

**Phosphorus phyto-availability and fertilizer value of petrochemical
and municipal wastewater sludges**

by

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Abstract

A growing population, urbanization and an increase in the number of industries is causing an increase in sewage sludge (SS) that needs to be either beneficially used or disposed of. Application of SS to agricultural lands is a well-known practice but the plant available phosphate and phosphate fertilizer value of SS has been of concern. This is especially due to the wide variety of soils that SS is applied to and the different phosphate removal processes that sewage waste water undergoes at the water care works and the source used to produce SS.

Phosphate phyto-availability and phosphate fertilizer value of petrochemical and municipal wastewater sludges (SS) were determined in four different soils using an incubation study over 168 days, a pot trial over 42 days and a field trial over one season. Phosphate phyto-availability was determined/calculated by means of an incubation approach. Soils were incubated with sludge as well as mono ammonium phosphate (MAP). The soils were then subjected to a Bray-1 extraction after a certain time (42 days, 168 days). The relative phosphate fertilizer value (RPFV) was then expressed as a percentage of the Bray-1 extractability of the sludge-amended soil, relative to the MAP-amended soil. The influence of soil properties, especially clay content, and sludge properties namely phosphate extraction method (chemical and biological) from waste water stream, was investigated to determine the effect on phyto-availability and fertilