growth medium is low (Brady & Weil, 2008), which is the case for most gold and coal tailings materials. Other benefits of liming are an increased bioavailability of plant nutrients, adsorption and precipitation of toxic metals, improved complexation of metals by soil organic matter, and heightened biological activity (Logan, 1992). In addition to these benefits, liming may also improve root growth (due to the limiting effect of lime on Al toxicity), which leads to better exploitation of water and mineral reserves (Poozesh *et al*., 2010).

Sparks (2003) and Thomas and Hargrove (1984) describe the neutralisation of an acidic growth medium through the addition of calcitic lime according to Equation 12 and 13. When in contact with water, $CaCO_3$ (calcitic lime) dissolves and hydrolyses to form OH^- ions, illustrated in Equation 12:

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \quad \text{(Eq. 12)}$$

The OH^- ions formed in Equation 12 then react with exchangeable Al^{3+} and H^+ ions formed through hydrolysis of Al^{3+}. A nett reaction of calcitic lime with an acidic soil is given in Equation 13:

$$2\ \text{Al-soil} + 3CaCO_3 + 3H_2O \rightarrow 3\ \text{Ca-soil} + 2Al(OH)_3 + 3CO_2 \quad \text{(Eq. 13)}$$

Exchangeable Ca^{2+} (and Mg^{2+} where dolomitic lime is used) and precipitates of $Al(OH)_3$ [and $Fe(OH)_3$] are the products of a completed liming reaction in an acidic soil where Al^{3+} ions (and Fe^{3+}) are replaced by Ca^{2+} ions (and Mg^{2+}) on the exchange complex (Brady & Weil, 2008; Singer & Munns, 1992; Sparks, 2003; Thomas & Hargrove, 1984). Blowes *et al*. (1994) also state that the precipitation of $Al(OH)_3$ (gibbsite) and $Fe(OH)_3$ (ferrihydrite) is favoured as $CaCO_3$ and $CaMg(CO_3)_2$ dissolve.

All these reactions are pushed to the right as a result of the insolubility of $Al(OH)_3$, weak dissociation of H_2O and the discharge of CO_2 gas into the atmosphere. The pH of the soil solution is increased because of the lower percentage acid saturation of the exchange complex owing to the adsorption of Ca^{2+} and Mg^{2+} (Brady & Weil, 2008).

The reaction rate of lime when incorporated into an acidic soil is largely dependent on the pH of the soil, the extent of lime-soil contact surfaces as well as the size of the limestone particles. The initial pH of the soil greatly influences this reaction rate as a result of the pH-dependent solubility of liming materials (Adams, 1984). Calcitic lime ($CaCO_3$) and dolomitic lime [$CaMg(CO_3)_2$] are the most commonly used minerals for the neutralisation of tailings (Ochieng *et al*., 2009).

Ochieng *et al*. (2009) give the following neutralisation reactions (Eqs. 14-17) for calcite and dolomite in acidic and mildly acidic to alkaline conditions:

Calcite:

$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$ pH ≤ 6.2 (Eq. 14)

$2CaCO_3 + 2H^+ \rightarrow 2Ca^{2+} + 2HCO_3^-$ pH ≥ 6.2 (Eq. 15)

Dolomite:

$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3$ pH ≤ 6.2 (Eq. 16)

$2CaMg(CO_3)_2 + 4H^+ \rightarrow 2Ca^{2+} + 2Mg^{2+} + 4HCO_3^-$ pH ≥ 6.2 (Eq. 17)

The nett oxidation/neutralisation reactions in a mildly to an extremely acidic environment are summarised by Ochieng *et al*. (2009) in Eqs. 18-20:

$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ (Eq. 18)

$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$ (Eq. 19)

$H_2CO_3 \leftrightarrow H_2O + CO_2$ (Eq. 20)

In a mildly to an extremely acidic environment with a pH ≤ 6, the molar ratio of [Ca] to [SO_4] is 1:2, therefore 0.5 or <1. Under less acidic conditions, the molar ratio would be >1 through the formation of bicarbonate (HCO_3^-) (Ochieng *et al*., 2009; Van Deventer *et al*., 2007).

Neutralising acidic tailings where the acidity is caused by the oxidation of sulphide minerals present in the material, is a more challenging task compared to the neutralisation of naturally acidic soils (Khozhina & Sherriff, 2006). The reason for this is that ongoing acidification (discussed in Section 2.5.1) dominates, even after the tailings have been treated with large amounts of lime (Van Deventer & Hattingh, 2008). Therefore, lime has to be applied in very large quantities to neutralise active acidity as well as future acidity (potential or latent acidity) produced as a result of FeS_2 oxidation (discussed in Section 2.5). The pH of the growth medium must also be monitored frequently (e.g. every week/month) to determine if additional lime applications are necessary (e.g. if the pH decreases to <5). This is a very costly and time-consuming practice (Van Deventer, 2007).

There are various factors that influence the rate of the neutralisation reaction brought on by lime when incorporated into a growth medium. These factors are, as listed by Adams (1984), the pH of the growth medium, the fineness or particle size of the lime as well as the degree of lime-soil intermixing. Because the solubility of lime is greatly dependent on pH, the neutralisation reaction rate of lime is higher at lower pH levels. The particle size distribution of the lime and the degree of lime-soil intermixing is also important for the reason that the neutralisation reaction takes place between two surfaces, namely (1) the exchange sites on the surface of the soil particle that are

occupied by H^+ and Al^{3+} ions and (2) the surface of the lime particle, that is, the source of the neutralising CO_3^{2-} ions. By using a finer crushed lime, a larger reaction surface on the lime particle is made available, making more CO_3^{2-} ions available in a shorter timeframe for the neutralisation reaction to take place (Adams, 1984; Barber, 1984; Thomas & Hargrove, 1984; Van Deventer, 2007). This is why the time-dependent reactivity of agricultural lime is defined by particle size (Bishop & Hedley, 2013).

The importance of including very fine particles of lime (<0.25 mm) was proven through an experiment conducted by Elphick (as cited in Bishop & Hedley, 2013). The experiment studied the dissolution rate of different lime particle size fractions (2.00-0.84 mm, 0.400-0.177 mm and 0.177-0.104 mm) under moisture conditions near field capacity to optimise lime dissolution. The results from this experiment showed that the smallest size fraction (0.177-0.104 mm) had the highest dissolution rate (Bishop & Hedley, 2013), proving that larger reaction surfaces of finer lime particles result in higher dissolution rates (Adams, 1984; Barber, 1984; Thomas & Hargrove, 1984) and that the effectiveness of agricultural lime increases with a reduction in particle size (Conyers *et al*.; Scott *et al*.) (as cited in Bishop & Hedley, 2013).

According to Fertmark (as cited in Bishop & Hedley, 2013), to obtain a high quantity of highly reactive 0.25 mm lime particles, >95% of the total weight of the agricultural lime must be capable of passing through a 2.00 mm sieve and >50% of the total weight must be capable of passing through a 0.5 mm sieve.

A study conducted by Alvarez *et al*. (as cited in Bishop & Hedley, 2013) concluded that lime particle sizes between 2.00 mm and 4.00 mm do not have a significant effect on soil acidity or alleviating Al toxicity.

Lastly, temperature and moisture also influence the rate of $Ca,Mg(CO_3)_2$ and $CaCO_3$ dissolution which is directly linked to the rate of the neutralisation reaction. Higher temperatures and the presence of water aid in the dissolution of lime and consequently increase the rate of neutralisation. Larger amounts of water also help move Ca^{2+}, Mg^{2+}, HCO_3^- and H_2CO_3 deeper into the soil profile (Thomas & Hargrove, 1984).

The chemical effectiveness or quality of a liming material is determined by means of its $CaCO_3$-equivalence (CCE). Defined as “the acid-neutralising capacity of the material by weight in relation to $CaCO_3$” (Barber, 1984), the CCE is a measure of the chemical purity of the lime. Because of the lower atomic weight of Mg, dolomitic limestone shows a higher neutralising capacity than calcitic limestone. The particle size of a liming material also contributes to its quality in the sense that a finer lime particle allows for a higher neutralisation reaction rate (Barber, 1984; Van Deventer, 2007).

2.7.1 Ongoing acidification of tailings material after initial neutralisation

A more sustainable solution for the rehabilitation of a TSF is obtained after the acidic tailings have been treated with the appropriate amount of lime to neutralise the active as well as the potential acidity of the material. This counts for dry and wet environments. Natural leaching caused by frequent rainfall or irrigation in wet environments will lead to a moderately acidic root zone that is free of salts. Conversely, the root zone of TSFs in dry environments will still contain a large number of salts but the material will have an alkaline pH. Even though pH conditions can be improved by treating the tailings with large amounts of lime, acidification will continue to take place (Van Deventer & Hattingh, 2008).

Van Deventer and Hattingh (2008) and Van Deventer *et al.* (2007) explain the abovementioned phenomenon in great detail and attributes it to a number of chemical reactions explained below (Eqs. 21-26), starting with the initial oxidation of FeS_2 (pyrite) under acidic conditions (Eq. 21) where $FeSO_4$ and H_2SO_4, the product of S oxidation, are formed.

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \qquad \text{(Eq. 21)}$$

From Equation 21, one mole of H_2SO_4 is produced for every mole of FeS_2. Complete oxidation and hydrolysis of the $FeSO_4$ formed in Equation 21 can produce an additional mole of H_2SO_4 (sulphuric acid) along with a rusty brown iron hydroxide mineral (ferrihydrate), represented in Equation 22. Environmental factors such as water content, pH, degree and rate of oxidation, time, the oxidation state of Fe, the concentration of SO_4 and alkali cations determine the species of Fe minerals formed from the oxidation of $FeSO_4$ (Singh *et al*., 1999). The ageing of iron hydroxide leads to the precipitation of either lepidocrocite (rapid oxidation of Fe^{3+}) or goethite (slow oxidation of Fe^{3+}). Lepidocrocite is brown to orange in colour, whereas goethite is more yellowish brown (Hattingh, 2005). Figure 7 is a photograph of ferrihydrate on the surface of a gold TSF in the North-West Province, South Africa.

$$FeSO_4 + 0.25\ O_2 + 1.5\ H_2O \rightarrow FeOOH + H_2SO_4 \qquad \text{(Eq. 22)}$$

Figure 7: A photograph of ferrihydrate (rusty brown iron hydroxide mineral) on the surface of a gold TSF. Photograph taken by Schimmer (2016), with permission.

The amount of acid released on account of the oxidation and hydrolysis of H_2SO_4 to Fe^{3+}-bearing sulphate minerals is more when the product of the reaction is FeOOH, as in Equation 22, compared to when the product is jarosite or schwertmannite (Van Deventer & Hattingh, 2008; Van Deventer *et al*., 2007). Jarosite and schwertmannite precipitate under pH conditions of <4 where the concentration of SO_4 is >1000 mg/l (Hattingh, 2005).

For example, when $KFe_3(SO_4)_2(OH)_6$ (jarosite) is formed as the product of $FeSO_4$ oxidation and hydrolysis (Eq. 23), merely 1/3 mole H_2SO_4 is produced for every mole of $FeSO_4$ present. On the other hand, if the jarosite formed in Equation 23 was to dissolve and precipitate as FeOOH (Eq. 24), an added 1.5 mole H_2SO_4 would be produced (Van Deventer & Hattingh, 2008; Van Deventer *et al*., 2007).

$$3\ FeSO_4 + 0.75\ O_2 + 4.5\ H_2O + K^+ \rightarrow KFe_3(SO_4)_2(OH)_6 + H_2SO_4 + H^+ \qquad \text{(Eq. 23)}$$

$$KFe_3(SO_4)_2(OH)_6 \rightarrow 3\ FeOOH + 1.5\ H_2SO_4 + 0.5\ K_2SO_4 \qquad \text{(Eq. 24)}$$

Then again, Van Deventer and Hattingh (2008) also state that if $Fe_8O_8(OH)_6SO_4$ (schwertmannite) would be the resulting product from the oxidation and hydrolysis of $FeSO_4$, 7/8 mole H_2SO_4 would be produced for every mole of $FeSO_4$ (Eq. 25). Also, if schwertmannite was to hydrolyse and form FeOOH, the reaction would produce an additional 1/8 mole of H_2SO_4 for every mole of Fe present (Eq. 26).

$$8\ FeSO_4 + 2\ O_2 + 10\ H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 7\ H_2SO_4 \qquad \text{(Eq. 25)}$$

$$Fe_8O_8(OH)_6SO_4 + 2\ H_2O \rightarrow 8\ FeOOH + H_2SO_4 \qquad \text{(Eq. 26)}$$

It is therefore of the utmost importance that the appropriate method is used to determine the lime requirements of acidic tailings materials, for example, the acid-base accounting (ABA) method. This method accounts for further acid generation in the tailings caused by the presence of sulphide minerals in the sample (Usher *et* al., 2003). Together with the appropriate method to determine the lime requirements of these acidic tailings, robust and strategic monitoring of the ameliorated tailings is crucial.

Tailings materials are unconventional growth mediums and most of these are not in chemical equilibrium, that is, changing redox potential, ongoing acidification and pH fluctuations within a short period, compared to natural soils where these factors are not so severe (Haagner, 2008). As a result of ongoing changes in the chemistry of the tailings material owing to the processes discussed above, the results of this research will contribute to the development of supplementary ameliorative measures to further improve the quality of the tailings material as a growth medium.

As stated by Van Deventer and Hattingh (2008), liming of acidic tailings is only a short-term solution due to ongoing acidification as previously discussed. Liming is still very essential, as an initial neutralising environment creates an ideal opportunity for a selection of grass species to be established during the gradual change in pH of the material back to an acidic environment. Examples of these species are *Hyparrhenia hirta*, *Hyparrhenia tamba* and *Cynodon dactylon*. During this time, these species build up higher tolerances to acidic growth environments and, in due time, become completely tolerant to the acidic conditions of the growth medium (tailings). On the other hand, if these species are to be established in the original acidic growth medium without any means of neutralising measures, they would not survive (Van Deventer, 2007; Van Deventer & Hattingh, 2008).

2.8 Phosphorus (P) in soil and other growth mediums

Known as the “master” of plant nutrients and “the key of life”, phosphorus (P) plays a vital role in photosynthesis and energy transfer processes in all forms of life and is also a primary component in plant cell membranes. The importance of adequate P nutrition in growth mediums is portrayed in the numerous roles that it fulfils in processes such as root development, nitrogen (N) fixation, respiration, seed production, flowering, carbon metabolism, water and nutrient transfer up xylem tissue as well as Ca and Mg uptake (Brady & Weil, 2008; Desta, 2015; Johnston & Steën, 2000; Justin *et al*., 2012; Rachana *et al*., 2012; Sanyal & De Datta, 1991).

Compared to other macronutrients (e.g. nitrogen, potassium, calcium and sulphur), labile forms of P in growth mediums are reasonably scarce on account of the low solubility of minerals and soil compounds containing P (Antoniadis *et al*., 2015). Phosphorus deficiency has a direct impact on plant growth and development as well as seed formation. The symptoms of a P deficiency

can be observed on the leaves and stems of young plants as abnormal dark green or even purple marks (Figure 8). Usually, a P-deficient plant has stunted roots and frail, thin stems. P deficiency may also lead to senescence and yellowing of the leaves in severe cases (Brady & Weil, 2008; Johnston & Steën, 2000; MVSA, 2007). In contrast, very high levels of P in solution may also reduce growth in some plant species by hindering the absorption of micro-elements such as copper (Cu), iron (Fe) and zinc (Zn) (Alvarenga, 2012).

A study by Poozesh *et al*. (2010) found that P had a protective effect on Al toxicity. According to Schuman and Wilson (as cited in Poozesh *et al*., 2010), this can be explained through the formation of non-toxic Al-P precipitates in the soil solution as a result of treating acidic soils with fertilisers that contain P.

Figure 8: A photograph presenting a phosphorus-deficient turnip plant used during a TSF rehabilitation pot trial. Photograph taken by Schimmer (2016), with permission. Note the purple discolouration of leaves as a result of P deficiency.

Phosphorus is always accompanied by oxygen ions (O^{2-}) in the form of phosphate anions (PO_4^{3-}). Because of its 3- valence, PO_4^{3-} anions can react with cations such as H^+, Mg^{2+}, Ca^{2+}, Fe^{3+} and Al^{3+} present in the soil solution (Hansel *et al*., 2014).

In soil or growth mediums, dissolved P is absorbed by plants in the form of inorganic orthophosphate ions, mainly $H_2PO_4^-$ and, to a smaller degree, HPO_4^{2-}. A small amount of inert soluble organic P is also absorbed, but only available after mineralisation (Brady & Weil, 2008;

Pretorius, 1991; Stroia *et al*., 2013). The species or type of orthophosphate ion present in solution is determined by the pH of the growth medium, as illustrated in Figure 9.

Higher concentrations of H^+ ions are in solution at lower pH values; therefore the monovalent ion $H_2PO_4^-$ dominates in strongly acidic growth mediums (pH 4 to 5.5). On the other hand, in alkaline solutions with a lower H^+ ion activity, a higher concentration of the HPO_4^{2-} ionic species is present. Nearly equal concentrations of $H_2PO_4^-$ and HPO_4^{2-} are present in near-neutral solutions (Batjes, 2011; Brady & Weil, 2008).

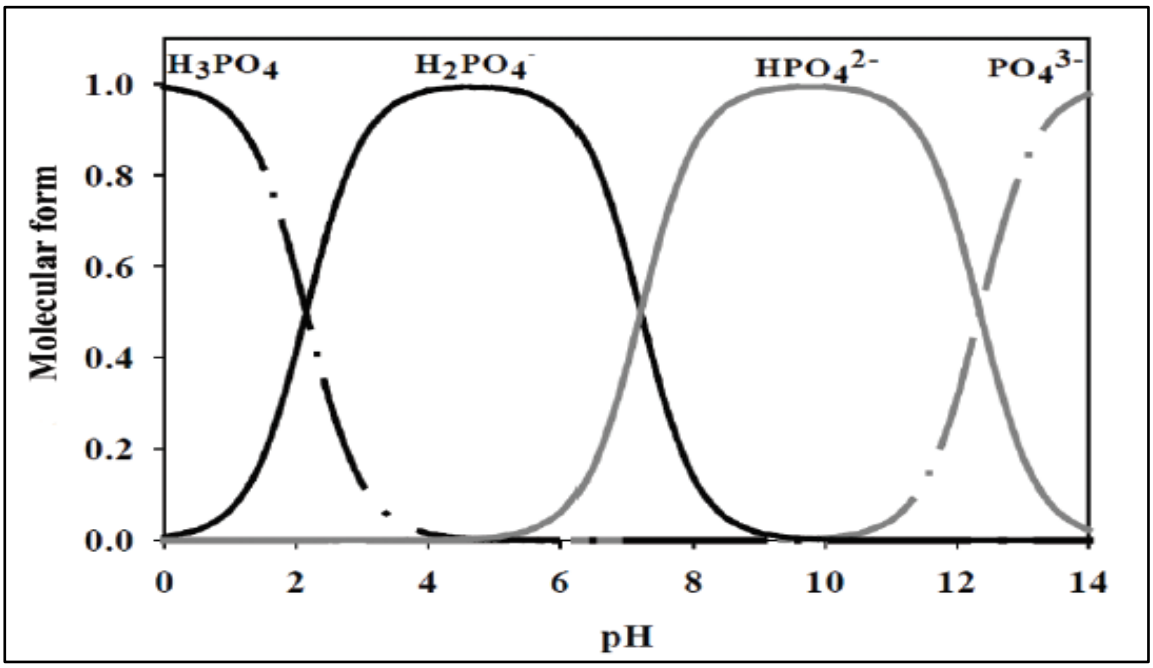


Figure 9: A graph illustrating the effect of pH on the concentrations of orthophosphate species in solution (Hansel *et al.*, 2014).

Phosphorus is relatively immobile in growth mediums, unlike other plant nutrients (e.g. nitrogen) (Yuan *et al*., 2005; MVSA, 2007) and exists in six different pools, as listed by Stevenson (1986):

- Weakly adsorbed (labile) inorganic phosphate
- Soluble inorganic and organic compounds
- Insoluble phosphates of Fe, Al and Ca
- Phosphates strongly fixed by hydrous Fe and Al oxides
- Phosphates fixed by silicate minerals
- Insoluble organic forms of phosphate (soil biomass, undecomposed animal and plant rests and humus)

2.8.1 Phosphorus transformations in growth mediums

As a function of its the degree of solubility, P is present in inorganic and organic forms in growth mediums. Inorganic P is present in the soil solution mainly as HPO_4^{2-} and $H_2PO_4^-$, which can be fixed by means of adsorption on Fe and Al oxides in acidic growth mediums. The process of P adsorption with Al and Fe oxides can either be weak (labile P) or strong (moderately labile P). Precipitation with oxides of Al and Fe in acidic growth mediums or Ca in alkaline soils containing free Ca, creates insoluble forms of phosphates, known as the "non-labile pool of P". Also consisting of phosphate ions, organic P is adsorbed onto organic compounds in the growth medium. The susceptibility to decomposition of the organic compound bound to the phosphate ions determines the availability or lability of organic P (Costa *et al.*, 2016).

The process of transforming non-labile P to labile P is very slow, whereas the transformation of labile P to unavailable non-labile P, for example, after fertiliser applications, may be a rapid transformation (MVSA, 2007; Rachana *et al*., 2012).

Figure 10 contains a simplified illustration of inorganic and organic P transformations and processes within a growth medium. Phosphate introduced into the growth medium (e.g. fertiliser) and phosphate ions already present in solution can undergo different types of reactions that remove these ions from the solution and form other P-containing compounds with very low or no solubility. Collectively, these reactions lead to *phosphorus fixation* (Brady & Weil, 2008).

Phosphorus fixation can, therefore, be defined as the transformation of soluble, plant-available forms of P into less soluble, plant-unavailable forms of P through a series of chemical reactions governed by chemical conditions within the growth medium. The most important reactions leading to the removal of P from the soil solution are *adsorption* and *precipitation* (Batjes, 2011).

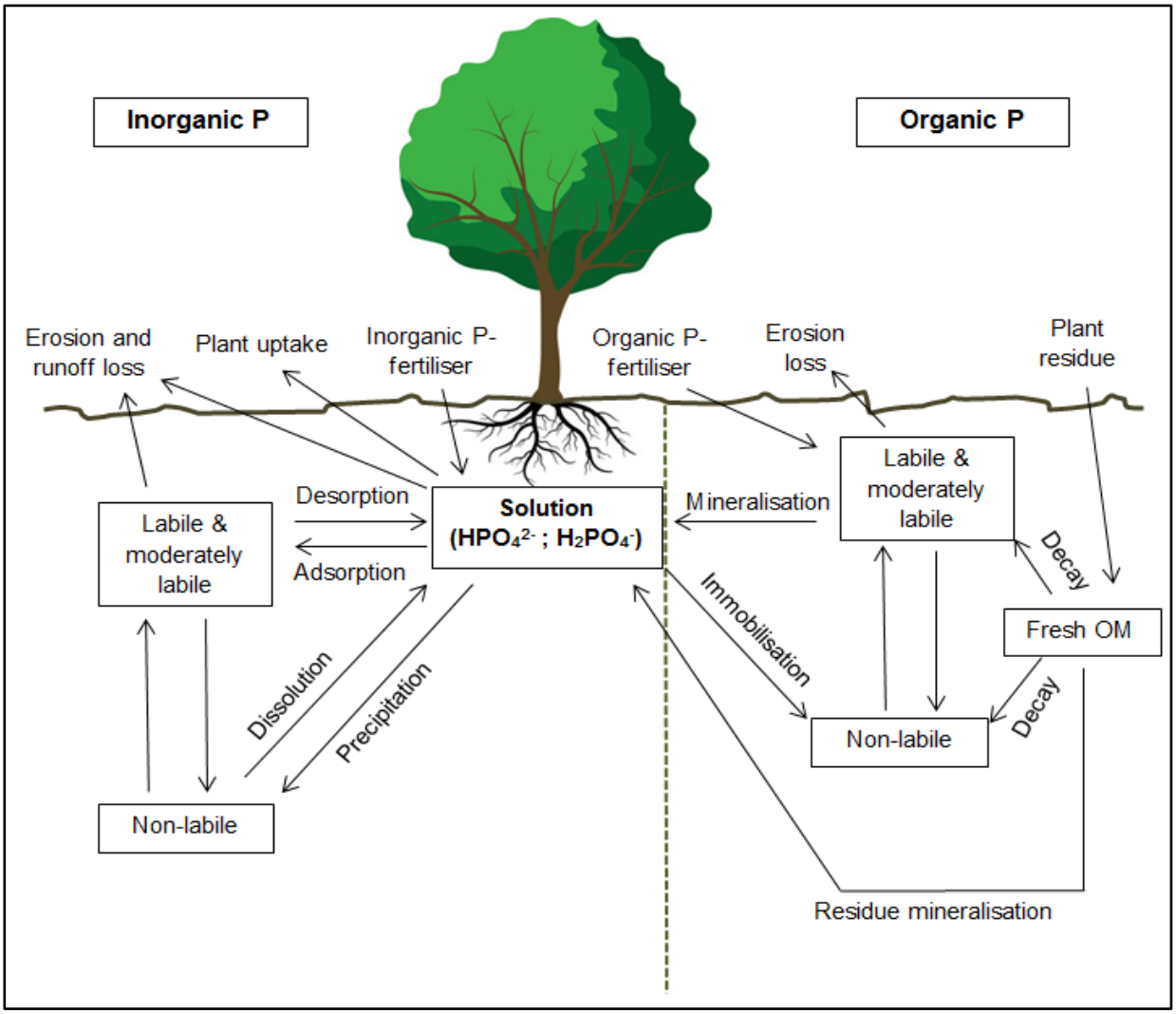


Figure 10: A simplified illustration of P processes and transformations in a growth medium (adapted from MVSA, 2007 and Yuan et al., 2005).

As explained by Stewart (1991) and Yuan *et al*. (2005), the process of *adsorption* refers to the phenomenon where P is bound to the surface of minerals or colloidal particles. Phosphate ions in solution (HPO_4^{2-} or $H_2PO_4^-$, depending on the pH of the solution) bind with positively charged ions, for example, Fe^{3+}, Al^{3+}, Mn^{2+}, Ca^{2+} or Mg^{2+}, to form less soluble phosphate compounds.

Precipitation takes place when soluble, more labile P is converted to an insoluble mineral form of P through the formation of insoluble Fe, Al and Ca phosphates. A reaction takes place between $H_2PO_4^-$ and strongly positively charged Fe^{3+}, Al^{3+} and Mn^{2+} ions in solution to form insoluble hydroxy-phosphate precipitates. The available concentration of phosphate in solution is controlled by the solubility of the mineral formed through the precipitation reaction. Very acidic growth mediums usually contain enough Fe^{3+}, Al^{3+} and/or Mn^{2+} in solution to chemically precipitate virtually all $H_2PO_4^-$ ions in solution (Alvarenga, 2012; Brady & Weil, 2008; Yuan *et al*., 2005). The precipitation reaction in acidic growth mediums is illustrated in Equation 27 with the use of the Al^{3+} ion as an example (Brady & Weil, 2008).

$$Al^{3+} + H_2PO_4^- + 2H_2O \leftrightarrow 2H^+ + Al(OH)_2H_2PO_4 \quad \text{(Eq. 27)}$$
(Soluble) (Insoluble)

The pH of the growth medium plays a vital role in adsorption and precipitation transformations. A greater amount of phosphate is adsorbed and precipitated at lower pH values for the reason that more positively charged ions (more specifically Al^{3+}, Fe^{3+} and Mn^{2+}) are present in high concentrations (Yuan *et al*., 2005). The amelioration of acidic growth mediums with lime to raise the pH of the solution may also lead to the fixation of P. The Ca^{2+} and Mg^{2+} originating from the dissolution of lime granules will displace H^+, Al^{3+}, Fe^{3+} and/or Mn^{2+} ions from the solution, resulting in an increase in pH and P fixation (Sarker *et al*., 2014).

Phosphorus fixation in acidic growth mediums containing hydrous-oxide minerals and silicate clays occurs when $H_2PO_4^-$ ions are adsorbed to the surfaces of insoluble Fe, Al and Mn oxides, for example, goethite ($Fe_2O_3 \cdot 3H_2O$) or gibbsite ($Al_2O_3 \cdot 3H_2O$), or react with 1:1-type silicate clays (e.g. kaolinite). Known to have large surface areas and, consequently, large anion exchange capacities (AEC), positively charged surfaces of materials such as kaolinite and Al and Fe oxides bind strongly with phosphate anions. Hydrous oxides of Fe, Al and Mn exist as crystalline and non-crystalline particles on their own as well as on the surfaces of clay minerals in the form of fine coatings. Characterised by large surface areas, these coatings have the ability to fix or retain a considerable amount of P. This implies that clay minerals or aluminosilicates also play a supplementary role in P fixation (Batjes, 2011; Brady & Weil, 2008; Stewart, 1991).

Antoniadis *et al*. (2015) studied the effect of liming and P addition on P availability in low-P and acidic soils with the use of pot trials. They found that the best practice in acidic low-P soils was to increase the pH of the growth medium through the addition of lime accompanied by P fertilisation.

The opposite of adsorption is *desorption* (Figure 10), where adsorbed P is released into a solution and made available for plant uptake. Even though adsorption is a rapid process and directly affected by the pH of the solution, the same is not true for desorption. Desorption may be a very slow process, and sometimes even impossible, depending on the type of compound formed after adsorption (Yuan *et al*., 2005).

For organic P (Figure 10), the first process of importance is the breakdown of fresh plant residue into simpler organic components termed “decomposition” or “decay”. After decomposition, the organic P is still unavailable for plant use. *Mineralisation* driven by microorganisms in the rhizosphere of a soil or growth medium has to occur to convert plant-unavailable organic P to plant-available inorganic P (Yuan *et al*., 2005).

Microorganisms and plant roots secrete enzymes (e.g. phytases and phosphatases) that are capable to mobilise and release P (and other elements) from organic compounds. Examples of

microorganisms that play a vital role in P mineralisation include those that form part of the genera *Enterobacter*, *Bacillus*, *Citrobacter*, and so forth. Other microorganisms, such as mycorrhizal fungi and actinomycetes, are also of great importance for P mineralisation (Hunter *et al*., 2014).

The process of *immobilisation* is the inverse of mobilisation, where plant-available inorganic P is converted back to plant-unavailable organic P (Yuan *et al*., 2005).

In summary, there are several factors that influence the adsorption, fixation or precipitation and also the plant availability of phosphate in a growth medium. After consulting various forms of literature and experimental studies, four factors were emphasised and discussed frequently. These factors are mineralogy and chemistry of the growth medium, clay content, pH and microbial activity.

2.8.2 Inorganic phosphate fertilisers in South Africa

The commercially viable phosphate deposits of South Africa containing the mineral apatite $Ca_{10}(PO_4)_6F_2$, exist in igneous as well as marine sedimentary geological environments. The latter is by far less significant for the reason that approximately 95% of phosphate fertilisers of South Africa is sourced from the igneous rocks of the 2 030-million-year-old Phalaborwa Complex (Roux *et al*., 1989). Stevenson (1986) and Tisdale *et al*. (1990) refer to apatite as “tri-calcium phosphate” with a chemical formula of $3[Ca_3(PO_4)_2]\cdot CaX_2$, where X may be Cl^-, F^-, OH^- or CO_3^{2-}. The greatest amount of phosphate mined in South Africa, particularly from the Phalaborwa Complex, contains fluorine (F). For this reason, most of the apatite has a chemical formula of $Ca_{10}(PO_4)_6F_2$ (fluroapatite) (MVSA, 2007; Roux *et al*., 1989).

Sedimentary phosphate deposits are of biological origin, largely from marine fauna. These deposits were formed as a result of the chemical breakdown of biological wastes (e.g. bones, manure, etc.) and surrounding rocks. The deposits hold a weak crystalline, amorphous apatite mineral that dissolves partially in diluted weak acids (e.g. citric acid) and can, therefore, be directly applied to the growth medium as a phosphate fertiliser in a finely milled form (MVSA, 2007; Roux *et al*., 1989). On- and offshore marine sedimentary phosphate deposits are present in the western and southern coastal areas of South Africa. Intermittent onshore deposits are present from Lamberts Bay (north) to Saldanha Bay (south), with ore grading from 8.0 to 12.8 wt% P_2O_5. The deposits consist of sand horizons rich in a carbonate apatite mineral termed “francolite”. Offshore deposits of phosphate-rich sedimentary material can be found on the continental shelf of the Agulhas Bank, extending in an easterly direction from Cape Town to Port Elizabeth and also in a northerly direction from Cape Town to Lamberts Bay. These deposits consist of approximately 16 wt% P_2O_5 on average (Roux *et al*., 1989).

Apatite-containing ore in igneous geological environments occurs as solidified magma intrusions. This hard apatite mineral is strongly crystalline and insoluble in diluted weak acids. As a result, it must be treated with strong acids before it can be utilised as a fertiliser (MVSA, 2007).

The Phosphate Development Corporation Ltd (Foskor) has exclusive mining rights to the phosphate contained within the Phalaborwa Complex. Most of the mining activities in the Phalaborwa Complex take place near the Kruger National Park, south of the town Phalaborwa in the Limpopo Province. This location is known for its high-quality apatite (e.g. phosphate) and vermiculite deposits. It is also the site of Africa's largest open-pit copper mine (Verwoerd & Du Toit, 2006). Containing 10 wt% P_2O_5 on average, the phosphate is mainly derived from apatite in the foskorite zone of the Complex (Roux *et al*., 1989; Verwoerd & Du Toit, 2006).

After ore extraction, the phosphates are crushed and beneficiated to gain higher apatite concentrations through the removal of unwanted minerals from the ore (e.g. vermiculite, magnetite and phlogopite) by means of a flotation process. After flotation, the processed ore is referred to as "phosphate concentrates" (and not "rock phosphates") (MVSA, 2007). The phosphate concentrates are then *heat-treated* or *acid-treated* to increase the solubility of the material (MVSA, 2007; Tisdale *et al*., 1990).

2.8.2.1 Heat-treated phosphates

Also referred to as "thermal phosphate fertilisers", these fertilisers are manufactured by means of melting phosphate concentrates in the presence of additives such as serpentine, lime or silica. The final fertiliser product is soluble in citric acid but not in water and contains complex calcium silicophosphates (MVSA, 2007; Tisdale *et al*., 1990). Tisdale *et al*. (1990) mention that these fertilisers have some disadvantages, which include the following:

- They are more expensive to produce, compared to acid-treated fertilisers.
- The plant-available P is often less than 100% of the total amount present.
- The fertiliser contains no water-soluble P.
- They are worthless in the manufacture of N-P-K fertilises for the reason that they are unable to undergo ammoniation.

Kalmafos is a heat-treated phosphate fertiliser used in South-Africa. It is manufactured by means of melting the phosphate concentrate in the presence of a magnesium silicate, serpentine, and rapidly cooling it afterwards (MVSA, 2007).

2.8.2.2 Acid-treated phosphates

Acid-treated phosphates are manufactured by way of treating phosphate concentrates with strong acids (e.g. sulphuric, nitric or phosphoric acid) to increase their solubility in water. These fertilisers are almost entirely water-soluble (MVSA, 2007; Tisdale *et al*., 1990).

Examples of acid-treated phosphates used in South Africa include (a) superphosphate, (b) enriched superphosphate, (c) double superphosphate, (d) nitrophosphate and (e) monoammonium phosphate (MAP) and diammonium phosphate (DAP).

(a) Single superphosphate

Phosphate concentrates are treated with H_2SO_4 (sulphuric acid). Mainly consisting of $3Ca(H_2PO_4)_2H_2O$ (monocalcium phosphate), it also contains $CaSO_4$ (gypsum). As a result, single superphosphate contains three plant nutrients, e.g. P, Ca and S. Equation 28 illustrates this chemical reaction (MVSA, 2007).

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2H_2O + 7CaSO_4 + 2HF \quad \text{(Eq. 28)}$$

The acidification of growth mediums caused by the presence of free acid in superphosphate is insignificantly small (MVSA, 2007). Approximately 90% of the product is water-soluble and plant-available. Single superphosphate, also known as “ordinary superphosphate” (OSP), is frequently mixed with other dry, pulverised or granular fertilisers in the manufacturing of mixed fertilisers that contain N, P and K. Single superphosphate fertiliser may also be applied directly to the growth medium (Tisdale *et al*., 1990).

(b) Enriched superphosphate

In a process very similar to that of the manufacturing of superphosphates, phosphate concentrates are treated with a mixture of H_2SO_4 (sulphuric acid) and H_3PO_4 (phosphoric acid), resulting in a lower concentration of $CaSO_4$ and a higher concentration of P contained in the end-product. Similar to single superphosphates, this superphosphate fertiliser also contains a mixture of monocalcium phosphate and gypsum. Nearly all of the P contained in the fertiliser is plant-available (MVSA, 2007; Tisdale *et al*., 1990).

(c) Double superphosphate

Also called “triple superphosphate”, this fertiliser is manufactured by means of treating phosphate concentrates with H_3PO_4 (phosphoric acid), according to Equation 29. No gypsum is formed from this reaction, which differs from the manufacturing of single and enriched superphosphates. This means that the $3Ca(H_2PO_4)_2H_2O$ is not diluted with $CaSO_4$ and contains nearly no sulphur; therefore, the P concentration in double superphosphate is higher than that of single and enriched superphosphates (MVSA, 2007; Tisdale *et al*., 1990).

$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 + 10H_2O \rightarrow 10Ca(H_2PO_4)\cdot H_2O + 2HF$ (Eq. 29)

A very small amount of free acid is present in double superphosphate fertilisers, but it has negligible acidifying effects on growth mediums (MVSA, 2007). Double superphosphates are usually manufactured in granular and pulverised forms (Tisdale *et al*., 1990).

(d) Nitrophosphate

Phosphate concentrates are treated with HNO_3 (nitric acid) in the manufacturing of nitrophosphate. An excess amount of acid is usually used in this process, which is then neutralised by way of ammonification where NH_3 is used. As a result, an NP product (nitrophosphate) is formed, consisting of dicalcium phosphate, monocalcium phosphate and ammonium nitrate (MVSA, 2007). Most nitrophosphates are less water-soluble than other acid-treated phosphates and they are always manufactured in a granular form (Tisdale *et al*., 1990).

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

Carefully considering and researching appropriate materials and methodologies before starting a research project is essential in every academic field. This study was conducted in three main phases. Phase 1 consisted of a pilot study and some desktop studies to identify suitable growth mediums or materials that would be used for the main experimental work. Phase 2 comprised two pot trials that were aimed at determining the influence of a neutralisation time lag on the availability of phosphorus (P) in the growth mediums identified in Phase 1. Phase 3 was aimed at determining if a neutralisation time lag would improve seedling survival rates in the respective growth mediums.

This chapter describes the materials used in the study and the methodology (experimental design and analytical methods) followed during every phase of the research project in detail.

3.2 Material selection (Phase 1)

Neutralisation pot trials (Figure 11a) were conducted on 13 different mine waste tailings found all over South Africa along with a naturally acidic soil, which served as the control medium, during November and December of 2016. Trials were conducted with the intention to determine which tailings material was best suited to use in the final fertiliser pot trials. Another objective of the trial was to determine the time at which the tailings would reach a pH where the P fertiliser would be available for plant use.

Owing to oxidation reactions within the tailings material taking place continuously, re-acidifying the material, aiming for a pH between 6.5 and 7.5 (optimal pH for phosphorus availability) was unrealistic. It was, therefore, decided that the aimed pH would be 5.5 and higher. At this level of acidity, phosphorus (P) is still less plant-available than at a pH of 6.5, but more available than it would be at a pH of <4, the pH of the material before lime treatment.

(a) Layout of the neutralisation pot trial.

(b) Weekly pH(H_2O) and EC monitoring.

Figure 11: Photographs of the pot layout and pH(H_2O) monitoring during the neutralisation pot trial. Photographs taken by Myburgh (2016).

Different types of gold, coal and fluorspar tailings were used in the neutralisation pot trial. The growth medium collection can be summarised as follows:

Control medium: Approximately 3 m^3 of the acidic soil was loaded in the field and transported to the research facility. The total bulk sample of the medium was air-dried and thoroughly mixed with a concrete mixer to ensure a homogenous sample.

Tailings materials: Approximately 3 m^3 of each were transported to the research facility. The identified tailings (two from New Machavie Gold Mine, one from Crown Gold Mine and one from Landau Colliery) were mixed individually with concrete mixers to ensure homogenous samples to be used in the pot trials.

The lime requirement of each and every material was determined beforehand according to the Net Acid Production (NAP) or Net Acid Generation (NAG) Test by Dr A.A. Bloem from Geolab. The tailings were brought to field capacity with deionised water and treated with dolomitic lime according to their lime requirements. Three replicas were made for each material so that an average between them could be determined, ensuring more reliable results.

Neutralisation of the mediums was monitored by measuring the pH(H_2O) of the leachate water from the mediums on a weekly basis (Figure 11b), with the use of the leaching procedure as discussed in subsection 3.5.2. After monitoring the pH(H_2O) of the different growth mediums over a period of seven weeks, the data collected were plotted on a line graph where the change in pH

of the different materials could be compared. The data were used to identify the four tailings used in the phosphate fertiliser pot trials.

3.3 Material descriptions

This section briefly discusses the geological settings of the host rocks where the tailings and soil originated from and the locations where the different growth mediums used in the study were obtained. The physiochemical characteristics of the growth mediums are discussed in Chapter 4.

3.3.1 Geological origin of the growth mediums

The tailings material used in the study along with the control medium originates from different geological environments that contribute to dissimilarities in various properties, such as chemical composition and texture. Figure 12 contains a stratigraphic column of the geology of South Africa with arrows pointing to the geological formations or supergroups that the materials originate from.

The NM700 and NMC1 tailings were collected at the New Machavie Gold Mine and originate from the Chuniespoort Group of the Transvaal Supergroup. The Crown tailings, mine waste material from Crown Mines, originate from the Central Rand Group of the Witwatersrand Supergroup. The coal tailings originate from the Ecca Group of the Karoo Supergroup. The coal tailings were obtained from Landau Colliery. Lastly, the control medium, a naturally acidic sandy soil, originate from the Pretoria Group, which also forms part of the Transvaal Supergroup.

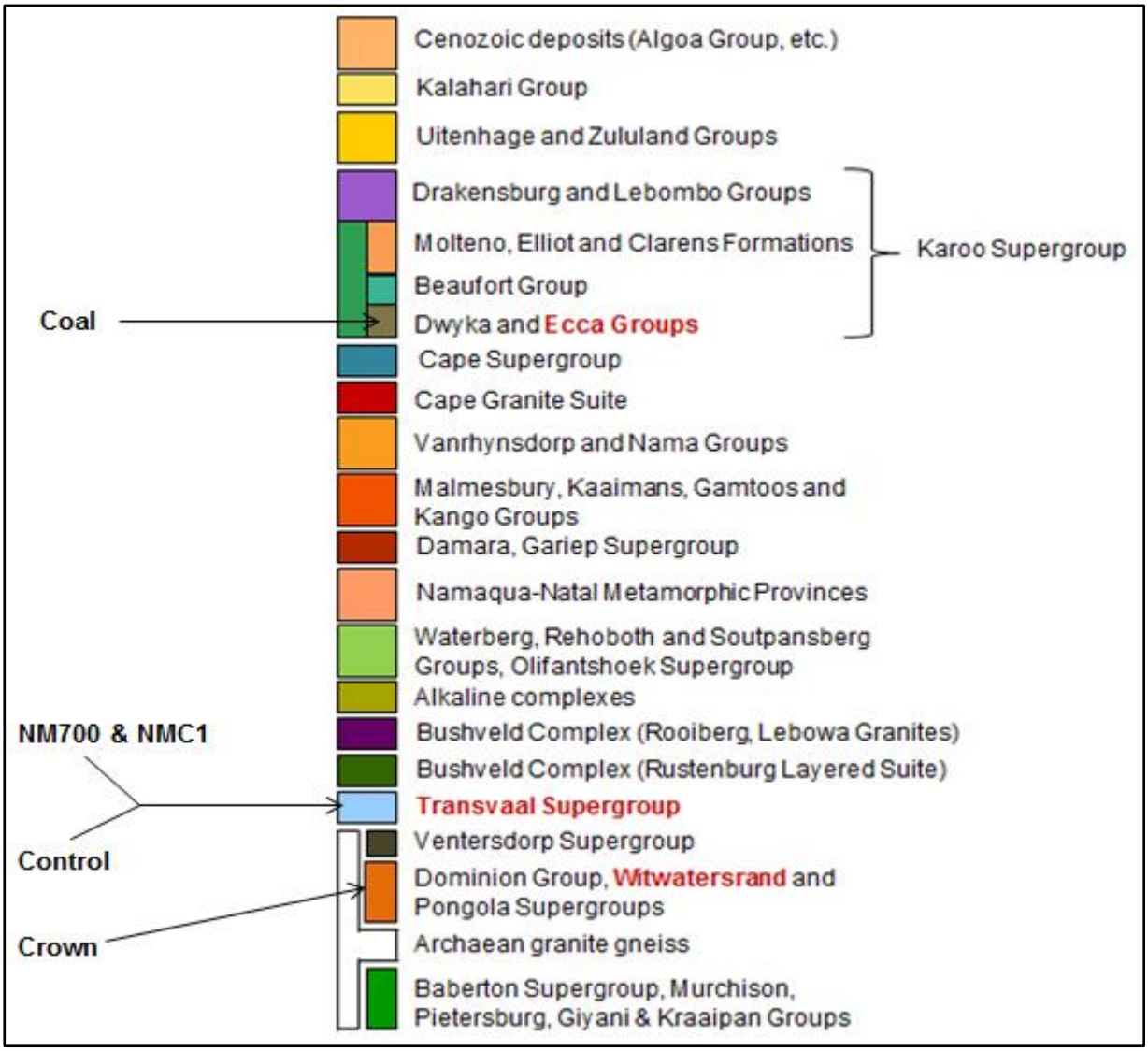


Figure 12: A summarised stratigraphic column of the geology of South Africa, illustrating the geological origin of the different growth mediums used in the study (adapted from McCarthy & Rubidge, 2005).

3.3.1.1 New Machavie (NM700 and NMC1)

The NM700 and the NMC1 tailings material were obtained from the New Machavie Gold Mine, also known as the Eleazer Mine. A locality map of the mine can be seen in Figure 13. The New Machavie Gold Mine is a Tlokwe Local Municipality-owned derelict mine located approximately 22 km west of Potchefstroom, in the North-West Province. Mining took place between the 1930s and 1940s, and during this time, five TSFs were constructed (Aucamp, 2000; Koch, 2014).

The coordinates of the sample localities are as follows:

NMC1: 26° 40’ 18.59” S; 26° 52’ 18.75” E

NM700: 26° 40’ 19.47” S; 26° 52’ 29.70” E

The geology of this mine mainly consists of sedimentary rocks belonging to the Transvaal Supergroup (deposited roughly 2 000 million years ago). A small portion on the western part of

the mine is underlain by volcanic rocks of the approximately 2 600-million-year-old Ventersdorp Supergroup (Aucamp, 2000; Botha, 2015; Eriksson *et al*., 2006; McCarthy & Rubidge, 2005).

As explained by Aucamp (2000) and Koch (2014), the Transvaal Supergroup is represented by the Blackreef Formation and the Monte Christo and Oaktree Formations (which form part of the Malmani Subgroup in the Chuniespoort Group). Feldspathic quartzite, shale and small-pebbled basal conglomerate are abundantly present in the Black Reef Formation. Dolomite rich in chert can be found in the Monte Christo Formation, together with stromatolites, erosion breccia and mudstones, whereas the underlying Oaktree Formation comprises mostly chert-free dolomite, large stromatolitic domes and carbonaceous shales (Aucamp, 2000; Botha, 2015; Koch, 2014). The Ventersdorp Supergroup will not be discussed as it is not of relevance for this study.

There are five different TSFs on the New Machavie premises, each with its own colour, texture and chemical composition. The reason for this is that five different gold reefs were actively mined at the New Machavie Gold Mine. For example, the dark colour of the NM700 tailings material originates from the conglomerates that are rich in inorganic carbon from the Black Reef Formation (Van Deventer, 2017). NMC1 tailings are lighter in colour and sandier; therefore, the tailings may originate from a feldspathic quartzite reef.

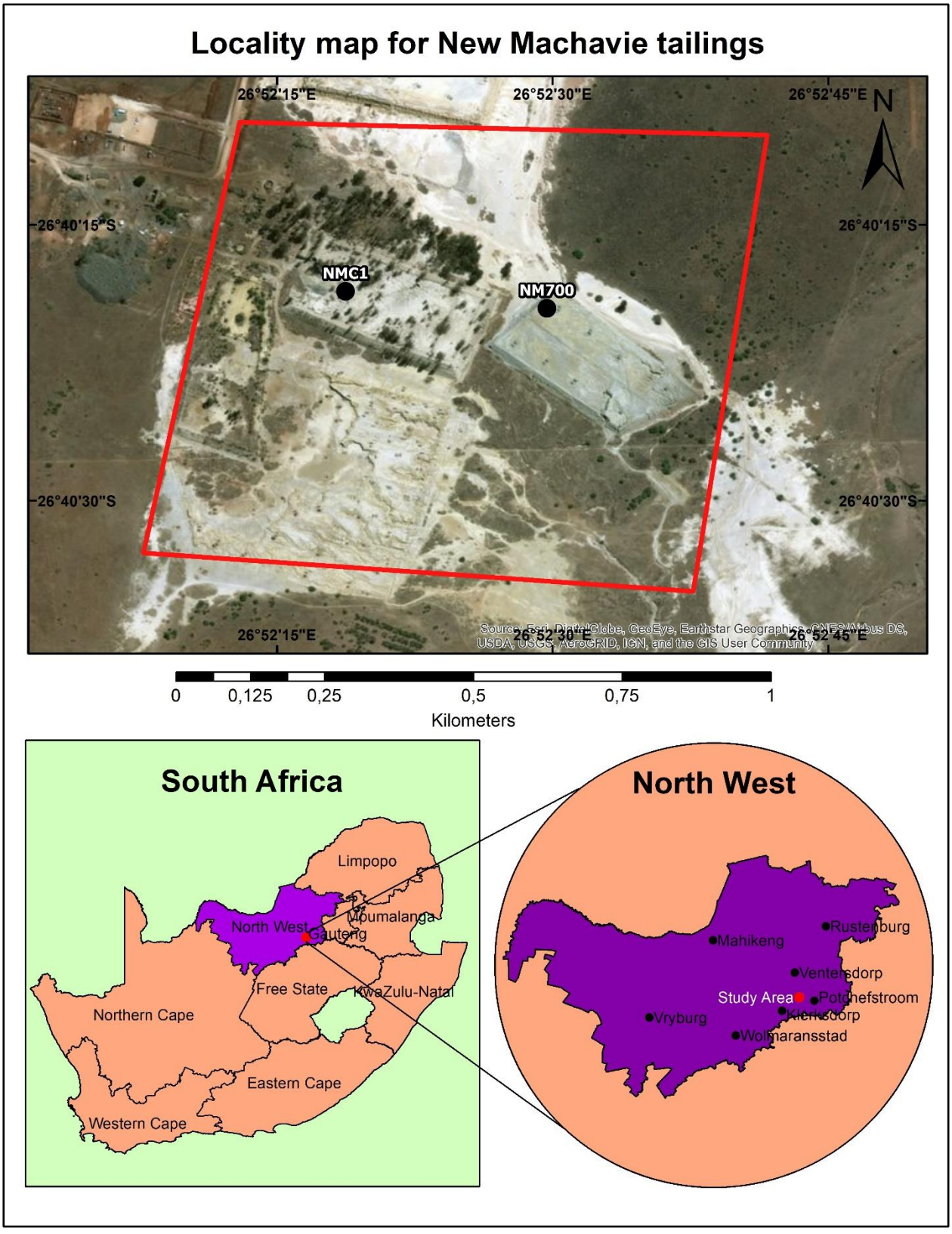


Figure 13: A locality map of the New Machavie (Eleazer) Gold Mine (GIS map compiled by S. Denysschen, 2017).

3.3.1.2 Crown

Crown tailings material was sampled from one of the TSFs at Crown Mines (Figure 15) in the Gauteng Province, which was the largest single gold mining company in the world for many years. The GPS coordinates of where the tailings material was collected are as follows:

26° 13' 32.37" S; 27° 57' 34.45" E

These tailings originate from the Witwatersrand Supergroup (aged between 2 300 million years ago [Ma] and 2 800 Ma) that hosts the most extraordinary gold resource in the world, producing approximately 31% of all the gold resources ever mined. The lower part of the Witwatersrand sedimentary sequence is called the "West Rand Group" and consists mainly of iron-rich shale and quartzite. Unconformably overlying the West Rand Group, is the Central Rand Group (Figure 3-5), characterised by gold-bearing quartz-pebble conglomerate reefs and quartzite at a maximum thickness of 2 880 m (McCarthy, 2006; McCarthy & Rubidge, 2005; Viljoen, 2009).

The three main auriferous conglomerate reefs or units are, as illustrated in Figure 14, (1) the Main Reef, (2) the Main Reef Leader and (3) the South Reef. The lower part of the Main Reef is largely comprised of poorly sorted conglomerate with pebbles of approximately 5 cm in diameter, intermittently accompanied by channels filled with boulders. The relatively thin Main Reef Leader, which was the most fruitful gold-producing reef of the Central Rand, displaying roughly 40 cm in thickness, often produced grades of 50 grams per ton and higher. This reef is coarser (pebbles being up to 8 mm in diameter) and better sorted than the Main Reef and often displays a dark colour due to the presence of chlorite (McCarthy, 2006; McCarthy & Rubidge, 2005; Viljoen, 2009).

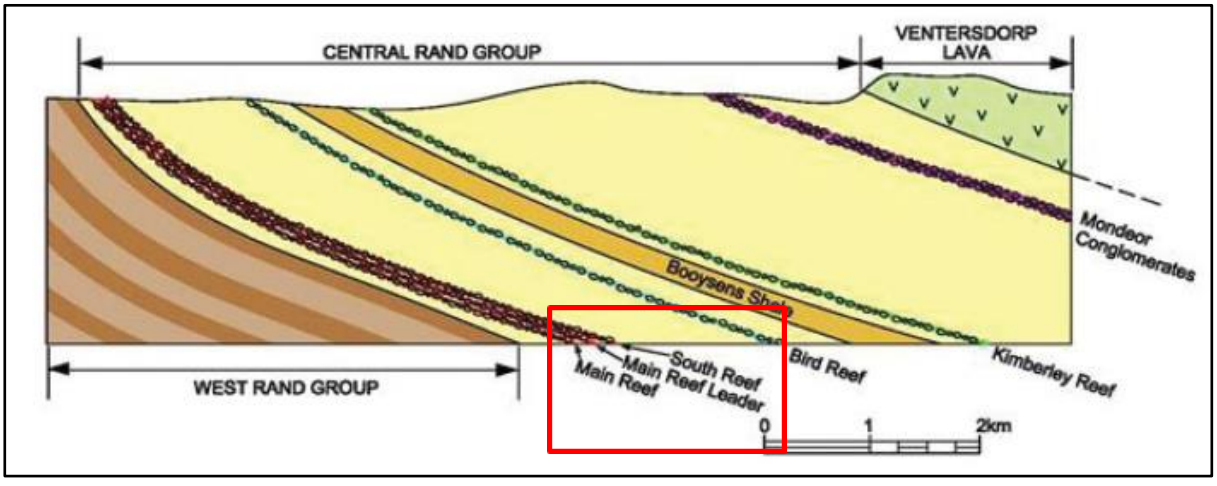


Figure 14: A cross section through the three gold-bearing conglomerates of the Central Rand Group (Viljoen, 2009).

The South Reef, with a somewhat lower grade than the Main Reef Leader, generally occurs as individual pebble bands parted by arenaceous material. Iron sulphide (FeS_2) is abundant within

these conglomerates, making up approximately 3% of the conglomerate (McCarthy, 2006; McCarthy & Rubidge, 2005; Viljoen, 2009).

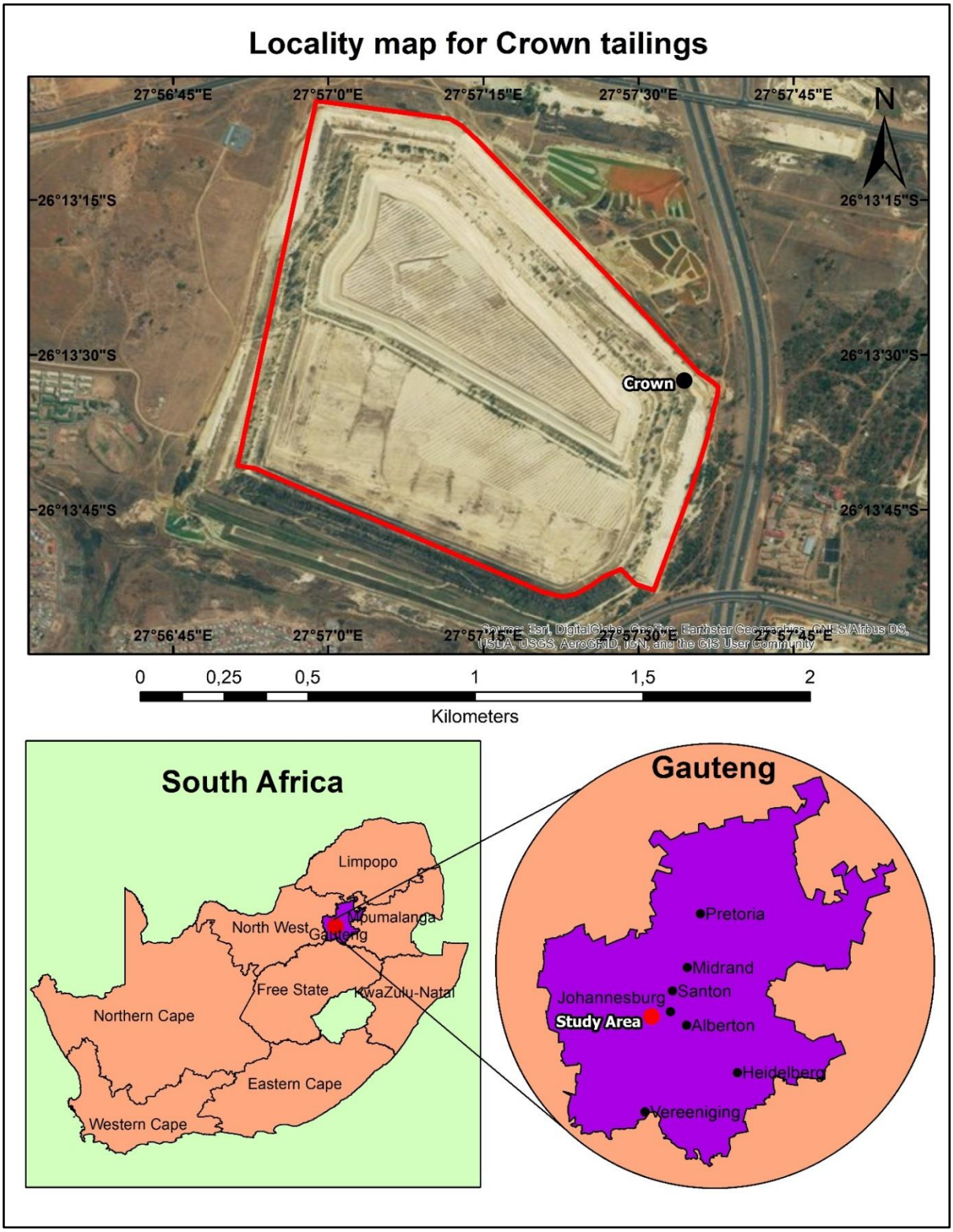


Figure 15: A Google locality map of the TSF belonging to Crown Mines where the material was collected (GIS map compiled by S. Denysschen, 2017).

3.3.1.3 Coal

The coal tailings used in the study, originate from the Landau Colliery (Figure 14) near Witbank in the Mpumalanga Province, where it was mined from the Witbank Coalfield. The GPS coordinates for the location of Landau Colliery are:

25° 55’ 08.41” S; 29° 09’ 59.42” E

The Witbank Coal Seam is located in the Northern part of the Karoo Basin. The coal seams, ranging between 0.5 m and 6.5 m in thickness, were deposited between layers of shale, sandstone, siltstone and grit within the Vryheid Formation of the Ecca Group (Du Plessis, 2008; Pretorius, 2014; Jeffrey, 2005). As illustrated in Figure 13, there are five mineable bituminous coal seams present within the Witbank Coalfield, numbered from 1 to 5 in ascending stratigraphic order.

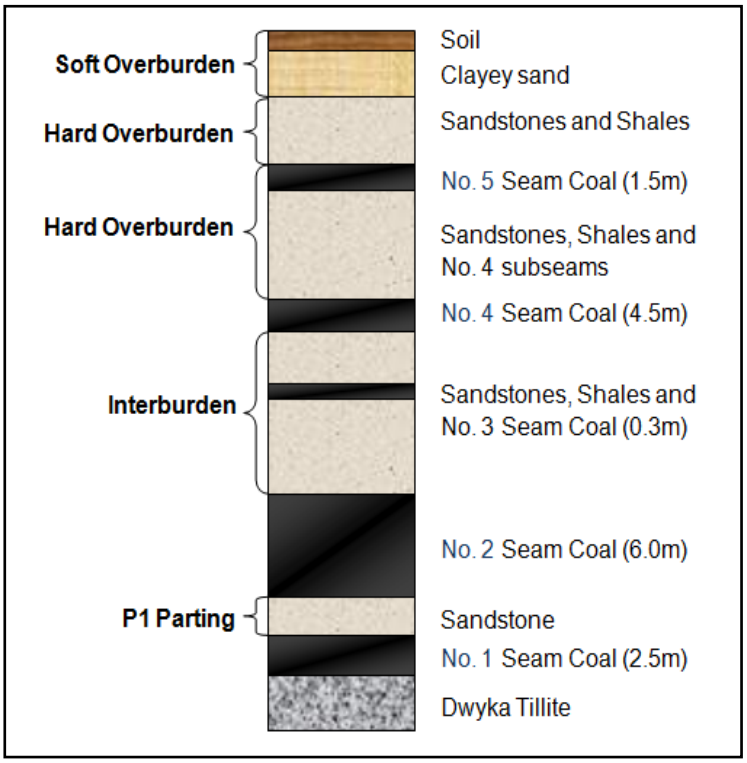


Figure 13: Stratigraphy of the Witbank Coalfield (adapted from Kleinkopje Colliery, 2013).

Jeffrey (2005) explains that the no. 1 seam, underlain by Dwyka Tillite, was intermittently formed as a result of pre-Karoo topography and frequently shows very low phosphorus content, where it is then mined separately as metallurgical feedstock. The no. 2 seam, being the most economically valuable coal seam, has up to six quality grades, whereas the no. 3 seam is generally uneconomic. The no. 4 seam is divided into Nos 4 A, 4 Upper and 4 Lower through partings consisting of mudstone or siltstone. This coal seam has some economic importance but

not nearly as much as the no. 2 coal seam. The no. 5 seam, consisting of erosional fragments, is also not of economic importance.

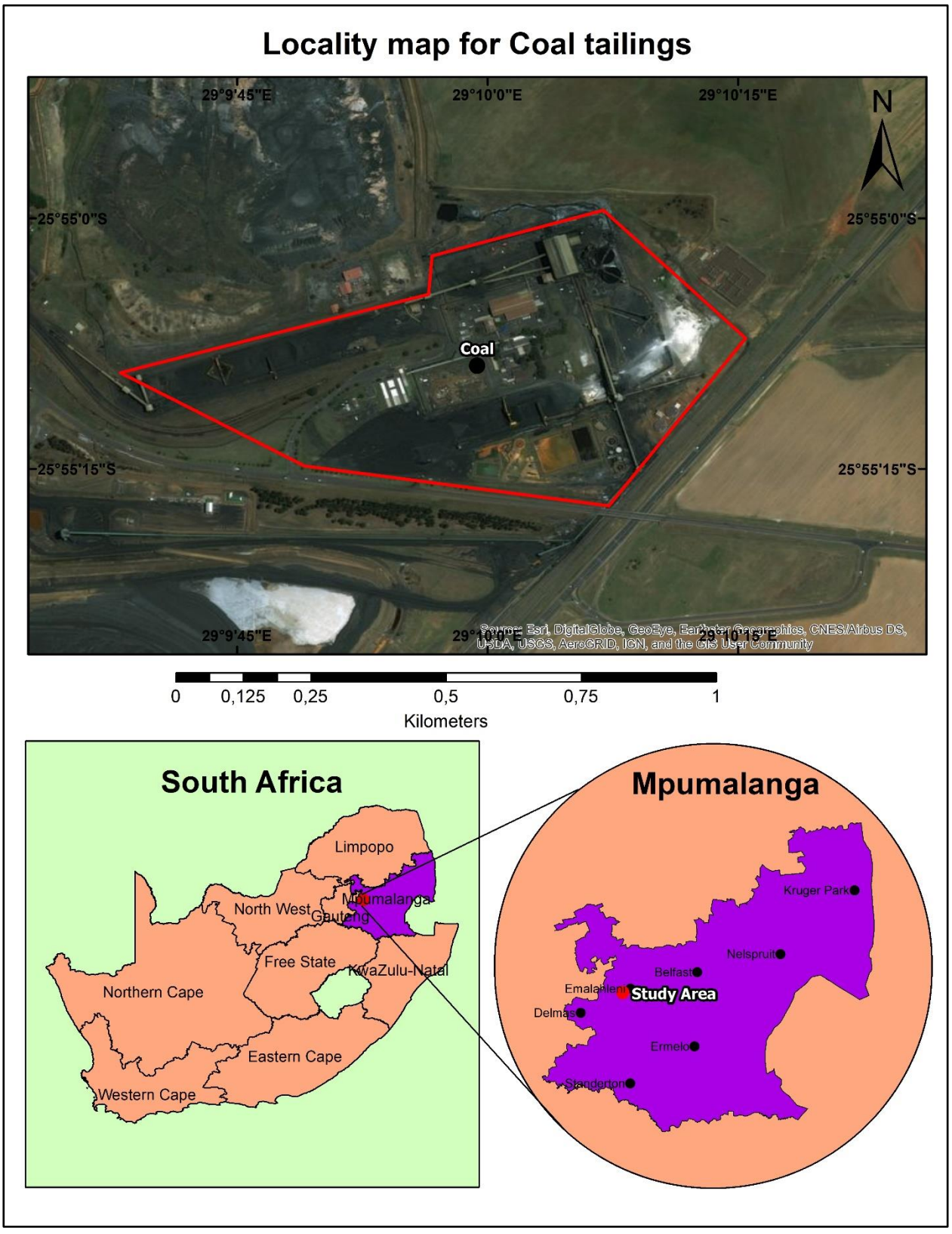


Figure 14: A locality map for Landau mine where the coal tailings material was collected (GIS map compiled by S. Denysschen, 2017).

3.3.1.4 Control medium (soil)

The control medium used in the study was obtained from an experimental farm southwest of Potchefstroom in the North-West Province (Figure 15). The GPS coordinates for the sample location are:

25° 46’ 31.1520” S; 26° 58’ 02.9640” E

The material originates from the Strubenkop formation of the 2 350- to 2 100-million-year-old Pretoria Group, which forms part of the Transvaal Supergroup. Irregular layers of mudstones and siltstones, accompanied by secondary interbedded fine-grained sandstones, are present in this geological formation (Eriksson *et al*., 2006; McCarthy & Rubidge, 2005).

Sediments of the Pretoria Group were deposited under marine conditions that ranged from muddy tidal flats (seen today as mudstones) to shallow marine sands (seen today as very prominent quartzite). As indicated by the Geological Map Series 2626 West-Rand, the lithology of the sample area comprises ferruginous shale and quartzite (Soil and Irrigation Research Institute, 1987).

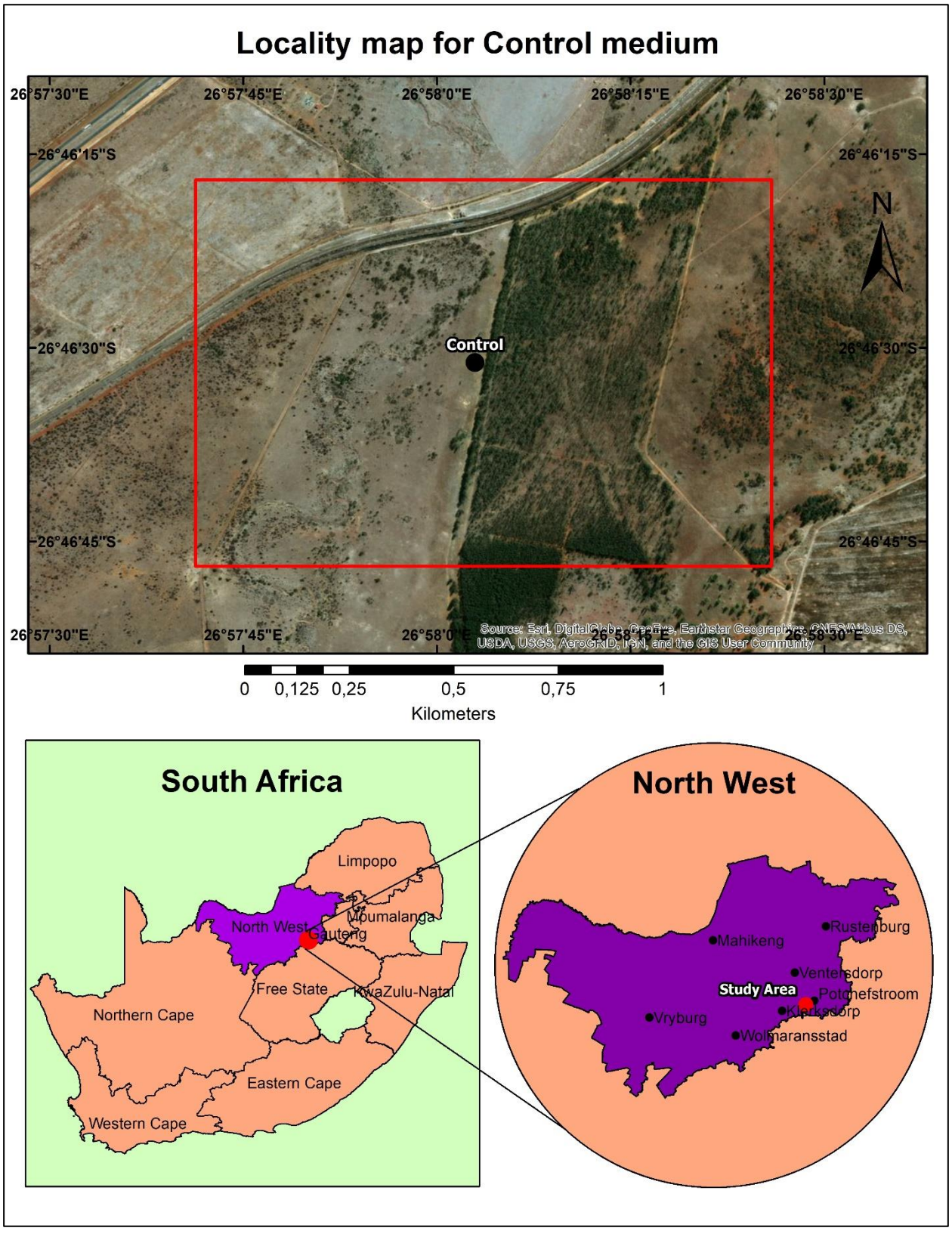


Figure 15: A locality map of the area where the control medium was collected (GIS map compiled by S. Denysschen, 2017).

3.4 Experimental design

3.4.1 Fertiliser pot trials (Phase 2)

The main experimental work of the study was carried out by way of pot trials. The growth mediums were separated into two groups, namely (1) Group A and (2) Group B, illustrated in Figure 16. The growth mediums were treated with lime and superphosphate respectively.

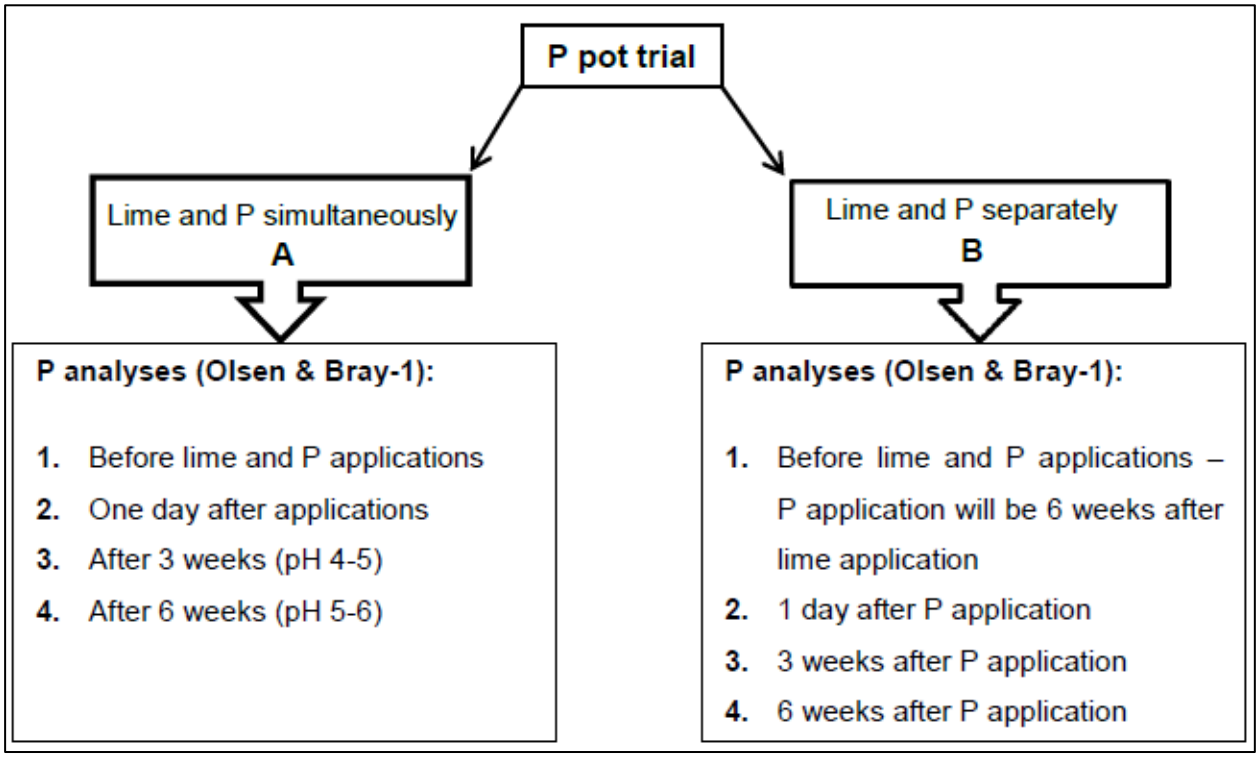


Figure 16: A graphic illustration of the fertiliser pot trial.

As illustrated in Figure 16, the mediums in Group A were treated simultaneously with lime and fertiliser. Phosphorus analyses with the use of the P Bray-1 and the Olsen P methods were conducted one day after, three weeks after and six weeks after the treatments took place. For Group B, the mediums were treated with lime only and left to stand for a neutralisation period of six weeks. This was done to allow the pH(H_2O) of the material to reach a more suitable level (pH 5.5-6.5) for improved plant availability of P. The mediums in Group B were treated with phosphate fertiliser as a superphosphate after the neutralisation period.

In preparation of the fertiliser pot trial, the materials were air-dried, thoroughly mixed and sifted to <2 mm in diameter, apart from the coal tailings that were sieved to <4 mm in diameter. Composite samples of the materials were taken and sent to the laboratories of GeoLab and EcoAnalytica respectively for the determination of the lime and fertiliser requirements. The lime requirements for the materials were given in t/ha, where the values were then recalculated to grams (g) applied to every 10ℓ nursery pot with the use of the dry bulk density (kg.m^3) and the weight of the tailings

in a 10ℓ pot. The lime requirements, as determined by GeoLab, are presented in Table 3. More detailed data on the lime requirements of the growth mediums are presented in Appendix A.

Table 3: Lime requirements and applications for the materials used in the fertiliser pot trial.

Material	Lime requirement (t/ha)
NM700	435
NMC1	56
Crown	25
Coal	200
Control	5

Dolomitic lime with a CCE (HCl) of 104.22% $CaCO_3$ was used throughout the study. The particle size of the dolomitic lime was as follows: 100% < 1.70 mm; 100% < 1.00 mm; 53.64% < 0.25 mm and; 31.44% < 0.106 mm.

Lime was sifted again with a <2 mm sieve before it was mixed with the growth mediums. The reason for this was to ensure evenly spread neutralisation throughout the growth mediums and to increase reaction surfaces; lime has a very low solubility and its neutralising action usually takes place at micro level, very close to the lime particle itself (Van der Watt, 1986).

The P Bray-1 results were used in determination of the superphosphate (8.3) applications. The results from the analyses, as determined by EcoAnalytica, are presented in Table 4. The P application rate was determined with a target growth medium P value of 15 mg/kg. The fertiliser recommendations were all enhanced, as recommended by Aajjane *et al*., (2014) as well as Johnston *et al.* (1991). A study conducted by Johnston *et al.* (1991) lists phosphorus desorption indices (PDI) of a wide range of acidic Natal soils to account for P fixation in acidic growth mediums. It was decided that a PDI of 0.5 (50%) would be used for the purpose of this research; hence, all the recommended applications were multiplied by two.

Table 4: P Bray-1 results and superphosphate applications for the materials used in the fertiliser pot trial.

Material	P Bray-1 (mg/kg)	Superphosphate application to every 10 ℓ pot after incorporation of PDI (g/kg material)	
		Pot trial 1	Pot trial 2
Control	3.25	0.28	0.64
NM700	14.20	0.12	0.40
Coal	14.00	0.02	0.39
NMC1	5.05	0.24	0.60
Crown	3.25	0.28	0.64

The lime and fertiliser ameliorants were weighed before mixing the materials with their respective ameliorants. The ameliorants and a small amount of deionised water were applied to the materials with the use of a cement mixer to ensure a uniform composition and chemical reactivity throughout the pot.

Nursery pots were marked with a weather-resistant permanent marker and placed in an orderly manner in an open area where they would receive the same amount of sunlight and occasional rain (Figure 17).

Figure 17: Photograph showing the various pots after amelioration. The pots were randomly placed afterwards.

Figure 18: Photographs showing the process of composite sampling of the material with the use of a PVC pipe. Photographs were taken by De Necker (2017), with permission.

Composite samples were taken from each pot with the use of a white PVC pipe for the monitoring of pH(H_2O), EC and phosphorus throughout the pot trial (Figure 18). Samples were then dried, sieved and placed in clearly marked re-sealable plastic bags before they were sent to the laboratories for chemical analyses according to the methods discussed in Section 3.4.

A second pot trial (Pot Trial 2) was conducted as a result of doubtful results obtained during the first pot trial for the two materials that received the highest lime applications (i.e. NM700 and coal). The same growth mediums were used with identical sampling methods and lime applications. The target growth medium P value for Pot trial 1 was 30 mg/kg.

This pot trial was conducted to determine the effect of high Ca concentrations on the P Bray-1 method. The concentration of Ca was analysed in the P Bray-1 extract to determine if high concentrations of Ca, as a result of high lime requirements in some tailings materials, influence the suitability of the P Bray-1 method.

The plant-available P was only monitored until three weeks after fertiliser applications due to funding limitations. This is the only difference from the first pot trial where the plant-available P was monitored until six weeks after fertiliser applications.

3.4.2 Seedling survival rate and plant growth experiment (Phase 3)

An experiment to compare seedling survival rates between Group A and Group B of Pot trial 2 was conducted during the month of October 2017. *Eragrostis curvula*, a perennial tuft grass commonly known as Oulandsgras (Afrikaans), Weeping love grass (English), African love grass (English), Matolo (Sesotho), Bojang-jwa-phofu (Tswana) or umSingizane (Zulu), was used for this

experiment. *Eragrostis curvula* is a strong-growing, dense and wide-spread grass species, which generally grows in disturbed soils (Van Oudtshoorn, 2012). As a result of its high biomass, this grass species is regularly used for vegetation establishment on TSFs (Van Deventer, 2015).

The growth mediums were prepared by way of breaking any surface crusts that formed over time (Figure 19). Ten *Eragrostis curvula* seeds, mixed with a small amount of compost, as seen in Figure 20, were sown in each pot and slightly covered with the respective growth mediums. Afterwards, the growth mediums were randomly placed in an area where they would receive generous amounts of sunlight and water from irrigation sprinklers. Germination success and the length of the longest *Eragrostis curvula* leaf in each growth medium in Group A and Group B were recorded after six weeks.

Figure 19: Preparing the control medium for sowing.

Figure 20: *Eragrostis curvula* seeds mixed with compost before sowing.

3.5 Analytical methods

Various chemical and physical properties of the growth mediums used in the study were analysed as part of a baseline assay. The results obtained from the baseline assays, more specifically the lime requirements and the P Bray-1 analyses, were used to determine the amount of lime and fertiliser added to the different growth mediums respectively.

The lime requirements of the growth mediums were determined by the laboratory of GEO LAB. The remaining soil analyses were carried out by the laboratories of EcoAnalytica. The researcher monitored and measured the pH(H_2O) throughout the study herself.

All the material was dried at 40°C and carefully crushed using a pestle and mortar. The samples were sieved with a 2 mm stainless steel sieve to remove particles larger than 2 mm from the sample. Lastly, the samples were placed in individual plastic bags, sealed and marked with a permanent marker.

3.5.1 Lime requirements (NAP/NAG test)

The lime requirements of the growth mediums were determined by means of the Net Acid Production (NAP) or Net Acid Generation (NAG) Test, one of the best-practised static tests for Acid-Base Accounting (ABA) (Saria *et al*., 2006). The NAP/NAG test is an alternative procedure to ABA for the prediction of further acid generation caused by the presence of sulphide minerals in the sample. Therefore, the analysis provided a lime requirement for every material based on future oxidation of pyrite (Usher *et al*., 2003).

Hydrogen peroxide (H_2O_2) was added to the sample to oxidise sulphides (e.g. FeS_2) present in the material to produce sulphuric acid (H_2SO_4). Acid produced during this reaction was instantaneously neutralised by acid-consuming minerals (e.g. carbonates) present in the material (Usher *et al*., 2003).

The pH of the slurry (NAG pH) was determined at the completion of the reaction to deliver a qualitative indication of the acid-generating potential (AP) of the material. The amount of acid present in the slurry was determined by way of titration. The results obtained from the titration were used to calculate the total amount of acid produced by the peroxide digestion, providing a quantitative assessment of the AP (Usher *et al*., 2003). This value was then used to determine a lime requirement for the material, which takes future acidification into account.

The laboratorial method followed for the NAP/NAG test was obtained from the report written by Usher *et al.* (2003). For the analysis, 250 ml of 15% H_2O_2 (at room temperature) was added to 2.5 g of a pulverised (<75 µm) sample in a wide-mouth conical flask. The mixture was then covered with a watch glass and placed in a fume hood where the sample was allowed to react

until fizzing or boiling has stopped. After fizzing has ceased, the sample was gently boiled over a hot plate for a minimum time of two hours or until effervescence stopped. Deionised water was added to the mixture to prevent the sample from boiling dry. The final pH (NAG pH) was then measured after the solution had been allowed to cool to room temperature. Deionised water was added to the flask containing the sample to give a final volume of 250 ml. The solution was then titrated to a pH of 4.5 while stirring with the appropriate NaOH concentration based on the NAG pH reading. Determination of the appropriate NaOH concentration was done as follows:

- NAG pH > 2 = 0.10 M NaOH
- NAG pH < 2 = 0.50 M NaOH

Lastly, a calculation was done to determine the NAG of the material, according to the following formula (Eq. 30):

$$\text{Net acid generation (NAG)} = 49 \times V \times M/W \qquad \text{(Eq. 30)}$$

Where:
NAG = Net acid generation (kg H_2SO_4/t)
V = Volume of base NaOH titrated (ml)
M = Molarity of base NaOH (moles/l)
W = Weight of sample reacted (g)

3.5.2 pH(H_2O)

The pH of the growth mediums was measured with the use of three procedures: the conventional procedure (1:2.5 soil-to-water ratio), the leaching procedure and the incubation procedure. Three different procedures were used to demonstrate why it would better to use the leaching procedure with tailings material that receives much higher lime applications than naturally acidic soils. Measuring the pH of the filtrate or leachate allowed the electrode to measure the immediate pH of the growth medium that received a very high lime treatment. Making use of the conventional procedure, where the suspension is left to stand for 50 minutes, the large amount of lime present in the material is forced to react with the water added to the material during this time. This led to an increase in pH, compared to the leaching procedure. The incubation procedure was used to demonstrate how a prolonged reaction time between the growth mediums and water used to create the soil-water suspension may lead to a higher pH value compared to the leaching method.

The pH meter used throughout the study was calibrated frequently with standard buffer solutions to ensure constant accuracy by compensating for any drift.

3.5.2.1 Conventional procedure

A 1:2.5 soil-to-water ratio suspension was prepared and left to stand for 50 minutes. After 50 minutes, the suspension was mixed with a glass rod and left to stand for another ten minutes. The pH(H_2O) of the suspension was then measured with the use of a multi-functional pH meter (The Non-Affiliated Soil Analyses Work Committee, 1990).

3.5.2.2 Leaching procedure

The pH(H_2O) was determined by way of filtering a 1:2,5 soil-to-water ratio suspension through a qualitative wet, strengthened filter paper (Figure 21), a procedure recommended by the soil scientist and director of GEO LAB (Grond- en Omgewingslaboratorium), Dr Bloem. After allowing all the water to filter through the medium (which takes approximately 15 minutes), a multi-functional pH meter was used to measure the pH(H_2O) of the filtrate.

Figure 21: Photograph illustrating the preparation of the filtrate used to measure pH(H_2O).

3.5.2.3 Incubation procedure

A 1:2.5 soil-to-water ratio suspension was prepared in 250ml Schott bottles. The bottles were then placed in an incubator where the suspensions were shaken at 120 rpm at a constant temperature of 25°C. The pH of the suspensions was measured after 24 hours with the use of a calibrated multi-functional pH meter.

3.5.3 pH(KCl)

For determining the pH(KCl) of the growth mediums, a dry 10 g sample of the selected growth medium and 25 ml KCl solution (1 mol.dm^{-3}) was mixed rapidly in a container for five seconds by using a glass rod. The mixture was mixed again after 50 minutes and allowed to stand for ten minutes. The pH of the solution was then measured with a calibrated pH meter and reported as pH(KCl) (The Non-Affiliated Soil Analyses Work Committee, 1990).

3.5.4 Electrical conductivity (EC)

The electrical conductivity (EC), recorded in mS.m^{-1}, was measured by way of the saturated extract method, as described in detail by The Non-Affiliated Soil Analyses Work Committee (1990). Deionised water was added to 250 g of the selected growth medium until the medium exhibited the properties of a saturated paste. Suction was applied to filter the paste through Whatman no. 50 paper in a Richards funnel, where the filtrate (saturation extract) was collected in a test tube.

A conductivity cell was calibrated with a 0.01 mol.dm^{-3} KCl solution with an EC of 141.18 mS.m^{-1} at 25 °C. After calibration, the conductivity cell was rinsed with the saturation extract to determine its electrical conductivity. This value is indicative of the total amount of dissolved salts present in the saturated extract.

3.5.5 Particle size distribution (PSD)

The particle size distribution (PSD) was determined by a mechanical method (sieving) and a hydrometer method and grouped into seven particle size classes as described by The Non-Affiliated Soil Analyses Work Committee (1990). A known mass of the sample was mechanically sieved through a series of sieves. After sieving the sample, the different sieves were weighed and recorded to calculate the weight percentage of the sample gathered in each sieve respectively. The sample was then classified into seven size classes, namely:

- course sand (2 – 0.5 mm)
- medium sand (0.5 – 0.25 mm)
- fine sand (0.25 – 0.106 mm)
- very fine sand (0.106 – 0.05 mm)
- coarse silt (0.05 – 0.02 mm)
- fine silt (0.02 – 0.002 mm)
- clay (<0.002 mm)

The hydrometer method, based on Stoke's Law, was used to determine the weight percentages of the silt and clay fractions (The Non-Affiliated Soil Analyses Work Committee, 1990).

3.5.6 Cation exchange capacity (CEC) and nutrient status

The cation exchange capacity (CEC) and the exchangeable and water-soluble cations were used to determine the nutrient status of the growth mediums. For this analysis, 10 g of the sample was mixed with 50 cm^3 ammonium acetate (1 $mol.dm^{-3}$). The ammonium acetate served as the extractant for exchangeable and water-soluble cations. This action saturated the exchange complex of the sample with an index cation (e.g. NH_4^+) by dislocating the exchangeable cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) from the exchange complex. The index cation was then displaced by a cation from another salt solution (e.g. K^+ from KCl). The CEC, recorded in cmol (+)/kg, was determined by way of steam distillation. Steam distillation separated the ammonia, where the amount of ammonia obtained (determined by titrating the solution with 0.05 $mol.dm^{-3}$ H_2SO_4) is equal to the CEC of the sample (The Non-Affiliated Soil Analyses Work Committee, 1990).

The calculation for determining the CEC of the sample was done with the use of the formula represented in Equation 31, as explained in detail by The Non-Affiliated Soil Analyses Work Committee (1990):

$$\text{Cation exchange capacity (CEC)} = (T_1 \times 20) - (X_2 - X_1) \times 0.2 \times T_2 \qquad \text{(Eq. 31)}$$

Where:

T_1 = Titration value for KCl solution

T_2 = Titration value for ammonium acetate solution

X_1 = Mass of tube plus sample (g)

X_2 = Mass of tube plus occluded solution (g)

3.5.7 Aluminium saturation (extractable or exchangeable Al)

The extractable aluminium (Al) was determined with the use of the KCl (1 $mol.dm^3$) as described by The Non-Affiliated Soil Analyses Work Committee (1990). The method is suitable for up to 200 $mg.kg^{-1}$ Al in a growth medium. This analysis entailed a treatment with an unbuffered salt (e.g. KCl) to displace extractable or exchangeable Al from the exchange complex. The concentration of displaced Al in the KCl extract was then recorded. Being a component of extractable acidity, the proportion of extractable Al can vary between 30 and 90%, depending on various properties of the growth medium (e.g. organic matter content, clay mineralogy, etc.).

For the extraction, 5 g of the sample was placed in a 100 cm^3 polythene centrifuge tube whereto 50 cm^3 of 1 $mol.dm^3$ KCl extractant was added. The sample was then shaken at 180 rpm for a duration of 30 minutes and centrifuged at 2 500 rpm for ten minutes. The mixture was filtered through Whatman no. 42 filter paper into an appropriate container. It was important to maintain

a temperature of 20 °C (±2 °C) throughout the duration of the extraction (The Non-Affiliated Soil Analyses Work Committee, 1990).

To determine the concentration of displaced Al in the extract, 1 cm^3 of the prepared extract was transferred into a small conical flask. A mixture of 10 cm^3 $mol.dm^3$ KCl, 10 cm^3 hexamine buffer, 10 cm^3 ascorbic acid and 10 cm^3 CAS reagent was added to the extract. The mixture was allowed to stand for a duration of 20 minutes before the absorbance was recorded at 567 nm against standards that were prepared beforehand (The Non-Affiliated Soil Analyses Work Committee, 1990).

The amount of Al saturation was then calculated according to Equation 32:

Al in growth medium ($mg.kg^{-1}$) = (k x 50) / 5 (Eq. 32)

Where:
k = Al content of KCl extract ($mg.dm^{-3}$)

3.5.8 Phosphorus (P)

Soluble P was determined by using two methods throughout the study, namely the P Bray-1 method and the Olsen P method. Two methods were used, the reason for which is that the suitability of the methods is dependent on the pH of the growth medium as well as the amount of $CaCO_3$ present in the growth medium.

As explained by Iatrou *et al*., (2014), the Olsen P method was developed to extract P in soils with pH values higher than 5. Where growth mediums are more acidic than pH 5, the Olsen P method will overestimate the amount of plant-available P. This method delivers the best results in calcareous soils with $CaCO_3$ values of greater than 2%. The 0.5 M $NaHCO_3$ extracting agent increases the solubility of P by way of decreasing the concentration of soluble Ca^{2+} through precipitation as $CaCO_3$ as well as soluble Fe^{3+} and Al^{3+} through the formation of Al and Fe oxyhydroxides. The alkaline extractant increases the pH of the solution further, decreasing the number of sorption sites and/or increases negative surface charges, which increases the desorption of P into solution (Sims, 2002b).

The Bray-1 method uses an acidic extracting agent (NH_4F and HCl) with a pH of 2.6 to solubilise Al, Ca and Fe phosphates through the protonation of PO_4^{3+} and the formation of Al^{3+} and Fe^{3+} complexes (Hahne *et al*., 1988; Sims, 2002a). This method should not be used on calcareous growth mediums, growth mediums with a pH >6.8, high base saturation values or large amounts of lime ($CaCO_3$ >2%) (Sims, 2002a). Sims (2002a) explains that when this method is used on growth mediums that have been treated with large amounts of lime, soluble Ca^{2+} from the lime

reacts with the F^- in the extracting agent and forms CaF_2, which immobilises P and reduces the efficiency of this P-extracting method. The large amount of lime also has the ability to neutralise the acidic extracting agent.

3.5.8.1 Olsen P method

The Olsen P method, also used by Antoniadis *et al*. (2015) and Poozesh *et al*. (2010) in their studies, is based on an extraction with 0.5 M sodium bicarbonate ($NaHCO_3$) to provide an index of plant-available P (ortho-phosphate) present in a growth medium. This method of P extraction was originally created for calcareous soils but Pretorius (1991) also states its usefulness for non-calcareous soils. A standard operating procedure issued by the International Rice Research Institute (IRRI) was used in the determination of plant-available P for the Olsen P method. As explained by IRRI (2011), a mixture of 2.5 g growth medium and 50 ml of 0.5 M $NaHCO_3$ with a pH of 8.5 was shaken at 180 rpm for 30 minutes. A filtrate was then prepared by way of filtering the mixture through Whatman no. 2 filter paper, whereafter 1 ml HCl was added to the filtrate (Figure 22).

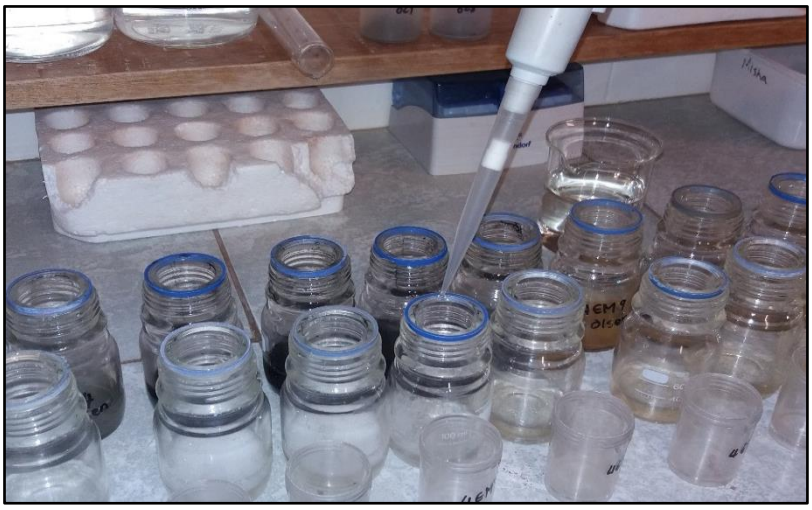


Figure 22: A photograph taken during the addition of 1 ml HCl to the filtrates.

The plant-available P was then determined colourimetrically with a continuous flow analyser by mixing the filtrate with ammonium molybdate using ascorbic acid ($C_6H_8O_6$) as the reducing agent.

3.5.8.2 P Bray-1 method

A mixture of 4 g growth medium and 30 ml P Bray solution (0.03 M NH_4F and 0.10 M HCl) were shaken at 180 rpm for 30 minutes. The mixture was then filtered through Whatman no. 2 filter paper (Figure 23) to create the extracts or filtrates used to measure the extractable P in the growth mediums. The extractable P was determined colourimetrically by a continuous flow analyser

where the concentration of extractable P was measured against the standard solutions (The Non-Affiliated Soil Analyses Work Committee, 1990).

Figure 23: Preparation of the P Bray-1 extracts.

After measuring the pH of the P Bray-1 extracts with a calibrated benchtop pH meter, the calcium (Ca) concentrations in the P Bray-1 extracts were determined by way of placing 5 ml of the extract in 50 ml volumetric flasks. The flasks were then filled up with a 1:100 Lanthanum (La) solution (Figure 24). The Ca concentration in the Bray-1 extract was determined by way of atomic absorption with the use of an auto analyser at the Eco Analytica laboratory.

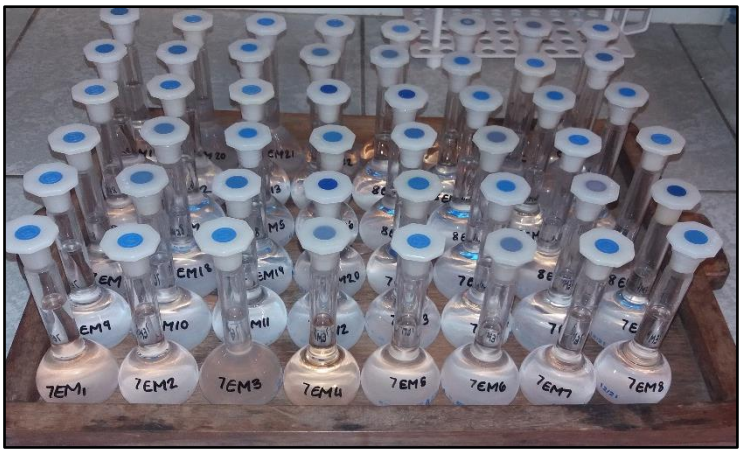


Figure 24: Volumetric flasks containing 5 ml Bray-1 extract and 45 ml Lanthanum solution.

3.6 Data analysis

Excel 2016 was used for data sorting and presentation. Pearson correlation coefficients (r) and p-values obtained by way of XLSTAT correlation analyses were used to describe the data obtained from the study, as seen in Chapter 4.

A correlation analyses, also called a correlation test, is a tool to calculate the association or relationship between two or more quantitative variables (Gogtay & Thatte, 2017). Correlation

analyses conducted with the use of XLSTAT deliver different kinds of correlation coefficients between variables and also state whether these correlations are statistically significant or not (XLSTAT, 2017).

The Pearson correlation coefficient, which can have a value between -1 and 1, describes the linear relationship between two ratio or interval variables being studied. This correlation measure assesses the association between two variables to determine whether they share variance, if the relationship between the variables is positive or negative, and the degree to which they correlate (Chee, 2015; Gogtay & Thatte, 2017).

ANOVA analyses were also conducted on the data to confirm statistical significance between different variables.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The results obtained throughout the study are presented and discussed in this chapter. The results are discussed in separate sections as the study has been conducted in three phases. The discussion of the results is presented in the following sequence:

1. **Phase 1:** Initial neutralisation incubation pot trial used for material selection
2. Textural characteristics of the growth mediums
3. Chemical characteristics of the growth mediums
4. Results of pH(H_2O) monitoring with the use of three different procedures
5. **Phase 2:** The effect of a neutralisation time lag of six weeks on the availability of phosphorus in the growth mediums (Pot trial A and B)
6. The effect of high Ca concentrations (as a result of high lime requirements) on the suitability of the Bray-1 method
7. **Phase 3:** The effect of a neutralisation time lag between lime and fertiliser applications on seedling survival rates in the growth mediums

4.2 Phase 1: Initial neutralisation incubation pot trial

As previously discussed, a neutralisation incubation pot trial was conducted at the beginning of the research project to identify the materials that would be used for the main experimental work. Thirteen different mine waste tailings from all over South Africa were used along with a naturally acidic soil, which served as the control medium throughout the research project.

Four tailings with varying lime requirements and varying results obtained during the neutralisation incubation pot trial were identified. They were (1) NM700, (2) NMC1, (3) Crown and (4) coal.

The change in pH (H_2O) of the tailings and the control medium (soil) over a period of seven weeks under natural conditions is presented in Figure 25. The data for the rest of the tailings used in the neutralisation pot trial are shown in Appendix F.

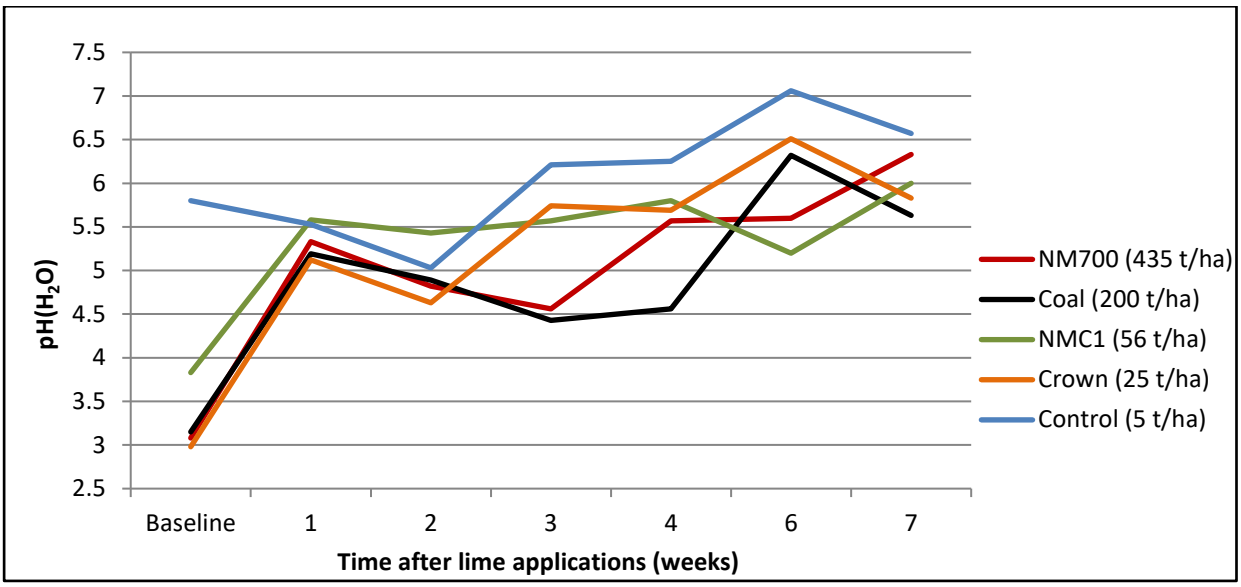


Figure 25: Change in pH(H_2O) of the growth mediums identified in the neutralisation pot trial over a period of seven weeks after lime treatment.

The results of the four identified tailings and the control medium obtained from the neutralisation pot trial are presented in Figure 25. The lime requirements of the respective growth mediums are presented in the legend. Average pH values were calculated from the three replicas of each material.

As evident in Figure 25, the pH(H_2O) of the mediums fluctuated greatly over the seven-week incubation period. These fluctuations are due to oxidation reactions that take place continuously, which can be amplified by the addition of water (i.e. rainfall) and an increase in temperature. The pH(H_2O) data obtained in week 5 were discarded as a result of a faulty pH meter. At week 6, the pH of all the mediums reached a pH >5.0. After week 6, the mediums acidified yet again as a result of continuous oxidation reactions taking place in the tailings material as well as the control medium.

The trial study ultimately proved that the degree of acidity in tailings material is ever-changing as long as there are unoxidised FeS_2, Fe^{3+} and Al^{3+} present in the material. Different pools of acidity exist in these growth mediums, accompanied by constant oxidation reactions that take place (Bloem, 2015; Van der Nest, 1991; Van Deventer, 2015; Van Deventer *et al*., 2007). This makes it a challenging task to identify an appropriate time for fertiliser treatments.

It was, therefore, decided that the most suitable time to apply P fertiliser is six weeks after lime treatment because all of the growth mediums reached a pH(H_2O) reading of >5.0.

The survival rate and growth performance of germinated seedlings may increase due to increased plant-available P. This will aid in ensuring initial ecosystem stabilisation owing to increased growth medium quality. Through obtaining initial ecosystem stabilisation, microbial communities

may start to settle within the system. This will further increase the quality of the tailings as a growth medium, allowing surrounding indigenous grass species that are adapted to the area and more tolerable to acidic growth environments to freely establish on the tailings material over time (Schimmer *et al*., 2015; Van Deventer & Hattingh, 2008).

4.2.1 Summary

The objective of Phase 1 was to identify a neutralisation incubation period for improved plant availability of P that could be used over a wide range of sulphide-rich acidic tailings. This was done by monitoring the change in pH of several acidic tailings over a period of seven weeks after lime treatment.

It was concluded that the most suitable neutralisation incubation period for sulphide-rich acidic tailings is six weeks after lime treatment.

The results obtained from Phase 1 of the study supported the first sub-hypothesis of the study in that the time lag of neutralisation of different acidic tailings varies due to different pools of acidity and ongoing acidification reactions within the tailings.

4.3 Textural characteristics of the growth mediums

Figure 26 shows a soil texture triangle for all of the growth mediums used in the study. Data for the textural characteristics of the growth mediums can be seen in Appendix C. The textural class of a growth medium is based on the various sizes of individual particles in a specific growth medium. Based on their size and shape, the particles are divided into three categories (sand, silt or clay). A final textural class is then allocated to the growth medium, based on the relative proportions of sand, silt or clay present in the sample. Sand particles are between 2.0 and 0.05 mm in diameter, silt particles are between 0.05 and 0.002 mm in diameter and clay particles are less than 0.002 mm in diameter (GKWG, 1991; Winegardner, 1995). There are 12 different major soil textural classes, namely sand, loamy sand, sandy loam, loam, silty loam, silt, sandy clay loam, silty clay loam, clay loam, sandy clay, silty clay and clay. A textural triangle can be used to determine and graphically illustrate the textural class name of a growth medium based on the results of a particle size analysis (Brady & Weil, 2008; Jones, 2012).

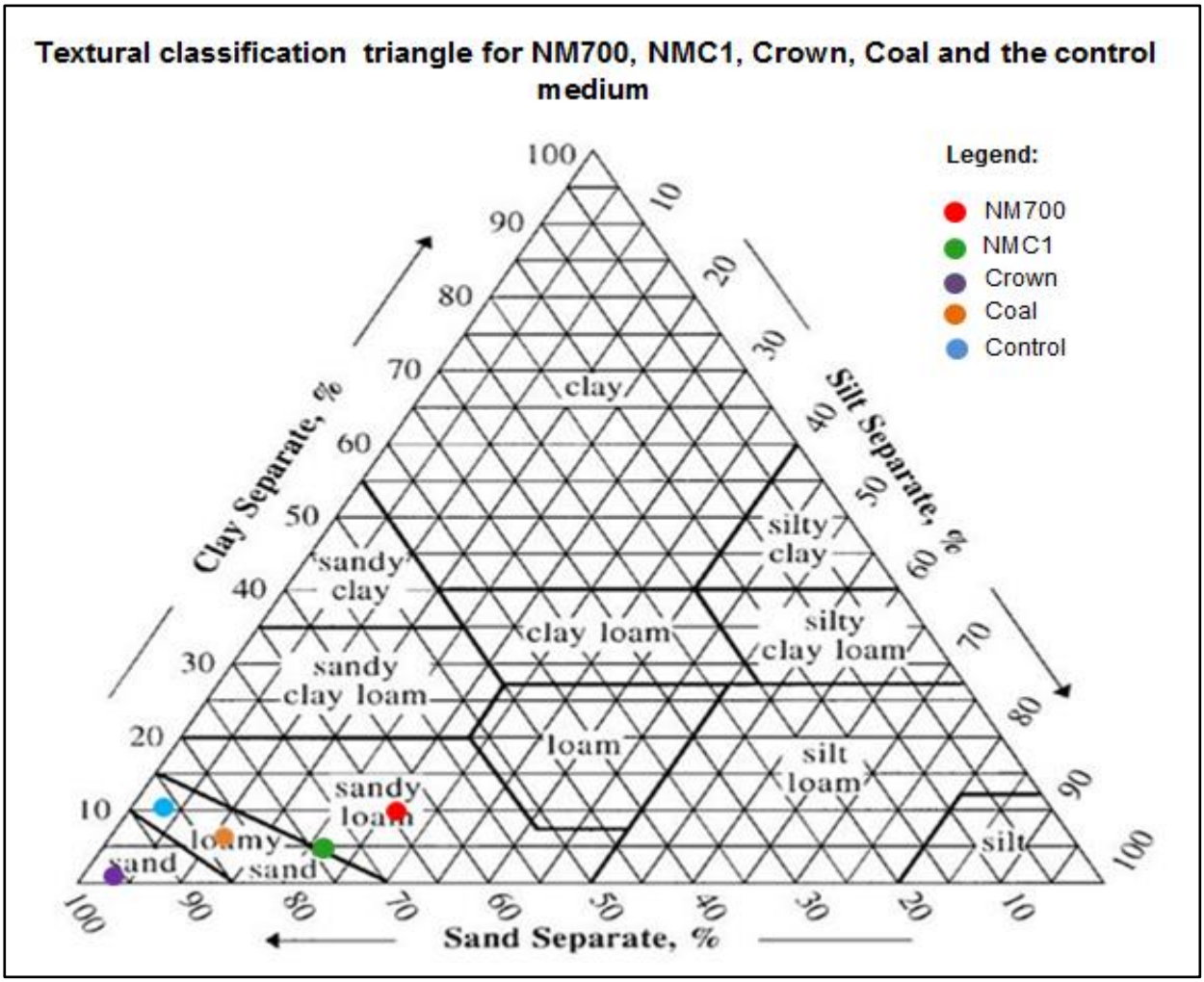


Figure 26: Textural classification triangle illustrating the textural classes of the growth mediums used in the study.

As shown in Figure 26, the sandy texture dominates the texture results. The Crown tailings were classified as sand, whereas the coal tailings and the control medium were classified as loamy sands. Both of the New Machavie tailings (NM700 and NMC1) were classified as sandy loams. The sandy texture of the growth mediums may be attributed to their geological origins. The conglomerates of the Witwatersrand Supergroup and the quartzites contained in the Transvaal Supergroup all weather to sandy soils due to the high concentration of quartz (SiO_2) in these rocks. The geology of the control medium also contains irregular layers of mudstones and siltstones, which explains the higher amount of silt present in this medium. On the other hand, the loamy sand texture of the coal tailings is attributable to the fact that the coal has undergone some degree of processing.

4.4 Baseline chemical characteristics of the growth mediums

The chemical characteristics of the growth mediums used in the study are presented in Figures 27 to 31.

Data for the chemical characteristics of the growth mediums can be seen in Appendix B. On account of financial constraints experienced throughout the research period, composite samples of the growth mediums were used to conduct the baseline analyses. Throughout this study, the term "baseline" refers to the value of a specific chemical attribute (e.g. pH, EC, P Bray-1, Olsen P, etc.) before any applications or ameliorants have been added to a specific growth medium.

4.4.1 Baseline pH(H_2O) and EC values

Figure 27 provides baseline pH(H_2O) and electrical conductivity (EC) values for the growth mediums used for the main experimental work. These baseline pH(H_2O) values were determined with the conventional 1:2.5 soil-to-water ratio suspension as described in Section 3.5.2. The EC values were determined as described in Section 3.5.4.

Figure 20 shows that the control medium had the highest pH(H_2O) value and the lowest EC value. The coal and NM700 growth mediums were among those with the lowest pH(H_2O) values and by far the highest EC values. NMC1 was the tailings material with the highest baseline pH(H_2O) value, whereas Crown showed the lowest EC value.

All of the growth mediums are extremely acidic (Sparks, 2003; Winegardner, 1995) which may cause many problems with regard to vegetation establishment. The availability and phytotoxicity of plant nutrients and other elements (e.g. Fe, Al, S, B, Cu, Mo, Zn, etc.) are directly influenced by the pH(H_2O) of a growth medium. Very low pH(H_2O) conditions may result in toxic levels of Al^{3+}, Mn^{2+} and other metal ions, as well as deficiencies in plant nutrients such as Ca, Mg, P and Mo (Foy, 1984; Hossner & Hons, 1992; Viljoen, 2013).

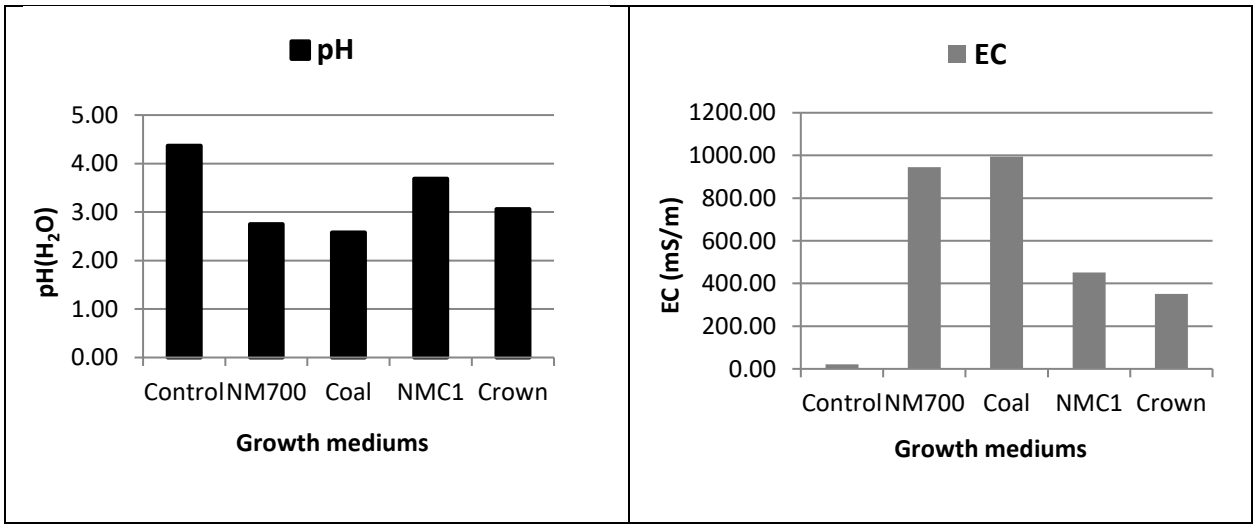


Figure 27: Baseline values for pH(H_2O) and electrical conductivity (EC) of the growth mediums used in the study.

According to a figure published in Beegle (2001) (Figure 1 in Chapter 2), all of the growth mediums, especially the tailings materials, will have insufficient amounts of plant-available P, accompanied by toxic levels of Al (pH < 4.0), Fe, Cu and B because of their extremely acidic nature. This will have limiting effects on plant growth, as explained by Poozesh *et al*. (2010).

In accordance with Beegle (2001), P is optimally available for plant use at pH(H_2O) values between 6.5 and 7.5. Beegle (2001) also illustrated that the plant availability of P starts to decrease at a pH(H_2O) of <6.5 and is least available at a pH(H_2O) of <4.0, whereas Hazelton and Murphy (2007) stated that P availability is reduced at pH(H_2O) of <5.0. All of the tailings material showed pH(H_2O) values of <4.0, meaning that very little, or zero, P applied in the form of fertiliser at this pH level, will be available for plant use.

Plants absorb phosphorus in the form of $H_2PO_4^-$ and HPO_4^{2-} to a smaller degree (Brady & Weil, 2008; Pretorius, 1991; Strioa *et al*., 2013). The type of orthophosphate ion present in the solution phase of a growth medium is determined by the pH(H_2O) of the growth medium (Hansel *et al*., 2014). As per Figure 8 in Chapter 2 of this report, it is evident that the orthophosphate ion species present in the solution phase of the growth mediums is $H_2PO_4^-$. The H_3PO_4 species is also present in the solution, but in much smaller concentrations.

When comparing the baseline pH(H_2O) values of the growth mediums with their respective lime requirements and total S percentages (%) (shown in Appendix A), it can be seen that growth mediums with higher baseline pH(H_2O) values overall show lower total S percentages along with lower lime requirements and vice versa. The opposite may also be true; that is why lime requirements determined by way of NAP/NAG analyses take future pyrite oxidation and, therefore, the generation of more acidity into account (Usher *et al*., 2003).

The importance of using the total S% of a growth medium, especially tailings material, is explained through growth mediums that have higher lime requirements than others with lower pH(H_2O) values (e.g. NM700 vs. coal and Crown vs. NMC1). Even though NM700 has a higher baseline pH(H_2O) than coal, it showed to have a much higher lime requirement (435 t/ha) than the coal medium (200 t/ha). This is attributable to the total S% value of the growth mediums; where the value for NM700 is 3.34%, that is, a great deal higher than for coal (1.64%). This means that NM700 has more unoxidised sulphur present in the material. Therefore, more lime must be applied to this material to neutralise acidity generated through future pyrite (FeS) oxidation.

The electrical conductivity (EC) of a growth medium, a measure of salinity which is recorded in mS/m, is a quantification of its ability to conduct electricity, which is directly related to the concentration of soluble salts or solutes in the soil solution (Brady & Weil, 2008; Grondklassifikasiewerkgroep, 1991; Van Deventer & Hattingh, 2008). All of the growth mediums

used in the study, except for the control medium, showed extremely high EC values ranging from 351 mS/m to 995 mS/m. The coal, NM700 and NMC1 tailings showed EC values much higher than the critical value of 460 mS/m reported by Daniell (2015) and Van Deventer (2015).

Damage caused by highly saline growth mediums commonly takes place during the germination and early growth stages (Van Deventer & Hattingh, 2008). High EC values in growth mediums make it difficult for plant roots to absorb water as a result of decreased osmotic potential (Brady & Weil, 2008). This means that the plant will use more energy to absorb water from the growth medium and to biochemically alter itself to survive in highly saline conditions such as these (Khozhina & Sherriff, 2006). The critical EC of a growth medium where growth is affected, depends largely on the plant species (Van Deventer & Hattingh, 2008).

Neutralising the growth mediums with the addition of lime will lead to an increase in base cations, increasing the EC of the growth mediums and, therefore, giving rise to a higher level of salinity (Khozina & Sherriff, 2006).

High concentrations of dissolved SO_4^{2-} ions in the coal (32 950.16 mg/l), NM700 (31 749.33 mg/l), NMC1 (11 092.59 mg/l) and Crown tailings (6 088.49 mg/l) owing to pyrite oxidation, contribute greatly to the particularly high EC readings. The results for Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} anion concentrations are presented in Appendix B.

The high SO_4^{2-} concentrations were clearly observed in the precipitation of $CaSO_4$ (gypsum), a week after the growth mediums were treated with lime in the initial neutralisation incubation pot trial (Appendix U). These observations coincide with the results obtained in a study done by Jurjovec *et al*., (2002) on acid neutralisation mechanisms in mine tailings. They found that SO_4^{2-} concentrations decreased at the beginning of their neutralisation experiment. The dissolution of carbonates (from the lime) enrich the solution phase with Ca, which causes SO_4^{2-} ions to react with the Ca^{2+} ions and precipitate as $CaSO_4$. Concentrations of SO_4^{2-} will increase again after the carbonate mineral sources are depleted (Jurjovec *et al*., 2002).

4.4.2 Baseline P Bray-1, Olsen P and pH(H_2O) values

As previously stated, phosphorus (P) levels were measured with the use of two methods: the Bray-1 method and the Olsen method. Figure 28 shows the baseline P Bray-1, Olsen P as well as pH(H_2O) results of the growth mediums used for the main experimental work of the study.

The P Bray-1 levels for the control medium, Crown and NMC1 are rated as “low”, whereas the P Bray-1 levels for NM700 and coal are rated as “medium” (Clements & McGowen) (as cited in Hazelton & Murphy, 2007).

According to Clements and McGowen (as cited in Hazelton & Murphy, 2007), the Olsen P values are “low” for all of the growth mediums presented in Figure 21.

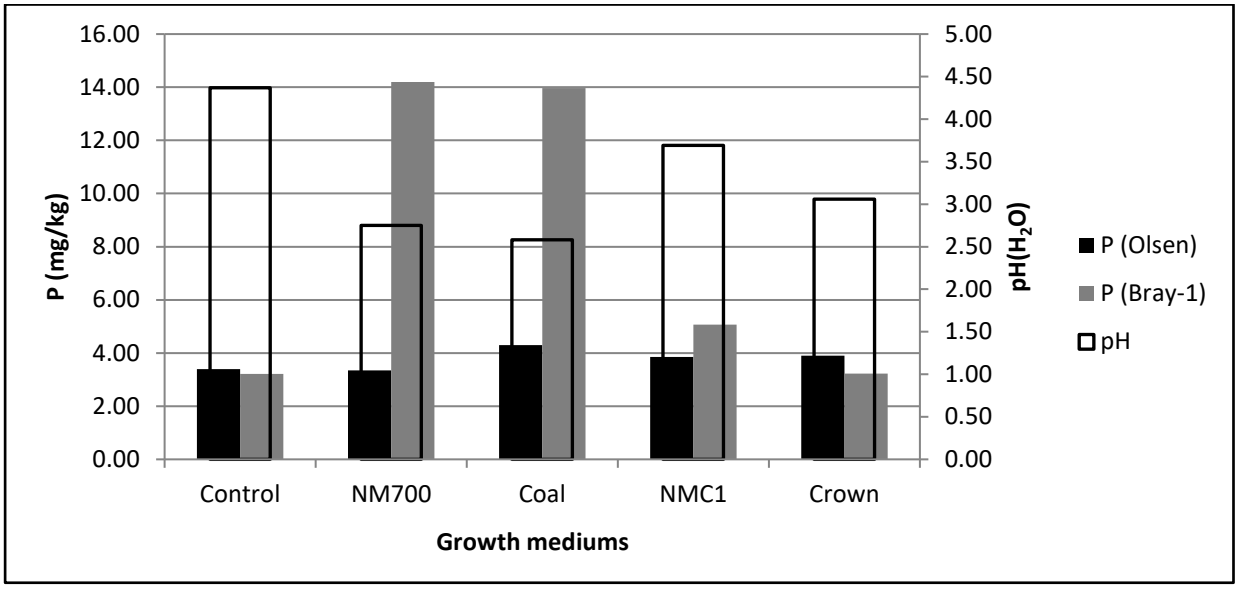


Figure 28: Baseline P Bray-1, Olsen P and pH(H_2O) results.

The difference between the results obtained from the Bray-1 and the Olsen analyses can be explained through the pH(H_2O) of the growth mediums (Figure 28). The Bray-1 method was initially designed for acidic growth mediums. On the other hand, the Olsen method delivers the best results when used on calcareous growth mediums with $CaCO_3$ >2% and pH values >5.0 (Iatrou *et al*., 2014; Sims, 2002a, 2002b).

The Bray-1 results are much higher than the Olsen results for the reason that all of the growth mediums have baseline pH values of >4.5, with coal showing the lowest baseline pH of 2.58. At these low pH levels accompanied by high Al saturation values, most of the P present in the growth mediums are in the form of Al phosphates or Al oxides (Costa *et al*., 2016; Stevenson, 1986). Sims (2002a) explains that the acidic extracting agent (pH <2.6) dissolves available forms of P from Al, Ca and Fe phosphates or oxides. The Olsen method, which is based on the use of a $NaHCO_3$ with an alkaline pH of 8.5, does not have this ability.

The pH(H_2O) results for all of the growth mediums are very low (<4.0 for the tailings material and just above 4 for the control medium). This means that the P present in the growth mediums is mostly unavailable for plant use (Hazelton & Murphy, 2007).

4.4.3 Cation exchange capacity (CEC) values

Figure 29 provides CEC values for the growth mediums used in the main experimental work of the study. The CEC value of a growth medium, measured in cmol(+)/kg, is a quantification of its ability to adsorb exchangeable cations from the soil solution (Brady & Weil, 2008). Exchangeable

cations are cations that are adsorbed weakly onto mineral particle surfaces. These cations can be easily displaced by another cation from the surface of the negatively charged particle into the soil solution (Van Deventer & Hattingh, 2008).

The NMC1 tailings material showed the highest CEC value among all of the growth mediums used in the study, whereas the CEC value for the Crown tailings material was the lowest. This means that, in terms of being a growth medium for plants, the individual particles of the NMC1 tailings have the greatest capacity to attract and exchange cations with the surrounding soil solution. The CEC values for NMC1, coal, NM700 and the control medium can all be classified as “moderate” (CEC = 12-25 cmol(+)/kg), while the CEC value for the Crown tailings is classified as “low” (CEC = 6-12 cmol(+)/kg) (Hazelton & Murphy, 2007).

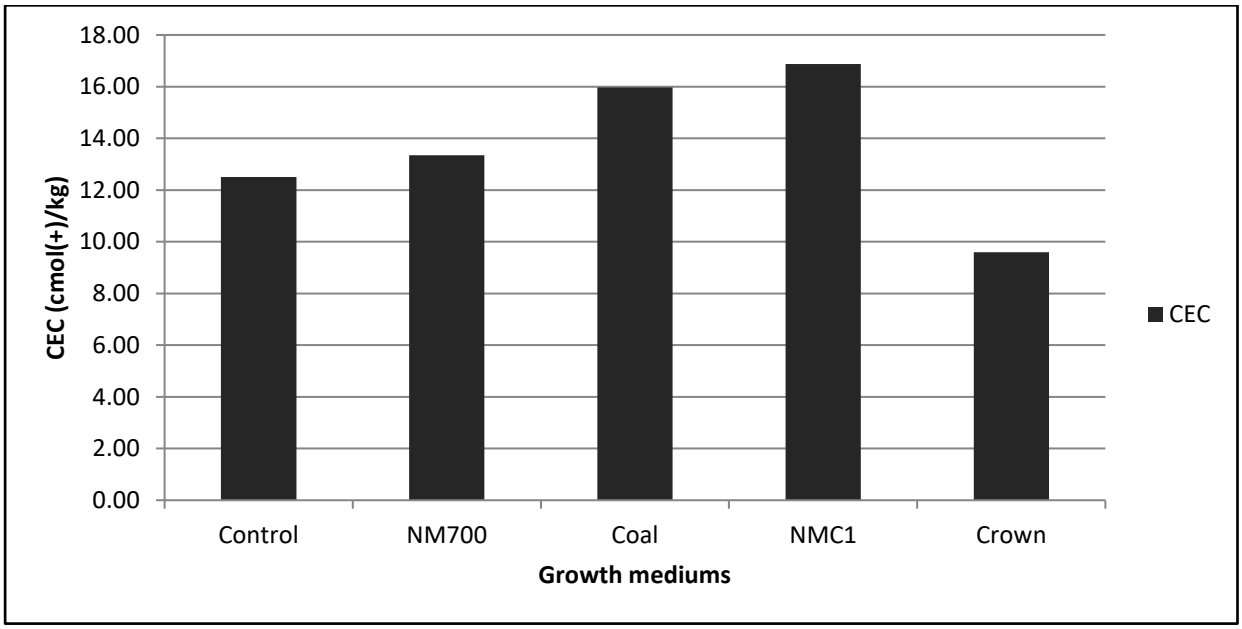


Figure 29: Cation exchange capacities of the growth mediums used in the study.

4.4.4 Exchangeable cations

The values for exchangeable cations (cmol(+)/kg) are presented in Figure 30. These values are representative of the amount of each cation as a proportion of the total CEC of the growth medium (Hazelton & Murphy, as cited in Myburgh, 2015).

The control medium showed very low levels of Ca and low levels of Mg, K and Na. All of the tailings material showed very low levels of K and Na. The NM700 tailings showed high levels of Mg accompanied by low levels of Ca, whereas moderate levels of Ca and Mg were present in the NMC1 tailings. The Crown tailings showed low levels of Ca and Mg, while the coal tailings showed moderate levels of Ca accompanied by low levels of Mg (Hazelton & Murphy, 2007).

All of the samples showed very low to low Na levels, with exchangeable sodium percentage (ESP) values of ≤1.04%. This can be seen as a positive attribute because these low levels indicate that erosion as a result of dispersion will not occur (Van Deventer, as cited in Myburgh, 2015).

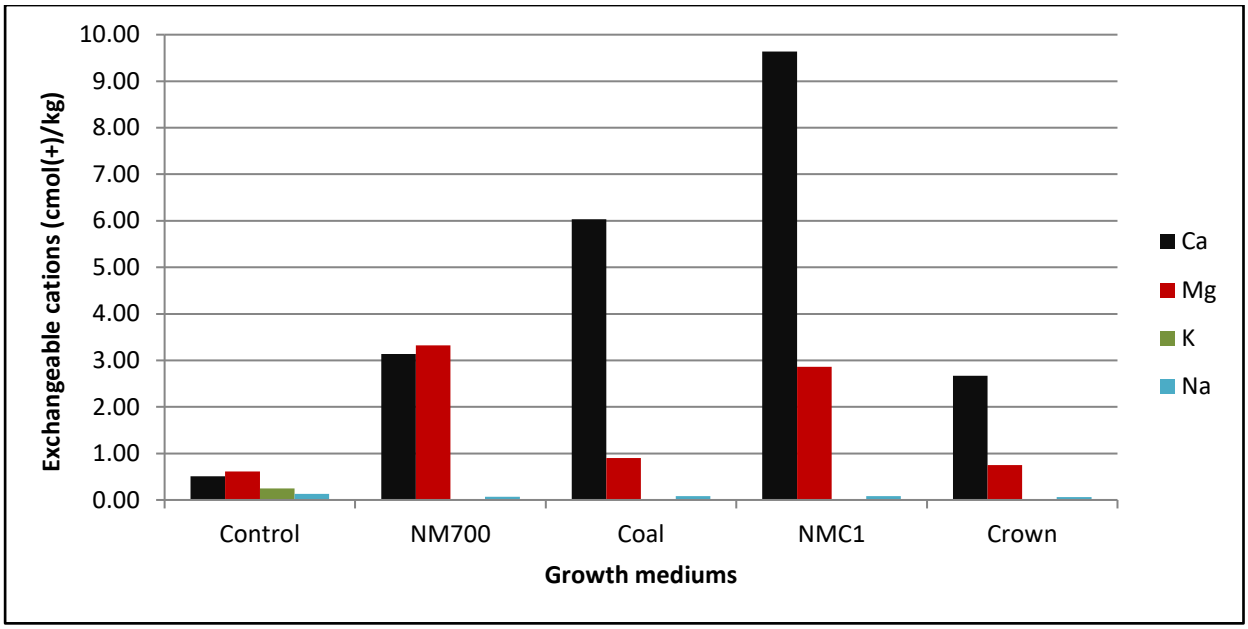


Figure 30: Baseline values for exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) of the growth mediums used in the study.

The exchangeable cation concentrations of the different tailings presented in Figure 30 are representations of not only the mineralogy and geochemistry of the host rock, but also the processing chemicals used to extract the economic minerals from the ore (Kossoff *et al*., 2014). This is proven through the higher concentrations of Ca and Mg found in the gold tailings materials, compared to those of the control medium. The main source of Ca and Mg present in these tailings is the calcitic or dolomitic lime used during the chemical extraction process (Beukes *et al*., as cited in Versfeld *et al*., 1998).

4.4.5 Aluminium and base saturation

Figure 31 illustrates the relationship among the aluminium (Al) saturation, base saturation and pH(H_2O) values of the growth mediums used in the study. The Al saturation (%) value represents the amount of exchangeable Al (Al^{3+}) as a percentage of the CEC of the growth medium (Baquy *et al*., 2017). As defined by Hazelton and Murphy (2007), the base saturation (%) of a growth medium is the percentage of its CEC that is saturated with Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} cations.

The control medium showed to have a very low base saturation value, accompanied by a higher Al saturation value. The NM700 and coal tailings had the highest Al saturation values by far with much lower base saturation results. These two growth mediums also had the lowest pH(H_2O) values.

Crown also showed to have a higher Al saturation than base saturation with a pH(H_2O) value close to that of NM700 and Coal. On the other hand, the NMC1 tailings showed to have a higher base saturation than Al saturation, meaning that there were much more base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) present on the exchange complex than Al^{3+} cations. It is evident that lower base saturation values make it possible for other acidity-causing cations such as Al^{3+} and H^+ to be adsorbed onto the exchange complex of a growth medium (Myburgh, 2015).

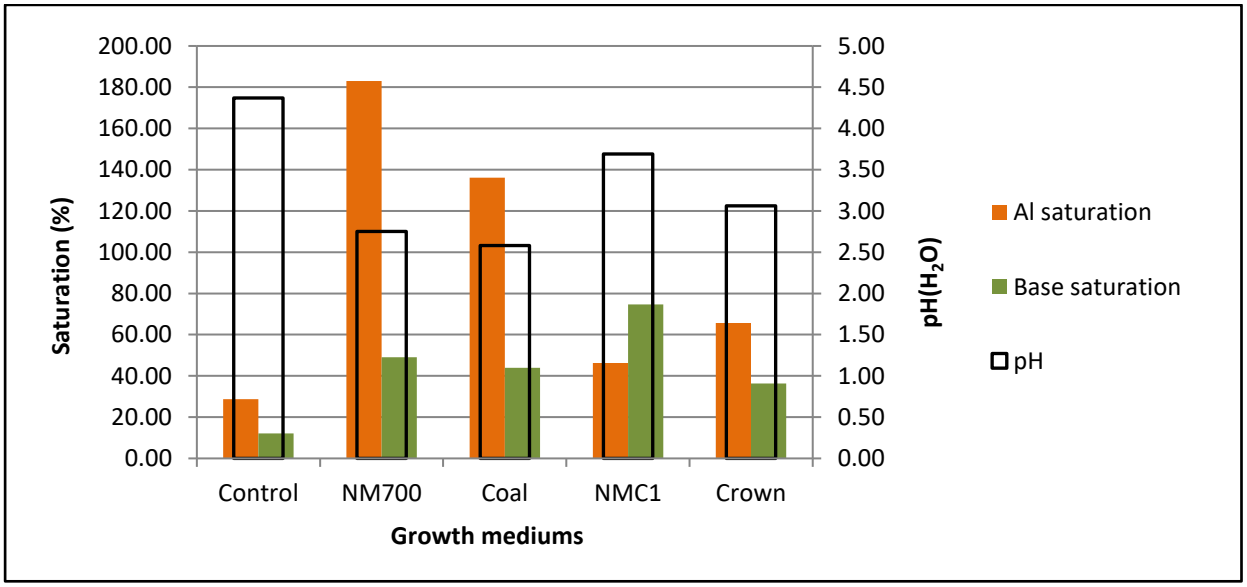


Figure 31: A comparison between aluminium saturation, base saturation and pH(H_2O) values of the growth mediums.

All of the growth mediums used in the study showed definite signs of Al toxicity. According to Foy (1984), Al toxicity occurs where more than 15 to 20% of the exchange complex of a growth medium is occupied by Al^{3+} ions. Aluminium toxicity is detrimental towards plant growth as it may cause stunted plant roots, limited plant growth and impaired microbial activity (Foy, 1984).

With high Al saturation values, such as those presented in Figure 31, it can be expected that Al will be present in the tissue of plants growing in these growth mediums. According to Meriño-Gergichevich *et al*. (as cited in Baquy *et al*., 2017), the existence of Al in plant tissue damages the chloroplast and mitochondrial membranes of the plant cells and interferes with Ca and Mg uptake from the growth medium. This will have deteriorating effects on the plant as Ca is needed for cell growth and plays an important role in the formation of proteins. An interference with the Mg uptake of the plant will interfere with photosynthesis as Mg forms the nucleus of the complex chlorophyll molecule. Magnesium also plays an important role in the translocation of P (MVSA, 2007).

The pH(H_2O) of the solution phase determines the dissolution equilibria of Al in a growth medium. Al-bearing minerals dissolve and release Al^{3+}, OH^- or H_3O^+ ions, as explained by Equation 33 (Van Rensburg, as cited in Myburgh, 2015):

$$Al(OH)_3 \rightarrow Al^{3+} + 3OH^- \quad \text{(Eq. 33)}$$

Owing to the strong affinity of hydroxyl (OH) for Al^{3+}, Al^{3+} may also react with water, releasing H^+ cations into the solution phase of the growth medium. This means that the presence of free Al^{3+} cations in a solution may generate further acidity through Equation 34 (Van Rensburg, as cited in Myburgh, 2015).

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad \text{(Eq. 34)}$$

A strongly negative linear correlation ($r^2 = 0.695$, therefore $r = -0.834$) was observed between pH(H_2O) and the Al saturation (Appendix D) – a result also obtained from studies conducted by Abreu *et al*. (2003) and Myburgh (2015). This means that as the pH(H_2O) values of the growth mediums decrease, the Al saturation values will strongly increase.

4.5 Measuring pH(H_2O) with the use of three different procedures

The pH(H_2O) of the growth mediums were monitored with the use of a leaching procedure, rather than the conventional procedure. This experiment was conducted to determine the relationship among pH(H_2O) readings obtained by way of these three different procedures and to explain why the leaching procedure was used throughout the study. The third procedure (incubation) was used to illustrate the influence of a prolonged reaction time between water and a highly limed growth medium on pH(H_2O) values.

Each of these procedures represents a different reaction time between the water and the growth mediums; from a very short time with the leaching procedure (approximately 15 minutes), to 50 minutes with the conventional procedure and 24 hours with the incubation procedure.

Detailed explanations of these three procedures (i.e. conventional, leaching and incubation) are presented in Section 3.5.2. Raw data for the pH(H_2O) values obtained by way of the three different procedures are presented in Appendix S.

4.5.1 Control medium

Figure 32 gives the pH values of the control medium measured by way of the leaching, conventional and incubation procedures over a period of six weeks after a 5 t/ha lime treatment.

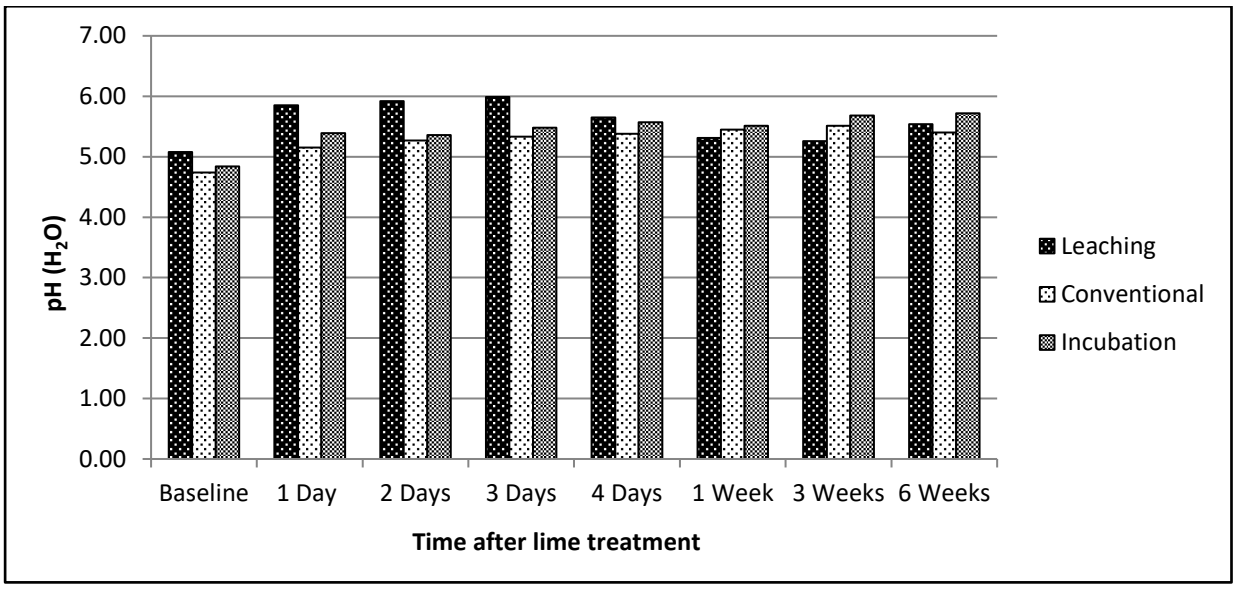


Figure 32: Change in pH(H_2O) readings of the control medium measured by way of the leaching-, conventional and incubation procedures over a period of six weeks after lime treatment.

An overall increase in pH was observed for the control medium over the neutralisation period of six weeks for all three methods. The greatest increase in pH was observed with the leaching procedure, where the pH increased from 5.04 to 5.85 within one day after lime treatment. A more gradual increase was observed after that to a pH value of 5.99 after three days, followed by a decreased pH value of 5.65 only a day later. The pH values obtained with the leaching procedure kept decreasing to 5.26 until another slight increase was observed after six weeks. The conventional and incubation procedures showed more gradual increases in pH values over the neutralisation period from 4.69 to 5.40 (conventional procedure) and 4.80 to 5.72.

The pH values of the leaching procedure were the highest for the baseline value and for the first four days. The opposite was true at one and three weeks after lime treatment, where the pH values obtained by this method were the lowest. The values obtained by the incubation procedure were slightly higher than those obtained by the conventional procedure throughout the six-week incubation period.

A statistical analysis was done on the pH values obtained with the use of the three procedures. The results showed a strong positive linear relationship between the conventional procedure and the incubation procedure ($r + 0.932$) of statistical significance ($p < 0.05$) (ANOVA $F = 12.784$; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.2 NM700 tailings material

The change in pH(H_2O) values of the NM700 tailings material measured by way of the leaching, conventional and incubation procedures is presented in Figure 33. The readings were taken over a six-week neutralisation period after a 435 t/ha lime treatment.

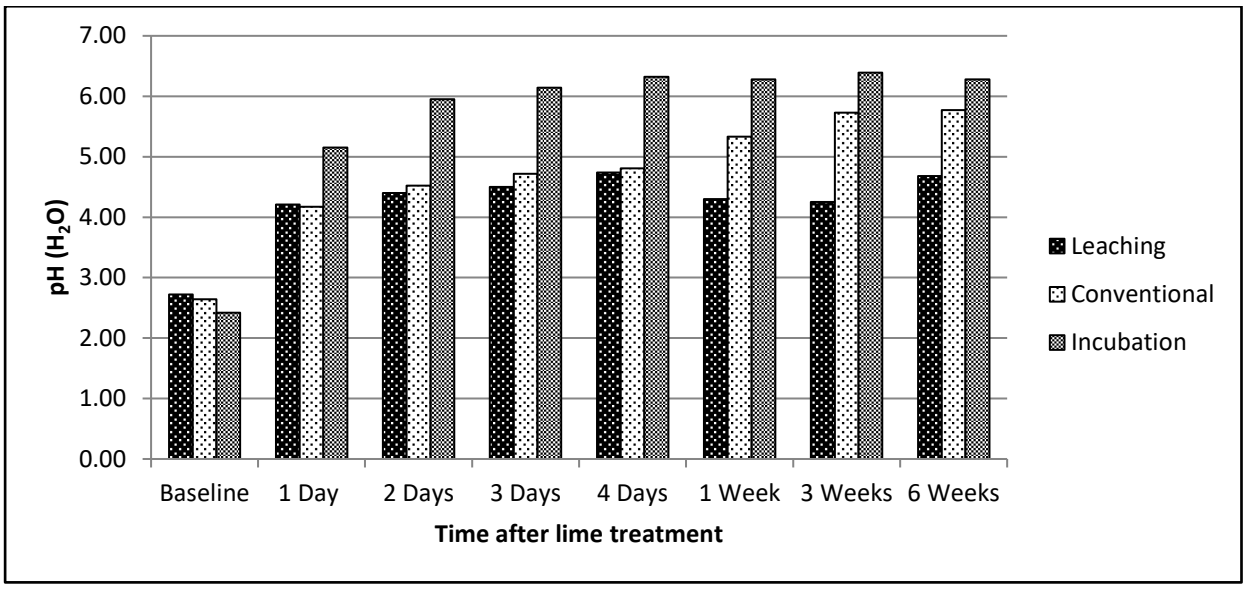


Figure 33: Change in pH(H_2O) values of the NM700 tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after lime treatment.

An overall increase in pH was observed for all three procedures, with the highest increase in pH being one day after lime treatment. A great increase was observed within the first two days after lime treatment for the incubation procedure, from a baseline pH value of 2.42 to 5.95, followed by a more gradual increase to 6.39 after six weeks. An overall gradual increase in pH was observed with the conventional procedure from a baseline pH of 2.64 to a pH of 5.77 six weeks after lime treatment. The pH values obtained from the leaching procedure increased significantly from a baseline pH of 2.72 to 4.74 four days after lime treatment. Values from the leaching procedure showed a slight decrease in pH to 4.30 (one week after lime treatment) and 4.25 (three weeks after lime treatment), followed by an increase to 4.68.

The incubation procedure provided the lowest baseline value but delivered much higher pH values than the conventional and leaching procedures throughout the neutralisation incubation period. The leaching procedure presented the highest baseline pH value but gave the lowest pH values from two days after lime treatment. The conventional procedure presented pH values slightly higher than the leaching procedure for the first four days; much greater differences between these two procedures were observed after the first week.

The statistical analyses of the results showed a strong positive correlation between the conventional procedure and the leaching procedure (r + 0.820), between the leaching procedure and the incubation procedure (r + 0.869), as well as between the conventional procedure and the incubation procedure (r + 0.862). All of these correlations had p values of <0.05, meaning that they were all of statistical significance (ANOVA F = 88.806; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.3 Coal tailings material

Figure 34 presents the change in pH(H_2O) values of the coal tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after a 200 t/ha lime treatment.

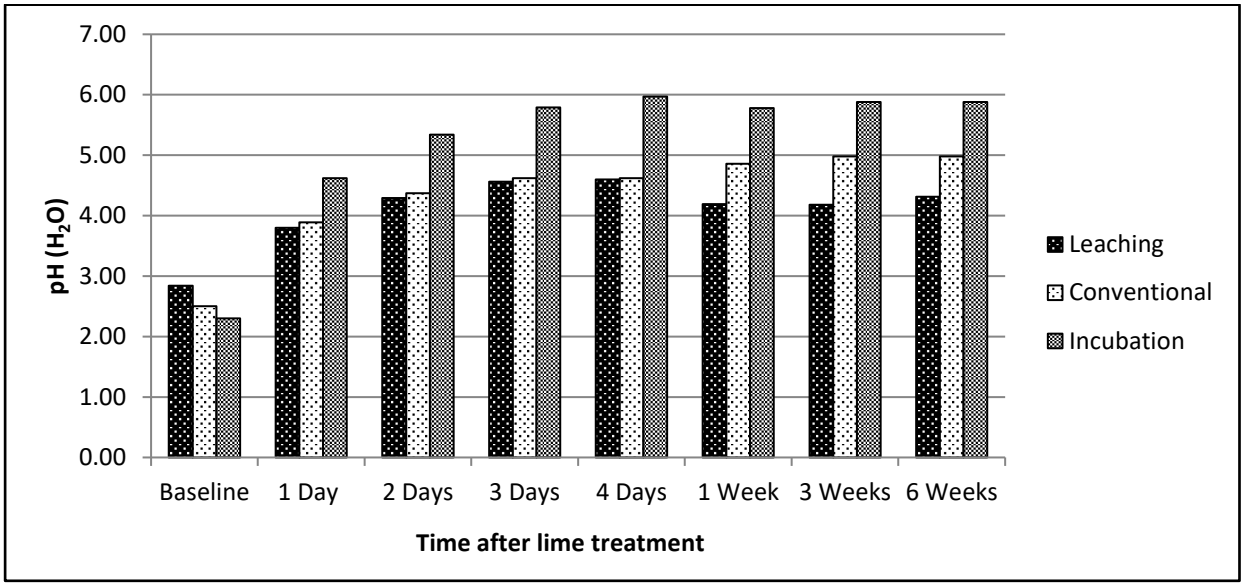


Figure 34: Change in pH(H_2O) values of the coal tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after lime treatment.

An overall increase in pH was observed with all three of the procedures, where the incubation procedure showed the greatest increase. The highest increase in pH was observed one day after lime treatment. The incubation procedure showed the lowest baseline pH value of 2.30 but increased much more than the other two procedures to a pH of 5.15 one day after lime treatment. The pH values from the incubation procedure increased gradually from there on to 5.97 four days after lime application. The pH levels decreased slightly and increased again to 5.88 after six weeks. The leaching procedure, which presented the highest baseline pH value of 2.84, delivered the lowest pH values of all three procedures used.

The pH values from the leaching procedure and the incubation procedure did not differ significantly during the first four days of neutralisation, but a greater difference was observed after the first week up until the sixth week of neutralisation. The pH values of the three procedures were very different after the sixth week of neutralisation where the pH values were 5.88 (incubation procedure), 4.98 (conventional procedure) and 4.31 (leaching procedure) respectively.

A strong positive linear relationship was observed between the conventional procedure and the incubation procedure (r + 0.960), the leaching procedure and the incubation procedure (r + 0.953), as well as between the leaching procedure and the conventional procedure (r + 0.914). All of

these results were statistically significant ($p < 0.05$) (ANOVA F = 89.453; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.4 NMC1 tailings material

Figure 35 presents the change in pH(H_2O) values of the coal tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after a 56 t/ha lime treatment.

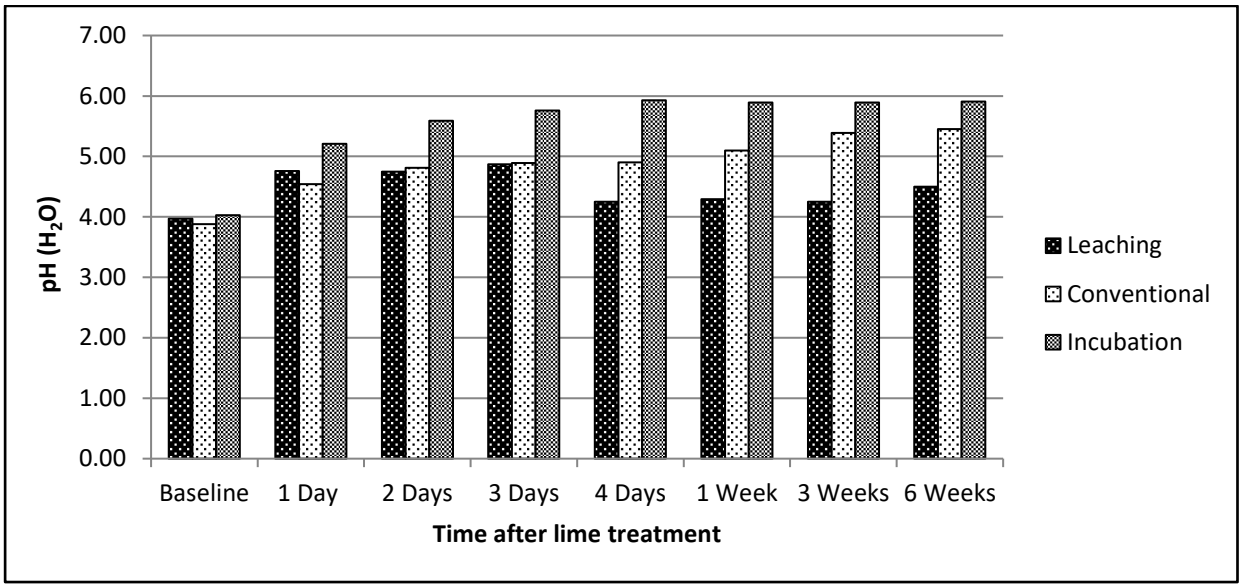


Figure 35: Change in pH(H_2O) values of the NMC1 tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after lime treatment.

A gradual increase in pH was observed with all three procedures. The greatest increase in pH was observed after the first day of lime treatment. The incubation procedure showed the greatest increase in pH straight through the neutralisation period, where the highest degree of neutralisation took place within the first four days. The pH values stabilised thereafter and reached a pH of 5.91 after six weeks. The conventional procedure presented the lowest baseline pH value of 3.88 but increased to pH levels higher than the values obtained with the leaching procedure. Lower pH values were obtained by the leaching procedure from three days after lime treatment throughout the remaining period.

The final pH values (six weeks after lime treatment) obtained from these procedures differed yet again. The values from the incubation procedure showed to be the highest (pH 5.91), followed by the conventional procedure (pH 5.45) and those of the leaching procedure as the lowest (pH 4.50).

The statistical analyses of the data showed a strong positive correlation between the conventional and the incubation procedures (r + 0.937). A weak positive correlation existed between the

leaching procedure and the conventional procedure (r + 0.378), as well as the leaching procedure and the incubation procedure (r + 0.474). All of these linear relationships were of statistical significance ($p < 0.05$) (ANOVA F = 139.562; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.5 Crown tailings material

The change in pH(H_2O) values of the Crown tailings material measured by way of the leaching, conventional and the incubation procedures is presented seen in Figure 36. The values were taken over a six-week neutralisation period after a 25 t/ha lime treatment.

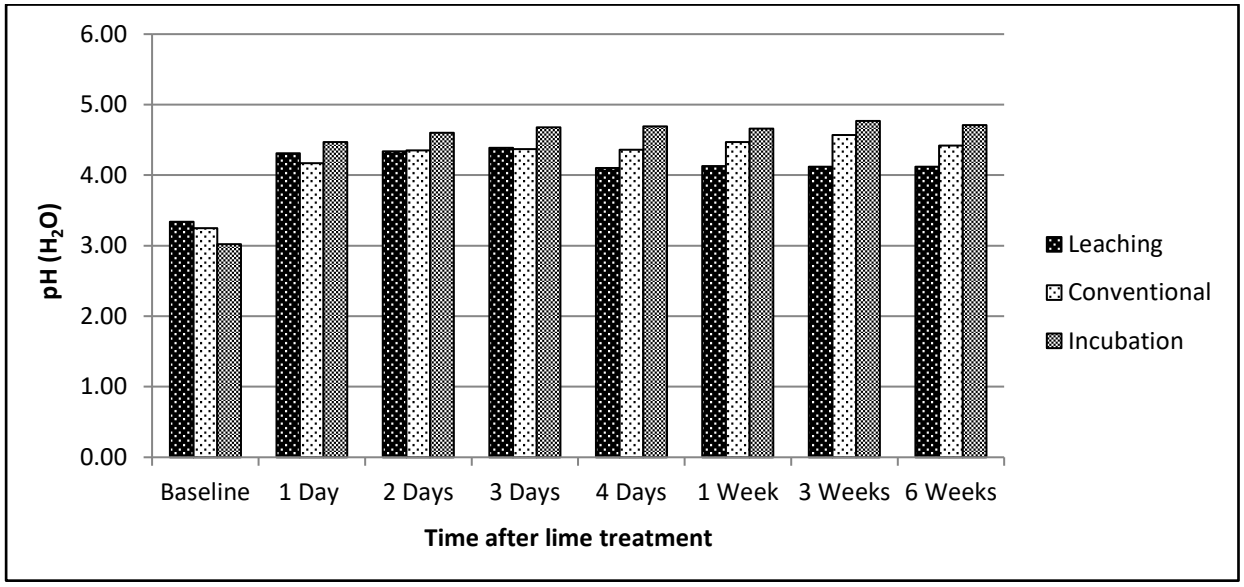


Figure 36: Change in pH(H_2O) values of the Crown tailings material measured by way of the leaching, conventional and incubation procedures over a period of six weeks after lime treatment.

An overall increase in pH was observed with all three procedures, with the highest increase being one day after lime treatment. The incubation procedure presented the lowest baseline pH value of 3.02 but provided the highest pH values from one day (pH 4.47) to six weeks after lime treatment (pH 4.71). The pH values obtained with the conventional procedure increased gradually from 4.17 one day after lime treatment to 4.42 six weeks after lime treatment. The results from the leaching procedure showed that the pH of the material increased from a baseline pH of 3.34 to a pH of 4.31 one day after lime treatment. The pH values increased gradually until the third day (pH 4.39) but decreased to 4.10 a day later. The pH values did not increase significantly thereafter, for the pH of the material, as determined by the leaching procedure, was 4.12 after six weeks.

The pH values obtained by way of the three procedures were also different after the six-week neutralisation incubation period. The highest pH value, obtained by the incubation procedure, was 4.71. This value was followed by the pH obtained with the conventional procedure (pH 4.42) and, lastly, by the leaching procedure (pH 4.12).

A strong positive linear relationship was observed between the conventional procedure and the incubation procedure (r + 0.954), between the leaching procedure and the incubation procedure (r + 0.904), as well as between the leaching procedure and the conventional procedure (r + 0.820). All of these results were of statistical significance ($p < 0.05$) (ANOVA F = 57.984; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.6 Integration of results

The highest pH values for the control medium were obtained with the leaching procedure for the first four days. After a week, the leaching procedure provided the lowest pH values throughout the remaining neutralisation incubation period. The pH values obtained with the incubation procedure were the highest after a week up until the sixth week. However, the difference between the results of the three procedures did not vary as much as with the tailings materials.

Greater differences between the pH values obtained with the three procedures were experienced with the tailings material compared to the control medium. Greater differences between the three procedures were observed in tailings with higher lime requirements (NM700 and coal). The results obtained with the incubation procedure showed the highest pH values, whereas the leaching procedure showed the lowest pH values for all of the tailings materials.

After the six-week neutralisation period, the results obtained through the conventional procedure presented pH values between those obtained by the incubation and leaching procedures. The reason for this was that with the conventional procedure (50 minutes) and the incubation procedure (24 hours), the large amount of lime present within the material was forced to react with the water added to the material during this time. This reaction released more CO_3^{2-} ions into the solution, increasing the pH to a higher level. A prolonged exposure to water, therefore, led to higher pH values when free lime was still present in the tailings material.

Since there were small differences between the baseline pH values (before lime treatment) obtained with all three procedures, it is recommended that the leaching procedure would be more suitable for pH monitoring in highly limed tailings materials. This procedure allows for a smaller reaction time between the water added to the sample and the large amount of lime, and will, therefore, provide a more immediate and representative pH value of the tailings material after it has been treated with a large amount of lime.

Statistical analysis of the pH results obtained by the three procedures for all of the growth mediums used in this study showed a moderately positive linear relationship between the conventional procedure and the incubation procedure (r + 0.687). A weak positive linear relationship was observed between the leaching procedure and the conventional procedure (r + 0.554), as well as between the leaching procedure and the incubation procedure (r + 0.200). All

of these relationships were of statistical significance ($p < 0.05$) (ANOVA F = 113.844; ANOVA F *crit* < ANOVA F) (Appendix T).

4.5.7 Summary

The data discussed in this section were aimed at completing the research objective of comparing three different procedures (leaching, conventional and incubation) of monitoring pH levels in the different acidic growth mediums after lime treatment.

It was concluded that the leaching procedure (as recommended by the soil scientist, Dr A.A. Bloem) is a more suitable procedure to monitor pH levels in highly limed tailings materials.

The three different procedures used in this experiment produced different pH values, with the greatest differences found in the growth mediums that had the highest lime requirements, proving the sub-hypothesis stated in Section 1.4.

4.6 Change in pH(H_2O) and EC of the growth mediums during Pot trial 1 and Pot trial 2

The pH(H_2O) and EC results discussed in this section were obtained with the use of the leaching procedure. These variables were monitored before lime was applied to the growth mediums (baseline values), one day after the lime applications and on a weekly basis thereafter in Pot trial 1.

The pH and EC monitoring in Pot trial 2 took place for the first four days after liming, as well as one week, three weeks and six weeks after liming. Additional pH and EC measurements were done on the materials in Pot trial 2 at 23 weeks after lime treatment to determine whether re-acidification of the material has taken place.

Raw data for the change in pH(H_2O) and EC of the growth mediums are presented in Appendices G and H for Pot trial 1 and Appendices I and K for Pot trial 2.

4.6.1 pH(H_2O)

The change in pH after lime treatment in Pot trial 1 over a period of 12 weeks is presented in Figure 37. Average temperatures during this time were 26.38 °C (maximum) and 7.13 °C (minimum). The total amount of rainfall experienced in this area was 74.6 mm.

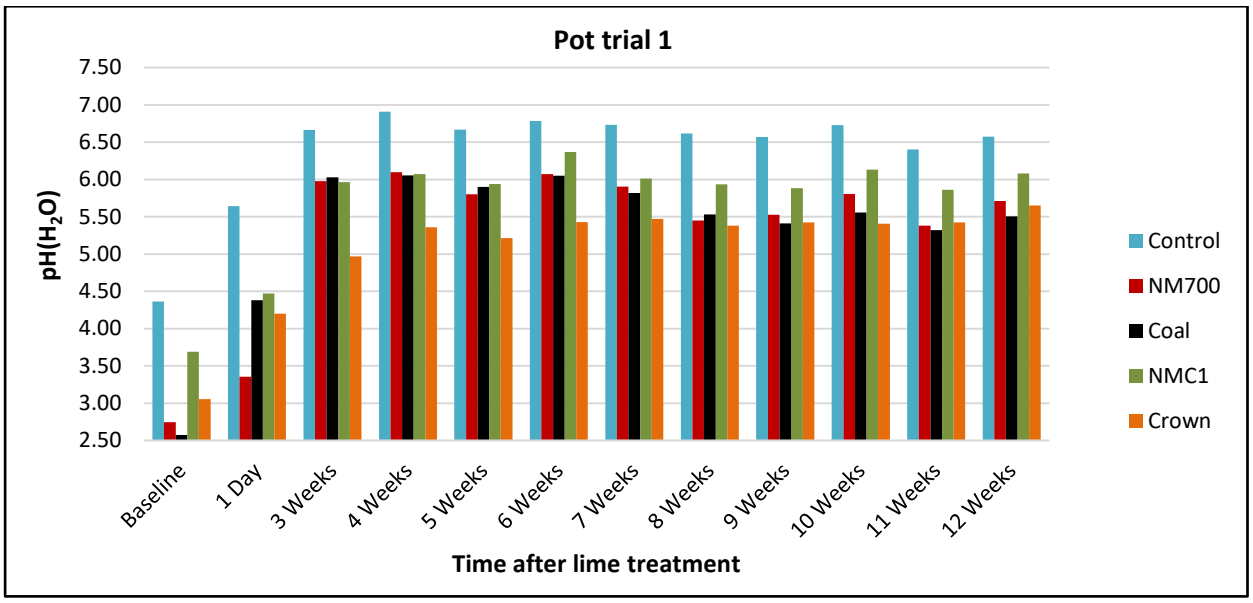


Figure 37: Change in pH(H_2O) of the growth mediums after lime treatment in Pot trial 1.

As seen in Figure 37, all of the growth mediums had baseline pH values of <4.50 (control: 4.37; NM700: 2.75; coal: 2.58; NMC1: 3.69; Crown: 3.06). The pH of the growth mediums increased significantly one day after lime application, with an even larger increase observed in pH values taken three weeks after lime treatment. All of the growth mediums had pH values of >5.0 after six weeks when fertiliser was applied to the growth mediums in Group B.

The smallest amount of fluctuation was observed in the control medium and the Crown tailings material from three weeks after lime treatment until the end of Pot trial 1. These are the two growth mediums with the lowest SO_4 concentrations, total S% and lime requirements, whereas the growth mediums with the highest SO_4 concentrations, total S% and lime requirements (NM700, coal and NMC1) showed the most fluctuation. This can be attributed to ongoing acidification reactions taking place in the sulphide-rich tailings materials. Additional acidity brought on by these reactions is then neutralised through the large amount of lime added to the growth medium as determined by way of the NAP/NAG analyses that account for ongoing acidification (Usher *et al*., 2003).

All of the growth mediums had much higher pH values at the end of Pot trial 1, that is, 12 weeks after lime treatments (control: 6.58; NM700: 5.71; coal: 5.50; NMC1: 6.08; Crown: 5.65).

The change in pH after lime treatment in Pot trial 2 is presented in Figure 36. The pH levels of the growth mediums were monitored daily for the first four days, and thereafter one week, three weeks, six weeks, seven weeks and eight weeks after lime treatment. A final pH measurement was made at 23 weeks after lime treatment to determine if re-acidification of the materials has taken place long after lime application.

Average temperatures during this time were 23.23 °C (maximum) and 2.53 °C (minimum) respectively. The total amount of rainfall experienced in this area was 0.2 mm.

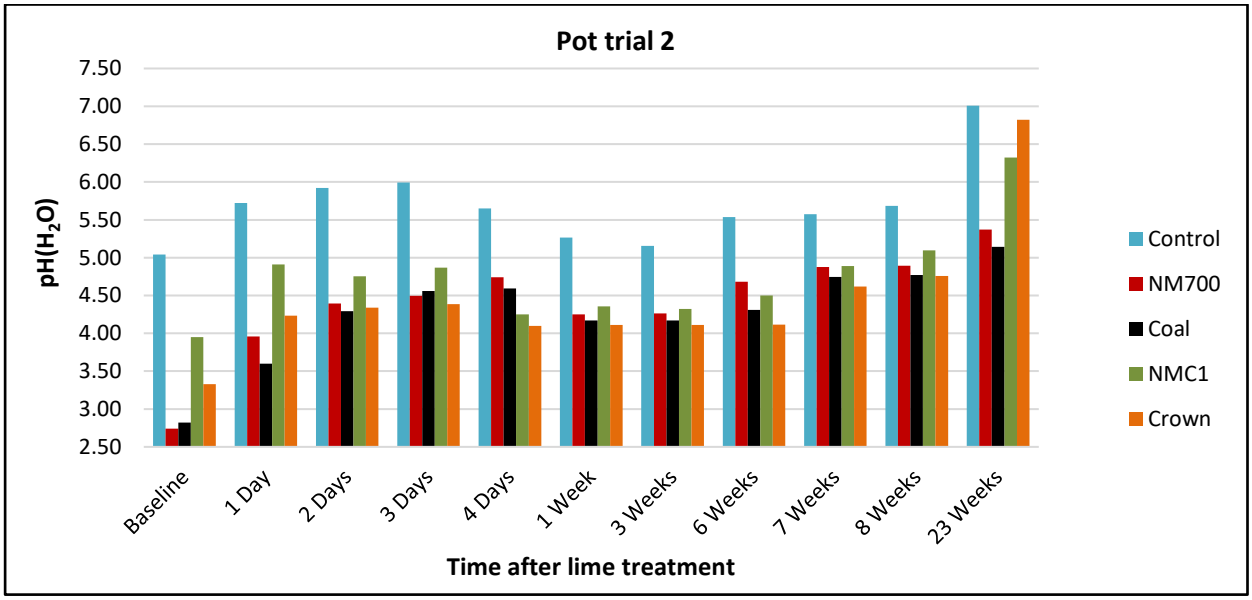


Figure 38: Change in pH(H_2O) of the growth mediums after lime treatment in Pot trial 2.

The baseline pH values were very low for all the growth mediums, especially the tailings material (control: 5.04; NM700: 2.74; coal: 2.82; NMC1: 3.95; Crown: 3.33) (Figure 38). The pH of the control medium increased gradually for the first four days, followed by a decline in pH after four days, one week and three weeks after lime treatment. The pH of the control medium increased again to 5.69, eight weeks after lime treatment. The same trend in fluctuation was also observed in the Crown tailings material, as with Pot trial 1 where these two growth mediums with the lowest SO_4 concentrations, total S% and lime requirements reacted very similarly after lime treatment.

The NM700 and coal tailings material – the two growth mediums with the highest SO_4 concentrations, total S% and lime requirements – reacted similarly after lime treatment. The pH values of these tailings increased gradually for the first four days after lime treatment, followed by a rapid decrease one week thereafter. The pH values of these tailings increased again and ended with a higher pH at eight weeks after lime treatment (NM700: 4.90; coal: 4.77).

The NMC1 tailings showed the most fluctuation in pH for the first four days after lime treatment. The pH of this growth medium increased gradually from one week after to eight weeks after lime treatment, where it had a pH of 5.10.

Fluctuations in pH observed in the growth mediums are due to the ongoing oxidation of sulphates that takes place as long as there are unoxidised forms of this substance present in the growth mediums, as described by Van Deventer *et al*. (2007) and Van Deventer and Hattingh (2008).

The greatest increases in pH during the pot trials were observed in the tailings with the lowest baseline pH values, owing to the fact that the solubility of lime is greatly dependent on the pH of the growth medium. The rate of the neutralisation reaction is higher at lower pH levels (Adams, 1984; Barber, 1984; Thomas & Hargrove, 1984; Van Deventer, 2007).

All of the growth mediums had much higher pH values 23 weeks after lime treatment. This means that re-acidification of the growth mediums, especially the tailings materials, did not take place and the lime requirements, as determined by the NAP/NAG, were sufficient.

There was a clear difference in the change of pH values during Pot trial 1 and Pot trial 2. The pH values of Pot trial 1 were always higher that the pH values measured in Pot trial 2 at the same time intervals, even though the materials were treated with the same amount of lime. A greater degree of fluctuation in pH values was also observed in Pot trial 1. This can be attributed to the difference in micro-climate between the two Pot trials. Pot trial 1 was conducted during a time where maximum and minimum temperatures were higher than during Pot trial 2. Pot trial 1 also received much more rainfall than Pot trial 2.

Higher temperatures and increased oxygen levels as a result of rainfall increased the reaction rate of oxidation in the tailings, producing more acidity (Akcil & Koldas, 2006; Nengovhela *et al*., 2006; Ritcey, 2005). At the same time, increased temperatures and moisture content also contributed to the dissolution of lime and increased the rate of neutralisation (Thomas & Hargrove, 1984).

4.6.2 Electrical conductivity (EC)

The change in EC values of the growth mediums measured during Pot trial 1 is presented in Figure 39.

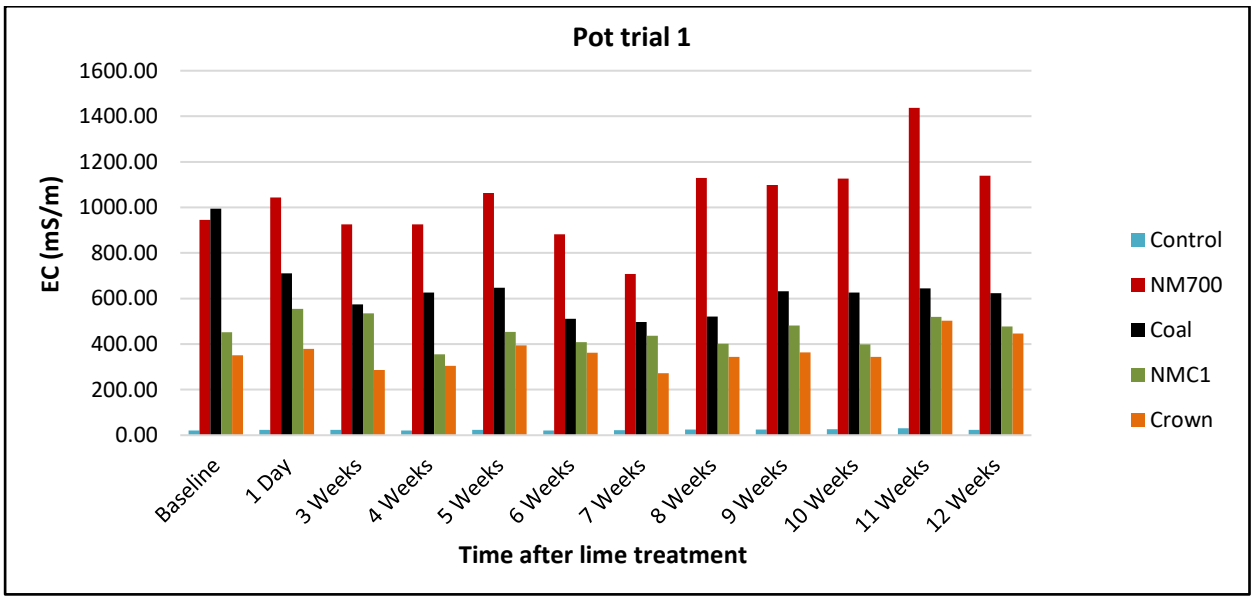


Figure 39: Change in EC of the growth mediums after lime treatment in Pot trial 1.

As seen in Figure 39, the EC values of the NM700, NMC1 and Crown tailings increased one day after lime had been applied to the growth mediums. This was due to the large amount of lime added to the materials. The dissolution of lime produces H_2CO_3 (at pH ≤6.2) and HCO_3^- (at pH ≥6.2), increasing the EC of the growth medium (Ochieng *et al*., 2009). According to this, higher lime requirements will result in greater EC increases after lime application. In contrast to the other growth mediums, the EC of the coal tailings decreased after lime treatment in Pot trial 1.

Precipitated $CaSO_4$ were observed on the surfaces of the tailings materials one week after lime treatment (Appendix U). Growth mediums with the highest EC values and SO_4 concentrations showed more $CaSO_4$ precipitation on the surface of the growth medium as water evaporated from the surface.

Decreases in EC values were observed in the three-week and seven-week values. These values correlate with rainfall data, which state that the area received 52 mm of rain within the first three weeks of the pot trial and 20 mm of rain two days before the seven-week values were recorded. Lower EC values at the end of Pot trial 1, 12 weeks after lime treatment, are attributable to leaching of free salts from the solution phase of the growth mediums over time.

Figure 40 presents the change in EC values the growth mediums underwent after lime applications in Pot trial 2. All of the growth mediums experienced an increase in EC after lime treatments. Less fluctuation in EC values was observed during Pot trial 2 as a result of far less rainfall and, consequently, less leaching during this time.

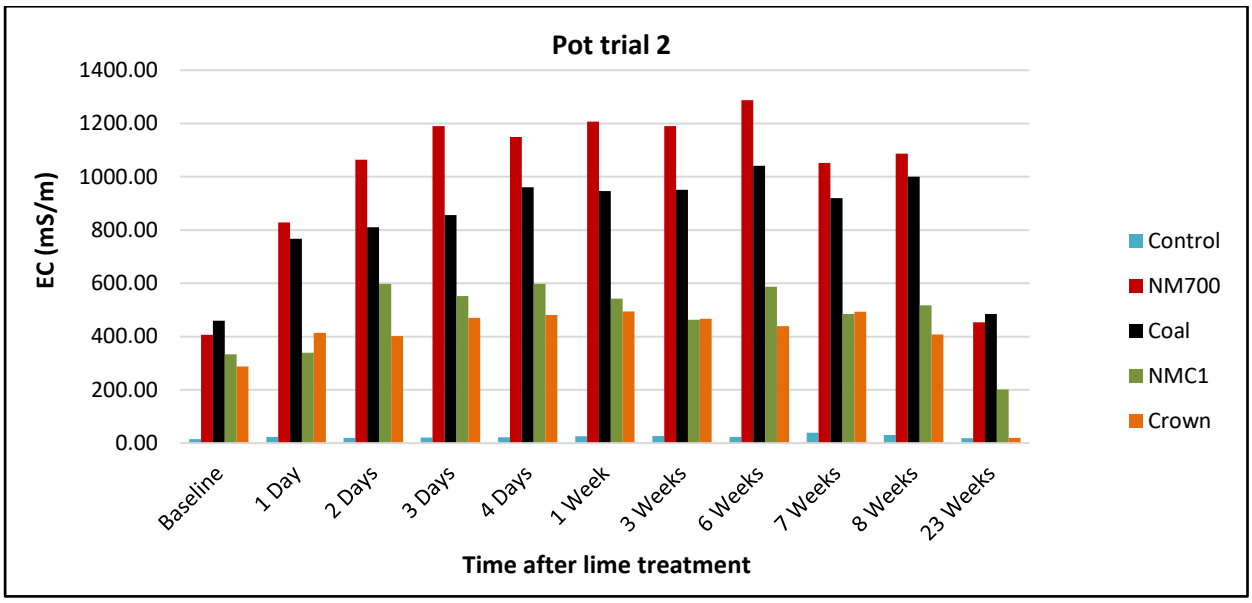


Figure 40: Change in EC of the growth mediums after lime treatment in Pot trial 2.

The EC values of the growth mediums were much lower 23 weeks after lime treatment. The pots were placed under irrigation sprinklers during the seedling survival experiment conducted on Pot trial 2 pots. This resulted in a lot of free salts being leached out of the growth mediums, especially from the top 15 cm, causing a major decrease in EC of the tailings materials.

The lower EC values were very beneficial toward the seedling survival rate experiment (see Section 4.9). High salinities cause the most damage during germination and the early stages of root development (Van Deventer & Hattingh, 2008); therefore, the lower EC values, as a result of leaching, resulted in good seedling survival rates and plant growth. This may have been the reason why the coal tailings material – a very hostile growth medium with the highest EC of all the growth mediums – showed much better seedling survival rates and plant growth than expected.

4.7 Phase 2: The influence of a neutralisation time lag on phosphorus availability

Two main pot trials were conducted throughout the research study, namely Pot trial 1 and Pot trial 2. The fertiliser requirements for Pot trial 1 were determined with a target value of 15 mg/kg P, whereas the fertiliser requirements for Pot trial 2 were determined with a target value of 30 mg/kg P. Group A of the pot trials was treated with lime and fertiliser as superphosphate simultaneously. Fertiliser was only applied to the growth mediums in Group B six weeks after lime treatments.

Monitoring of pH, P Bray and Olsen P levels after respective lime and fertiliser treatments for the first pot trial, took place at one day, three weeks and six weeks after the treatments, whereas monitoring for the second pot trial took place at one day, one week and three weeks after the

treatments. The growth mediums received exactly the same amount of lime in both of the pot trials. Raw data of the Pot trials can be seen in Appendices I and K for Pot trial 1 and Appendices N and P for Pot trial 2.

The results for every growth medium used in the study are discussed separately in the following sections (this includes both pot trials), followed by an integration of results from all the different growth mediums. Note that “baseline” values are pH, Olsen and Bray-1 values before any lime or fertiliser treatments have been added to the growth mediums.

Raw data obtained during Pot trial 1 is presented in Appendix I (Group A) and Appendix K (Group B).

Raw data for Pot trial 2 is presented in Appendix N (Group A) and Appendix P (Group B).

4.7.1 Control medium

Figure 41 presents the results obtained during Pot trial 1 and Pot trial 2 for the control medium. This growth medium was treated with 5 t/ha lime, 0.28 g/kg superphosphate in Pot trial 1 and 0.64 g/kg superphosphate in Pot trial 2 respectively.

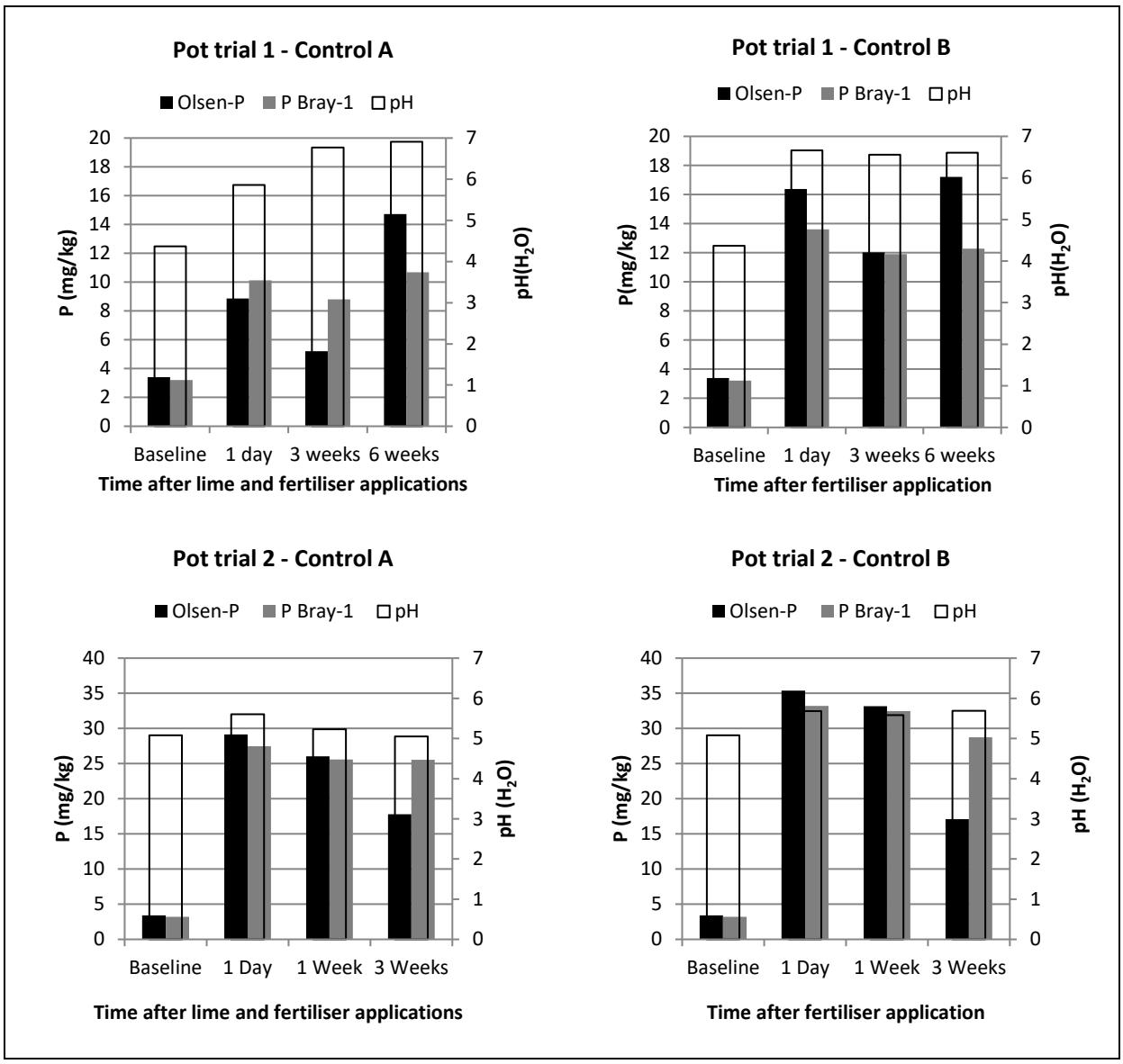


Figure 41: Olsen P, P Bray-1 and pH results for the control medium during Pot trial 1 and Pot trial 2.

a) Pot trial 1

The results for Pot trial 1 (Group A and B) showed an increase in P as obtained from the Olsen and the Bray-1 methods. The pH, Olsen P and P Bray-1 values of the medium one day after the growth medium has been treated with fertiliser, were higher for Group B (pH: 6.66; Olsen P: 16.38 mg/kg; P Bray: 13.61 mg/kg) than Group A (pH: 5.86; Olsen P: 8.86 mg/kg; P Bray 10.13 mg/kg). The P Bray and Olsen P results for both groups decreased three weeks after fertiliser application.

Six weeks after the soil had been treated with fertiliser, P values for Group B (Olsen P: 17.22 mg/kg; P Bray: 12.29 mg/kg) were higher than those of Group A (Olsen P: 14.73 mg/kg; P Bray: 10.69 mg/kg). Even though the pH in Group A (6.91) was higher than Group B (6.61) six weeks after fertiliser application, P-Bray 1 values were higher in Group B.

There was no statistically significant relationship between P Bray-1 and Olsen P results (r + 0.536; p > 0.05), between pH and P Bray-1 results (r – 0.145; p > 0.05) or between pH and Olsen P results (r + 0.21; p > 0.05) in Group A during Pot trial 1 (ANOVA F = 5.915; ANOVA F *crit* < ANOVA F) (Appendix J).

A statistically significant relationship was obtained between the pH of the control medium an P extracted by the Bray-1 method (r + 0.640; p < 0.05) in Group B during Pot trial 1. No statistically significant relationship existed between pH and Olsen P results (r + 0.450; p > 0.05) or between Olsen P and P Bray-1 results (r – 0.046; p > 0.05) in Group B of Pot trial 1 (ANOVA F = 68.939; ANOVA F *crit* < ANOVA F) (Appendix L).

The average pH value for the control medium in Group A over the course of Pot trail 1 was 6.51. On average, the Olsen method extracted less P from the growth medium (9.67 mg/kg) than the Bray-1 method (9.92 mg/kg) (Appendix J). In Group B, an average pH of 6.61 was recorded. An average of 15.28 mg/kg P was recorded by the Olsen P analysis whereas an average of 12.65 mg/kg P was recorded by the Bray-1 analysis in Group B for Pot trial 1 (Appendix L).

The results obtained for the control medium in Pot trial 1 proved that higher levels of extractable P had been obtained after six weeks of being treated with fertiliser when the fertiliser had been applied after a neutralisation incubation period of six weeks.

b) Pot trial 2

The results for Pot trial 2 (Figure 41) showed an increase in P, one day after being treated with fertiliser in Group A (Olsen P: 29.14 mg/kg; P Bray: 27.45 mg/kg) as well as Group B (Olsen P: 35.39 mg/kg; P Bray: 33.21 mg/kg), with the greatest increase being when the fertiliser was applied six weeks after lime application (Group B). One week after fertiliser treatment, Group B also showed higher levels of extractable P as well as a higher pH value than Group A. P Bray and Olsen P values for Group A and Group B decreased one week after fertiliser application. The amount of P extracted by the Olsen method decreased three weeks after fertiliser applications in Group A and Group B. The Bray-1 method extracted approximately the same amount of P at one week and at three weeks after lime and fertiliser treatments in Group A, whereas P Bray-1 values decreased in Group B over this time.

After comparing the results obtained from Group A and Group B at six weeks after fertiliser treatment, it was noted that Group B had higher pH and P Bray-1 values (pH: 5.69; P Bray: 28.76 mg/kg) than Group A (pH: 5.05; P Bray: 25.55 mg/kg). Six weeks after fertiliser applications, the average Olsen P value for Group B (17.12 mg/kg) was lower than Group A (17.80 mg/kg). The results obtained at the end of Pot trial 2 showed that higher P Bray-1 values have been obtained in a naturally acidic soil when fertiliser was applied after a neutralisation period of six weeks.

The Olsen method extracted more P from the control medium in Group A and Group B during Pot trial 2 for the baseline value, one day and one week after fertiliser treatments; however, the Bray-1 method extracted more P from the control medium three weeks after the respective fertiliser treatments.

There was a statistically significant positive correlation between pH and Olsen P results ($r + 0.711$; $p < 0.05$) in Group A for Pot trial 2 (Appendix O). No statistically significant correlation was obtained between pH and P Bray-1 results ($r + 0.248$; $p > 0.05$) or between P Bray-1 and Olsen P results ($r + 0.477$; $p > 0.05$) in Group A of Pot trial 2 (ANOVA F + 78.643; ANOVA F *crit* < ANOVA F) (Appendix O).

A statistically significant positive correlation was obtained between Olsen P and P Bray-1 results ($r + 0.813$; $p < 0.05$) in Group B. No statistically significant correlation was found between pH and P Bray-1 results ($r – 0.408$; $p > 0.05$) or between pH and Olsen P results ($r – 0.306$; $p > 0.05$) for Group B in Pot trial 2 (ANOVA F = 60.942; ANOVA F *crit* < ANOVA F) (Appendix Q).

The average pH value for the control medium in Group A over the course of Pot trail 2 was 5.29. On average, the Olsen method extracted less P from the growth medium (24.33 mg/kg) than the Bray-1 method (26.20 mg/kg) (Appendix O). In Group B, an average pH of 5.65 was recorded. An average of 28.56 mg/kg P was recorded by the Olsen P analysis whereas an average of 31.48 mg/kg P was recorded by the Bray-1 analysis in Group B for Pot trial 2 (Appendix Q).

Sarker *et al*. (2014) found a stronger positive correlation ($r + 0.946$; $p < 0.05$) between the Olsen P and P Bray-1 methods, meaning that Olsen P values can be used to predict Bray-1 values for P according to their data. Mallarino (1995) also observed a positive correlation ($r + 0.77$) between the Olsen and Bray-1 methods for soils with a pH of <7.05. Both these studies found positive correlations of statistical significance ($p < 0.05$) between these two methods, meaning that as one value for P increased (Olsen or Bray-1), so did the other.

Statistically insignificant relationships between pH and Olsen P results obtained through this study agree with the results recorded by Justin *et al*. (2012) from a study conducted on extraction methods of soil P in some acidic soils of Western Kenya. This implies that one cannot predict the amount of P extracted by either one of these methods by considering only the pH of the growth medium.

4.7.2 NM700 tailings material

A visual representation of the results obtained during Pot trial 1 and Pot trial 2 for the NM700 tailings material is presented in Figure 42. The tailings were treated with 435 t/ha lime and 0.12 g/kg superphosphate in Pot trial 1, and 0.40 g/kg superphosphate in Pot trial 2 respectively.

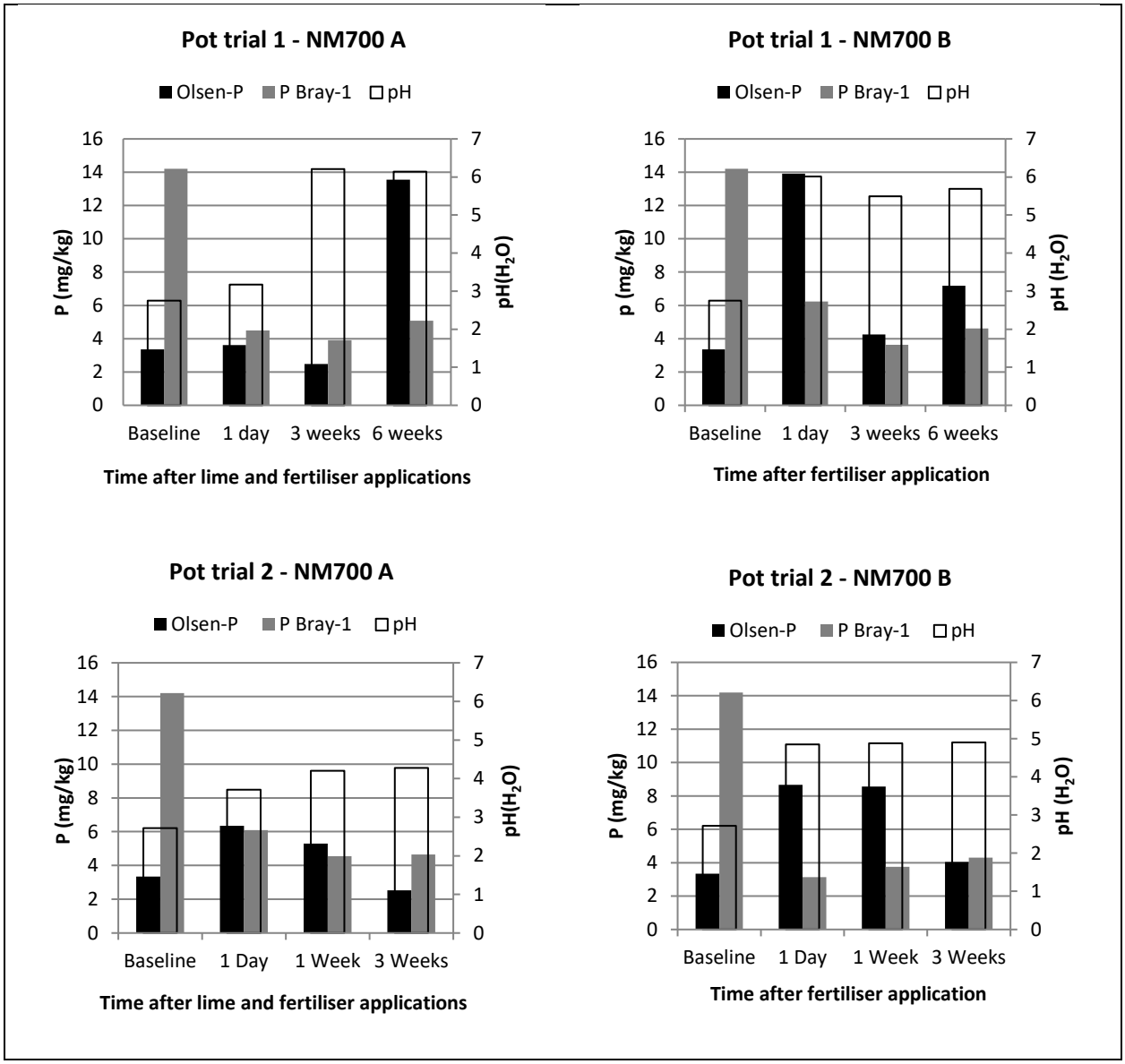


Figure 42: Olsen P, P Bray-1 and pH results for the NM700 tailings material during Pot trial 1 and Pot trial 2.

a) Pot trial 1

The results obtained during Pot trial 1 for Group A and Group B of the NM700 tailings material showed that the amount of P extracted by the Bray-1 method had decreased from a baseline P value of 14.20 mg/kg to 4.50 mg/kg P (Group A) and 6.23 mg/kg P (Group B), one day after lime and fertiliser treatments. The amount of P extracted by the Bray-1 method was higher in Group B than in Group A one day after the respective fertiliser treatments.

The P Bray-1 results for Group A and Group B remained lower after lime and fertiliser treatments than before the tailings had been treated (baseline values). Peculiar P Bray-1 results obtained from tailings with high lime requirements (e.g. NM700 and coal) led to the formation of an additional research objective: to determine the effect of high Ca concentrations on the ability of the Bray-1 method to extract P from a highly limed growth medium.

Group A of Pot trial 1 showed a slight increase in P as determined by the Olsen method from a baseline value of 3.35 mg/kg P to 6.62 mg/kg P one day after lime and fertiliser treatments. This was followed by a decrease to 2.48 mg/kg P after three weeks. After six weeks, where the pH of the tailings had increased from 2.75 to 6.14, the Olsen P results had increased to 13.55 mg/kg P.

The Olsen P results of Group B (Pot trial 1) showed an increase in P from 3.35 mg/kg P to 13.91 mg/kg P, one day after fertiliser application at a pH of 6.01. With a decrease in pH to 5.49 three weeks after fertiliser treatment came a decrease in the Olsen results to 4.26 mg/kg P. The amount of P extracted by the Olsen method increased again after six weeks to 7.18 mg/kg P.

A comparison between Group A and Group B (Pot trial 1) show that more P was extracted with the Olsen method as well as the Bray-1 method in Group A, six weeks after being treated with lime and fertiliser simultaneously, than in Group B, where the tailings were treated with fertiliser after a neutralisation incubation period of six weeks.

There was a statistically significant positive correlation between Olsen P and P Bray-1 results in Group A ($r + 0.737$; $p < 0.05$). No statistically significant relationship was found between pH and P Bray-1 results ($r – 0.082$; $p > 0.05$) or between pH and Olsen P results ($r + 0.391$; $p > 0.05$) in Group A (ANOVA F = 1.312; ANOVA F *crit* > ANOVA F) (Appendix J). The ANOVA p-value obtained from the analysis of variance was > 0.05, meaning that the relationships between pH, Olsen P and P Bray-1 in Group A of Pot trial 1 for the NM700 tailings are not of statistical significance.

A positive, statistically significant, correlation was found between Olsen P and P Bray-1 results ($r + 0.977$; $p < 0.0001$) in Group B. This strong positive correlation proves that the amount of P extracted by the Olsen method can be used to predict the amount of P that would be extracted by the Bray-1 method in Group B of the NM700 tailings and vice versa. This coincides with the results obtained by Mallarino (1995) and Sarker *et al*. (2014), for they also observed a positive correlation between these two methods. Statistically significant relationships also existed between pH and Olsen P results ($r + 0.739$; $p < 0.05$) and pH and P Bray-1 results ($r + 0.755$; $p < 0.05$) in Group B (ANOVA F = 5.899; ANOVA F *crit* < ANOVA F) (Appendix L).

The average pH value for the NM700 tailings in Group A over the course of Pot trail 1 was 5.17. On average, the Olsen method extracted more P from the growth medium (6.55 mg/kg) than the Bray-1 method (4.46 mg/kg) (Appendix J). In Group B, an average pH of 5.73 was recorded. An average of 8.45 mg/kg P was recorded by the Olsen P analysis whereas an average of 4.79 mg/kg P was recorded by the Bray-1 analysis in Group B for Pot trial 1 (Appendix L).

b) Pot trial 2

The P Bray-1 values of Group A and Group B in Pot trial 2 were also lower after fertiliser treatments than before the treatments (baseline), despite the fact the pH of the tailings had increased. P Bray-1 values in Group A decreased from a baseline value of 14.20 mg/kg P to 6.10 mg/kg P one day after simultaneous lime and fertiliser treatments. These results were even lower one week after (4.54 mg/kg P) and three weeks after (4.65 mg/kg P) lime and fertiliser treatments.

The same was observed for Group B where P Bray-1 values decreased from 14.20 mg/kg P to 3.13 mg/kg P one day after fertiliser treatments. Slight increases in Bray-1 results were observed one week after (3.75 mg/kg P) and three weeks after fertiliser treatment (4.30 mg/kg P). As with Group A, no increase higher than the baseline P Bray-1 value was observed in Group B of Pot trial 2.

The amount of P extracted by the Olsen method increased from 3.35 mg/kg P to 6.35 mg/kg P in Group A and 8.66 mg/kg in Group B. One week after the respective fertiliser treatments, 5.30 mg/kg P was extracted by the Olsen method in Group A and 8.56 mg/kg P in Group B. Three weeks after fertiliser treatments, higher Olsen P values were obtained in Group B (4.04 mg/kg P) than in Group A (2.52 mg/kg P). These results proved the hypotheses to be true: allowing a neutralisation incubation period of six weeks before fertiliser treatments did, in fact, lead to higher P values, as determined by the Olsen method.

There was statistically significant negative correlation between pH and P Bray-1 results in Group A ($r - 0.901$; $p < 0.0001$). A statistically significant correlation was also observed between pH and Olsen P results ($r - 0.559$; $p < 0.05$). No statistically significant correlation was found between Olsen P and P Bray-1 results ($r + 0.432$; $p > 0.05$) in Group A (ANOVA F = 65.196; ANOVA F *crit* < ANOVA F) (Appendix O).

There was no statistically significant relationship between pH and Olsen P results ($r - 0.403$; $p>0.05$), pH and P Bray-1 results ($r + 0.199$; $p > 0.05$) or between Olsen P and P Bray-1 results ($r - 0.462$; $p > 0.05$) in Group B (ANOVA F = 1926.462; ANOVA F *crit* < ANOVA F) (Appendix Q).

An average pH of 4.06 was recorded for the NM700 tailings in Group A of Pot trial 2. On average, the Olsen method extracted less P from the growth medium (4.73 mg/kg) than the Bray-1 method (5.09 mg/kg) in Group A (Appendix O). In Group B, an average pH of 4.87 was recorded. An average of 7.09 mg/kg P was recorded by the Olsen P analysis whereas a lower average of 3.73 mg/kg P was recorded by the Bray-1 analysis in Group B of Pot trial 2 (Appendix Q).

4.7.3 Coal tailings material

Figure 43 presents the results obtained from Pot trial 1 and Pot trial 2 for the coal tailings material. This growth medium was treated with 200 t/ha lime, 0.024 g/kg superphosphate in Pot trial 1 and 0.39 g/kg superphosphate in Pot trial 2 respectively.

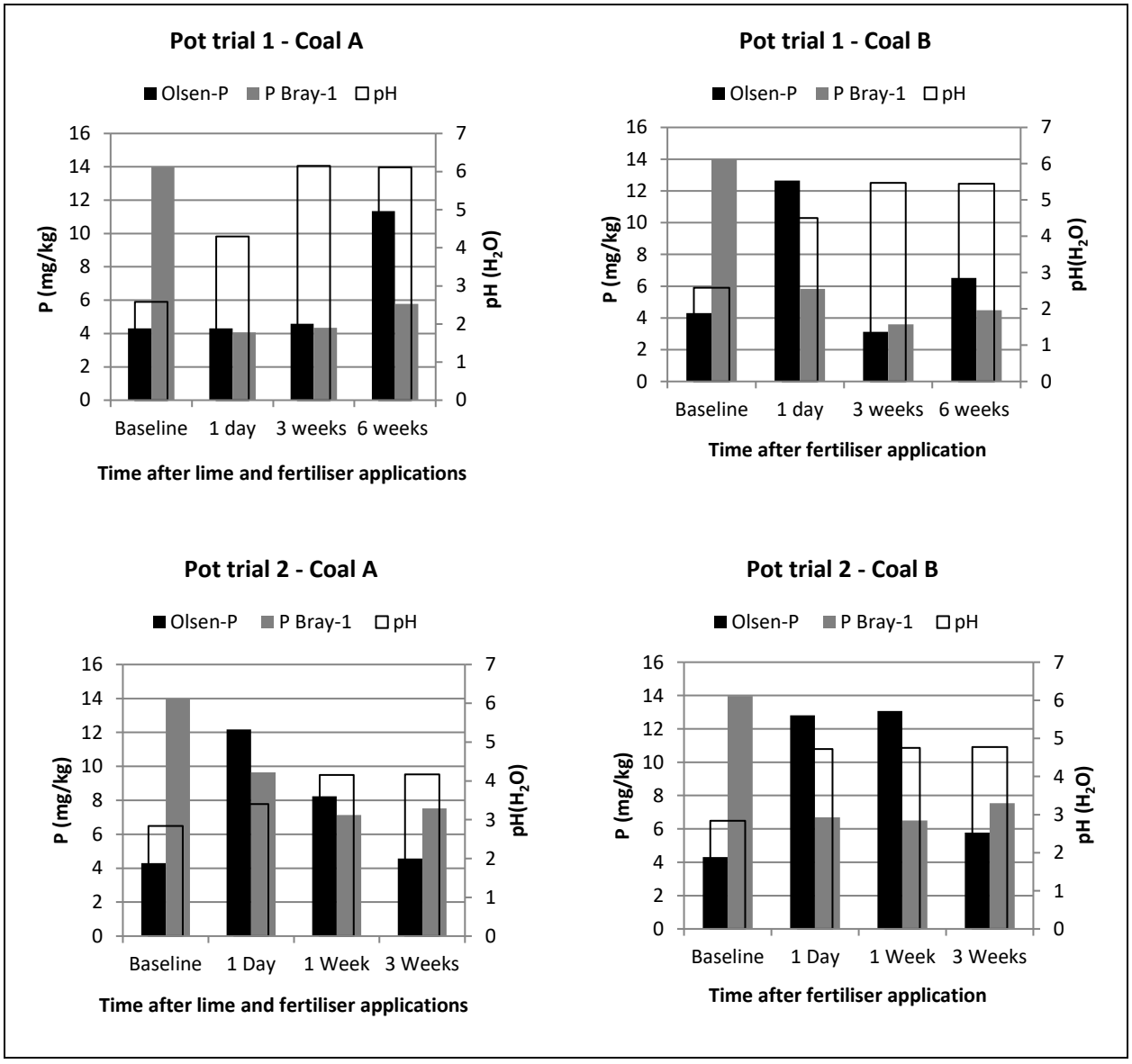


Figure 43: Olsen P, P Bray-1 and pH results for the coal tailings material during Pot trial 1 and Pot trial 2.

a) Pot trial 1

The results gathered during Pot trial 1 for Group A as well as Group B of the coal tailings material showed that the P Bray-1 values decreased from a baseline P value of 13.97 mg/kg P to 4.06 mg/kg P in Group A and 5.83 mg/kg P in Group B, one day after respective lime and fertiliser treatments. After six weeks, the P Bray-1 results were as low as 5.78 mg/kg P in Group A and 4.49 mg/kg P in Group B, despite definite increases in pH over this period. Similar P Bray-1 results were obtained for another highly limed tailings material, NM700 (435 t/ha).

As previously discussed, decreases in P Bray-1 values after lime- and fertiliser treatments were obtained from highly limed tailings, which led to the formulation of an additional research objective: to determine the effect of high Ca concentrations on the ability of the Bray-1 method to extract P from a highly limed growth medium. The results of this experiment are discussed in Section 4.8.

The Olsen P results for Pot trial 1 showed an increase from a baseline Olsen P value of 4.30 mg/kg P to 4.31 mg/kg P in Group A one day after lime and fertiliser treatment. pH values increased from 2.58 to 4.30. After three weeks, Olsen P values were 4.58 mg/kg P. P extracted by the Olsen method in Group A continued to increase to a value of 11.34 mg/kg P, six weeks after simultaneous lime and fertiliser applications.

Group B, which received fertiliser at a higher pH than Group A, showed greater increase in Olsen P values from 4.30 mg/kg P before any lime or fertiliser applications to 12.65 mg/kg P, one day after fertiliser treatment. Despite a further increase in pH to 5.47, the Olsen P results decreased to 3.12 mg/kg P three weeks after fertiliser treatment. The Olsen P results increased again to 6.51 mg/kg P, six weeks after fertiliser treatment.

There was a statistically significant positive correlation between Olsen P and P Bray-1 results in Group A ($r + 0.930$; $p < 0.0001$). No statistically significant correlation was observed between pH and Olsen P results ($r + 0.446$; $p > 0.05$) or between pH and P Bray-1 results ($r + 0.550$; $p > 0.05$) in Group A (ANOVA $F = 2.280$; ANOVA F *crit* > ANOVA F) (Appendix J). The p-value obtained from the analysis of variance was > 0.05, meaning that the relationships between pH, Olsen P and P Bray-1 in Group A of Pot trial 1 for the Coal tailings are not of statistical significance.

There was a statistically significant positive correlation between Olsen P and P Bray-1 results in Group B ($r + 0.903$; $p < 0.0001$). No statistically significant correlation was observed between pH and Olsen P results ($r – 0.232$; $p > 0.05$) or between pH and P Bray-1 results ($r – 0.154$; $p > 0.05$) in Group B (ANOVA $F = 3.126$; ANOVA F *crit* > ANOVA F) (Appendix L). The ANOVA p-value obtained from the analysis of variance was > 0.05, meaning that the relationships between pH, Olsen P and P Bray-1 in Group B of Pot trial 1 for the Coal tailings are not of statistical significance.

The average pH value for the coal tailings in Group A over the course of Pot trail 1 was 5.54. On average, the Olsen method extracted more P from the growth medium (6.87 mg/kg) than the Bray-1 method (4.75 mg/kg) (Appendix J). In Group B, an average pH of 5.14 was recorded. An average of 7.44 mg/kg P was recorded by the Olsen P analysis whereas a lower average of 4.62 mg/kg P was recorded by the Bray-1 analysis in Group B for Pot trial 1 (Appendix L).

b) Pot trial 2

The P Bray-1 results of Group A and Group B from Pot trial 2 were also lower after fertiliser treatments, despite definite increases in the pH of the tailings. Group B had lower Bray-1 results (6.69 mg/kg P) than Group A (9.65 mg/kg P), despite the fact that Group B received fertiliser at a higher pH than Group A. The P Bray-1 results for Group A and Group B decreased further to 7.14 mg/kg P (Group A) and 6.50 mg/kg P (Group B). Three weeks after the respective fertiliser treatments, the Bray-1 method extracted 7.53 mg/kg P in Group A and 7.54 mg/kg P in Group B. As in Pot trial 1, the P Bray-1 results did not increase to levels higher than the baseline value of 13.97 mg/kg P after the fertiliser applications.

The Olsen P results increased from a baseline value of 4.30 mg/kg P to 12.18 mg/kg P in Group A and 12.81 mg.kg P in Group B, one day after fertiliser applications. One week after the fertiliser treatments, the Olsen method extracted 8.24 mg/kg P in Group A and 13.07 mg/kg P in Group B. These values decreased to 4.57 mg.kg P in Group A and 5.78 mg.kg P in Group B, three weeks after the fertiliser treatments. The higher Olsen P results in Group B obtained at the end of Pot trial 2 proved that more P can be extracted by the Olsen method when fertiliser is applied after a neutralisation incubation period of six weeks.

There were statistically significant negative correlations between pH and P Bray-1 results ($r - 0.897$; $p < 0.0001$) and between pH and Olsen P results ($r - 0.799$; $p < 0.001$). A statistically significant positive correlation was obtained between Olsen P and P Bray-1 results ($r + 0.645$; $p < 0.05$) in Group A (ANOVA F = 538.743; ANOVA F *crit* < ANOVA F) (Appendix O).

No statistically significant correlations were found between Olsen P and P Bray-1 results ($r - 0.473$; $p > 0.05$), between pH and Olsen P results ($r - 0.262$; $p > 0.05$) or between pH and P Bray-1 results ($r + 0.124$; $p > 0.05$) in Group B (ANOVA F = 531.533; ANOVA F *crit* < ANOVA F) (Appendix Q).

The average pH value for the coal tailings in Group A over the course of Pot trail 2 was 3.90. On average, the Olsen method extracted more P from the growth medium (8.33 mg/kg) than the Bray-1 method (8.12 mg/kg) (Appendix O). In Group B, an average pH of 4.75 was recorded. An average of 10.55 mg/kg P was recorded by the Olsen P analysis whereas a lower average of 6.91 mg/kg P was recorded by the Bray-1 analysis in Group B for Pot trial 2 (Appendix Q).

4.7.4 NMC1 tailings material

A visual representation of the results obtained during Pot trial 1 and Pot trial 2 for the NMC1 tailings material is presented in Figure 44. The tailings were treated with 56 t/ha lime, 0.24 g/kg superphosphate in Pot trial 1 and 0.60 g/kg superphosphate in Pot trial 2 respectively.

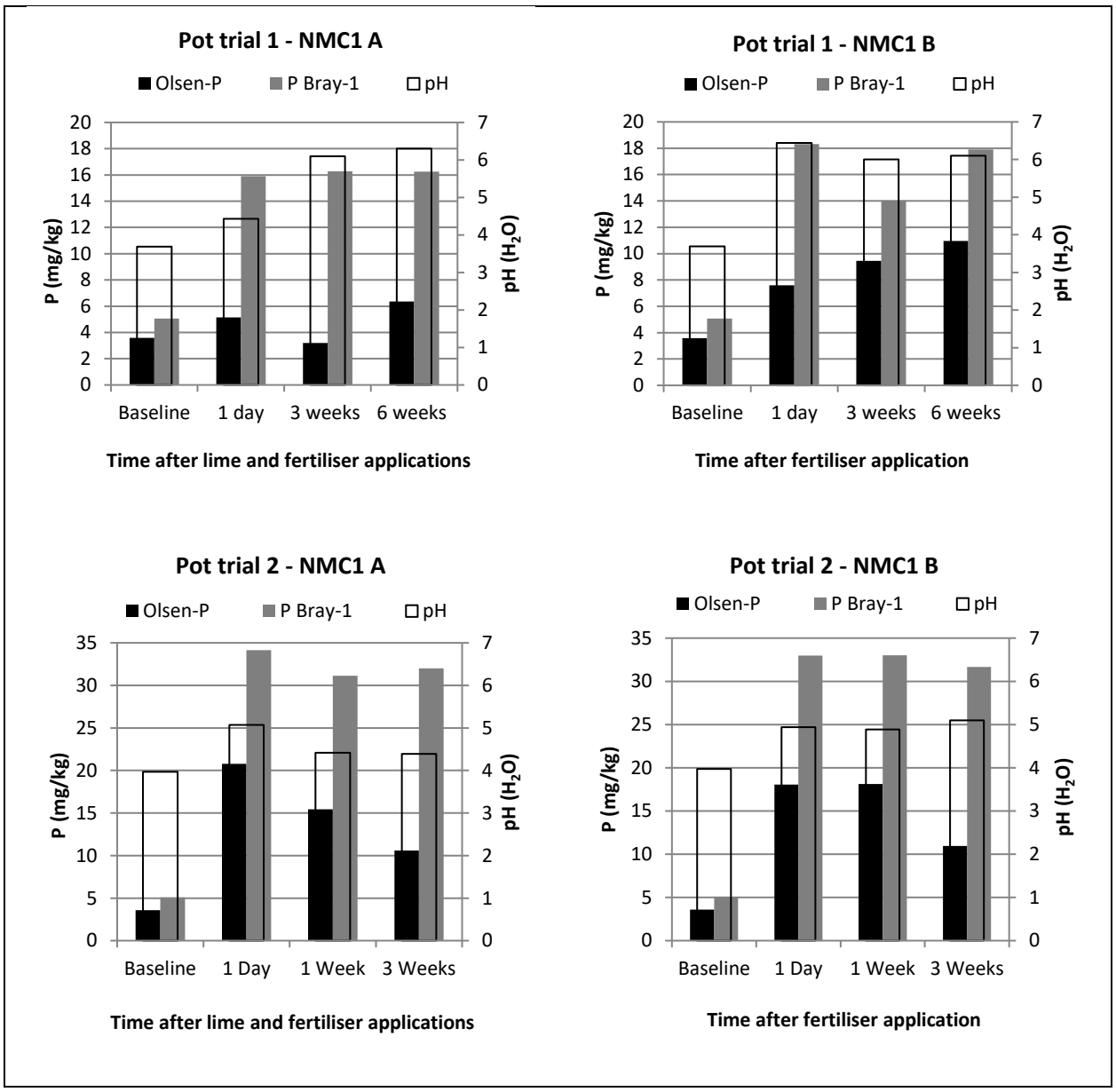


Figure 44: Olsen P, P Bray-1 and pH results for the NMC1 tailings material during Pot trial 1 and Pot trial 2.

a) Pot trial 1

Figure 44 shows that P Bray-1 values in Pot trial 1 increased from a baseline value of 5.07 mg/kg P to 15.91 mg/kg P in Group A and 18.32 mg/kg P in Group B, one day after fertiliser treatments. Three weeks after fertiliser treatments, the P Bray-1 values increased to 16.28 mg/kg P in Group A and decreased to 14.03 mg/kg P in Group B. After six weeks, the P Bray-1 results were 16.25 mg/kg P in Group A and 17.90 mg/kg P in Group B.

A more significant difference between the two groups was observed in the Olsen P results. One day after fertiliser treatment, the Olsen P increased from a baseline value of 3.58 mg/kg P to 5.15 mg/kg P in Group A and 7.60 mg/kg P in Group B where the growth medium was treated with fertiliser at a higher pH (pH 6.44). The Olsen method extracted a lower 3.20 mg/kg P in Group A

and a higher 9.46 mg/kg P in Group B. Six weeks after fertiliser treatment, the Olsen P values were 6.36 mg/kg P for Group A and 10.97 mg/kg P for Group B. These results also proved that extractable P was increased when applying superphosphate after a neutralisation incubation period of six weeks. Greater differences between Group A and Group B were observed in P extracted by the Olsen method, compared to P extracted by the Bray-1 method.

There was no statistically significant correlation in Group A between pH and Olsen P results ($r - 0.065$; $p > 0.05$), between pH and P Bray-1 results ($r + 0.140$; $p > 0.05$) or between Olsen P and P Bray-1 results ($r + 0.094$; $p > 0.05$) (ANOVA F = 265.385; ANOVA F *crit* < ANOVA F) (Appendix J).

Statistically significant correlations were observed for Group B between pH and P Bray-1 results ($r + 0.640$; $p < 0.05$) and between pH and Olsen P results ($r - 0.620$; $p < 0.05$). No statistically significant correlation was observed between Olsen P and P Bray-1 results ($r - 0.095$; $p > 0.05$) (ANOVA F = 128.672; ANOVA F *crit* < ANOVA F) (Appendix L).

The average pH value for the NMC1 tailings in Group A over the course of Pot trail 1 was 5.61. On average, the Olsen method extracted less P from the growth medium (4.82 mg/kg) than the Bray-1 method (16.17 mg/kg) (Appendix J). In Group B, an average pH of 6.18 was recorded. An average of 9.24 mg/kg P was recorded by the Olsen P analysis whereas a higher average of 16.77 mg/kg P was recorded by the P Bray-1 analysis in Group B for Pot trial 1 (Appendix L).

b) Pot trial 2

In Pot trial 2, P Bray-1 values increased in Group A (34.14 mg/kg) and Group B (32.99 mg/kg), one day after fertiliser applications. After one week, Group A had a P Bray-1 value of 31.05 mg/kg, whereas Group B had a higher value of 33.01 mg/kg. Three weeks after fertiliser treatments, P Bray-1 values were 32.01 mg/kg in Group A and 31.66 mg/kg in Group B.

The amount of P extracted by the Olsen method in Pot trial 2 increased from a baseline value of 3.58 mg/kg P to 20.79 mg/kg P in Group A and 18.06 mg/kg P in Group B, one day after the respective fertiliser applications. A week after the fertiliser applications, Olsen P values decreased in Group A to 15.44 mg/kg P and in Group B to 18.11 mg/kg P. Three weeks after the fertiliser applications, Olsen P values were 10.58 mg/kg in Group A and 10.95 mg/kg in Group B.

There was a statistically significant positive correlation in Group A between pH and Olsen P results ($r + 0.872$; $p < 0.0001$). No statistically significant correlation was observed between pH and P Bray-1 results ($r + 0.546$; $p > 0.05$) or between Olsen P and P Bray-1 results ($r + 0.386$; $p > 0.05$) (ANOVA F = 643.788; ANOVA F *crit* < ANOVA F) (Appendix O).

A statistically significant positive correlation was observed in Group B between Olsen P and P Bray-1 results ($r + 0.777$; $p < 0.05$). A statistically significant negative correlation existed between pH and Olsen P results ($r - 0.618$; $p < 0.05$). There was no statistically significant correlation between pH and P Bray-1 results ($r - 0.413$; $p > 0.05$) in Group B (ANOVA F = 189.455; ANOVA F *crit* < ANOVA F) (Appendix Q).

The average pH value for the NMC1 tailings in Group A over the course of Pot trail 2 was 4.63. On average, the Olsen method extracted less P from the growth medium (15.60 mg/kg) than the Bray-1 method (32.43 mg/kg) (Appendix O). In Group B, an average pH of 4.98 was recorded. An average of 15.71 mg/kg P was recorded by the Olsen P analysis whereas a higher average of 32.55 mg/kg P was recorded by the P Bray-1 analysis in Group B for Pot trial 2 (Appendix Q).

4.7.5 Crown tailings material

Figure 45 presents the results obtained from Pot trial 1 and Pot trial 2 for the Crown tailings material. This tailings material was treated with 25 t/ha lime, 0.28 g/kg superphosphate in Pot trial 1 and 0.64 g.kg superphosphate in Pot trial 2 respectively.

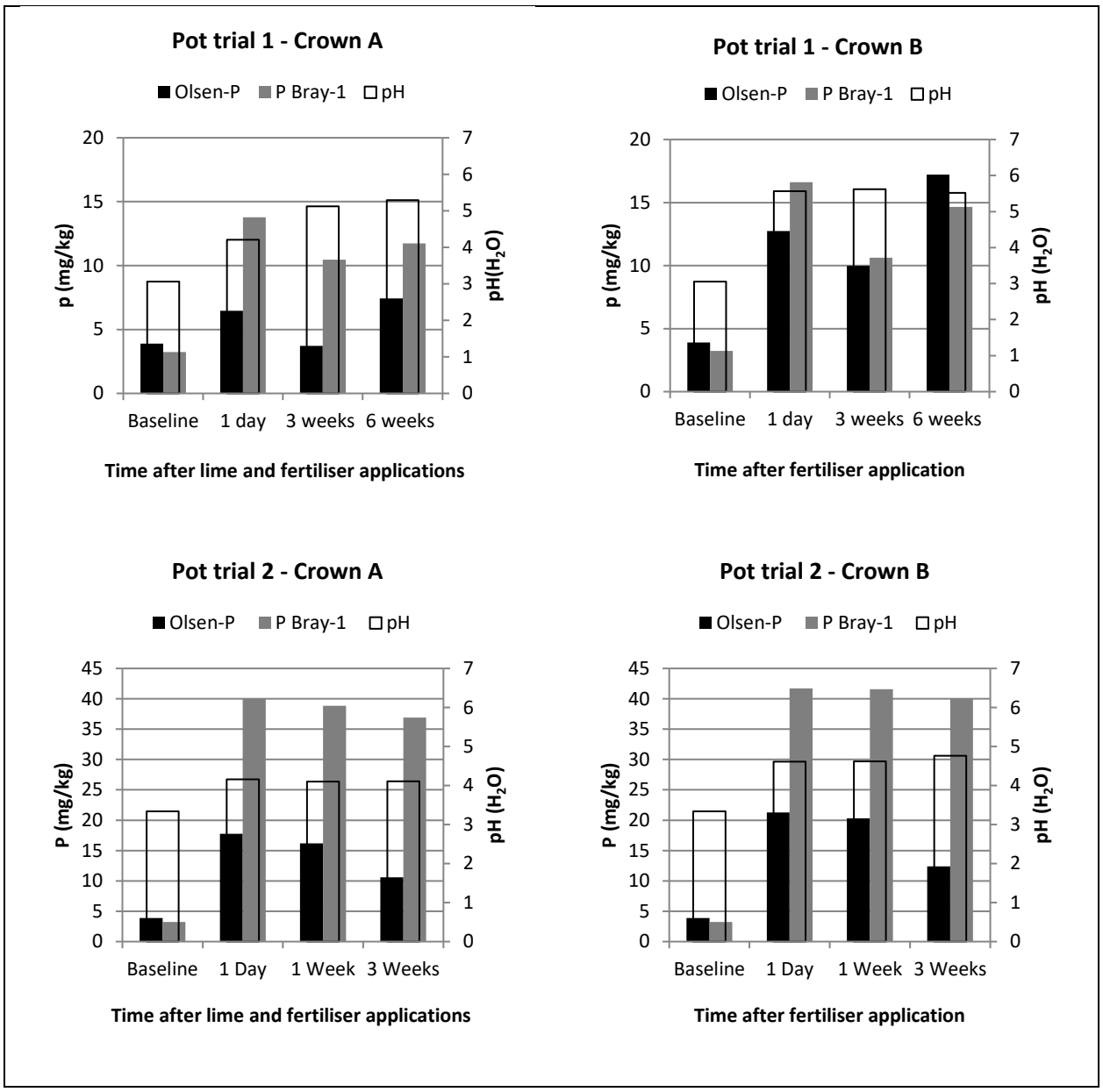


Figure 45: Olsen P, P Bray-1 and pH results for the Crown tailings material during Pot trial 1 and Pot trial 2.

a) Pot trial 1

The P Bray-1 levels of the Crown tailings material increased from a baseline P Bray-1 value of 3.23 mg/kg to 13.79 mg/kg in Group A and 16.62 mg/kg in Group B, one day after fertiliser treatments in Pot trial 1 (Figure 36). After three weeks, these values decreased to 10.47 mg/kg P in Group A and 10.62 mg/kg P in Group B. At the end of Pot trial 1, six weeks after the respective fertiliser treatments, P Bray-1 values were higher in Group B (14.66 mg/kg) than in Group A (11.73 mg/kg). The same results were obtained for the NMC1 tailings material.

Greater differences between Group A and Group B of the Crown tailings in Pot trial 1 were observed in the Olsen P results, an observation also made in the NMC1 tailings. The Olsen P levels increased from a baseline of 3.90 mg/kg P to 6.47 mg/kg P in Group A and 12.73 mg/kg P

in Group B. A much higher Olsen P result was obtained in Group B, where fertiliser was applied to the growth medium at a higher pH of 5.57. Three weeks after the respective fertiliser applications, Group B also had a higher Olsen P value (9.98 mg/kg) than Group A (3.73 mg/kg). Olsen P values of Group B (17.22 mg/kg) was much higher compared to Group A (7.43 mg/kg) at the end of Pot trial 1. The higher P Bray-1 and Olsen P results in Group B of Pot trial 1 proved that the amount of extractable P is increased when fertiliser is applied after a neutralisation incubation period of six weeks.

There was a statistically significant negative correlation in Group A pH and P Bray-1 results ($r - 0.654$; $p < 0.05$). No statistically significant correlation was observed between pH and Olsen P results ($r - 0.062$; $p > 0.05$) or between Olsen P and P Bray-1 results ($r + 0.465$; $p > 0.05$) (ANOVA $F = 80.001$; ANOVA F *crit* < ANOVA F) (Appendix J).

Statistical data from Group B showed no significant correlations between pH and Olsen P results ($r - 0.415$; $p > 0.05$), pH and P Bray-1 results ($r - 0.329$; $p > 0.05$) or between Olsen P and P Bray-1 results ($r + 0.356$; $p > 0.05$) (ANOVA $F = 41.739$; ANOVA F *crit* < ANOVA F) (Appendix L).

The average pH value for the Crown tailings in Group A over the course of Pot trail 1 was 4.87. On average, the Olsen method extracted less P from the growth medium (5.85 mg/kg) than the Bray-1 method (12.16 mg/kg) (Appendix J). In Group B, an average pH of 5.57 was recorded. An average of 13.24 mg/kg P was recorded by the Olsen P analysis whereas a higher average of 14.06 mg/kg P was recorded by the P Bray-1 analysis in Group B for Pot trial 1 (Appendix L).

b) Pot trial 2

During Pot trial 2, the Crown tailings also showed an increase in P Bray-1 results. One day after fertiliser treatments, the P Bray-1 values were 39.96 mg/kg P at a pH of 4.16 in Group A and 41.70 mg/kg P at a pH of 4.61 in Group B. The P Bray-1 levels decreased in Group A (38.83 mg/kg P) remained constant in Group B (41.56 mg/kg P), one week after fertiliser applications. Six weeks after the respective fertiliser applications, the pH and P Bray-1 levels were higher in Group B (pH: 4.76; 39.99 mg/kg P) than in Group A (pH: 4.11; 36.90 mg/kg).

P extracted by the Olsen method increased to 17.77 mg/kg P at a pH of 4.16 in Group A and 21.26 mg/kg P at a pH of 4.61 in Group B from a baseline of 3.90 mg/kg P, one day after fertiliser applications. One week after the applications, the Olsen P values decreased in both groups. At the end of Pot trial 2, three weeks after the respective fertiliser applications, more P was extracted with the use of the Olsen method in Group B (12.39 mg/kg P) with a pH of 4.76 than in Group A (10.61 mg/kg P) with a pH of 4.11.

There was a statistically significant positive correlation between Olsen P and P Bray-1 results (r +0.771; $p < 0.05$) in Group A. No correlation was found between pH and Olsen P results (r + 0.301; $p > 0.05$) or between pH and P Bray-1 results (r + 0.081; $p > 0.05$) (ANOVA F = 475.439; ANOVA F *crit* < ANOVA F) (Appendix O).

Data from Group B showed a statistically significant negative correlation between pH and Olsen P results (r – 0.744; $p < 0.05$). There was also a statistically significant correlation between Olsen P and P Bray-1 results (r + 0.615; $p < 0.05$). No correlation was observed between pH and P Bray-1 results (r – 0.147; $p > 0.05$) (ANOVA F = 2157.148; ANOVA F *crit* < ANOVA F) (Appendix Q).

The average pH value for the Crown tailings in Group A over the course of Pot trail 2 was 4.12. On average, the Olsen method extracted less P from the growth medium (14.85 mg/kg) than the Bray-1 method (38.56 mg/kg) (Appendix O). In Group B, an average pH of 4.66 was recorded. An average of 17.99 mg/kg P was recorded by the Olsen P analysis whereas a higher average of 41.08 mg/kg P was recorded by the P Bray-1 analysis in Group B for Pot trial 2 (Appendix Q).

4.7.6 Integration of results

The two growth mediums with the highest lime requirements (NM700: 435 t/ha; coal: 200 t/ha) the lowest P Bray-1 values at the end of Pot trial 1 and Pot trial 2 (Groups A and B), compared to the other three growth mediums, which all reached or nearly reached the target P values in Pot trial 1 (15 mg/kg P) and Pot trial 2 (30 mg/kg P). These results are attributed to great increases in the concentration of free Ca in the solution phase of the tailings as a result of high lime applications. The high concentration of free Ca^{2+} cations react with F^- anions of the NH_4F extracting agent used in the Bray-1 method. Calcium fluoride (CaF_2) forms as a result of this reaction, which reduces the ability of the extracting agent to extract P (Sims, 2002a). Section 4.8 contains a more detailed discussion on this occurrence.

The NM700 and the coal tailings showed the lowest P Bray-1 results at the end of both of the pot trials. They also had the highest Al saturation values of all the growth mediums used in the study (NM700: 183%; coal: 136.05%). Apart from the influence of high concentrations of free Ca^{2+} in the solution phase of the growth mediums, high Al saturation values could have caused P retention or fixation in the growth mediums. Stewart (1991) and Yuan *et al*. (2005) explain that the positively charged Al^{3+} cations bind with the negatively charged phosphate anions, resulting in the formation of less soluble phosphate compounds.

Heavy liming that took place with the NM700 and the coal tailings may not only have interfered with the accuracy of the Bray-1 method, but the large amount of lime may have also caused the plant availability of soluble phosphates to decrease in these tailings as a result of the chemical

precipitation of calcium phosphates on carbonate surfaces (Bohn *et al*., as cited in Aajjane *et al*., 2014).

Higher concentrations of P were extracted with the Olsen and the Bray-1 methods in Group B of the control medium, the NMC1 tailings and the Crown tailings at the end of Pot trail 1. These results proved that the six-week neutralisation incubation period before any fertiliser applications allowed for higher extractable P values in these growth mediums. Fertiliser was applied to the growth mediums at a higher pH in Group B (control: 6.66; NMC1: 6.44; Crown: 5.57) than in Group A (control: 4.37; NMC1: 3.69; Crown: 3.06). This resulted in increased plant availability of P in Group B due to higher pH levels at which the growth mediums were treated with fertiliser.

Lalljee (1997) found a significant positive correlation between pH and P fixation (r + 0.78). Even though he used a different method (Truog method) to determine P, he also observed that P levels decrease with a decrease in pH.

Lower extractable P was obtained with the Olsen and the Bray-1 method in Group B of the NM700 and the coal tailings during Pot trial 1. The P Bray-1 results were not trustworthy for these two tailings materials as a result of high lime applications. Because the Olsen method is pH-dependent (Iatrou *et al*., 2014), the higher Olsen P results in Group A can be explained by the fact that the NM700 and the coal tailings had higher pH values in Group A (NM700: 6.14; coal: 6.11) than in Group B (NM700: 5.69; coal: 5.45).

Higher P Bray-1 results were obtained in Group B at the end of Pot trial 2 for the control medium, coal tailings and the Crown tailings. P extracted with the Olsen method was higher in Group B for the NM700, coal, NMC1 and the Crown tailings. Pot trial 2 only lasted three weeks and not six weeks as Pot trial 1 did, due to time and financial constraints. More accurate results might have been obtained if it were possible to monitor P levels over a longer period than that of Pot trial 1. However, the higher Olsen P results in Group B of all of the tailings also proved that a neutralisation incubation period improved the plant availability of P in tailings materials.

The results obtained through the pot trials showed higher plant-available P values in growth mediums that had been treated with P fertiliser at higher pH values (>5.0). This supports the literature explaining the influence of high concentrations of Al^{3+} and Fe^{3+} in the solution phase of the growth medium on plant-available P due to very low pH values before lime treatment. High concentrations of these positively charged cations bind with phosphate anions (HPO_4^{2-} or $H_2PO_4^-$) to form less soluble compounds (e.g. $Al(OH)_2H_2PO_4$) that are unavailable for plant use (Hansel *et al*., 2014; Stewart, 1991; Yuan *et al*., 2005).

Implementing a neutralisation incubation period means that P fertilisers are applied at higher pH values, leading to higher plant-available P levels.

A decrease in plant-available P levels over time was observed numerously after fertiliser applications, especially during Pot trial 2. The same observation was made by Pretorius (1991). Attributed to adsorption and precipitation reactions that take place after P fertiliser applications, this is a normal occurrence in most acidic growth mediums (Bloem, 2018; Pretorius, 1991). It is therefore very important that P fertiliser is applied directly before sowing (Bloem, 2018).

4.7.7 Summary

The objective of Phase 2 was to determine if the plant availability of P improved after allowing a neutralisation incubation period before fertiliser applications, compared to a scenario where lime and fertiliser were applied simultaneously.

The results obtained from this phase showed that a neutralisation incubation period before fertiliser applications contributed towards higher Olsen P and P Bray-1 values in the control medium, NMC1 tailings and the Crown tailings in the first pot trial. The results from the second pot trial generally delivered higher plant-available P levels in the growth mediums that had been treated with fertiliser after a neutralisation incubation period.

These results support the main hypothesis of the project through proving that plant-available P measurements in highly limed tailings vary when a neutralisation incubation period of six weeks is implemented before fertiliser applications, compared to the common practice of applying lime and fertiliser simultaneously.

4.8 Effect of high Ca concentrations on the suitability of the P Bray-1 method

During Pot trial 1, the P Bray-1 results for the NM700 and the coal tailings material were inconclusive. Lower levels of P were extracted with the Bray-1 method after the application of superphosphate than before any lime or fertiliser was added to these two growth mediums; however, this did not happen with the other three growth mediums. These two tailings materials received much higher lime treatments compared to the rest of the growth mediums that formed part of the research study (Table 3 and Table A1 in Appendix A). The NM700 tailings were treated with 435 t/ha lime and the coal tailings with 200 t/ha lime, much more than the NMC1 tailings (56 t/ha), the Crown tailings (25 t/ha) and the control medium (5 t/ha).

P Bray-1 and Ca measured on the P Bray-1 extract before the growth mediums were treated with lime and fertiliser are presented in Appendix M.

The results presented in Appendix V show how the amount of P extracted by the Bray-1 method decreased with an increase in Ca present in the Bray-1 extract (due to the addition of lime) with the NM700 and coal tailings material, but not in the other growth mediums. Similar results were

obtained by Hahne *et al*. (1988), who used the Bray-2 method (also an acidic extracting agent made up of NH_4F and HCl) to determine the effect of $CaCO_3$ (calcitic lime) additions on the Bray-2 extraction of P. They reported a remarkable decrease in the amount of extractable P with the addition of $CaCO_3$ to three different phosphate compounds, $AlPO_4$, $Ca_3(PO_4)_2$ and $FePO_4$, in solution.

An experiment was conducted to determine whether high concentrations of free Ca present in a growth medium, as a result of high lime applications, could negatively affect the suitability of the Bray-1 method to extract P. In order to do this, the concentration of Ca was also analysed in the P Bray-1 extract. The results of these analyses can be seen in Appendix P. The amount of P extracted with the Bray-1 analyses was then correlated with the amount of Ca present in these Bray-1 extracts. The results of this correlation are illustrated in Figure 46.

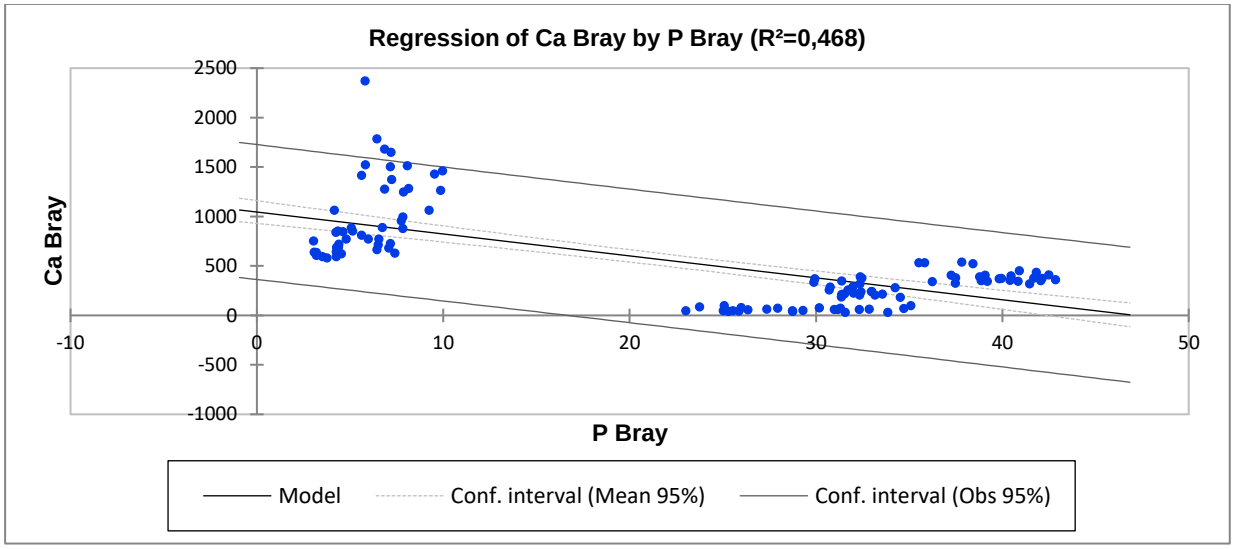


Figure 46: A correlation between the amount of P extracted by the Bray-1 method and the concentration of Ca present in the extracts.

The amount of P extracted by the Bray-1 method showed to be lower with higher concentrations of Ca present in the extract (Figure 46). This experiment proved that a moderately negative correlation (r - 0.684) existed between the amount of P extracted by the Bray-1 method and the concentration of Ca in the extract – a statistically significant correlation ($p < 0.05$) (ANOVA F = 151.609; ANOVA F *crit* < ANOVA F) (Appendix R).

Frank *et al*. (1998), Hahne *et al*. (1988) and Sims (2002a) warn against using the Bray-1 method in growth mediums with large amounts of lime ($CaCO_3$ > 2%). This method is based on an acidic extracting agent (pH 2.6) made up of ammonium fluoride (NH_4F) and hydrogen chloride (HCl) to solubilise Al, Ca and Fe phosphates through the protonation of PO_4^{3+} and the formation of Al^{3+} and Fe^{3+} complexes (Hahne *et al*., 1988; Sims, 2002a).

Sims (2002a) explains that the large amount of Ca^{2+} ions in solution from the lime reacts with F^- and Cl^- ions in the extracting agent. This reaction results in the formation of CaF_2, which then immobilises P and consequently leads to low P values, reducing the efficiency of the Bray-1 method to extract P.

The large amount of Ca found in the Bray-1 extract is not just free Ca present in the solution phase of the growth mediums; the high Ca values also originate from Ca ions brought into solution by the acidic Bray-1 extract through the dissolution of undissolved lime in the samples (Bloem, 2018). The presence of free lime in the growth medium would have also reduced the acidity of the HCl in the extracting agent.

It is therefore recommended to rather use the Olsen P method, which was initially designed for calcareous growth mediums with a pH of >5 (Iatrou *et al*., 2014), to monitor P levels in tailings material that has been treated with large quantities of lime. Even though the pH of tailings that have such high lime requirements (approx. >100 t/ha) frequently reach pH levels of <5 after lime treatment, the Olsen P method often showed to extract a more representative amount of P from the highly limed tailings than the Bray-1 method, especially during Pot trial 1.

The 0.5 M $NaHCO_3$ extracting agent increases the solubility of P by decreasing the concentration of Ca^{2+} ions in solution through precipitation as $CaCO_3$. It also causes a decrease in the concentration of Fe^{3+} and Al^{3+} ions in solution through the formation of Al and Fe oxyhydroxides. The alkaline-extracting agent increases the pH of the solution that causes a reduced amount of sorption sites and/or increased negative charges on Al and Fe oxides, which increases the desorption of available P into solution (Sims, 2002b).

4.8.1 Summary

The objective of this experiment was to determine whether the reliability of the Bray-1 method was affected by high concentrations of Ca in the growth medium as a result of heavy liming.

The results showed a negative correlation between P extracted by the Bray-1 method and the concentration of Ca in the extract, proving that the ability of the Bray-1 method to extract P from a growth medium decreases with an increase in the concentration of Ca^{2+}.

4.9 Phase 3: Seedling survival rates and plant performance

Higher Olsen P results in Group B of all of the tailings proved that a neutralisation incubation period before fertiliser applications improves the plant availability of P in acidic tailings materials. A final experiment was conducted on the pots of Pot trial 2 during the month of October 2017 to determine whether the increased plant availability of P, as a result of the neutralisation incubation

period, would result in improved seedling survival rates and better plant performance (also referred to as plant growth).

The growth mediums were irrigated every second day with irrigation sprinklers while receiving generous amounts of sunlight throughout the experiment. Germination success and the length of the longest *Eragrostis curvula* leaf were recorded to determine plant performance for Group A and Group B, six weeks after the seeds were planted (Appendix W). The results for Group A and Group B of the growth mediums were then compared to each other to determine whether the application of fertiliser after a neutralisation incubation period (Group B) would lead to better germination rates and plant growth, compared to when lime and fertiliser were applied simultaneously (Group A).

Figure 47 contains photographs of growth mediums taken on the day the recordings were done, six weeks after sowing. One replica of every growth medium is represented to demonstrate the difference in seedling survival rate and plant growth observed between the different growth mediums.

Figure 47: Photographs taken six weeks after sowing to illustrate the difference in plant growth and seedling survival observed between the different growth mediums.

The control medium exhibited the highest seedling survival rates and plant growth values. Of all the tailings materials, the highest seedling survival rates and plant growth values were observed in the coal and NMC1 tailings. The NM700 tailings showed to have the lowest seedling survival rates and plant growth values by far, as seen in Figures 47, 48 and 49.

The results for seedling survival rates in Group A and Group B of the growth mediums are presented in Figure 48. The average length of the tallest or longest grass leaf grown in the growth

mediums (Group A and Group B), which was used as a measure of plant growth, is shown in Figure 49.

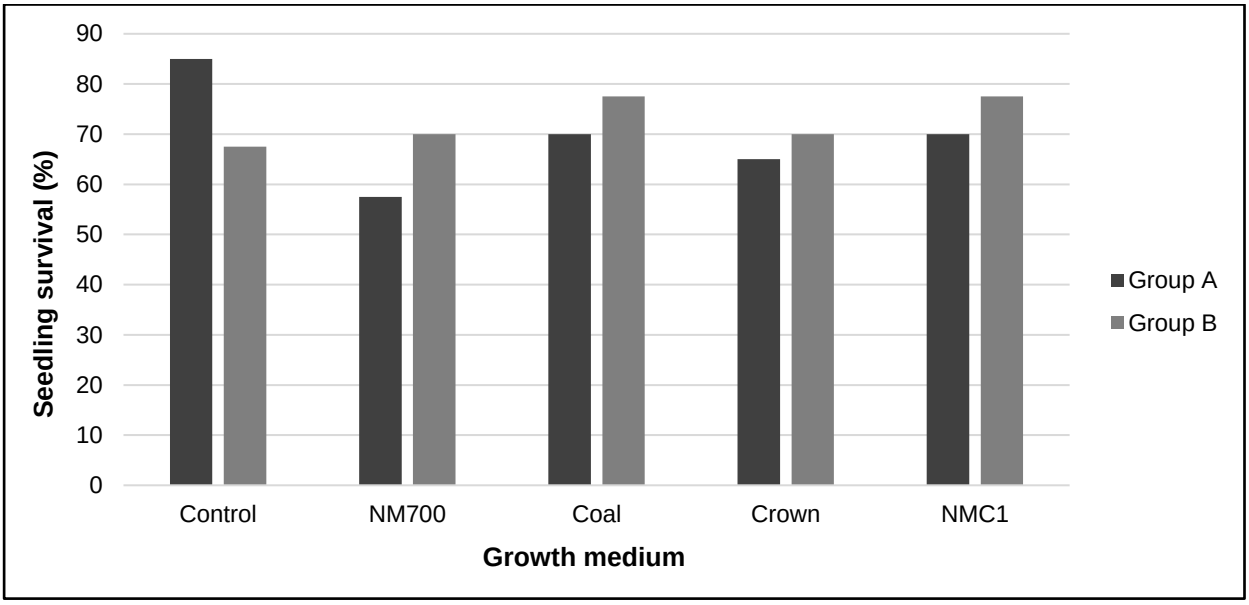


Figure 48: Average seedling survival rate of *Eragrostis curvula* in Group A and Group B of the growth mediums used in the study.

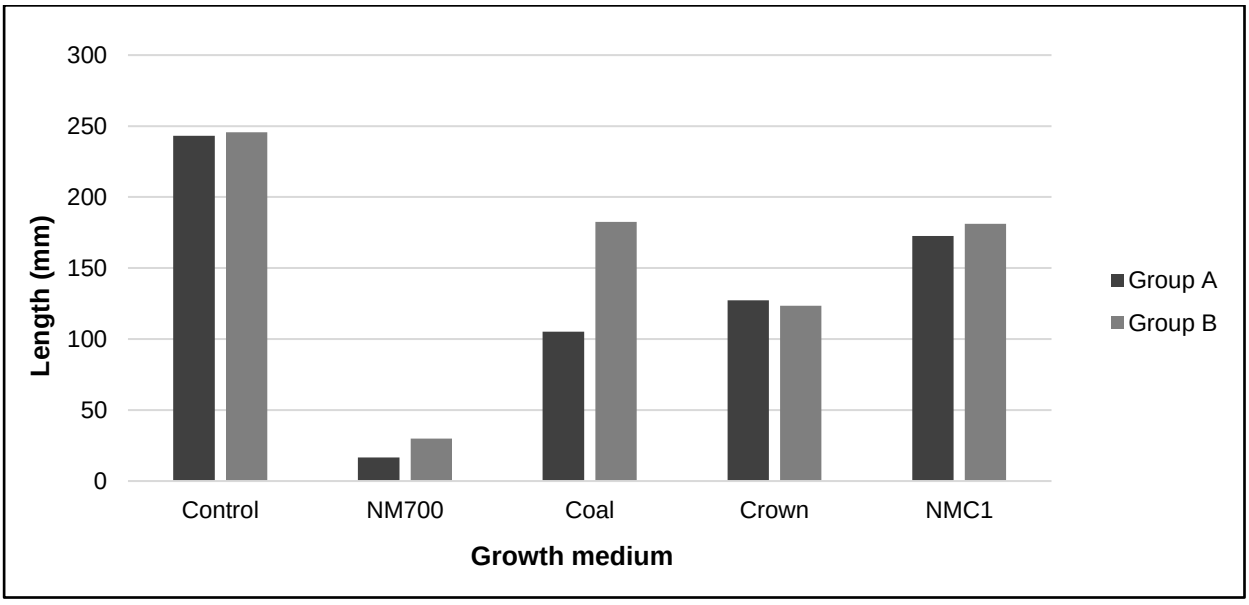


Figure 49: Average length of the longest *Eragrostis curvula* leaf for every growth medium in Group A and Group B.

The control medium had a higher seedling survival rate in Group A (85.00%) than in Group B (67.50%) but showed slightly better plant growth in Group B (245.75%) than in Group A (243.25%). These results imply that the neutralisation incubation period before fertiliser application resulted only in improved plant growth for the control medium and not improved seedling survival rates. The lower germination rate may be attributed to a very hard, resistant surface crust that was observed on the control medium at times when the soil was dry. This may

have caused a smaller germination rate in pots that received less water if the irrigation sprinklers did not irrigate evenly.

All of the tailings material presented higher seedling survival rates in Group B (NM700: 70.00%; coal: 77.50%; Crown: 70.00%; NMC1: 77.50%) than in Group A (NM700: 57.50%; coal: 70.00%; Crown: 65.00%; NMC1: 70.00%).

Improved plant growth was observed in Group B of NM700 (A: 57.50 mm; B: 30.00 mm), coal (A: 105.25 mm; B: 182.50 mm) and NMC1 (A: 172.50 mm; B: 181.25 mm), whereas the Crown tailings showed slightly better plant growth in Group A (A: 127.25 mm; B: 123.50 mm).

Dark purple leaves were observed on *Eragrostis curvula* planted in Group A and Group B of the Crown tailings (Figure 50), aiming towards P deficiency as described by MVSA (2007).

Figure 50: The purple discolouration of leaves observed in the Crown tailings material is a symptom of P deficiency (MVSA, 2007).

Horta and Torrent (2007) found that plant-available P and P extracted by the Olsen method were strongly correlated ($r + 0.93$; $p < 0.001$), a result that implies that the amount of P extracted by the Olsen method can be used as a measure of plant-available P.

All of the tailings showed that the neutralisation incubation period before fertiliser application resulted in increased plant availability in P (observed through higher Olsen P results in Group B

at the end of the pot trials). This was proved again in the results obtained from this experiment, where the higher levels of plant-available P that was observed in Group B, also showed higher seedling survival rates in the tailings. Better plant growth was also observed in Group B of most of the growth mediums. These results support Brady and Weil (2008), Johnston and Steën (2000) and the MVSA (2007) in that P does, in fact, play an important role in seedling survival rate and plant growth.

A positive correlation was observed between average grass height and P extracted by way of the Olsen method ($r + 0.789$; $p < 0.05$) (ANOVA $F = 44.334$; ANOVA F *crit* < ANOVA F) (Appendix X), implying that better plant growth was observed in growth mediums that had higher Olsen P values. No correlation was observed between average grass height and P extracted by the Bray-1 method ($r + 0.500$; $p < 0.05$) (Appendix X). These results support the findings by Horta and Torrent (2007) in that Olsen P results can be used as a measure for phyto-available P.

The results obtained from this experiment supported the statement made at the end of Section 4.2. Higher seedling survival rates were observed in Group B as a result of increased plant-available P. Higher seedling survival rates will then enhance the quality of the tailings as a growth medium by improving initial stabilisation of a newly created ecosystem. This may encourage the natural establishment of surrounding indigenous grass species that are adapted to the area and tolerable towards acidic growth mediums to take place as time passes (Schimmer *et al*., 2015; Van Deventer & Hattingh, 2008).

4.9.1 Summary

The objective of Phase 3 was to determine if seedling survival rate and growth performance were improved when fertiliser was applied after a neutralisation incubation period.

The results obtained from this experiment showed higher seedling survival rates in growth mediums that had been treated with fertiliser after a neutralisation incubation period. Higher growth performances were obtained in most of the mediums that had been treated with fertiliser after a neutralisation time lag.

Different seedling survival rates and growth performances were obtained between Group A and Group B, supporting the fourth sub-hypothesis of the research project.

CHAPTER 5

CONCLUSIONS

The conclusions based on the results of the research work and testing the hypotheses of this research study are summarised as follows:

5.1 Neutralisation incubation pot trial

Phase 1 of the study entailed a neutralisation incubation pot trial with 13 different tailings materials to identify five growth mediums that would be used for the main research work. Apart from identifying the growth mediums, the pH values of the tailings were also monitored on a weekly basis to determine when the tailings reached a value pH of >5 (where it is expected for P to be more plant-available).

It was found that the most suitable time to apply P as superphosphate would be six weeks after lime treatment, answering the first research question.

The different acidic tailings used in this pot trial showed varying neutralisation time lags, proving the first sub-hypothesis of the research study.

5.2 Comparing three different procedures of measuring pH in highly limed growth mediums

Three procedures (i.e. the leaching, conventional and incubation procedures) for measuring the pH of tailings that have been treated with a large amount of lime were also studied as part of Phase 1. Larger differences in the results of the three procedures were obtained in tailings that had received greater amounts of lime.

The leaching procedure was found to be more suitable for the monitoring of pH levels in highly limed tailings materials. The leaching procedure allows a much-shortened reaction time between the highly limed sample and the water added. Longer reaction times (as with the conventional and incubation procedures) force the large amount of lime in the sample to react, leading to a less representative pH value. The leaching procedure provided a more representative and immediate pH value for highly limed tailings materials, answering the second research question.

Because the three procedures used in this experiment delivered different pH values, where the greatest differences were observed in the highest limed growth mediums, the results support the second sub-hypothesis of the research study.

5.3 The influence of neutralisation time lag on the plant availability of P

The most important phase of the study, Phase 2, comprised the main experimental work. This was to determine whether the plant availability of P is improved by applying superphosphate after a neutralisation incubation period of six weeks (Group B), as opposed to applying the substances at the same time (Group A).

Two different analytical methods were used to determine P availability in the growth mediums (i.e. the Olsen method and the Bray-1 method). The Olsen method was used as an indicator for plant-available P in the growth mediums (Horta & Torrent, 2007).

The main hypothesis of the research was proved through the results obtained during the two pot trials. Plant-available P measurements in growth mediums that had been treated with fertiliser after the neutralisation incubation period of six weeks were different from the growth mediums that had been treated with lime and fertiliser simultaneously. Higher Olsen P results in Group B of all of the tailings, as well as the control medium, proved that a neutralisation incubation period before fertiliser application had improved the plant availability of P in the growth mediums.

5.4 Effect of high lime applications on the reliability of the P Bray-1 method

The effect of high concentrations of free Ca on the reliability of the P Bray-1 method was also investigated as part of Phase 2 of the study.

The motivation behind this experiment was that during Pot trial 1, lower P Bray-1 results were obtained after P fertiliser applications in the two growth mediums that had been treated with the most lime (NM700 and coal); however, the results obtained with the Olsen method showed increased levels of P, as expected.

It was found that high concentrations of free Ca in the solution phase of the growth mediums, as a result of heavy liming, negatively affected the suitability of the P Bray-1 method as a measure of plant-available P.

The Olsen P method was not affected by the high concentrations of Ca, making this method a more reliable method to determine plant-available P levels in heavy limed growth mediums.

5.5 Influence of neutralisation incubation before fertiliser application on seedling survival rate and plant performance

The main objective of Phase 3 was to determine if the neutralisation incubation period before fertiliser application would also lead to improved seedling survival rates and plant performance.

This experiment offered supporting evidence in that higher seedling survival rate values were obtained in Group B of the growth mediums where higher concentrations of P were extracted with the Olsen method. Higher plant performance values were obtained for most of the growth mediums, except for the Crown tailings. This finding may be attributed to Group B of the Crown tailings being accidentally placed in an area that received less water from the irrigation sprinklers, resulting in reduced plant growth, answering the third research question of the study.

The results obtained from the experiment, therefore, supports the third sub-hypotheses by proving that real-time germination rates and plant performances vary between when lime and fertiliser were applied simultaneously and when fertiliser was applied after a neutralisation incubation period.

By achieving the main aim and objectives of the research study, the project was successful in answering all of the research questions and proving the main and sub-hypotheses stated in Sections 1.4, 1.5 and 1.6.

This study ultimately produced insightful data, verifying that a neutralisation incubation period before fertiliser applications results in increased plant availability of P. Improved plant availability of this essential plant nutrient will contribute towards improving the quality of mine rehabilitation practices.

CHAPTER 6

RECOMMENDATIONS FOR FURTHER RESEARCH

Recommendations for future studies regarding this subject are as follows:

- Pot trials were used for the main experimental work in this research study. Further research should also incorporate field trials to extend the nature of the data collected. Field trials would deliver more detailed data sets that would incorporate the micro-environments of the specific TSFs.
- Additional studies (field and pot trials) on this research topic should be conducted on other types of acidic or sulphide-rich tailings material to extend the application of the results on other rehabilitation projects.
- Further studies should also include tailings material that extends over a wider variety of lime requirements.
- P monitoring has to be done more frequently (i.e. weekly) and over a longer period to obtain more detailed data sets and better statistical correlations between different variables. This would, however, be very expensive; therefore, more attention has to be given to obtaining sufficient funding for research projects such as this one. Funding was a big constraint during this study, which resulted in less frequent P monitoring and the use of only five growth mediums.
- The Olsen P method should always be used in conjunction with the P Bray-1 method when working with highly limed tailings materials. High concentrations of free Ca in the solution phase of the material (as a result of heavy liming) influence P Bray-1 results, despite the fact that the Bray-1 method had been developed for acidic growth mediums. See Section 4.8 for a more detailed discussion regarding this subject.
- It is of the utmost importance to monitor the pH of tailings material after lime treatment. This would be a labour-intensive and expensive practice but it would definitely improve the quality and sustainability of rehabilitation projects. Frequent monitoring would help environmentalists keep track of neutralisation after lime applications so that fertilisers are applied at pH levels where plant nutrients are optimally available for plant use. This would save significant expenditure since a smaller amount of plant nutrients will get lost as a result of fixation.
- It would be a great advantage to also investigate the influence of neutralisation time lag on the plant availability of potassium (K) in acid mine tailings.

REFERENCES

Aajjane, A., Karam, A. & Parent, L.E. 2014. Availability of Three Phosphorus Fertilizers to Corn Grown in Limed Acid-Producing Mine Tailings. *Journal of Bioremediation & Biodegradation,* 5(4):1-5.

Abreu, C.H., Muraoka, T. & Lavorante, A.F. 2003. Relationship between acidity and chemical properties of Brazilian soils. *Scientia Agricola*, 60(2):337-343.

Adams, F. 1984. Crop Response to Lime in the Southern United States. (*In* Adams, F., *ed*. Soil Acidity and Liming – Agronomy Monograph no. 12. 2nd ed. Madison, Wisconsin: American Society of Agronomy. p. 211-265).

Akcil, A. & Koldas, S. 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14:1139-1145.

Alvarenga, E.H.C. 2012. Bioavailability of Nutrients in Bio-solids. Oulu: University of Oulu. (Dissertation – MSc).

Antoniadis, V., Hatzis, F., Bachtsevanidis, D. & Koutroubas, S.D. 2015. Phosphorus availability in low-P and acidic soils as affected by liming and P-addition. *Communications in Soil Science and Plant Analysis*, 46:1288-1298.

Aucamp, P.J. 2000. Trace element pollution of soils by abandoned gold mine tailings near Potchefstroom, South Africa. Potchefstroom: NWU. (Dissertation – MSc).

Baquy, M.A., Li, J., Xu, C., Mehmood, K. & Xu, R. 2017. Determination of critical pH and Al concentration of acidic ultisols for wheat and canola crops. *Solid Earth*, 8:149-159.

Barber, S.A. 1984. Liming Materials and Practices. (*In* Adams, F., *ed*. Soil Acidity and Liming – Agronomy Monograph no. 12. 2nd ed. Madison, Wisconsin: American Society of Agronomy. p. 171-209).

Batjes, N.H. 2011. Global distribution of soil phosphorus retention potential. ISRIC Report 2011/06. http://www.isric.org/sites/default/files/isric_report_2011_06.pdf Date of access: 20 February 2018.

Beegle, D.B. 2001. Soil Acidity and Aglime. https://extension.psu.edu/soil-acidity-and-aglime Date of access: 17 February 2017.

Bell, F.G., Bullock, S.E.T., Halbich, T.F.J. & Lindsay, P. 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. *International Journal of Coal Geology*, 45:195-216.

Bejan, D. & Bruce, N.J. 2015. Acid mine drainage: electrochemical approaches to prevention and remediation of acidity and toxic metals. *Journal of Applied Electrochemistry*, 45: 1239-1254.

Bezuidenhout, N. & Rosseau, P.D.S. 2006. Investigations into the depth and rate of weathering on Witwatersrand gold tailings dam surfaces as key information for long-term ARD risk assessments. Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), St. Louis, MO, 26-30 March 2006.

Bishop, P. & Hedley, M. 2013. Effectiveness of Screened Ag-lime – A Review. Paper presented at the 26th Annual FLRC Workshop held at Massey University, February 2013. http://lfrc.massey .ac.nz/publications.html. Date of access: 15 January 2018.

Bloem, A.A. 2015. Soil Acidity. (Unpublished PowerPoint presentation presented at the NWU, Potchefstroom Campus for the OMWE 611 module).

Bloem, A.A. 2018. The effect of high Ca concentrations on the P Bray-1 method and adsorption and precipitation reactions of P in soils [email correspondence]. 15 January 2018, Potchefstroom.

Blowes, D.W., Ptacek, C.J., Frind, E.O., Johnston, R.H., Robertson, W.D. & Molson, J.W. 1994. Acid-neutralisation reactions in inactive mine tailings impoundments and their effect on the transport of dissolved metals. Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, 24-29 April 1994.

Botha, A.J. 2015. Surface impacts of gold mining activities on the Kromdraai/Koekemoerspruit: A situation analysis. Potchefstroom: NWU. (Dissertation – MSc).

Brady, N.C. & Weil, R.R. 2008. The Nature and Properties of Soils. 14th ed. Upper Saddle River, NJ: Pearson Prentice Hall.

Changul, C., Sutthirat, C., Padmanahban, G. & Tongcumpou, C. 2010. Chemical characteristics and acid mine drainage assessment of mine tailings from Akara Gold mine in Thailand. *Environmental Earth Science*, 60:1583-1595.

Chee, J.D. Pearson's Product-Moment Correlation: Sample Analysis. file:///C:/Users/Ida/Downloads/JCheePearsonsProduct_MomentCorrelation.pdf Date of access: 5 June 2018.

Costa, M.G., Gama-Rodrigues, A.C., De Moraes Goncalves, J.L., Gama-Rodrigues, E.F., Da Silva Sales, M.V. & Aleixo, S. 2016. Labile and Non-Labile Fractions of Phosphorus and Its Transformations in Soil under Eucalyptus Plantations, Brazil. *Forests*, 7(15):1-15.

Daniell, A. 2015. Geochemical monitoring of soil pollution from the MWS-5 gold tailings facility on the Farm Stilfontein. Potchefstroom: NWU. (Dissertation – MSc).

Desta, H.A. 2015. Reclamation of phosphorus fixation by organic matter in acidic soils. *Global Journal of Agriculture and Agricultural Sciences*, 3(6):271-278.

Do Carmo Horta, M. & Torrent, J. 2007. The Olsen P method as an agronomic and environmental test for predicting phosphate release form acid soils. *Nutrient Cycles Agroecosystems*, 77:283-292.

Dold, B. 2014. Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4:621-641.

Du Plessis, G.P. 2008. The relationship between geological structures and dolerite intrusions in the Witbank Highveld Coalfield, South Africa. Bloemfontein: UFS. (Dissertation – MSc).

Durand, J.F. 2012. The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa. *Journal of African Earth Sciences*, 68:24-43.

Envirogreen, 2004. Evaluation of the rehabilitation and surface stability of the Brakpan tailings dam (Ergo). Report prepared for AngloGold. (Unpublished).

Eriksson, P.G., Altermann, W. & Hartzer, F.J. 2006. The Transvaal Supergroup and its precursors. (*In* Johnson, M.R., Anhaeusser, C.R. & Thomas, R.J., *eds*. The geology of South Africa. Pretoria: Geological Society of South Africa, Johannesburg/Council for Geoscience. p. 237-260).

Foy, C.D. 1984. Physiological Effects of Hydrogen, Aluminium and Manganese Toxicities in Acid Soil. (*In* Adams, F. *ed*. Soil Acidity and Liming – Agronomy Monograph no. 12. 2nd ed. - Madison, Wisconsin: American Society of Agronomy. p. 57-97).

Frank, K., Beegle, D. & Denning, J. 1998. Phosphorus. (*In* Brown, J.R., *ed*. Recommended Chemical Soil Test Procedures for the North Central Region. p. 21-26. http://msue.anr.msu.

edu/uploads/234/68557/Rec_Chem_Soil_Test_Proce55c.pdf Date of access: 22 November 2017).

GKWG (Grondklassifikasiewerkgroep). 1991. Grondklassifikasie – 'n Taksonomiese sisteem vir Suid-Afrika. Pretoria: Departement van Landbou-ontwikkeling.

Gogtay, N.J. & Thatte, U.M. 2017. Principles of Correlation Analysis. *Journal of The Association of Physicians of India*, 65:78-81.

Gunsinger, M.R., Ptacek, C.J., Blowes, D.W., Jambor, J.L. & Moncur, M.C. 2006. Mechanisms controlling acid neutralisation and metal mobility within a Ni-rich tailings impoundment. *Applied Geochemistry*, 21:1301-1321.

Haagner, A.S.H. 2008. The role of vegetation in characterising landscape function on rehabilitating gold tailings. Potchefstroom: NWU. (Dissertation – MSc).

Hahne, H.C.H., Van der Merwe, A.J. & Loock, A.H. 1988. Review of phosphorus extraction methods and functional components of the Bray 2 and ISFEI/AMBIC extractants. Proceedings Phosphorus Symposium. Soil and Irrigation Research Institute, Pretoria.

Hansel, F.D., Amado, T.J.C., Bortolotto, R.P., Trindade, B.S. & Hansel, D.S.S. 2014. Influence of different phosphorus sources on fertilization efficiency. *Brazilian Journal of Applied Technology for Agricultural Science, Guarapuava*, 7(1):103-111.

Hansen, R.N. 2015. Contaminant leaching from gold mine tailings dams in the Witwatersrand Basin, South Africa: A new geochemical modelling. *Applied Geochemistry*, 61(2015):217-223.

Hattingh, J.M. 2005. Stabilising the slopes of mine waste disposal facilities with vegetation – An internal report for Envirogreen. (Unpublished).

Hattingh, J.M. & Van Deventer, P.W. 2004. The effect of the chemical properties of tailings and water application on the establishment of a vegetative cover on gold tailings dams. Water Research Commission Report No. 899/1/04. Pretoria.

Hattingh, R.P. 2003. Guidance for the rehabilitation of contaminated gold tailings dam footprints. Water Research Commission Report No.1001/2/03. Pretoria.

Hazelton, P. & Murphy, B. 2007. Interpreting soil test results: What do all the numbers mean? 2nd ed. Collingwood, Aus: CSIRO Publishing.

Horta, M. & Torrent, J. 2007. The Olsen P method as an agronomic and environmental test for predicting phosphate release from acid soils. *Nutrient Cycling in Agroecosystems*, 77:283-292.

Hossner, L.R. & Hons, F.M. 1992. Reclamation of Mine Tailings. (*In* Lal, R. & Stewart, B.A., *ed.* Soil Restoration – Advances in Soil Science: Volume 17. New York: Springer-Verlag. p. 311-350).

Hunter, P.J., Teakle, G.R. & Bending, G.D. 2014. Root traits and microbial community interactions in relation to phosphorus availability and acquisition, with particular reference to *Brassica*. *Frontiers in Plant Science*, 5(27):1-18.

Iatrou, A., Papadopoulos, A., Papadopoulos, F., Dichala, O., Psoma, P. & Bountla, A. 2014. Determination of Soil Available Phosphorus using the Olsen and Mehlich 3 Methods for Greek Soils Having Variable amounts of Calcium Carbonate. *Communications in Soil Science and Plant Analysis*, (45):2207-2214.

IRRS (International Rice Research Institute). 2011. Available phosphorus (Olsen Phosphorus). file:///C:/Users/23378506/Downloads/QM-AD002-AP12%20-Available%20Phosphorus%20_Olsen%20P_-rev03-09jan2011_condensed.pdf Date of access: 26 April 2017.

Jackson, L.M. & Parbhakar-Fox, A. 2016. Mineralogical and geochemical characterization of the Old Tailings Dam, Australia: Evaluating the effectiveness of a water cover for long term AMD control. *Applied Geochemistry*, 68:64-78.

James, A.R. 1997. The prediction of pollution loads from coarse sulphide-containing waste materials. Water Research Commission Report no. 559/1/97.

Jeffrey, L.S. 2005. Characterization of the coal resources of South Africa. *The Journal of the South African Institute of Mining and Metallurgy*, 95-102.

Johnston, A.E. & Steën, I. 2000. Understanding phosphorus and its use in agriculture. http://www.fertilizerseurope.com/fileadmin/user_upload/publications/agriculture_publications/EFMA_Phosphorus_booklet__2_.pdf Date of access: 30 August 2016.

Johnston, M.A., Miles, N. & Thibaud, G.R. 1991. Quantities of phosphorus fertiliser to raise the soil test value. *South African Journal of Plant and Soil*, 8(1):17-21.

Jones, J.B. 2012. Plant Nutrition and Soil Fertility Manual. 2nd ed. Broken Sound Parkway, USA: CRC Press.

Jurjovec, J., Ptacek, C.J. & Blowes, D.W. 2002. Acid neutralization mechanisms and metal release in mine tailings: A laboratory column experiment. *Geochimica et Cosmochimica Acta*, 66(9):1511-1523.

Justin, M.K., John, S.K., Fred, S.K. & Peter, K.O. 2012. Comparison of soil phosphorus extraction by Olsen and double acid methods in acid soils of Western Kenya. *East African Journal of Pure and Applied Science*, 2(1):1-5.

Kalra, Y.P. 1995. Determination of pH of Soils by Different Methods: Collaborative Study. *Journal of AOAC International*, 79(2):310-324.

Khozhina, E.I. & Sheriff, B.L. 2006. Background research of the tailings area of a Ni-Cu mine for the determination of an optimal method for revegetation. *Forest, Snow and Landscape Research*, 80(3):367-386.

Kleinkopje Colliery. 2013. Kleinkopje Life of Mine 2013 Report. (Unpublished).

Koch, J. 2014. Migration and gamma ray assessment of uranium on a gold tailings disposal facility. Potchefstroom: North-West University. (Dissertation – MSc).

Kossoff, D., Dubbin, W.E., Alfredsson, M., Edwards, S.J., Macklin, M.G. & Hudson-Edwards, K.A. 2014. Mine tailings dams: Characteristics, failure, environmental impacts and remediation. *Applied Geochemistry*, 51:229-245.

Landau Colliery, 2001. The Environmental Management Programme Report for Landau Colliery: A Section of South African Coal Estates. http://www.sahra.org.za/sahris/sites/default/files/additionaldocs/Landau_ML101995_EMPR_Main_DMEstamped_Compressed_0.pdf Date of access: 5 April 2017.

Lee, J. & Kim, Y. 2008. A quantitative estimation of the factors affecting pH changes using simple geochemical data form acid mine drainage. *Environmental Geology*, 55(1):66-75.

Logan, T.J. 1992. Reclamation of Chemically Degraded Soils. (*In* Lal, R. & Stewart, B.A., *eds*. Advances in Soil Science: Volume 17 – Soil Restoration. New York: Springer-Verlag. p. 13-35).

Mallarino, A.P. Comparison of Mehlich-3, Olsen, and Bray-P1 procedures for phosphorus in calcareous soils. http://www.agronext.iastate.edu/soilfertility/info/ComparisonofMehlich-3OlsenandBray-P1Procedures.pdf Date of access: 14 December 2017.

Marais, M. 2013. Practical Implications of Legislation Pertaining to Remediation and Mine Closure. Basic Principles of Ecological Rehabilitation and Mine Closure: Resource Kit 2. (Unpublished).

McCarthy, T. & Rubidge, B. 2005. The Story of Earth and Life: A southern African perspective on a 4.6-billion-year journey. Cape Town: Struik Nature.

McCarthy, T.S. 2006. The Witwatersrand Supergroup. (*In* Johnson, M.R., Anhaeusser, C.R. & Thomas, R.J., *eds*. The geology of South Africa. Pretoria: Geological Society of South Africa, Johannesburg/Council for Geoscience. p. 155-186).

Mingorance, M.D., Franco, I. & Rossini-Oliva, S. 2016. Application of different soil conditioners to restorate mine tailings with native (*Cistus ladanifer L.*) and non-native species (*Medicago sativa L.*). *Journal of Geochemical Exploration*. http://dx.doi.org/10.1016/j.gexplo.2016.02.010 Date of access: 4 August 2016.

Muller, I. 2014. Seed viability and re-growth of grasses used for mine waste rehabilitation. Potchefstroom: NWU. (Dissertation – MSc).

MVSA (Die Misstofvereniging van Suid-Afrika). 2007. Bemestingshandleiding. 7de uitgawe. Lynwoodrif, SA: Die Misstofvereniging van Suid-Afrika.

Myburgh, E. 2015. Soil quality of topsoil and subsoil substrates at Kleinkopje Colliery. Potchefstroom: NWU. (Mini-dissertation – BSc Hons).

Nengovhela, A.C., Yibas, B. & Ogola, J.S. 2006. Characterisation of gold tailings dams of the Witwatersrand Basin with reference to their acid mine drainage potential, Johannesburg, South Africa. *Water SA*, 32(4):499-506.

Nicholson, R.V., Gillham, R.W. & Reardon, E.J. 1988. Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. *Geochimica et Cosmochimica Acta*, 52:1077-1085.

Ochieng, L., Harck, T. & Peters, M. 2009. Net Neutralisation Potential (NNP) in Kimberley Diamond Tailings and Slimes Waste Materials. Paper presented at the International Mine Water Conference, Pretoria, SA, 19-23 October 2009.

Poozesh, V., Castillon, P., Cruz, P. & Bertoni, G. 2010. Re-evaluation of the liming-fertilization interaction in grasslands on poor and acid soils. *Grass and Forage Science*, 65:260:272.

Pretorius, J.M. 2014. Growth potential of various plant species for vegetative rehabilitation of different mine tailings. Potchefstroom: NWU. (Dissertation – MSc).

Pretorius, M. 1991. ’n Vergelyking van verskillende metodes vir die ekstraksie en bepaling van fosfor in gronde. Potchefstroom: NWU. (Verhandeling – MSc).

Rachana, J., Saxena, J. & Sharma, V. 2012. Phosphate Solubilising Microorganisms: Characterization of Phoaphate Solubilizing Fungi from Semi-Arid Agricultural Soil for Potential Use as Biofertilisers. India: Lap Lambert Academic Publishing.

Ritcey, G.M. 2005. Tailings management in gold plants. *Hydrometallurgy*, 78:3-20.

Rösner, T. & Van Schalkwyk, A. 2000. The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa. *Bulletin of Engineering Geology and the Environment*, 59:137-148.

Roux, E.H., De Jager, D.H., Du Plooy, J.H., Nicotra, A., Van der Linde, G.J. & De Waal, P. 1989. Phosphate in South Africa. *Journal of the South African Institute of Mining and Metallurgy*, 89(5):129-139.

Sanyal, S.K. & De Datta, S.K. 1991. Chemistry of phosphorus transformations in soil. (*In* Stewart, B.A., *ed.* Advances in Soil Science: Volume 16. New York: Springer-Verlag. p. 1-120).

Saria, L., Shimaoka, T. & Miyawaki, K. 2006. Leaching of heavy metals in acid mine drainage. *Waste Management and Research*, 24:134-140.

Sarker, A., Kashem, M.A., Osman, K.T., Hossain, I. & Ahmed, F. 2014. Evaluation of Available Phosphorus by Soil Test Methods in an Acidic Soil Incubated with Different Levels of Lime and Phosphorus. *Open Journal of Soil Science*, 4:103-108.

Schimmer, C., Schmidhuber, E. & Van Deventer, P.W. 2015. Alternative multiphase rehabilitation approach for an extreme hostile gold tailings storage facility. Paper presented at the 3rd Annual LaRSSA Conference, Muldersdrift, SA, 8-11 September.

Schoenberger, E. 2016. Environmentally sustainable mining: The case of tailings storage facilities. *Resources Policy*, 49(2016):119-128.

Shober, A.L. 2015. Phosphorus Cycling in the Agricultural Landscape. http://extension.udel.edu/factsheets/phosphorus-cycling-in-the-agricultural-landscape/ Date of access: 29 May 2017.

Sims, J.T. 2002a. Soil Test Phosphorus: Bray and Kurtz P-1. (*In* Pierzynski, G.M., *ed*. Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters. Southern Cooperative Series. p. 13-14. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.454.4558&rep=rep1&type=pdf Date of access: 22 November 2017).

Sims, J.T. 2002b. Soil Test Phosphorus: Olsen P. (*In* Pierzynski, G.M., *ed*. Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters. Southern Cooperative Series. p. 20-21. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.454.4558&rep=rep1&type=pdf Date of access: 22 November 2017).

Singer, M.J. & Munns, D.N. 1992. Soils – An Introduction. 2nd ed. New York: Macmillan Publishing Company.

Singh, B., Wilson, M.J., McHardy, W.J., Fraser, A.R. & Merrington, G. 1999. Mineralogy and chemistry of ochre sediments from an acid mine drainage near a disused mine in Cornwall, UK. *Clay Minerals*, 34:301-317.

Snyder, C. s.a. Efficient Fertilizer Use – Soil pH Management. http://www.plantstress.com /articles/toxicity_m/soilph%20amend.pdf Date of access: 17 February 2017.

SIR (Soil and Irrigation Research Institute). 1987. Land Types of the Maps 2626 West Rand, 2726 Kroonstad. Memoirs on the Agricultural Natural Resources of South Africa, No. 4. Department of Agriculture and Water Supply, Pretoria.

South Africa. 1965. Atmospheric Pollution Prevention Act 45 of 1965. Pretoria: Government Printer.

South Africa. 1983. Conservation of Agricultural Resources Act 43 of 1983. Pretoria: Government Printer.

South Africa. 1996. Constitution of the Republic of South Africa 1996. Pretoria: Government Printer.

South Africa. 1998a. National Environmental Management Act 107 of 1998. Pretoria: Government Printer.

South Africa. 1998b. National Water Act 36 of 1998. Pretoria: Government Printer.

South Africa. 1999. Nuclear Energy Act 1999. Pretoria: Government Printer.

South Africa. 2002. Mineral and Petroleum Resources Development Act 28 of 2002. Pretoria: Government Printer.

South Africa. 2004. National Environmental Management: Biodiversity Act 10 of 2004. Pretoria: Government Printer.

South Africa. 1989. Environmental Conservation Act 73 of 1989. Pretoria: Government Printer.

Sparks, D.L. 2003. Environmental Soil Chemistry. 2nd ed. San Diego, CA: Academic Press.

Ssenku, J.E., Ntale, M., Backeus, I., Lehtila, K. & Oryem-Origa, H. 2014. Dynamics of plant species during phytostabilisation of copper mine tailings and pyrite soils, Western Uganda. *Journal of Environmental Engineering & Ecological Science*, 3(4):1-12.

Stevenson, F.J. 1986. Cycles of Soil. New York: John Wiley & Sons.

Stewart, B.A. 1991. Advances in Soil Science: Volume 16. New York: Springer-Verlag.

Stroia, C., Berbecea, A., Baghina, N., Gaica, I., Stroia, M. & Radulov, I. 2013. Phosphorus dynamics on acidic grassland soil. *Research Journal of Agricultural Science*, 45(1):78-83.

Swart, E. 2003. The South African legislative framework for mine closure. *The Journal of The South African Institute of Mining and Metallurgy*: 489-492.

The Non-Affiliated Soil Analyses Work Committee. 1990. Handbook of standard soil testing methods for advisory purposes. Pretoria: Soil Science Society of South Africa.

Thomas, G.W. & Hargrove, W.L. 1984. The Chemistry of Soil Acidity. (*In* Adams, F., *ed*. Soil Acidity and Liming – Agronomy Monograph no. 12. 2nd ed. Madison, Wisconsin: American Society of Agronomy. p. 3-56).

Tisdale, S.L., Nelson, W.L. & Beaton, J.D. 1990. Soil fertility and fertilizers. 4th ed. New York: Macmillan Publishing Company.

Usher, B.H., Cruywagen, L.M., De Necker, E. & Hodgson, F.D.I. 2003. On-site and Laboratory Investigations of Spoil in Opencast Collieries and the Development of Acid-Base Accounting Procedures. WRC Report No. 1055/1/03, Pretoria.

Van Der Nest, L.J. 1991. ‘n Evaluering van analiesetegnieke vir die bepaling van kalkbehoefte van goudmynslikdam-materiaal vir die vestiging van plantegroei. Potchefstroom: NWU. (Tesis – MSc).

Van der Watt, H.V.H. 1986. Die oplosbaarheid en mobiliteit van kalk in sand. *South African Journal of Plant & Soil*, 3(3):140-146.

Van Deventer, P.W. 2007. Memorandum: Lime application on coal discard material. A report to Bulk Mech and Frazer Alexander Tailings. (Unpublished).

Van Deventer, P.W. 2008. Effectiveness of covers & analogue models. (*In* Van Deventer, P.W. 2015. Principles of rehabilitation of disturbed areas. Potchefstroom: NWU, Potchefstroom Campus. (Study guide OMWE 611 PEC)).

Van Deventer, P.W. 2015. Principles of rehabilitation of disturbed areas. Potchefstroom: NWU, Potchefstroom Campus. (Study guide OMWE 611 PEC).

Van Deventer, P.W. 2017. The geology of the New Machavie Gold Mine [personal correspondence]. 2 Jun., Potchefstroom.

Van Deventer, P.W. & Hattingh, J.M. 2008. Principles of rehabilitation of disturbed areas. (*In* Van Deventer, P.W. 2013. Gronddegradasie en Rehabilitasie. Potchefstroom: NWU, Potchefstroom Campus. (Study guide GDKN 221 PAC)).

Van Deventer, P.W., Hattingh, A.M., Botha, F. & Du Plessis, F. 2009. GDARD: Conceptual study on reclamation of mine residue areas for development purposes. Gauteng Department of Agriculture and Rural Development (GDARD). (Unpublished).

Van Deventer, P.W., Hattingh, J. & Bloem, D. 2007. Post-Rehabilitation Acidification of Gold Tailings. A report for Frazer Alexander Tailings. (Unpublished).

Van Oudtshoorn, F. 2012. Gids tot Grasse van Suider-Afrika. Pretoria: Briza Publikasies.

Versfeld, DB., Everson, C.S. & Poulter, A.G. 1998. The Use of Vegetation in the Amelioration of the Impacts of Mining on Water Quality – An Assessment of Species and Water Use. http://www.wrc.org.za/Knowledge%20Hub%20Documents/Research%20Reports/413-1-98.pdf Date of access: 13 November 2017.

Verwoerd, W.J. & Du Toit, M.C. 2006. The Phalaborwa and Schiel Complexes. (*In* Johnson, M.R., Anhaeusser, C.R. & Thomas, R.J., *eds*. The geology of South Africa. Geological Society of South Africa, Johannesburg/Council for Geoscience, Pretoria, p. 291-299).

Viljoen, C. 2013. Chemical Properties of Substrate. Basic Principles of Ecological Rehabilitation and Mine Closure: Resource Kit 3. (Unpublished).

Viljoen, M. 2009. The life, death and revival of the central Rand Goldfield. Paper presented at the World Gold Conference, hosted by The Southern African Institute of Mining and Metallurgy, Misty Hills, SA, 26-30 October.

Winegardner, D.L. 1995. An introduction to soils for environmental professionals. Boca Raton, Florida: Lewis Publishers.

XLSTAT. 2017. Correlation tests. https://www.xlstat.com/en/solutions/features/correlation-tests Date of access: 4 June 2018.

Yibas, B., Pulles, W. & Nengovhela, C. 2010. Kinetic development of oxidation zones in tailings dams with specific reference to the Witwatersrand gold mine tailings dams. WRC Report No. 1554/1/10, Pretoria.

Yuan, Y., Binger, R.L., Theurer, F.D., Rebich, R.A. & Moore, P.A. 2005. Phosphorus component in AnnAGNPS. *Transactions of the ASAE*, 46(6):2145-2154.

APPENDICES

<u>Appendix A:</u> Lime requirements of the growth mediums used throughout the study, obtained by way of NAP analyses.

Table A1: Lime requirements of the various tailings materials.

Sample	pH(KCl)	Res lime (t/ha lime)	Titr acid (t/ha lime)	Lime req 1 (t/ha)	Nett lime req (t/ha)	Total S (%)
Crown	2.90	0.00	14	11	25	0.31
NMC1	3.70	0.00	19	37	56	0.68
NMC2	2.80	0.00	21	35	56	0.55
NM700	2.40	0.00	141	294	435	3.34
NMTP	3.30	0.00	3	6	9	0.11
NMGeel	2.60	0.00	21	77	98	0.94
NMTPT	3.10	0.00	4	16	20	0.19
NMTS	4.20	0.00	4	6	10	0.18
Coal1	2.50	0.00	69	131	200	1.64
Coal2	6.20	0.00	1	41	42	0.52
Control	4.00	0.00	5		5	
T23	5.60	0.00	1	20	21	0.30
Domrif	3.50	0.00	15	86	101	1.26
T7 (Fluorspar)	7.10	7.00	0	14	7	0.23

† Lime req 1 = Lime requirement generated through future pyrite oxidation

<u>Appendix B:</u> Results for the baseline chemical analyses conducted to determine the chemical attributes of the growth mediums used in pot trial A and B.

Table B1: Nutrient status, pH(H_2O), EC and pH(KCl) results.

Growth medium	Nutrient status (mg/kg)						pH (H_2O)	EC (mS/m)	pH (KCl)
	Ca	Mg	K	Na	P (Bray-1)	P (Olsen)			
Control	101.75	74.50	97.75	30.80	3.21	3.40	4.37	20.50	3.82
NM700	269.00	403.75	0.50	16.25	14.20	3.35	2.75	945.50	2.50
Coal	1209.25	109.50	0.50	16.50	13.97	4.30	2.58	995.00	2.42
Crown	533.75	91.50	0.50	13.75	3.23	3.90	3.06	351.00	3.03
NMC1	1932.25	347.50	0.50	18.00	5.07	3.85	3.69	451.50	3.77

Table B2: Al saturation results.

Growth medium	Al saturation (%)
Control	28.70
NM700	183.00
Coal	136.05
Crown	65.70
NMC1	46.25

Table B3: Exchangeable cations, CEC, S-value and base saturation.

Growth medium	Exchangeable cations (cmol(+)/kg)				CEC	S-value	Base saturation
	Ca	Mg	K	Na			
Control	0.51	0.61	0.25	0.13	12.50	1.51	12.08
NM700	3.14	3.32	0.01	0.07	13.34	6.54	49.06
Coal	6.03	0.90	0.00	0.08	15.97	7.01	44.00
Crown	2.67	0.75	0.00	0.06	9.59	3.48	36.36
NMC1	9.64	2.86	0.00	0.08	16.88	12.58	74.60

Table B4: Anions (Cl^-, NO_3^-, PO_4^{3-} & SO_4^{2-}).

Sample	Saturated paste			
	Cl	NO_3	PO_4	SO_4
	mg/l			
NM700	6.95	9.46	1.93	31749.33
Coal	2.08	5.77	1.47	32950.16
Control	3.73	41.48	<0.01	76.82
Crown	1.31	4.54	<0.01	6088.49
NMC1	5.09	3.59	<0.01	11092.59

<u>Appendix C:</u> Results for the seven class textural analyses conducted on the growth mediums used in the main experimental work of the study.

Table C1: Particle size distribution results of the growth mediums used in the main experimental work.

	Particle size distribution (%)							
Sample	**>2 mm**	**Very coarse sand**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**Silt**	**Clay**
NM700	0.0	0.5	0.8	1.5	20.9	40.5	26.3	9.6
Coal	0.1	23.1	18.7	18.2	15.0	7.9	11.0	6.1
Control	0.0	0.7	5.4	31.7	28.2	20.7	3.1	10.2
Crown	0.0	0.0	0.4	7.7	58.3	29.8	2.9	0.9
NMC1	0.0	0.1	0.1	1.1	18.9	53.1	22.8	3.8

Appendix D: Correlation between pH(H_2O) and Al saturation values of the growth mediums.

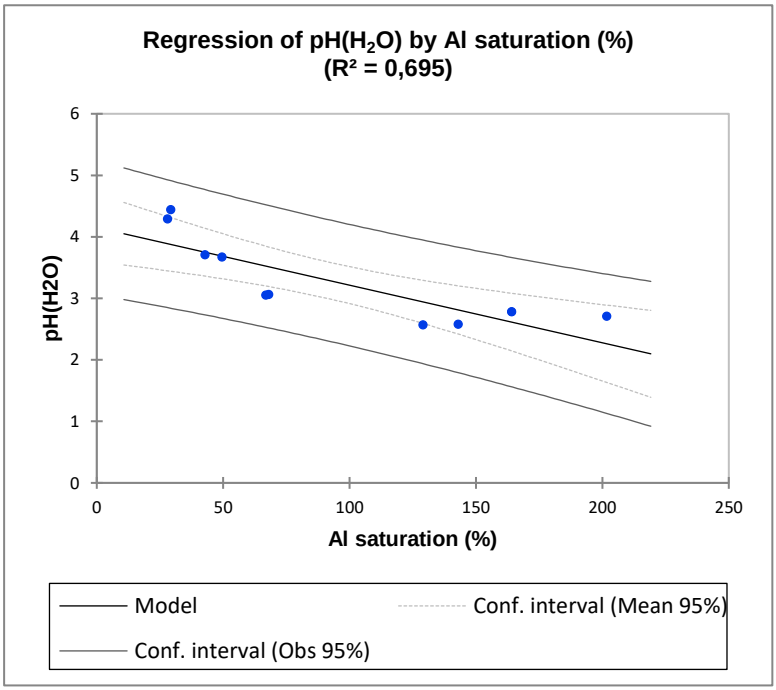


Figure D1: Linear relationship between pH(H_2O) and Al saturation values of baseline assays.

Table D1: Correlation matrix (r values) between pH(H_2O) and Al saturation.

	Al saturation (%)	**pH(H_2O)**
Al saturation (%)	**1**	-0.834
pH(H_2O)	-0.834	**1**

Appendix E: Results from the first pot trial done with NMC2 tailings.

Table E1: NMC2 pot trial results.

	Sample	P Bray-1 (mg/kg)	pH(H_2O)
Baseline	NMC2-1	9.18	2.73
	NMC2-2	9.18	2.73
	NMC2-3	9.18	2.73
	NMC2-4	9.18	2.73
1 Day after lime and fertiliser applications	NMC2-1	18.39	2.87
	NMC2-2	16.29	2.87
	NMC2-3	12.24	2.94
	NMC2-4	15.09	2.91
10 Days after lime and fertiliser applications	NMC2-1	10.42	3.93
	NMC2-2	11.40	3.95
	NMC2-3	10.91	4.02
	NMC2-4	10.99	4.02

Appendix F: pH(H_2O) and EC results of neutralisation incubation pot trial used to identify growth mediums for main fertiliser pot trials.

Table F1: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 1 – 28 Nov 2016).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	5.50	60.49	**T7-1**	5.84	80.96
LNR-2	5.52	39.56	**T7-2**	5.80	113.62
LNR-3	5.56	43.93	**T7-3**	5.76	183.77
Crown-1	5.06	410.09	**T23-1**	5.56	238.28
Crown-2	5.17	412.73	**T23-2**	5.65	193.66
Crown-3	5.13	448.73	**T23-3**	5.65	193.89
NM700-1	5.38	4.15	**Domrif-1**	4.34	1085.60
NM700-2	5.19	4.46	**Domrif-2**	4.37	768.20
NM700-3	5.41	3.83	**Domrif-3**	4.36	1016.60
NMC2-1	5.29	828.00	**NMTP-1**	5.46	98.67
NMC2-2	5.27	867.10	**NMTP-2**	5.42	110.40
NMC2-3	5.29	938.40	**NMTP-3**	5.32	189.98
Coal1-1	5.17	673.90	**NMTPT-1**	4.82	192.74
Coal1-2	5.16	784.30	**NMTPT-2**	5.02	170.89
Coal1-3	5.25	742.90	**NMTPT-3**	5.17	140.99
Coal2-1	5.07	756.70	**NMC1-1**	5.58	391.00
Coal2-2	5.12	586.50	**NMC1-2**	5.60	344.31
Coal2-3	5.15	568.10	**NMC1-3**	5.56	372.37
NMGeel-1	5.00	648.60	**NMTS-1**	5.47	167.21
NMGeel-2	5.02	476.10	**NMTS-2**	5.53	158.24
NMGeel-3	5.09	545.10	**NMTS-3**	5.51	181.93

Appendix F (continued)

Table F2: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 2 – 06 Dec 2016).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	5.11	51.98	**T7-1**	5.40	96.37
LNR-2	4.96	57.04	**T7-2**	5.39	1531.18
LNR-3	5.03	47.15	**T7-3**	5.54	117.76
Crown-1	4.43	459.54	**T23-1**	5.54	209.99
Crown-2	4.73	393.76	**T23-2**	5.58	191.82
Crown-3	4.74	338.33	**T23-3**	5.52	256.68
NM700-1	4.78	724.50	**Domrif-1**	4.97	938.40
NM700-2	4.80	975.20	**Domrif-2**	4.78	910.80
NM700-3	4.88	561.20	**Domrif-3**	4.57	954.50
NMC2-1	5.20	524.40	**NMTP-1**	5.67	124.66
NMC2-2	5.15	542.80	**NMTP-2**	5.61	142.83
NMC2-3	5.14	660.10	**NMTP-3**	5.59	138.23
Coal1-1	4.92	844.10	**NMTPT-1**	5.67	143.29
Coal1-2	4.84	821.10	**NMTPT-2**	5.63	175.26
Coal1-3	4.91	788.90	**NMTPT-3**	5.61	195.50
Coal2-1	5.12	795.80	**NMC1-1**	5.44	320.16
Coal2-2	5.21	1301.80	**NMC1-2**	5.42	444.36
Coal2-3	5.21	1067.20	**NMC1-3**	5.42	457.01
NMGeel-1	4.82	625.60	**NMTS-1**	5.87	125.12
NMGeel-2	4.90	584.20	**NMTS-2**	5.68	160.77
NMGeel-3	4.91	660.10	**NMTS-3**	5.60	170.20

Appendix F (continued)

Table F3: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 3 – 13 Dec 2016).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	6.21	48.76	**T7-1**	5.87	136.16
LNR-2	6.21	47.38	**T7-2**	5.95	116.84
LNR-3	6.21	48.53	**T7-3**	5.91	132.02
Crown-1	5.74	260.13	**T23-1**	5.82	201.71
Crown-2	5.73	287.04	**T23-2**	5.85	179.17
Crown-3	5.76	255.30	**T23-3**	5.82	203.09
NM700-1	4.54	607.20	**Domrif-1**	3.84	860.20
NM700-2	4.56	1044.20	**Domrif-2**	3.98	933.80
NM700-3	4.57	736.00	**Domrif-3**	4.05	816.50
NMC2-1	4.69	524.40	**NMTP-1**	5.78	140.30
NMC2-2	4.52	547.40	**NMTP-2**	5.90	84.41
NMC2-3	4.62	545.10	**NMTP-3**	5.86	91.08
Coal1-1	4.34	648.60	**NMTPT-1**	5.88	196.19
Coal1-2	4.41	770.50	**NMTPT-2**	5.78	178.48
Coal1-3	4.54	807.30	**NMTPT-3**	5.82	152.72
Coal2-1	5.49	717.60	**NMC1-1**	5.55	436.08
Coal2-2	5.54	558.90	**NMC1-2**	5.59	395.83
Coal2-3	5.56	542.80	**NMC1-3**	5.57	448.96
NMGeel-1	5.55	444.82	**NMTS-1**	5.72	198.03
NMGeel-2	5.57	444.82	**NMTS-2**	5.78	171.58
NMGeel-3	5.61	389.85	**NMTS-3**	5.78	153.64

Appendix F (continued)

Table F4: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 4 – 20 Dec 2016).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	6.21	52.21	**T7-1**	5.51	225.63
LNR-2	6.22	52.90	**T7-2**	5.62	204.47
LNR-3	6.33	46.46	**T7-3**	5.72	283.13
Crown-1	5.70	419.98	**T23-1**	4.99	225.63
Crown-2	5.79	327.06	**T23-2**	5.26	204.47
Crown-3	5.58	390.77	**T23-3**	5.23	283.13
NM700-1	5.56	1085.60	**Domrif-1**	4.81	788.90
NM700-2	5.56	1127.00	**Domrif-2**	4.84	765.90
NM700-3	5.58	1032.70	**Domrif-3**	4.88	660.10
NMC2-1	5.28	418.37	**NMTP-1**	5.91	134.32
NMC2-2	5.28	531.30	**NMTP-2**	5.98	151.80
NMC2-3	5.30	542.80	**NMTP-3**	5.99	115.00
Coal1-1	4.37	759.00	**NMTPT-1**	5.39	292.10
Coal1-2	4.62	657.80	**NMTPT-2**	5.63	185.38
Coal1-3	4.69	807.30	**NMTPT-3**	5.55	203.78
Coal2-1	4.96	657.80	**NMC1-1**	5.72	480.70
Coal2-2	5.08	572.70	**NMC1-2**	5.81	483.00
Coal2-3	5.15	738.30	**NMC1-3**	5.88	368.46
NMGeel-1	5.31	324.30	**NMTS-1**	5.53	184.23
NMGeel-2	5.32	349.14	**NMTS-2**	5.55	226.32
NMGeel-3	5.14	828.00	**NMTS-3**	5.59	219.42

Appendix F (continued)

Table F5: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 6 – 03 Jan 2017).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	7.01	23.69	**T7-1**	6.32	69.00
LNR-2	7.12	19.09	**T7-2**	6.46	63.02
LNR-3	7.04	22.54	**T7-3**	6.56	72.22
Crown-1	6.51	157.32	**T23-1**	6.45	142.60
Crown-2	6.50	141.68	**T23-2**	6.50	139.15
Crown-3	6.52	149.96	**T23-3**	6.55	125.81
NM700-1	5.55	326.14	**Domrif-1**	6.65	420.44
NM700-2	5.50	356.27	**Domrif-2**	6.14	439.07
NM700-3	5.75	345.00	**Domrif-3**	6.14	433.55
NMC2-1	6.30	234.60	**NMTP-1**	5.80	69.69
NMC2-2	6.38	207.69	**NMTP-2**	6.01	32.43
NMC2-3	6.33	250.70	**NMTP-3**	6.04	38.41
Coal1-1	6.31	308.89	**NMTPT-1**	5.58	59.34
Coal1-2	6.33	305.44	**NMTPT-2**	5.66	52.90
Coal1-3	6.33	316.48	**NMTPT-3**	5.69	57.73
Coal2-1	6.37	315.10	**NMC1-1**	5.38	217.58
Coal2-2	6.41	263.58	**NMC1-2**	5.04	217.58
Coal2-3	6.46	320.85	**NMC1-3**	5.18	180.32
NMGeel-1	5.89	180.55	**NMTS-1**	5.91	108.33
NMGeel-2	6.30	313.26	**NMTS-2**	5.99	106.72
NMGeel-3	6.45	201.02	**NMTS-3**	6.01	106.95

Appendix F (continued)

Table F6: pH(H_2O) and EC results for initial neutralisation incubation pot trial (Week 7 – 11 Jan 2017).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
LNR-1	6.60	18.17	**T7-1**	6.90	43.70
LNR-2	6.60	11.04	**T7-2**	6.80	50.83
LNR-3	6.50	10.81	**T7-3**	7.00	50.83
Crown-1	5.90	160.08	**T23-1**	6.20	136.85
Crown-2	5.90	132.25	**T23-2**	6.00	147.43
Crown-3	5.70	173.65	**T23-3**	6.01	145.13
NM700-1	6.30	294.63	**Domrif-1**	4.90	381.11
NM700-2	6.50	284.51	**Domrif-2**	5.20	388.70
NM700-3	6.20	271.86	**Domrif-3**	4.80	409.17
NMC2-1	5.50	257.14	**NMTP-1**	6.20	16.10
NMC2-2	5.30	235.75	**NMTP-2**	6.10	13.57
NMC2-3	5.50	201.48	**NMTP-3**	6.30	13.34
Coal1-1	5.80	307.74	**NMTPT-1**	6.70	24.84
Coal1-2	5.50	316.48	**NMTPT-2**	6.50	25.53
Coal1-3	5.60	262.20	**NMTPT-3**	6.50	21.85
Coal2-1	6.00	276.46	**NMC1-1**	6.00	213.90
Coal2-2	6.20	240.81	**NMC1-2**	6.10	125.12
Coal2-3	6.10	268.18	**NMC1-3**	5.90	227.24
NMGeel-1	5.60	165.60	**NMTS-1**	6.10	116.38
NMGeel-2	5.50	26.96	**NMTS-2**	6.20	82.57
NMGeel-3	5.70	211.14	**NMTS-3**	6.30	79.12

Appendix G: pH(H_2O) and EC results for Pot trial 1 (Group A) after lime and fertiliser treatments

Table G1: pH(H_2O) and EC results for Pot trial 1 (Group A) (1 day and 3 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
1 day after lime and fertiliser applications			**3 weeks after lime and fertiliser applications**		
NM700-1	3.12	1173.00	**NM700-1**	6.08	690.00
NM700-2	3.04	943.00	**NM700-2**	6.19	736.00
NM700-3	3.32	1104.00	**NM700-3**	6.29	1104.00
NM700-4	3.19	1242.00	**NM700-4**	6.29	1173.00
Coal-1	4.32	759.00	**Coal-1**	6.45	552.00
Coal-2	4.48	713.00	**Coal-2**	6.48	368.00
Coal-3	4.45	736.00	**Coal-3**	5.58	621.00
Coal-4	4.25	713.00	**Coal-4**	6.07	598.00
Control-1	5.86	23.92	**Control-1**	6.77	32.66
Control-2	5.83	26.45	**Control-2**	6.81	25.07
Control-3	5.85	25.99	**Control-3**	6.71	21.16
Control-4	5.89	23.23	**Control-4**	6.78	16.79
Crown-1	4.27	345.00	**Crown-1**	5.59	271.40
Crown-2	4.21	363.40	**Crown-2**	5.90	197.80
Crown-3	4.20	402.50	**Crown-3**	4.39	317.40
Crown-4	4.14	395.60	**Crown-4**	4.61	308.20
NMC1-1	4.37	575.00	**NMC1-1**	6.03	552.00
NMC1-2	4.43	598.00	**NMC1-2**	6.03	575.00
NMC1-3	4.43	598.00	**NMC1-3**	6.01	483.00
NMC1-4	4.50	552.00	**NMC1-4**	6.31	414.00

Appendix G (continued)

Table G2: pH(H_2O) and EC results for Pot trial 1 (Group A) (4 and 5 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC mS/m	Sample	pH(H2O)	EC mS/m
4 weeks after lime and fertiliser applications			**5 weeks after lime and fertiliser applications**		
NM700-1	6.11	1012.00	**NM700-1**	5.33	1196.00
NM700-2	6.25	943.00	**NM700-2**	5.68	1196.00
NM700-3	6.18	874.00	**NM700-3**	5.94	920.00
NM700-4	6.17	966.00	**NM700-4**	5.94	1081.00
Coal-1	5.91	506.00	**Coal-1**	5.88	529.00
Coal-2	6.03	598.00	**Coal-2**	5.92	483.00
Coal-3	6.15	713.00	**Coal-3**	5.86	575.00
Coal-4	6.34	529.00	**Coal-4**	5.73	713.00
Control-1	6.94	28.98	**Control-1**	6.62	23.92
Control-2	7.00	21.62	**Control-2**	6.65	26.22
Control-3	7.06	20.47	**Control-3**	6.73	22.77
Control-4	7.12	20.24	**Control-4**	6.77	24.15
Crown-1	6.34	230.00	**Crown-1**	5.77	351.90
Crown-2	6.34	241.50	**Crown-2**	5.58	374.90
Crown-3	4.73	299.00	**Crown-3**	4.78	455.00
Crown-4	4.67	310.50	**Crown-4**	4.67	446.20
NMC1-1	5.97	324.30	**NMC1-1**	5.61	506.00
NMC1-2	5.93	432.40	**NMC1-2**	5.87	384.10
NMC1-3	6.11	345.00	**NMC1-3**	5.92	552.00
NMC1-4	5.91	407.10	**NMC1-4**	5.98	460.00

Appendix G (continued)

Table G3: pH(H_2O) and EC results for Pot trial 1 (Group A) (6 and 7 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
6 weeks after lime and fertiliser applications			**7 weeks after lime and fertiliser applications**		
NM700-1	5.99	874.00	**NM700-1**	5.99	506.00
NM700-2	6.12	736.00	**NM700-2**	5.68	966.00
NM700-3	6.31	713.00	**NM700-3**	5.80	805.00
NM700-4	6.12	713.00	**NM700-4**	5.81	989.00
Coal-1	5.93	598.00	**Coal-1**	5.81	443.90
Coal-2	6.06	441.60	**Coal-2**	5.99	416.30
Coal-3	6.23	460.00	**Coal-3**	5.99	529.00
Coal-4	6.20	407.10	**Coal-4**	5.61	328.90
Control-1	6.96	17.02	**Control-1**	6.48	31.28
Control-2	6.87	16.10	**Control-2**	6.68	19.55
Control-3	6.93	18.63	**Control-3**	6.67	24.84
Control-4	6.87	24.84	**Control-4**	6.87	17.48
Crown-1	5.41	395.60	**Crown-1**	5.39	273.70
Crown-2	5.70	333.50	**Crown-2**	5.48	253.00
Crown-3	5.05	347.30	**Crown-3**	4.82	326.60
Crown-4	4.99	374.90	**Crown-4**	4.95	278.30
NMC1-1	6.32	294.40	**NMC1-1**	5.99	384.10
NMC1-2	6.22	404.80	**NMC1-2**	5.66	552.00
NMC1-3	6.24	529.00	**NMC1-3**	5.81	552.00
NMC1-4	6.42	425.50	**NMC1-4**	6.03	345.00

Appendix G (continued)

Table G4: pH(H_2O) and EC results for Pot trial 1 (Group A) (8 and 9 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
8 weeks after lime and fertiliser applications			**9 weeks after lime and fertiliser applications**		
NM700-1	5.48	1035.00	**NM700-1**	5.32	1357.00
NM700-2	5.44	1035.00	**NM700-2**	5.38	1035.00
NM700-3	5.44	1127.00	**NM700-3**	5.80	736.00
NM700-4	5.46	1265.00	**NM700-4**	5.73	782.00
Coal-1	5.53	506.00	**Coal-1**	5.41	598.00
Coal-2	5.48	529.00	**Coal-2**	5.30	667.00
Coal-3	5.62	529.00	**Coal-3**	5.48	667.00
Coal-4	5.45	552.00	**Coal-4**	5.24	805.00
Control-1	6.41	46.00	**Control-1**	6.49	28.06
Control-2	6.71	21.39	**Control-2**	6.66	23.92
Control-3	6.73	30.13	**Control-3**	6.63	28.29
Control-4	6.75	27.14	**Control-4**	6.55	31.05
Crown-1	5.26	340.40	**Crown-1**	5.48	342.70
Crown-2	5.48	262.20	**Crown-2**	5.59	285.20
Crown-3	4.90	351.90	**Crown-3**	4.91	363.20
Crown-4	4.63	529.00	**Crown-4**	4.93	391.00
NMC1-1	5.89	289.80	**NMC1-1**	5.72	434.70
NMC1-2	5.90	388.70	**NMC1-2**	5.64	575.00
NMC1-3	6.06	361.10	**NMC1-3**	5.84	529.00
NMC1-4	5.72	529.00	**NMC1-4**	5.86	460.00

Appendix G (continued)

Table G5: pH(H_2O) and EC results for Pot trial 1 (Group A) (10 and 11 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
10 weeks after lime and fertiliser applications			**11 weeks after lime and fertiliser applications**		
NM700-1	5.62	1311.00	**NM700-1**	5.24	1840.00
NM700-2	5.74	1012.00	**NM700-2**	5.15	1702.00
NM700-3	5.60	1104.00	**NM700-3**	5.21	1541.00
NM700-4	5.61	1265.00	**NM700-4**	5.32	1311.00
Coal-1	5.41	552.00	**Coal-1**	5.25	667.00
Coal-2	5.35	713.00	**Coal-2**	5.22	667.00
Coal-3	5.40	690.00	**Coal-3**	5.28	874.00
Coal-4	5.35	712.00	**Coal-4**	5.10	782.00
Control-1	6.56	22.31	**Control-1**	6.24	35.88
Control-2	6.26	31.28	**Control-2**	6.46	27.14
Control-3	6.38	41.17	**Control-3**	6.43	39.10
Control-4	6.72	26.45	**Control-4**	6.46	31.97
Crown-1	5.14	506.00	**Crown-1**	4.93	483.00
Crown-2	5.28	319.70	**Crown-2**	5.26	377.20
Crown-3	4.87	397.90	**Crown-3**	4.56	621.00
Crown-4	4.95	363.40	**Crown-4**	4.58	552.00
NMC1-1	5.87	379.50	**NMC1-1**	5.53	395.60
NMC1-2	6.07	317.40	**NMC1-2**	5.78	483.00
NMC1-3	5.91	598.00	**NMC1-3**	5.74	759.00
NMC1-4	6.24	301.30	**NMC1-4**	5.80	529.00

Appendix G (continued)

Table G6: pH(H_2O) and EC results for Pot trial 1 (Group A) (12 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	EC mS/m
12 weeks after lime and fertiliser applications		
NM700-1	5.51	1633.00
NM700-2	5.84	920.00
NM700-3	5.78	1219.00
NM700-4	5.78	1081.00
Coal-1	5.75	483.00
Coal-2	5.58	598.00
Coal-3	5.68	713.00
Coal-4	5.22	966.00
Control-1	6.40	25.30
Control-2	6.51	27.37
Control-3	6.66	19.55
Control-4	6.60	30.13
Crown-1	5.59	342.70
Crown-2	5.43	393.30
Crown-3	4.87	416.30
Crown-4	4.90	310.50
NMC1-1	5.84	427.80
NMC1-2	6.14	292.10
NMC1-3	6.08	621.00
NMC1-4	6.17	377.20

<u>Appendix H</u>: pH(H_2O) and EC results for Pot trial 1 (Group B) after respective lime and fertiliser treatments.

Table H1: pH(H_2O) and EC results for Pot trial 1 (Group B) (1 day and 3 weeks after lime treatment).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
1 day after lime application			**3 weeks after lime application**		
NM700-1	3.44	989.00	**NM700-1**	5.74	736.00
NM700-2	3.26	1150.00	**NM700-2**	5.76	1265.00
NM700-3	3.75	874.00	**NM700-3**	5.81	759.00
NM700-4	3.72	874.00	**NM700-4**	5.65	943.00
Coal-1	4.47	690.00	**Coal-1**	6.02	644.00
Coal-2	4.64	713.00	**Coal-2**	5.87	713.00
Coal-3	4.42	736.00	**Coal-3**	5.89	552.00
Coal-4	4.03	621.00	**Coal-4**	5.88	552.00
Control-1	5.39	20.70	**Control-1**	6.58	20.93
Control-2	5.44	18.86	**Control-2**	6.53	20.47
Control-3	5.33	20.70	**Control-3**	6.68	23.00
Control-4	5.56	25.99	**Control-4**	6.44	28.29
Crown-1	4.24	384.10	**Crown-1**	5.19	232.30
Crown-2	4.21	340.10	**Crown-2**	4.82	315.10
Crown-3	4.11	404.80	**Crown-3**	4.94	322.00
Crown-4	4.21	394.70	**Crown-4**	4.31	328.90
NMC1-1	4.47	529.00	**NMC1-1**	5.76	271.40
NMC1-2	4.57	483.00	**NMC1-2**	5.81	782.00
NMC1-3	4.53	506.00	**NMC1-3**	5.78	782.00
NMC1-4	4.48	598.00	**NMC1-4**	5.98	418.60

Appendix H (continued)

Table H2: pH(H_2O) and EC results for Pot trial 1 (Group B) (4 and 5 weeks after lime treatment).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
4 weeks after lime application			**5 weeks after lime application**		
NM700-1	5.92	1173.00	**NM700-1**	5.73	874.00
NM700-2	6.03	759.00	**NM700-2**	5.85	1173.00
NM700-3	6.07	690.00	**NM700-3**	6.02	1058.00
NM700-4	6.05	989.00	**NM700-4**	5.92	1012.00
Coal-1	6.04	621.00	**Coal-1**	5.95	712.00
Coal-2	5.88	759.00	**Coal-2**	5.86	874.00
Coal-3	6.01	644.00	**Coal-3**	6.01	644.00
Coal-4	6.09	644.00	**Coal-4**	6.00	644.00
Control-1	6.79	17.48	**Control-1**	6.68	20.47
Control-2	6.76	20.93	**Control-2**	6.70	18.17
Control-3	6.80	18.40	**Control-3**	6.61	23.92
Control-4	6.79	18.40	**Control-4**	6.59	26.22
Crown-1	5.25	299.00	**Crown-1**	5.20	349.60
Crown-2	4.75	374.90	**Crown-2**	5.29	361.10
Crown-3	5.29	377.20	**Crown-3**	5.21	395.00
Crown-4	5.51	299.00	**Crown-4**	5.20	423.20
NMC1-1	6.14	305.90	**NMC1-1**	5.98	391.00
NMC1-2	6.14	388.70	**NMC1-2**	6.02	483.00
NMC1-3	6.24	278.30	**NMC1-3**	6.09	345.00
NMC1-4	6.14	356.50	**NMC1-4**	6.04	506.00

Appendix H (continued)

Table H3: pH(H_2O) and EC results for Pot trial 1 (Group B) (6 and 7 weeks after lime treatment).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
6 weeks after lime application (pH where fertiliser was applied)			**7 weeks after lime application (1 week after fertiliser application)**		
NM700-1	6.22	828.00	**NM700-1**	5.98	621.00
NM700-2	5.75	1035.00	**NM700-2**	5.92	736.00
NM700-3	5.83	1288.00	**NM700-3**	5.94	552.00
NM700-4	6.24	874.00	**NM700-4**	6.10	483.00
Coal-1	6.18	552.00	**Coal-1**	5.80	529.00
Coal-2	5.89	529.00	**Coal-2**	5.77	575.00
Coal-3	6.02	483.00	**Coal-3**	5.77	621.00
Coal-4	5.89	621.00	**Coal-4**	5.80	529.00
Control-1	6.62	20.47	**Control-1**	6.68	25.30
Control-2	6.70	23.92	**Control-2**	6.90	19.55
Control-3	6.68	21.85	**Control-3**	6.90	19.32
Control-4	6.64	24.38	**Control-4**	6.68	21.39
Crown-1	5.62	358.80	**Crown-1**	5.62	285.20
Crown-2	5.52	345.00	**Crown-2**	5.68	255.30
Crown-3	5.53	377.20	**Crown-3**	6.01	204.70
Crown-4	5.59	361.10	**Crown-4**	5.81	299.00
NMC1-1	6.38	358.80	**NMC1-1**	6.16	365.70
NMC1-2	6.39	377.10	**NMC1-2**	6.27	345.00
NMC1-3	6.41	420.90	**NMC1-3**	6.14	441.60
NMC1-4	6.56	457.70	**NMC1-4**	6.03	506.00

Appendix H (continued)

Table H4: pH(H_2O) and EC results for Pot trial 1 (Group B) (8 and 9 weeks after lime treatment).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
8 weeks after lime application (2 weeks after fertiliser application)			**9 weeks after lime application (3 weeks after fertiliser application)**		
NM700-1	5.47	989.00	**NM700-1**	5.27	1265.00
NM700-2	5.21	1426.00	**NM700-2**	5.41	1472.00
NM700-3	5.58	1127.00	**NM700-3**	5.56	1219.00
NM700-4	5.50	1035.00	**NM700-4**	5.73	920.00
Coal-1	5.67	441.00	**Coal-1**	5.59	575.00
Coal-2	5.52	598.00	**Coal-2**	5.40	644.00
Coal-3	5.58	483.00	**Coal-3**	5.53	529.00
Coal-4	5.41	529.00	**Coal-4**	5.35	575.00
Control-1	6.48	23.46	**Control-1**	6.41	29.67
Control-2	6.59	20.93	**Control-2**	6.54	24.15
Control-3	6.65	17.71	**Control-3**	6.64	19.55
Control-4	6.62	16.56	**Control-4**	6.63	19.32
Crown-1	5.54	296.70	**Crown-1**	5.60	400.20
Crown-2	5.77	234.60	**Crown-2**	5.67	299.00
Crown-3	5.83	296.70	**Crown-3**	5.47	552.00
Crown-4	5.62	437.00	**Crown-4**	5.75	276.00
NMC1-1	5.88	506.00	**NMC1-1**	6.01	354.20
NMC1-2	5.92	414.00	**NMC1-2**	5.96	483.00
NMC1-3	5.93	439.30	**NMC1-3**	6.00	506.00
NMC1-4	6.16	287.50	**NMC1-4**	6.04	506.00

Appendix H (continued)

Table H5: pH(H_2O) and EC results for Pot trial 1 (Group B) (10 and 11 weeks after lime treatment).

Sample	pH(H2O)	EC (mS/m)	Sample	pH(H2O)	EC (mS/m)
10 weeks after lime application (4 weeks after fertiliser application)			**11 weeks after lime application (5 weeks after fertiliser application)**		
NM700-1	6.00	1219.00	**NM700-1**	5.58	1035.00
NM700-2	6.40	966.00	**NM700-2**	5.30	1541.00
NM700-3	5.48	1058.00	**NM700-3**	5.71	1242.00
NM700-4	6.00	1081.00	**NM700-4**	5.52	1288.00
Coal-1	5.65	506.00	**Coal-1**	5.49	76.00
Coal-2	5.85	644.00	**Coal-2**	5.43	782.00
Coal-3	5.77	667.00	**Coal-3**	5.41	598.00
Coal-4	5.68	529.00	**Coal-4**	5.38	713.00
Control-1	6.91	22.54	**Control-1**	6.19	30.82
Control-2	6.95	28.06	**Control-2**	6.43	28.52
Control-3	7.08	20.70	**Control-3**	6.45	24.84
Control-4	6.95	23.92	**Control-4**	6.55	23.46
Crown-1	6.16	264.50	**Crown-1**	5.28	453.10
Crown-2	5.85	370.30	**Crown-2**	5.36	397.90
Crown-3	5.87	266.80	**Crown-3**	5.40	434.70
Crown-4	5.14	259.90	**Crown-4**	5.34	483.00
NMC1-1	6.00	340.40	**NMC1-1**	6.04	397.90
NMC1-2	6.52	358.80	**NMC1-2**	5.86	621.00
NMC1-3	6.01	393.30	**NMC1-3**	6.06	483.00
NMC1-4	6.43	506.00	**NMC1-4**	6.09	483.00

Appendix H (continued)

Table H6: pH(H_2O) and EC results for Pot trial 1 (Group B) (12 weeks after lime treatment).

Sample	pH(H2O)	EC mS/m
12 weeks after lime application (6 weeks after fertiliser application)		
NM700-1	5.82	759
NM700-2	5.77	966
NM700-3	5.68	1196
NM700-4	5.5	1334
Coal-1	5.64	483
Coal-2	5.31	598
Coal-3	5.45	529
Coal-4	5.4	621
Control-1	6.56	23.46
Control-2	6.61	23.46
Control-3	6.65	21.39
Control-4	6.61	23.23
Crown-1	5.47	529
Crown-2	5.53	377.2
Crown-3	5.53	397.9
Crown-4	5.53	402.5
NMC1-1	5.95	529
NMC1-2	6.15	386.4
NMC1-3	6.25	407.1
NMC1-4	6.06	782

Appendix I: P Bray-1, Olsen P and pH(H_2O) results for Pot trial 1 (Group A) after lime and fertiliser treatments

Table I1: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 – Group A (1 day after lime and fertiliser applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH(H2O)
NM700-1	4.52	2.73	3.12	**Crown-1**	12.42	6.09	4.27
NM700-2	4.64	3.15	3.04	**Crown-2**	12.53	7.35	4.21
NM700-3	4.16	2.94	3.32	**Crown-3**	15.52	6.51	4.20
NM700-4	4.66	5.67	3.19	**Crown-4**	16.07	6.30	4.14
Coal-1	3.79	5.67	4.32	**NMC1-1**	13.72	4.62	4.37
Coal-2	4.00	4.83	4.48	**NMC1-2**	15.95	4.83	4.43
Coal-3	4.31	3.15	4.45	**NMC1-3**	15.44	5.88	4.43
Coal-4	4.15	3.57	4.25	**NMC1-4**	18.53	5.25	4.50
Control-1	9.64	7.98	5.86				
Control-2	11.13	7.98	5.83				
Control-3	10.50	12.39	5.85				
Control-4	9.73	7.98	5.89				

Table I2: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 – Group A (3 weeks after lime and fertiliser applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH(H2O)
NM700-1	4.29	2.52	6.08	**Crown-1**	10.13	3.78	5.59
NM700-2	3.79	1.89	6.19	**Crown-2**	10.22	3.78	5.90
NM700-3	3.60	3.57	6.29	**Crown-3**	10.46	2.73	4.39
NM700-4	3.60	1.89	6.29	**Crown-4**	11.06	4.62	4.61
Coal-1	4.14	3.05	6.45	**NMC1-1**	14.51	2.31	6.03
Coal-2	4.02	3.78	6.48	**NMC1-2**	15.26	3.57	6.03
Coal-3	4.03	1.68	5.58	**NMC1-3**	19.35	3.57	6.01
Coal-4	5.42	11.34	6.07	**NMC1-4**	16.00	3.36	6.31
Control-1	7.37	4.20	6.77				
Control-2	8.45	5.25	6.81				
Control-3	10.24	5.67	6.71				
Control-4	9.19	5.67	6.78				

Appendix I (continued)

Table I3: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 – Group A (6 weeks after lime and fertiliser applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH(H2O)
NM700-1	5.67	13.23	5.99	**Crown-1**	11.48	7.25	5.41
NM700-2	5.18	11.97	6.12	**Crown-2**	11.17	8.19	5.70
NM700-3	4.92	15.12	6.31	**Crown-3**	12.24	6.30	5.05
NM700-4	4.54	13.86	6.12	**Crown-4**	12.58	7.25	4.99
Coal-1	5.57	11.66	5.93	**NMC1-1**	15.92	7.40	6.32
Coal-2	5.80	10.71	6.06	**NMC1-2**	15.11	5.67	6.22
Coal-3	6.08	11.97	6.23	**NMC1-3**	17.17	5.04	6.24
Coal-4	5.67	11.03	6.20	**NMC1-4**	17.13	6.30	6.42
Control-1	8.49	16.38	6.96				
Control-2	11.78	15.75	6.87				
Control-3	11.66	15.75	6.93				
Control-4	10.82	11.03	6.87				

Appendix J: XLSTAT and ANOVA results for Group A in Pot trial 1

Table J1: Summary statistics for Group A of the Control medium in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	7,370	11,780	9,917	1,309
P Olsen	13	4,200	16,380	9,669	4,264
pH	13	5,830	6,960	6,511	0,467

Table J2: Pearson correlation matrix values for Group A of the Control medium in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	0,536	-0,145
P Olsen	0,536	**1**	0,214
pH	-0,145	0,214	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table J3: Pearson p-values for Group A of the Control medium in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,059	0,637
P Olsen	0,059	**0**	0,482
pH	0,637	0,482	**0**

Table J4: ANOVA summary for Group A of the Control medium in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	119	9,916667	1,868697
P Olsen	12	116,025	9,66875	19,8379
pH	12	78,13	6,510833	0,23759

Table J5: ANOVA results for Group A of the Control medium in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	86,5344	2	43,2672	5,915079	0,006376	3,284918
Within Groups	241,3861	33	7,314729			
Total	327,9205	35				

Appendix J (continued)

Table J6: Summary statistics for Group A of the NM700 tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	3,600	5,670	4,464	0,600
P Olsen	13	1,890	15,120	6,545	5,078
pH	13	3,040	6,310	5,172	1,421

Table J7: Pearson correlation matrix values for Group A of the NM700 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	**0,737**	-0,082
P Olsen	**0,737**	**1**	0,391
pH	-0,082	0,391	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table J8: Pearson p-values for Group A of the NM700 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	**0,004**	0,791
P Olsen	**0,004**	**0**	0,186
pH	0,791	0,186	**0**

Table J9: ANOVA summary for Group A of the NM700 tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	53,57	4,464167	0,393027
P Olsen	12	78,54	6,545	28,12645
pH	12	62,06	5,171667	2,203324

Table J10: ANOVA results for Group A of the NM700 tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	26,86587	2	13,43294	1,311691	0,283042	3,284918
Within Groups	337,9508	33	10,24093			
Total	364,8166	35				

Appendix J (continued)

Table J11: Summary statistics for Group A of the Coal tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	3,790	6,080	4,748	0,832
P Olsen	13	1,680	11,970	6,869	3,898
pH	13	4,250	6,480	5,542	0,856

Table J12: Pearson correlation matrix values for Group A of the Coal tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	**0,930**	0,550
P Olsen	**0,930**	**1**	0,446
pH	0,550	0,446	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table J13: Pearson p-values for Group A of the Coal tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	**< 0.0001**	0,052
P Olsen	**< 0.0001**	**0**	0,127
pH	0,052	0,127	**0**

Table J14: ANOVA summary for Group A of the Coal tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	56,98	4,748333	0,754561
P Olsen	12	82,43	6,869167	16,57303
pH	12	66,5	5,541667	0,799324

Table J15: ANOVA results for Group A of the Coal tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	27,55827	2	13,77914	2,280444	0,118124	3,284918
Within Groups	199,3961	33	6,042305			
Total	226,9543	35				

Appendix J (continued)

Table J16: Summary statistics for Group A of the NMC1 tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	13,720	19,350	16,174	1,554
P Olsen	13	2,310	7,400	4,817	1,370
pH	13	4,370	6,420	5,609	0,841

Table J17: Pearson correlation matrix values for Group A of the NMC1 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	0,094	0,140
P Olsen	0,094	**1**	-0,065
pH	0,140	-0,065	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table J18: Pearson p-values for Group A of the NMC1 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,760	0,648
P Olsen	0,760	**0**	0,832
pH	0,648	0,832	**0**

Table J19: ANOVA summary for Group A of the NMC1 tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	194,09	16,17417	2,635081
P Olsen	12	57,8	4,816667	2,047533
pH	12	67,31	5,609167	0,771499

Table J20: ANOVA results for Group A of the NMC1 tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	964,9604	2	482,4802	265,3851	4,6E-21	3,284918
Within Groups	59,99525	33	1,818038			
Total	1024,956	35				

Appendix J (continued)

Table J21: Summary statistics for Group A of the Crown tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	10,130	16,070	12,157	1,835
P Olsen	13	2,730	8,190	5,845	1,642
pH	13	4,140	5,900	4,872	0,625

Table J22: Pearson correlation matrix values for Group A of the Crown tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	0,465	**-0,654**
P Olsen	0,465	**1**	-0,062
pH	**-0,654**	-0,062	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table J23: Pearson p-values for Group A of the Crown tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,109	**0,015**
P Olsen	0,109	**0**	0,841
pH	**0,015**	0,841	**0**

Table J24: ANOVA summary for Group A of the Crown tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	145,88	12,15667	3,671988
P Olsen	12	70,145	5,845417	2,940607
pH	12	58,46	4,871667	0,425633

Table J25: ANOVA results for Group A of the Crown tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	375,4052	2	187,7026	80,00704	2,2E-13	3,284918
Within Groups	77,42051	33	2,346076			
Total	452,8257	35				

Appendix K: P Bray-1, Olsen P and pH(H_2O) results for Pot trial 1 (Group B) after respective lime and fertiliser treatments

Table K1: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 – Group B (1 day after fertiliser applications – 6 weeks after lime applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)
NM700-1	7.40	17.85	6.22	**Crown-1**	16.97	12.81	5.62
NM700-2	6.30	14.49	5.75	**Crown-2**	15.68	13.97	5.52
NM700-3	5.68	11.76	5.83	**Crown-3**	16.70	10.29	5.53
NM700-4	5.55	11.55	6.24	**Crown-4**	18.08	12.60	5.59
Coal-1	6.28	18.48	6.18	**NMC1-1**	18.02	8.93	6.38
Coal-2	5.79	10.71	5.89	**NMC1-2**	19.01	6.09	6.39
Coal-3	5.55	12.81	0.02	**NMC1-3**	17.41	6.09	6.41
Coal-4	5.71	8.61	5.89	**NMC1-4**	19.12	7.98	6.56
Control-1	12.46	17.22	6.62				
Control-2	13.37	16.59	6.70				
Control-3	13.69	19.74	6.68				
Control-4	14.92	11.97	6.64				

Table K2: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 – Group B (3 weeks after fertiliser applications – 9 weeks after lime applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)
NM700-1	3,73	4,70	5,27	**Crown-1**	10,46	9,51	5,60
NM700-2	3,92	4,35	5,41	**Crown-2**	10,90	10,12	5,67
NM700-3	3,47	4,09	5,56	**Crown-3**	10,48	9,82	5,47
NM700-4	3,38	3,89	5,73	**Crown-4**	10,80	10,93	5,75
Coal-1	4,03	3,79	5,59	**NMC1-1**	14,86	8,91	6,01
Coal-2	3,72	2,68	5,40	**NMC1-2**	13,69	9,36	5,96
Coal-3	3,37	2,22	5,53	**NMC1-3**	14,46	10,17	6,00
Coal-4	3,22	3,79	5,35	**NMC1-4**	13,10	9,41	6,04
Control-1	11,31	11,14	6,41				
Control-2	12,11	12,60	6,54				
Control-3	13,14	10,88	6,64				
Control-4	11,68	14,33	6,63				

Appendix K (continued)

Table K3: P Bray-1, Olsen P and pH(H_2O) for Pot trial 1 - Group B (6 weeks after fertiliser applications – 12 weeks after lime applications).

Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)	Sample	P Bray-1 (mg/kg)	Olsen (mg/kg)	pH (H2O)
NM700-1	5.11	7.25	5.82	**Crown-1**	16.24	15.96	5.47
NM700-2	4.72	7.77	5.77	**Crown-2**	15.13	16.17	5.53
NM700-3	4.07	6.09	5.68	**Crown-3**	14.06	17.43	5.53
NM700-4	4.10	7.56	5.50	**Crown-4**	13.22	19.32	5.53
Coal-1	4.66	6.41	5.64	**NMC1-1**	18.17	11.13	5.95
Coal-2	4.41	6.93	5.31	**NMC1-2**	19.61	11.97	6.15
Coal-3	4.49	5.67	5.45	**NMC1-3**	16.93	10.71	6.25
Coal-4	4.25	7.14	5.40	**NMC1-4**	16.87	10.08	6.06
Control-1	10.68	18.27	6.56				
Control-2	11.79	17.01	6.61				
Control-3	13.82	16.80	6.65				
Control-4	12.85	16.80	6.61				

Appendix L: XLSTAT and ANOVA results for Group B in Pot trial 1

Table L1: Summary statistics for Group B of the Control medium in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	10,680	14,920	12,652	1,158
P Olsen	13	10,882	19,740	15,279	2,849
pH	13	6,410	6,700	6,608	0,073

Table L2: Pearson correlation matrix values for Group B of the Control medium in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	-0,046	**0,640**
P Olsen	-0,046	**1**	0,450
pH	**0,640**	0,450	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table L3: Pearson p-values for Group B of the Control medium in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,881	**0,019**
P Olsen	0,881	**0**	0,123
pH	**0,019**	0,123	**0**

Table L4: ANOVA summary for Group B of the Control medium in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	151,82	12,65167	1,462415
P Olsen	12	183,3529	15,2794	8,857354
pH	12	79,29	6,6075	0,005839

Table L5: ANOVA results for Group B of the Control medium in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	474,5555	2	237,2778	68,93864	1,65E-12	3,284918
Within Groups	113,5817	33	3,441869			
Total	588,1372	35				

Appendix L (continued)

Table L6: Summary statistics for Group B of the NM700 tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	3,380	7,400	4,786	1,196
P Olsen	13	3,892	17,850	8,446	4,323
pH	13	5,270	6,240	5,732	0,277

Table L7: Pearson correlation matrix values for Group B of the NM700 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	**0,977**	**0,755**
P Olsen	**0,977**	**1**	**0,739**
pH	**0,755**	**0,739**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table L8: Pearson p-values for Group B of the NM700 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	**< 0.0001**	**0,003**
P Olsen	**< 0.0001**	**0**	**0,004**
pH	**0,003**	**0,004**	**0**

Table L9: ANOVA summary for Group B of the NM700 tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	57,43	4,785833	1,561317
P Olsen	12	101,3575	8,446456	20,38941
pH	12	68,78	5,731667	0,083506

Table L10: ANOVA results for Group B of the NM700 tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	86,65934	2	43,32967	5,899412	0,00645	3,284918
Within Groups	242,3766	33	7,344745			
Total	329,0359	35				

Appendix L (continued)

Table L11: Summary statistics for Group B of the Coal tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	3,220	6,280	4,623	0,960
P Olsen	13	2,221	18,480	7,437	4,508
pH	13	0,020	6,180	5,138	1,563

Table L12: Pearson correlation matrix values for Group B of the Coal tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	**0,903**	-0,154
P Olsen	**0,903**	**1**	-0,232
pH	-0,154	-0,232	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table L13: Pearson p-values for Group B of the Coal tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	**< 0.0001**	0,615
P Olsen	**< 0.0001**	**0**	0,446
pH	0,615	0,446	**0**

Table L14: ANOVA summary for Group B of the Coal tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	55,48	4,623333	1,005224
P Olsen	12	89,23879	7,436566	22,1718
pH	12	61,65	5,1375	2,666348

Table L15: ANOVA results for Group B of the Coal tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	53,85739	2	26,92869	3,125989	0,057117	3,284918
Within Groups	284,277	33	8,614456			
Total	338,1344	35				

Appendix L (continued)

Table L16: Summary statistics for Group B of the NMC1 tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	13,100	19,610	16,771	2,131
P Olsen	13	6,090	11,970	9,236	1,743
pH	13	5,950	6,560	6,180	0,201

Table L17: Pearson correlation matrix values for Group B of the NMC1 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	-0,095	**0,640**
P Olsen	-0,095	**1**	**-0,620**
pH	**0,640**	**-0,620**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table L18: Pearson p-values for Group B of the NMC1 tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,758	**0,019**
P Olsen	0,758	**0**	**0,024**
pH	**0,019**	**0,024**	**0**

Table L19: ANOVA summary for Group B of the NMC1 tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	201,25	16,77083	4,955717
P Olsen	12	110,8354	9,236287	3,313329
pH	12	74,16	6,18	0,043982

Table L20: ANOVA results for Group B of the NMC1 tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	713,1041	2	356,5521	128,6723	2,61E-16	3,284918
Within Groups	91,44331	33	2,771009			
Total	804,5474	35				

Appendix L (continued)

Table L21: Summary statistics for Group B of the Crown tailings in Pot trial 1.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
P Bray-1	13	10,460	18,080	14,060	2,696
P Olsen	13	9,510	19,320	13,244	3,175
pH	13	5,470	5,750	5,568	0,079

Table L22: Pearson correlation matrix values for Group B of the Crown tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**1**	0,356	-0,329
P Olsen	0,356	**1**	-0,415
pH	-0,329	-0,415	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table L23: Pearson p-values for Group B of the Crown tailings in Pot trial 1.

Variables	P Bray-1	P Olsen	pH
P Bray-1	**0**	0,232	0,273
P Olsen	0,232	**0**	0,159
pH	0,273	0,159	**0**

Table L24: ANOVA summary for Group B of the Crown tailings in Pot trial 1.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray-1	12	168,72	14,06	7,928636
P Olsen	12	158,9335	13,24446	10,99988
pH	12	66,81	5,5675	0,00682

Table L25: ANOVA results for Group B of the Crown tailings in Pot trial 1.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	526,8935	2	263,4468	41,73891	9,17E-10	3,284918
Within Groups	208,2887	33	6,311779			
Total	735,1823	35				

Appendix M: Baseline pH(H_2O), Olsen P, P Bray-1, Ca (P Bray-1 extract) and pH of the Bray extract for Pot trial 2

Table M1: Baseline results for Pot trial 2.

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700	2.74	3.35	14.20	317.50	2.37
Coal	2.82	4.30	13.97	1159.50	2.42
Control	5.04	3.40	3.21	66.00	3.02
Crown	3.33	3.90	3.23	288.75	2.99
NMC1	3.95	3.58	5.07	498.00	2.81

Appendix N: pH(H_2O), Olsen P, P Bray-1, Ca (P Bray-1 extract) and pH of the P Bray-1 extract for Group A during Pot trial 2

Table N1: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH (Bray-1 extract) results for Pot trial 2 - Group A (1 day after lime and fertiliser treatments).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	3.38	5.46	7.16	1500.75	2.41
NM700-2	3.74	7.35	5.82	1521.75	2.54
NM700-3	3.72	5.46	5.62	1413.00	2.56
NM700-4	4.00	7.14	5.80	2367.75	2.60
Coal-1	3.36	12.39	9.24	1060.50	2.50
Coal-2	3.54	14.07	9.86	1260.75	2.54
Coal-3	3.30	11.76	9.54	1428.00	2.52
Coal-4	3.40	10.50	9.97	1460.25	2.52
Control-1	5.50	31.71	30.18	73.50	3.03
Control-2	5.43	28.98	25.30	39.00	3.03
Control-3	5.60	29.19	29.31	48.00	3.03
Control-4	5.87	26.67	25.02	45.75	3.01
Crown-1	4.18	16.38	40.91	448.50	2.55
Crown-2	4.20	17.54	37.26	403.88	2.82
Crown-3	4.13	16.59	39.84	367.50	2.89
Crown-4	4.13	20.58	41.83	433.50	2.91
NMC1-1	5.07	21.42	37.49	322.88	3.07
NMC1-2	5.16	21.00	34.25	279.00	3.08
NMC1-3	5.19	21.21	32.46	373.50	3.07
NMC1-4	4.86	19.53	32.36	316.50	3.07

Appendix N (continued)

Table N2: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH(Bray-1 extract) results for Pot trial 2 - Group A (1 week after lime and fertiliser treatments).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	4.16	4.41	5.14	851.25	3.22
NM700-2	4.20	5.67	4.62	845.25	3.26
NM700-3	4.24	5.25	4.15	1062.00	3.23
NM700-4	4.20	5.88	4.25	836.25	3.14
Coal-1	4.12	6.93	8.08	1512.00	3.05
Coal-2	4.15	7.35	7.19	1645.50	3.16
Coal-3	4.17	10.29	6.44	1782.75	3.17
Coal-4	4.15	8.40	6.86	1677.75	3.15
Control-1	5.27	24.57	23.01	45.00	3.05
Control-2	5.23	23.94	25.87	42.00	3.13
Control-3	5.22	27.09	25.54	44.25	3.09
Control-4	5.20	28.56	27.94	69.75	3.09
Crown-1	4.10	15.75	37.51	378.00	3.02
Crown-2	3.98	15.12	39.07	402.75	2.96
Crown-3	4.14	17.22	39.96	371.25	3.01
Crown-4	4.16	16.59	38.79	388.50	3.04
NMC1-1	4.46	16.38	31.38	344.25	3.10
NMC1-2	4.44	14.07	30.77	283.60	3.12
NMC1-3	4.39	15.96	31.73	256.50	3.14
NMC1-4	4.40	15.33	30.72	255.00	3.13

Appendix N (continued)

Table N3: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH (Bray-1 extract) results for Pot trial 2 – Group A (3 weeks after lime and fertiliser treatments).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	4.30	2.52	5.07	884.25	2.99
NM700-2	4.26	2.52	4.34	849.75	3.01
NM700-3	4.28	2.73	4.80	770.25	3.01
NM700-4	4.26	2.31	4.40	719.25	3.04
Coal-1	4.22	4.20	6.86	1273.50	3.01
Coal-2	4.13	3.99	7.24	1370.25	2.97
Coal-3	4.16	4.83	8.14	1281.75	2.96
Coal-4	4.15	5.25	7.87	1244.25	2.99
Control-1	5.11	17.64	23.75	84.00	2.86
Control-2	5.06	17.22	27.37	62.25	2.84
Control-3	5.04	18.06	25.99	77.25	2.84
Control-4	5.00	18.27	25.07	97.50	2.82
Crown-1	4.12	9.24	35.52	528.75	2.54
Crown-2	4.10	11.76	38.43	522.00	2.55
Crown-3	4.12	10.71	35.83	528.75	2.56
Crown-4	4.09	10.71	37.82	535.50	2.58
NMC1-1	4.38	9.98	29.89	333.00	2.82
NMC1-2	4.38	10.08	31.98	286.50	3.01
NMC1-3	4.38	12.18	29.94	368.25	3.04
NMC1-4	4.43	10.08	36.24	340.50	3.04

Appendix O: XLSTAT and ANOVA results for Group A in Pot trial 2

Table O1: Summary statistics for Group A of the Control medium in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	5,000	5,870	5,294	0,249
P Olsen	13	17,220	31,710	24,325	5,019
P Bray	13	23,010	30,180	26,196	2,044
Ca Bray	13	39,000	97,500	60,688	18,578
pH Bray	13	2,820	3,130	2,985	0,108

Table O2: Pearson correlation matrix values for Group A of the Control medium in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**0,711**	0,248	-0,550	0,489
P Olsen	**0,711**	**1**	0,477	-0,537	**0,816**
P Bray	0,248	0,477	**1**	0,068	0,175
Ca Bray	-0,550	-0,537	0,068	**1**	**-0,728**
pH Bray	0,489	**0,816**	0,175	**-0,728**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table O3: Pearson p-values for Group A of the Control medium in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**0,006**	0,414	0,052	0,090
P Olsen	**0,006**	**0**	0,100	0,059	**0,001**
P Bray	0,414	0,100	**0**	0,824	0,568
Ca Bray	0,052	0,059	0,824	**0**	**0,005**
pH Bray	0,090	**0,001**	0,568	**0,005**	**0**

Table O4: ANOVA summary for Group A of the Control medium in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	63,53	5,294167	0,067717
P Olsen	12	291,9	24,325	27,47697
P Bray	12	314,35	26,19583	4,559572
Ca Bray	12	728,25	60,6875	376,5128
pH Bray	12	35,82	2,985	0,012627

Table O5: ANOVA results for Group A of the Control medium in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	25708,63	4	6427,158	78,64282	4,32E-22	2,539689
Within Groups	4494,926	55	81,72593			
Total	30203,56	59				

Appendix O (continued)

Table O6: Summary statistics for Group A of the NM700 tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	3,380	4,300	4,062	0,282
P Olsen	13	2,310	7,350	4,725	1,731
P Bray	13	4,150	7,160	5,098	0,843
Ca Bray	13	719,250	2367,750	1135,125	464,533
pH Bray	13	2,410	3,260	2,918	0,292

Table O7: Pearson correlation matrix values for Group A of the NM700 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**-0,559**	**-0,901**	**-0,602**	**0,865**
P Olsen	**-0,559**	**1**	0,432	**0,706**	-0,427
P Bray	**-0,901**	0,432	**1**	**0,663**	**-0,863**
Ca Bray	**-0,602**	**0,706**	**0,663**	**1**	**-0,754**
pH Bray	**0,865**	-0,427	**-0,863**	**-0,754**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table O8: Pearson p-values for Group A of the NM700 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**0,047**	**< 0.0001**	**0,029**	**0,000**
P Olsen	**0,047**	**0**	0,141	**0,007**	0,146
P Bray	**< 0.0001**	0,141	**0**	**0,014**	**0,000**
Ca Bray	**0,029**	**0,007**	**0,014**	**0**	**0,003**
pH Bray	**0,000**	0,146	**0,000**	**0,003**	**0**

Table O9: ANOVA summary for Group A of the NM700 tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	48,74	4,061667	0,086506
P Olsen	12	56,7	4,725	3,267409
P Bray	12	61,17	5,0975	0,776166
Ca Bray	12	13621,5	1135,125	235408
pH Bray	12	35,01	2,9175	0,092911

Table O10: ANOVA results for Group A of the NM700 tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12278341	4	3069585	65,19595	3,17E-20	2,539689
Within Groups	2589535	55	47082,45			
Total	14867876	59				

Appendix O (continued)

Table O11: Summary statistics for Group A of the Coal tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	3,300	4,220	3,904	0,361
P Olsen	13	3,990	14,070	8,330	3,295
P Bray	13	6,440	9,970	8,108	1,205
Ca Bray	13	1060,500	1782,750	1416,438	201,537
pH Bray	13	2,500	3,170	2,878	0,263

Table O12: Pearson correlation matrix values for Group A of the Coal tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**-0,799**	**-0,897**	0,375	**0,957**
P Olsen	**-0,799**	**1**	**0,645**	-0,004	**-0,673**
P Bray	**-0,897**	**0,645**	**1**	-0,505	**-0,937**
Ca Bray	0,375	-0,004	-0,505	**1**	**0,587**
pH Bray	**0,957**	**-0,673**	**-0,937**	**0,587**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table O13: Pearson p-values for Group A of the Coal tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**0,001**	**< 0.0001**	0,206	**< 0.0001**
P Olsen	**0,001**	**0**	**0,017**	0,989	**0,012**
P Bray	**< 0.0001**	**0,017**	**0**	0,078	**< 0.0001**
Ca Bray	0,206	0,989	0,078	**0**	**0,035**
pH Bray	**< 0.0001**	**0,012**	**< 0.0001**	**0,035**	**0**

Table O14: ANOVA summary for Group A of the Coal tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	46,85	3,904167	0,142063
P Olsen	12	99,96	8,33	11,84553
P Bray	12	97,29	8,1075	1,583675
Ca Bray	12	16997,25	1416,438	44309,81
pH Bray	12	34,54	2,878333	0,075179

Table O15: ANOVA results for Group A of the Coal tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	19103173	4	4775793	538,7433	2,16E-43	2,539689
Within Groups	487558	55	8864,691			
Total	19590731	59				

Appendix O (continued)

Table O16: Summary statistics for Group A of the NMC1 tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	4,380	5,190	4,628	0,322
P Olsen	13	9,975	21,420	15,601	4,256
P Bray	13	29,890	37,485	32,434	2,301
Ca Bray	13	255,000	373,500	313,290	38,980
pH Bray	13	2,815	3,140	3,057	0,082

Table O17: Pearson correlation matrix values for Group A of the NMC1 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**0,872**	0,546	0,203	0,165
P Olsen	**0,872**	**1**	0,386	-0,008	0,489
P Bray	0,546	0,386	**1**	0,068	0,172
Ca Bray	0,203	-0,008	0,068	**1**	-0,372
pH Bray	0,165	0,489	0,172	-0,372	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table O18: Pearson p-values for Group A of the NMC1 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**< 0.0001**	0,054	0,507	0,591
P Olsen	**< 0.0001**	**0**	0,193	0,980	0,090
P Bray	0,054	0,193	**0**	0,827	0,575
Ca Bray	0,507	0,980	0,827	**0**	0,210
pH Bray	0,591	0,090	0,575	0,210	**0**

Table O19: ANOVA summary for Group A of the NMC1 tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	55,54	4,628333	0,113088
P Olsen	12	187,215	15,60125	19,76173
P Bray	12	389,205	32,43375	5,77396
Ca Bray	12	3759,48	313,29	1657,576
pH Bray	12	36,685	3,057083	0,007311

Table O20: ANOVA results for Group A of the NMC1 tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	866916	4	216729	643,7881	1,81E-45	2,539689
Within Groups	18515,56	55	336,6465			
Total	885431,6	59				

Appendix O (continued)

Table O21: Summary statistics for Group A of the Crown tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	3.980	4.200	4.121	0.053
P Olsen	13	9.240	20.580	14.849	3.294
P Bray	13	35.520	41.830	38.563	1.830
Ca Bray	13	367.500	535.500	442.407	65.073
pH Bray	13	2.540	3.040	2.785	0.203

Table O22: Pearson correlation matrix values for Group A of the Crown tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	0.301	0.081	-0.113	-0.098
P Olsen	0.301	**1**	**0.771**	**-0.808**	**0.718**
P Bray	0.081	**0.771**	**1**	-0.491	0.382
Ca Bray	-0.113	**-0.808**	-0.491	**1**	**-0.898**
pH Bray	-0.098	**0.718**	0.382	**-0.898**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table O23: Pearson p-values for Group A of the Crown tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	0.318	0.793	0.712	0.751
P Olsen	0.318	**0**	**0.002**	**0.001**	**0.006**
P Bray	0.793	**0.002**	**0**	0.088	0.198
Ca Bray	0.712	**0.001**	0.088	**0**	**< 0.0001**
pH Bray	0.751	**0.006**	0.198	**< 0.0001**	**0**

Table O24: ANOVA summary for Group A of the Crown tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	49,45	4,120833	0,003045
P Olsen	12	178,185	14,84875	11,83976
P Bray	12	462,76	38,56333	3,654702
Ca Bray	12	5308,88	442,4067	4619,423
pH Bray	12	33,425	2,785417	0,044988

Table O25: ANOVA results for Group A of the Crown tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1762914	4	440728,6	475,4389	6,1E-42	2,539689
Within Groups	50984,62	55	926,993			
Total	1813899	59				

Appendix P: pH(H_2O), Olsen P, P Bray-1, Ca (P Bray-1 extract) and pH of the P Bray-1 extract for Group B during Pot trial 2

Table P1: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH (Bray-1 extract) results for Pot trial 2 – Group B (1 day after fertiliser treatments – 6 weeks after lime treatment).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	4.70	9.66	3.05	751.50	3.38
NM700-2	5.01	7.77	3.07	638.25	3.38
NM700-3	4.87	8.40	3.20	604.50	3.40
NM700-4	4.80	8.82	3.19	633.00	3.40
Coal-1	4.74	13.23	5.98	769.88	3.36
Coal-2	4.74	15.54	6.54	768.75	3.38
Coal-3	4.71	12.39	7.17	723.75	3.43
Coal-4	4.70	10.08	7.08	680.25	3.34
Control-1	5.69	35.91	32.33	58.50	3.38
Control-2	5.71	35.07	31.57	29.25	3.16
Control-3	5.63	35.49	33.85	27.00	3.27
Control-4	5.68	35.07	35.09	96.00	3.21
Crown-1	4.73	21.42	42.14	370.50	2.77
Crown-2	4.61	22.05	40.47	399.00	3.06
Crown-3	4.56	21.21	41.69	374.25	3.20
Crown-4	4.55	20.37	42.49	408.00	3.22
NMC1-1	4.89	16.17	33.57	213.00	3.27
NMC1-2	4.99	19.11	32.98	238.50	3.32
NMC1-3	4.93	18.90	32.99	238.50	3.30
NMC1-4	4.95	18.06	32.41	234.75	3.26

Appendix P (continued)

Table P2: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH (Bray-1 extract) results for Pot trial 2 – Group B (1 week after fertiliser treatments – 7 weeks after lime treatment).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	4.83	11.13	4.53	621.75	3.64
NM700-2	4.97	7.35	3.76	579.75	3.62
NM700-3	4.86	6.51	3.19	612.75	3.61
NM700-4	4.84	9.24	3.53	591.00	3.59
Coal-1	4.73	13.86	6.51	712.50	3.59
Coal-2	4.72	10.92	6.45	663.00	3.56
Coal-3	4.79	16.38	7.40	627.75	3.57
Coal-4	4.74	11.13	5.62	808.50	3.57
Control-1	5.52	31.08	31.31	71.63	3.31
Control-2	5.57	28.77	30.98	57.00	3.31
Control-3	5.64	32.76	34.71	69.00	3.33
Control-4	5.57	40.11	32.86	62.25	3.34
Crown-1	4.71	20.37	42.86	358.13	3.22
Crown-2	4.61	20.58	40.48	366.75	3.21
Crown-3	4.58	19.53	42.06	348.75	3.24
Crown-4	4.58	20.79	40.84	342.00	3.21
NMC1-1	4.94	20.79	34.52	181.50	3.31
NMC1-2	4.86	16.59	32.01	222.00	3.26
NMC1-3	4.88	18.48	32.34	204.00	3.28
NMC1-4	4.88	16.59	33.17	202.50	3.28

Appendix P (continued)

Table P3: pH(H_2O), Olsen P, P Bray-1, Ca (Bray-1 extract) and pH (Bray-1 extract) results for Pot trial 2 – Group B (3 weeks after fertiliser treatments – 9 weeks after lime treatment).

Sample	pH(H2O)	Olsen P (mg/kg)	P Bray-1 (mg/kg)	Ca (Bray-1 extract) (mg/kg)	pH (Bray-1 extract)
NM700-1	4.93	3.78	4.26	639.00	3.42
NM700-2	4.86	4.20	4.26	593.00	3.42
NM700-3	4.94	4.62	4.39	688.50	3.39
NM700-4	4.85	3.57	4.27	684.75	3.41
Coal-1	4.76	5.46	7.83	877.50	3.38
Coal-2	4.83	5.46	6.73	887.25	3.42
Coal-3	4.73	6.72	7.75	954.00	3.37
Coal-4	4.76	5.46	7.84	994.50	3.37
Control-1	5.59	18.27	31.18	56.25	3.09
Control-2	5.65	17.85	28.75	39.75	3.08
Control-3	5.83	16.17	26.35	53.25	3.04
Control-4	5.67	16.17	28.74	45.00	3.05
Crown-1	4.74	12.18	41.46	315.00	2.72
Crown-2	4.74	11.34	39.19	343.13	3.04
Crown-3	4.81	12.18	38.87	349.50	3.15
Crown-4	4.74	13.86	40.42	353.25	3.15
NMC1-1	5.22	10.82	31.38	210.00	3.23
NMC1-2	4.98	10.29	31.36	183.75	3.22
NMC1-3	5.18	11.97	32.38	388.75	3.22
NMC1-4	5.00	10.71	31.53	217.50	3.21

Appendix Q: XLSTAT and ANOVA results for Group B in Pot trial 2

Table Q1: Summary statistics for Group B of the Control medium in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	5.520	5.830	5.646	0.078
P Olsen	13	16.170	40.110	28.560	8.524
P Bray	13	26.350	35.090	31.477	2.473
Ca Bray	13	27.000	96.000	55.407	18.268
pH Bray	13	3.040	3.380	3.214	0.120

Table Q2: Pearson correlation matrix values for Group B of the Control medium in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	-0.306	-0.408	-0.189	-0.505
P Olsen	-0.306	**1**	**0.813**	0.220	**0.844**
P Bray	-0.408	**0.813**	**1**	0.390	**0.699**
Ca Bray	-0.189	0.220	0.390	**1**	0.320
pH Bray	-0.505	**0.844**	**0.699**	0.320	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table Q3: Pearson p-values for Group B of the Control medium in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	0.310	0.166	0.535	0.078
P Olsen	0.310	**0**	**0.001**	0.469	**0.000**
P Bray	0.166	**0.001**	**0**	0.188	**0.008**
Ca Bray	0.535	0.469	0.188	**0**	0.286
pH Bray	0.078	**0.000**	**0.008**	0.286	**0**

Table Q4: ANOVA summary for Group B of the Control medium in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	67,75	5,6458333	0,00659
P Olsen	12	342,72	28,56	79,25973
P Bray	12	377,72	31,476667	6,66937
Ca Bray	12	664,88	55,406667	364,0577
pH Bray	12	38,57	3,2141667	0,015627

Table Q5: ANOVA results for Group B of the Control medium in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	21939,55	4	5484,8863	60,94196	1,44E-19	2,539689
Within Groups	4950,099	55	90,001806			
Total	26889,64	59				

Appendix Q (continued)

Table Q6: Summary statistics for Group B of the NM700 tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	4,700	5,010	4,872	0,079
P Olsen	13	3,570	11,130	7,088	2,431
P Bray	13	3,050	4,530	3,725	0,558
Ca Bray	13	579,750	751,500	636,479	47,668
pH Bray	13	3,380	3,640	3,472	0,103

Table Q7: Pearson correlation matrix values for Group B of the NM700 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	-0,403	0,199	-0,426	0,040
P Olsen	-0,403	**1**	-0,462	-0,065	0,373
P Bray	0,199	-0,462	**1**	-0,042	0,143
Ca Bray	-0,426	-0,065	-0,042	**1**	**-0,559**
pH Bray	0,040	0,373	0,143	**-0,559**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table Q8: Pearson p-values for Group B of the NM700 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	0,172	0,514	0,146	0,897
P Olsen	0,172	**0**	0,112	0,833	0,210
P Bray	0,514	0,112	**0**	0,891	0,641
Ca Bray	0,146	0,833	0,891	**0**	**0,047**
pH Bray	0,897	0,210	0,641	**0,047**	**0**

Table Q9: ANOVA summary for Group B of the NM700 tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	58,46	4,871667	0,006815
P Olsen	12	85,05	7,0875	6,44762
P Bray	12	44,7	3,725	0,339245
Ca Bray	12	7637,75	636,4792	2478,846
pH Bray	12	41,66	3,471667	0,011488

Table Q10: ANOVA results for Group B of the NM700 tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3830810	4	957702,5	1926,462	2,18E-58	2,539689
Within Groups	27342,16	55	497,1303			
Total	3858152	59				

Appendix Q (continued)

Table Q11: Summary statistics for Group B of the Coal tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	4,700	4,830	4,746	0,034
P Olsen	13	5,460	16,380	10,553	3,802
P Bray	13	5,620	7,840	6,908	0,697
Ca Bray	13	627,750	994,500	788,969	112,513
pH Bray	13	3,340	3,590	3,445	0,093

Table Q12: Pearson correlation matrix values for Group B of the Coal tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	-0,262	0,124	0,316	0,074
P Olsen	-0,262	**1**	-0,473	**-0,794**	0,451
P Bray	0,124	-0,473	**1**	0,391	-0,408
Ca Bray	0,316	**-0,794**	0,391	**1**	-0,508
pH Bray	0,074	0,451	-0,408	-0,508	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table Q13: Pearson p-values for Group B of the Coal tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	0,388	0,686	0,293	0,809
P Olsen	0,388	**0**	0,102	**0,001**	0,121
P Bray	0,686	0,102	**0**	0,187	0,167
Ca Bray	0,293	**0,001**	0,187	**0**	0,076
pH Bray	0,809	0,121	0,167	0,076	**0**

Table Q14: ANOVA summary for Group B of the Coal tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	56,95	4,745833	0,001281
P Olsen	12	126,63	10,5525	15,77277
P Bray	12	82,9	6,908333	0,529397
Ca Bray	12	9467,63	788,9692	13810,03
pH Bray	12	41,34	3,445	0,009482

Table Q15: ANOVA results for Group B of the Coal tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5879333	4	1469833	531,5334	3,09E-43	2,539689
Within Groups	152089,8	55	2765,269			
Total	6031423	59				

Appendix Q (continued)

Table Q16: Summary statistics for Group B of the NMC1 tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	4,860	5,220	4,975	0,110
P Olsen	13	10,290	20,790	15,707	3,591
P Bray	13	31,360	34,520	32,553	0,908
Ca Bray	13	181,500	388,750	227,896	51,759
pH Bray	13	3,210	3,320	3,263	0,035

Table Q17: Pearson correlation matrix values for Group B of the NMC1 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**-0,618**	-0,413	0,525	-0,519
P Olsen	**-0,618**	**1**	**0,777**	-0,212	**0,934**
P Bray	-0,413	**0,777**	**1**	-0,087	**0,779**
Ca Bray	0,525	-0,212	-0,087	**1**	-0,273
pH Bray	-0,519	**0,934**	**0,779**	-0,273	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table Q18: Pearson p-values for Group B of the NMC1 tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**0,024**	0,161	0,066	0,069
P Olsen	**0,024**	**0**	**0,002**	0,487	**< 0.0001**
P Bray	0,161	**0,002**	**0**	0,777	**0,002**
Ca Bray	0,066	0,487	0,777	**0**	0,367
pH Bray	0,069	**< 0.0001**	**0,002**	0,367	**0**

Table Q19: ANOVA summary for Group B of the NMC1 tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	59,7	4,975	0,013209
P Olsen	12	188,48	15,70667	14,07039
P Bray	12	390,64	32,55333	0,899424
Ca Bray	12	2734,75	227,8958	2922,573
pH Bray	12	39,16	3,263333	0,00137

Table Q20: ANOVA results for Group B of the NMC1 tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	445227,9	4	111307	189,4549	1,82E-31	2,539689
Within Groups	32313,14	55	587,5116			
Total	477541	59				

Appendix Q (continued)

Table Q21: Summary statistics for Group B of the Crown tailings in Pot trial 2.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH	13	4.550	4.810	4.663	0.086
P Olsen	13	11.340	22.050	17.990	4.038
P Bray	13	38.870	42.860	41.081	1.205
Ca Bray	13	315.000	408.000	360.688	24.320
pH Bray	13	2.720	3.240	3.099	0.170

Table Q22: Pearson correlation matrix values for Group B of the Crown tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**1**	**-0.744**	-0.447	-0.522	-0.499
P Olsen	**-0.744**	**1**	**0.615**	**0.647**	0.306
P Bray	-0.447	**0.615**	**1**	0.262	-0.005
Ca Bray	-0.522	**0.647**	0.262	**1**	0.330
pH Bray	-0.499	0.306	-0.005	0.330	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table Q23: Pearson p-values for Group B of the Crown tailings in Pot trial 2.

Variables	pH	P Olsen	P Bray	Ca Bray	pH Bray
pH	**0**	**0.004**	0.125	0.067	0.083
P Olsen	**0.004**	**0**	**0.025**	**0.017**	0.309
P Bray	0.125	**0.025**	**0**	0.388	0.988
Ca Bray	0.067	**0.017**	0.388	**0**	0.270
pH Bray	0.083	0.309	0.988	0.270	**0**

Table Q24: ANOVA summary for Group B of the Crown tailings in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH	12	55,96	4,663333	0,008079
P Olsen	12	215,88	17,99	17,787
P Bray	12	492,97	41,08083	1,585317
Ca Bray	12	4328,26	360,6883	645,2417
pH Bray	12	37,19	3,099167	0,031463

Table Q25: ANOVA results for Group B of the Crown tailings in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1147005	4	286751,2	2157,148	9,95E-60	2,539689
Within Groups	7311,189	55	132,9307			
Total	1154316	59				

Appendix R: Pearson correlation matrix and ANOVA results for Ca Bray vs P Bray

Table R1: Pearson correlation matrix values for all Ca Bray and P Bray results in Pot trial 2.

	P Bray	Ca Bray
P Bray	**1**	-0,684
Ca Bray	-0,684	**1**

Table R2: ANOVA summary for all Ca Bray and P Bray results in Pot trial 2.

Groups	*Count*	*Sum*	*Average*	*Variance*
P Bray	120	2713,705	22,61421	204,3934
Ca Bray	120	65248,63	543,7386	214746,4

Table R3: ANOVA results for all Ca Bray and P Bray results in Pot trial 2.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16294237	1	16294237	151,609	2,77E-27	3,880827
Within Groups	25579140	238	107475,4			
Total	41873377	239				

Appendix S: Results for pH(H_2O) values as performed by way of three different procedures during Pot trial 2

Table S1: pH(H_2O) results as performed by way of three procedures (baseline).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	2.74	2.65	2.41
NM700-2	2.74	2.65	2.41
NM700-3	2.74	2.65	2.41
NM700-4	2.74	2.65	2.41
Coal-1	2.82	2.50	2.28
Coal-2	2.82	2.50	2.28
Coal-3	2.82	2.50	2.28
Coal-4	2.82	2.50	2.28
Control-1	5.04	4.69	4.80
Control-2	5.04	4.69	4.80
Control-3	5.04	4.69	4.80
Control-4	5.04	4.69	4.80
Crown-1	3.33	3.21	3.01
Crown-2	3.33	3.21	3.01
Crown-3	3.33	3.21	3.01
Crown-4	3.33	3.21	3.01
NMC1-1	3.95	3.85	4.02
NMC1-2	3.95	3.85	4.02
NMC1-3	3.95	3.85	4.02
NMC1-4	3.95	3.85	4.02

Appendix S (continued)

Table S2: pH(H_2O) results as performed by way of three procedures (1 day after lime applications).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.04	4.12	5.05
NM700-2	4.35	4.19	5.17
NM700-3	4.17	4.19	5.21
NM700-4	4.27	4.17	5.15
Coal-1	3.65	3.82	4.58
Coal-2	3.82	3.86	4.56
Coal-3	3.86	3.92	4.64
Coal-4	3.87	3.94	4.69
Control-1	5.48	4.95	5.42
Control-2	5.77	5.22	5.35
Control-3	6.01	5.25	5.40
Control-4	6.12	5.16	5.37
Crown-1	4.31	4.15	4.41
Crown-2	4.34	4.16	4.44
Crown-3	4.28	4.16	4.48
Crown-4	4.30	4.22	4.55
NMC1-1	4.76	4.53	5.25
NMC1-2	4.89	4.59	5.25
NMC1-3	4.67	4.49	5.17
NMC1-4	4.70	4.56	5.18

Appendix S (continued)

Table S3: pH(H_2O) results as performed by way of three procedures (2 days after lime applications).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.54	4.66	5.99
NM700-2	4.37	4.55	5.99
NM700-3	4.39	4.51	5.82
NM700-4	4.28	4.34	6.00
Coal-1	4.48	4.55	5.42
Coal-2	4.07	4.14	5.11
Coal-3	4.35	4.41	5.43
Coal-4	4.27	4.38	5.40
Control-1	5.83	5.23	5.33
Control-2	5.90	5.32	5.38
Control-3	5.99	5.30	5.36
Control-4	5.97	5.24	5.37
Crown-1	4.36	4.38	4.63
Crown-2	4.35	4.35	4.65
Crown-3	4.29	4.31	4.54
Crown-4	4.36	4.36	4.59
NMC1-1	4.67	4.74	5.40
NMC1-2	4.78	4.83	5.57
NMC1-3	4.82	4.86	5.69
NMC1-4	4.74	4.80	5.68

Appendix S (continued)

Table S4: pH(H_2O) results as performed by way of three procedures (3 days after lime applications).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.24	4.70	6.01
NM700-2	4.65	4.78	6.15
NM700-3	4.56	4.72	6.20
NM700-4	4.54	4.69	6.20
Coal-1	4.61	4.67	5.77
Coal-2	4.48	4.56	5.74
Coal-3	4.47	4.51	5.81
Coal-4	4.67	4.72	5.83
Control-1	5.91	5.36	5.55
Control-2	6.00	5.38	5.46
Control-3	6.02	5.28	5.47
Control-4	6.04	5.29	5.44
Crown-1	4.39	4.39	4.51
Crown-2	4.32	4.39	4.68
Crown-3	4.43	4.37	4.84
Crown-4	4.41	4.32	4.70
NMC1-1	4.92	4.95	5.71
NMC1-2	4.85	4.83	5.76
NMC1-3	4.82	4.85	5.74
NMC1-4	4.89	4.91	5.81

Appendix S (continued)

Table S5: pH(H_2O) results as performed by way of three procedures (4 days after lime applications).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.80	4.86	6.29
NM700-2	4.73	4.83	6.31
NM700-3	4.70	4.76	6.34
NM700-4	4.73	4.79	6.33
Coal-1	4.58	4.60	5.88
Coal-2	4.66	4.68	5.90
Coal-3	4.69	4.70	6.01
Coal-4	4.45	4.50	6.07
Control-1	5.89	5.48	5.71
Control-2	5.92	5.36	5.51
Control-3	5.49	5.36	5.53
Control-4	5.31	5.31	5.52
Crown-1	4.13	4.31	4.70
Crown-2	4.09	4.38	4.75
Crown-3	4.08	4.34	4.55
Crown-4	4.10	4.40	4.77
NMC1-1	4.25	4.82	5.83
NMC1-2	4.24	4.91	5.92
NMC1-3	4.25	4.94	5.99
NMC1-4	4.27	4.94	5.99

Appendix S (continued)

Table S6: pH(H_2O) results as performed by way of three procedures (1 week after lime applications).

Sample	pH(H2O) Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.32	5.30	6.26
NM700-2	4.28	5.29	6.23
NM700-3	4.30	5.37	6.28
NM700-4	4.29	5.36	6.33
Coal-1	4.19	4.83	5.69
Coal-2	4.19	4.83	5.76
Coal-3	4.21	4.95	5.82
Coal-4	4.17	4.81	5.84
Control-1	5.33	5.47	5.54
Control-2	5.27	5.45	5.50
Control-3	5.30	5.45	5.48
Control-4	5.32	5.41	5.51
Crown-1	4.12	4.45	4.68
Crown-2	4.12	4.47	4.70
Crown-3	4.12	4.50	4.70
Crown-4	4.14	4.46	4.57
NMC1-1	4.28	5.02	5.76
NMC1-2	4.31	5.11	5.88
NMC1-3	4.28	5.14	5.95
NMC1-4	4.28	5.14	5.96

Appendix S (continued)

Table S7: pH(H_2O) results as performed by way of three procedures (3 weeks after lime applications).

Sample	pH(H_2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.25	5.74	6.41
NM700-2	4.30	5.75	6.32
NM700-3	4.23	5.74	6.40
NM700-4	4.22	5.68	6.41
Coal-1	4.22	5.00	5.83
Coal-2	4.16	4.99	5.91
Coal-3	4.18	5.04	5.91
Coal-4	4.14	4.88	5.85
Control-1	5.26	5.55	5.74
Control-2	5.27	5.54	5.70
Control-3	5.26	5.50	5.65
Control-4	5.24	5.46	5.62
Crown-1	4.18	4.66	4.83
Crown-2	4.12	4.60	4.98
Crown-3	4.07	4.49	4.68
Crown-4	4.09	4.51	4.57
NMC1-1	4.27	5.35	5.89
NMC1-2	4.25	5.39	5.96
NMC1-3	4.25	5.40	6.02
NMC1-4	4.24	5.40	6.06

Appendix S (continued)

Table S8: pH(H_2O) results as performed by way of three procedures (6 weeks after lime applications).

Sample	pH(H2O)		
	Leaching procedure	Conventional procedure	Suspension shaken for 24 hrs
NM700-1	4.44	5.74	6.24
NM700-2	4.50	5.78	6.26
NM700-3	5.18	5.74	6.28
NM700-4	4.60	5.83	6.32
Coal-1	4.29	4.97	5.75
Coal-2	4.30	4.94	5.76
Coal-3	4.34	5.02	5.74
Coal-4	4.31	4.98	5.74
Control-1	5.49	5.42	5.84
Control-2	5.54	5.41	5.75
Control-3	5.54	5.40	5.69
Control-4	5.58	5.37	5.58
Crown-1	4.11	4.43	4.79
Crown-2	4.11	4.43	4.72
Crown-3	4.14	4.44	4.61
Crown-4	4.10	4.37	4.72
NMC1-1	4.42	5.41	5.85
NMC1-2	4.50	5.45	5.88
NMC1-3	4.54	5.48	5.95
NMC1-4	4.54	5.46	5.96

Appendix T: Statistics for pH(H_2O) values obtained by way of three different procedures

Table T1: Summary statistics of pH(H_2O) (three procedures) for the Control medium.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	36	5,040	6,120	5,581	0,335
Conventional	36	4,690	5,620	5,306	0,258
Shaken 24hrs	36	4,800	6,000	5,496	0,311

Table T2: Pearson correlation matrix values of pH(H_2O) (three procedures) for the Control medium.

Variables	Leaching	Incubation	Conventional
Leaching	**1**	0,304	0,321
Incubation	0,304	**1**	**0,932**
Conventional	0,321	**0,932**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T3: Pearson p-values of pH(H_2O) (three procedures) for the Control medium.

Variables	Leaching	Incubation	Conventional
Leaching	**0**	0,071	0,056
Incubation	0,071	**0**	**< 0,0001**
Conventional	0,056	**< 0,0001**	**0**

Table T4: ANOVA summary of pH(H_2O) (three procedures) for the Control medium.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	32	180,76	5,64875	0,084308
Conventional	32	172,26	5,383125	0,020338
Shaken 24hrs	32	178,64	5,5825	0,038903

Table T5: ANOVA results of pH(H_2O) (three procedures) for the Control medium.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1,223425	2	0,6117125	12,784	0,0000124	3,094337
Within Groups	4,450038	93	0,047849866			
Total	5,673463	95				

Appendix T (continued)

Table T6: Summary statistics of pH(H_2O) (three procedures) for the NM700 tailings.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	36	2,740	5,180	4,295	0,612
Conventional	36	2,650	5,880	4,824	0,961
Shaken 24hrs	36	2,410	6,520	5,650	1,252

Table T7: Pearson correlation matrix values of pH(H_2O) (three procedures) for the NM700 tailings.

Variables	Conventional	Leaching	Shaken 24hrs
Conventional	**1**	**0,820**	**0,862**
Leaching	**0,820**	**1**	**0,869**
Shaken 24hrs	**0,862**	**0,869**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T8: Pearson p-values of pH(H_2O) (three procedures) for the NM700 tailings.

Variables	Conventional	Leaching	Shaken 24hrs
Conventional	**0**	**< 0,0001**	**< 0,0001**
Leaching	**< 0,0001**	**0**	**< 0,0001**
Shaken 24hrs	**< 0,0001**	**< 0,0001**	**0**

Table T9: ANOVA summary of pH(H_2O) (three procedures) for the NM700 tailings.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	32	143,65	4,489063	0,071738
Conventional	32	163,05	5,095313	0,357232
Shaken 24hrs	32	193,77	6,055313	0,245271

Table T10: ANOVA results of pH(H_2O) (three procedures) for the NM700 tailings.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	39,91763	2	19,95882	88,80573	2,69E-22	3,094337
Within Groups	20,90147	93	0,224747			
Total	60,8191	95				

Appendix T (continued)

Table T11: Summary statistics of pH(H_2O) (three procedures) for the Coal tailings.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	36	2,820	4,740	4,163	0,553
Conventional	36	2,500	5,520	4,474	0,826
Shaken 24hrs	36	2,280	6,110	5,274	1,154

Table T12: Pearson correlation matrix values of pH(H_2O) (three procedures) for the Coal tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**1**	**0,914**	**0,953**
Conventional	**0,914**	**1**	**0,960**
Shaken 24hrs	**0,953**	**0,960**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T13: Pearson p-values of pH(H_2O) (three procedures) for the Coal tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**0**	**< 0,0001**	**< 0,0001**
Conventional	**< 0,0001**	**0**	**< 0,0001**
Shaken 24hrs	**< 0,0001**	**< 0,0001**	**0**

Table T14: ANOVA summary of pH(H_2O) (three procedures) for the Coal tailings.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	32	138,57	4,330313	0,083868
Conventional	32	151,05	4,720313	0,205093
Shaken 24hrs	32	180,75	5,648438	0,203091

Table T15: ANOVA results of pH(H_2O) (three procedures) for the Coal tailings.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	29,34368	2	14,67184	89,45295	2,16E-22	3,094337
Within Groups	15,25362	93	0,164017			
Total	44,59729	95				

Appendix T (continued)

Table T16: Summary statistics of pH(H_2O) (three procedures) for the NMC1 tailings.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	36	3,950	4,990	4,507	0,329
Conventional	36	3,850	5,490	4,928	0,490
Shaken 24hrs	36	4,020	6,240	5,611	0,633

Table T17: Pearson correlation matrix values of pH(H_2O) (three procedures) for the NMC1 tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**1**	**0,378**	**0,474**
Conventional	**0,378**	**1**	**0,937**
Shaken 24hrs	**0,474**	**0,937**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T18: Pearson p-values of pH(H_2O) (three procedures) for the NMC1 tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**0**	**0,023**	**0,004**
Conventional	**0,023**	**0**	**< 0,0001**
Shaken 24hrs	**0,004**	**< 0,0001**	**0**

Table T19: ANOVA summary of pH(H_2O) (three procedures) for the NMC1 tailings.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	32	146,44	4,57625	0,076927
Conventional	32	162,01	5,062813	0,102602
Shaken 24hrs	32	185,9	5,809375	0,085838

Table T20: ANOVA results of pH(H_2O) (three procedures) for the NMC1 tailings.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	24,69009	2	12,34504	139,5618	9,94E-29	3,094337
Within Groups	8,226384	93	0,088456			
Total	32,91647	95				

Appendix T (continued)

Table T21: Summary statistics of pH(H_2O) (three procedures) for the Crown tailings.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	36	3,330	4,730	4,159	0,341
Conventional	36	3,210	4,660	4,264	0,393
Shaken 24hrs	36	3,010	5,240	4,533	0,583

Table T22: Pearson correlation matrix values of pH(H_2O) (three procedures) for the Crown tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**1**	**0,820**	**0,904**
Conventional	**0,820**	**1**	**0,954**
Shaken 24hrs	**0,904**	**0,954**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T23: Pearson p-values of pH(H_2O) (three procedures) for the Crown tailings.

Variables	Leaching	Conventional	Shaken 24hrs
Leaching	**0**	**< 0,0001**	**< 0,0001**
Conventional	**< 0,0001**	**0**	**< 0,0001**
Shaken 24hrs	**< 0,0001**	**< 0,0001**	**0**

Table T24: ANOVA summary of pH(H_2O) (three procedures) for the Crown tailings.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	32	136,41	4,2628125	0,0316789
Conventional	32	140,66	4,395625	0,013348
Shaken 24hrs	32	151,13	4,7228125	0,0477693

Table T25: ANOVA results of pH(H_2O) (three procedures) for the Crown tailings.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3,5871021	2	1,79355104	57,983569	4,48E-17	3,094337
Within Groups	2,8766813	93	0,03093206			
Total	6,4637833	95				

Appendix T (continued)

Table T26: Summary statistics of pH(H_2O) (three procedures) for all the growth mediums treated with lime.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
Leaching	160	3,650	6,120	4,661	0,571
Conventional	160	3,820	5,880	4,931	0,503
Shaken 24hrs	160	4,410	6,520	5,564	0,571

Table T27: Pearson correlation matrix values of pH(H_2O) (three procedures) for all the growth mediums treated with lime.

Variables	Leaching	Shaken 24hrs	Conventional
Leaching	**1**	**0,200**	**0,554**
Shaken 24hrs	**0,200**	**1**	**0,687**
Conventional	**0,554**	**0,687**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table T28: Pearson p-values of pH(H_2O) (three procedures) for all the growth mediums treated with lime.

Variables	Leaching	Shaken 24hrs	Conventional
Leaching	**0**	**0,011**	**< 0,0001**
Shaken 24hrs	**0,011**	**0**	**< 0,0001**
Conventional	**< 0,0001**	**< 0,0001**	**0**

Table T29: ANOVA summary of pH(H_2O) (three procedures) for all the growth mediums treated with lime.

Groups	*Count*	*Sum*	*Average*	*Variance*
Leaching	160	745,83	4,661438	0,325621
Conventional	160	789,03	4,931438	0,252898
Shaken 24hrs	160	890,19	5,563688	0,325662

Table T30: ANOVA results of pH(H_2O) (three procedures) for all the growth mediums treated with lime.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	68,62374	2	34,31187	113,844	3,80E-41	3,014626
Within Groups	143,7649	477	0,301394			
Total	212,3886	479				

<u>Appendix U:</u> Photographs taken of $CaSO_4$ precipitation observed on the tailings material one week after lime applications. Note that no $CaSO_4$ precipitation was observed on the control medium

<u>Appendix V:</u> Change in Ca Bray, P Bray and Olsen P values after lime and fertiliser treatments during Pot trial 2 (Group A and B)

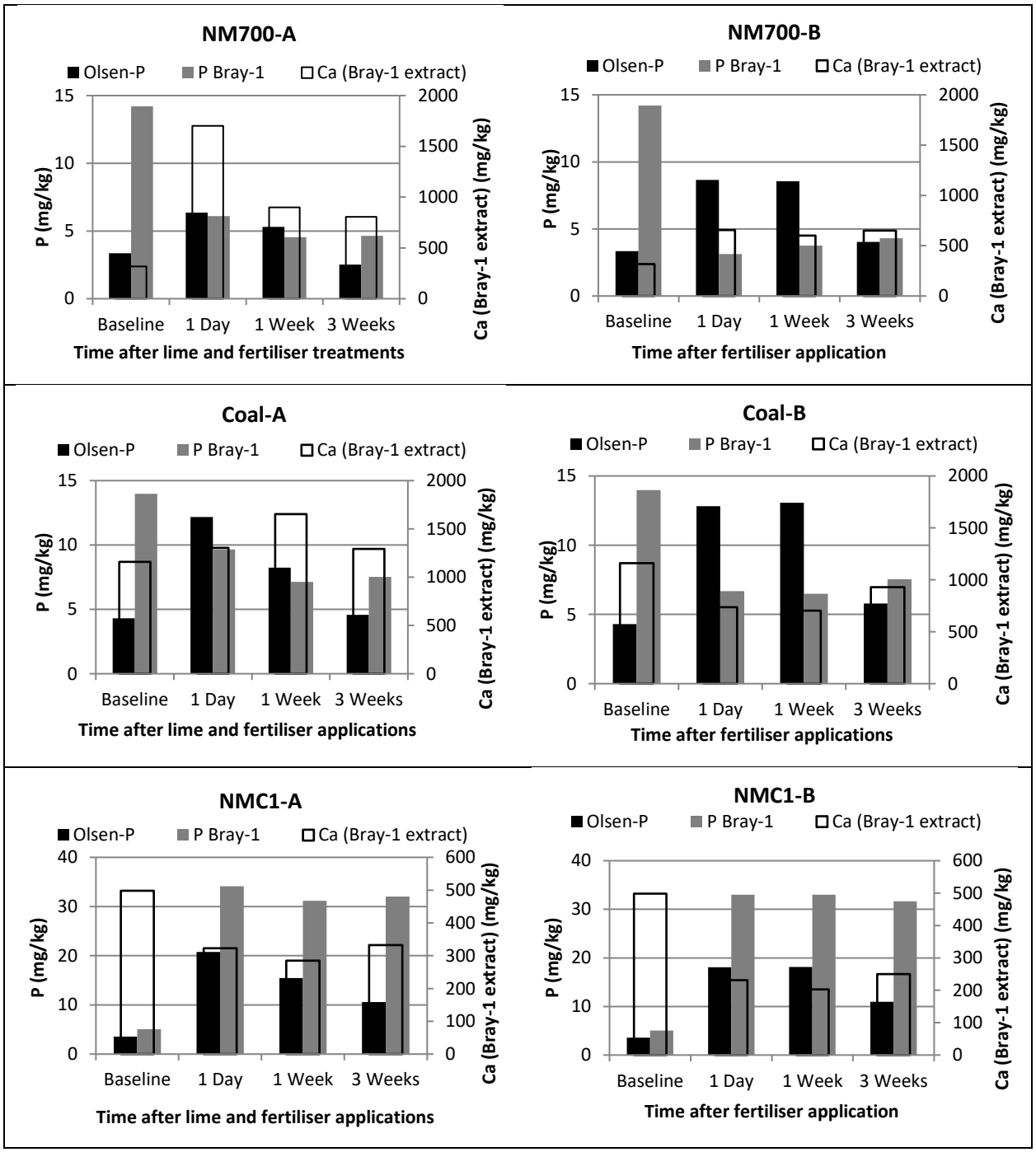


Figure P1: Pot trial 2 results for Group A and Group B (NM700, coal and NMC1).

Appendix V (continued)

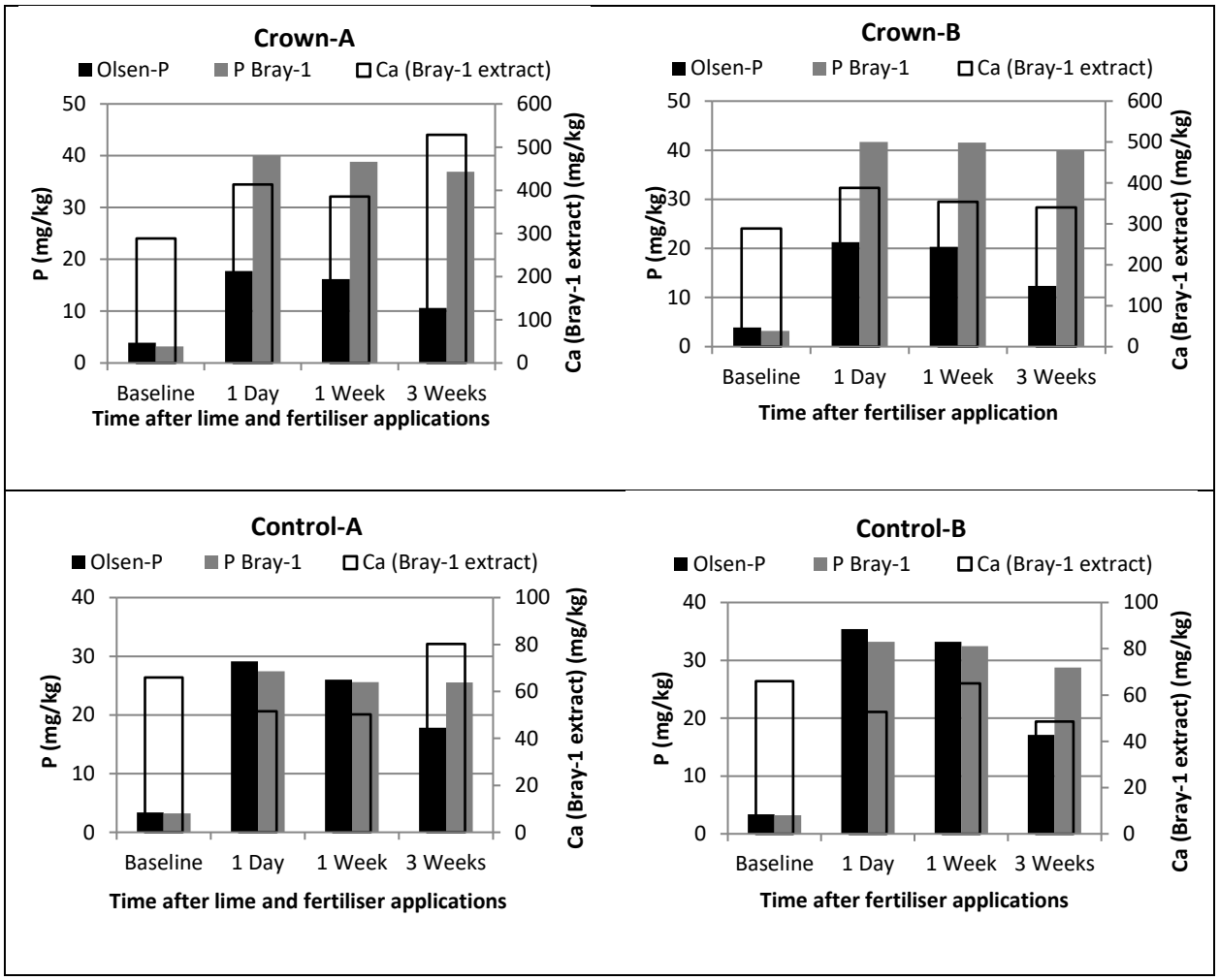


Figure P2: Pot trial 2 results for Group A and Group B (Crown and Control).

Appendix W: Results for seedling survival rates and plant growth (Pot trial 2)

Table W1: Seedling survival rates.

Seedling survival per pot (%)		
Sample	**Group**	
	A	**B**
NM700-1	60	70
NM700-2	50	90
NM700-3	70	60
NM700-4	40	60
Coal-1	70	80
Coal-2	60	70
Coal-3	70	80
Coal-4	80	80
Control-1	90	80
Control-2	90	50
Control-3	70	60
Control-4	90	80
Crown-1	60	70
Crown-2	50	60
Crown-3	90	70
Crown-4	60	80
NMC1-1	70	90
NMC1-2	80	80
NMC1-3	70	60
NMC1-4	60	80

Appendix W (continued)

Table W2: Plant growth results.

Length of the highest grass leaf (mm)		
Sample	**Group**	
	A	**B**
NM700-1	13.00	30.00
NM700-2	15.00	40.00
NM700-3	15.00	22.00
NM700-4	23.00	28.00
Coal-1	62.00	155.00
Coal-2	114.00	180.00
Coal-3	120.00	210.00
Coal-4	125.00	185.00
Control-1	269.00	280.00
Control-2	281.00	270.00
Control-3	256.00	171.00
Control-4	167.00	262.00
Crown-1	110.00	112.00
Crown-2	80.00	125.00
Crown-3	149.00	140.00
Crown-4	170.00	117.00
NMC1-1	151.00	179.00
NMC1-2	178.00	219.00
NMC1-3	190.00	158.00
NMC1-4	171.00	169.00

<u>Appendix X:</u> Statistics for seedling survival rates and plant growth (Pot trial 2 – Group A and B data)

Table X1: Summary statistics for seedling survival rate and plant growth experiment.

Variable	Observations	Minimum	Maximum	Mean	Std. deviation
pH End	40	4,090	5,830	4,720	0,478
P Olsen	40	2,310	18,270	9,634	5,173
P Bray	40	4,260	41,460	21,887	13,756
Survival%	40	40,000	90,000	70,750	12,888
Grass height	40	13,000	281,000	142,775	79,982
pH 23 Weeks	40	4,990	7,210	6,133	0,789
EC 23 Weeks	40	14,950	552,000	236,199	207,175

Table X2: Pearson correlation matrix values for seedling survival rate and plant growth experiment.

Variables	EC 23 Weeks	Survival%	pH End	Grass height	P Bray	pH 23 Weeks	P Olsen
EC 23 Weeks	**1**	-0,232	**-0,496**	**-0,688**	**-0,805**	**-0,836**	**-0,866**
Survival%	-0,232	**1**	0,247	**0,438**	0,103	0,080	0,291
pH End	**-0,496**	0,247	**1**	**0,538**	0,177	**0,417**	**0,596**
Grass height	**-0,688**	**0,438**	**0,538**	**1**	**0,500**	**0,552**	**0,789**
P Bray	**-0,805**	0,103	0,177	**0,500**	**1**	**0,867**	**0,748**
pH 23 Weeks	**-0,836**	0,080	**0,417**	**0,552**	**0,867**	**1**	**0,891**
P Olsen	**-0,866**	0,291	**0,596**	**0,789**	**0,748**	**0,891**	**1**

Values in bold are different from 0 with a significance level alpha=0,05

Table X3: Pearson p-values for seedling survival rate and plant growth experiment.

Variables	EC 23 Weeks	Survival%	pH End	Grass height	P Bray	pH 23 Weeks	P Olsen
EC 23 Weeks	**0**	0,149	**0,001**	**< 0,0001**	**< 0,0001**	**< 0,0001**	**< 0,0001**
Survival%	0,149	**0**	0,125	**0,005**	0,526	0,623	0,068
pH End	**0,001**	0,125	**0**	**0,000**	0,274	**0,007**	**< 0,0001**
Grass height	**< 0,0001**	**0,005**	**0,000**	**0**	**0,001**	**0,000**	**< 0,0001**
P Bray	**< 0,0001**	0,526	0,274	**0,001**	**0**	**< 0,0001**	**< 0,0001**
pH 23 Weeks	**< 0,0001**	0,623	**0,007**	**0,000**	**< 0,0001**	**0**	**< 0,0001**
P Olsen	**< 0,0001**	0,068	**< 0,0001**	**< 0,0001**	**< 0,0001**	**< 0,0001**	**0**

Appendix X (continued)

Table X4: ANOVA summary for seedling survival rate and plant growth experiment.

Groups	*Count*	*Sum*	*Average*	*Variance*
pH End of pot trial	40	188,78	4,7195	0,228928
P Olsen	40	385,355	9,633875	26,75869
P Bray	40	875,49	21,88725	189,2168
Survival%	40	2830	70,75	166,0897
Grass height	40	5711	142,775	6397,102
pH 23 Weeks	40	245,33	6,13325	0,622115
EC 23 Weeks	40	9447,94	236,1985	42921,43

Table X5: ANOVA results for seedling survival rate and plant growth experiment.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1888699	6	314783,2	44,33438	1,11E-37	2,131866
Within Groups	1938357	273	7100,207			
Total	3827056	279				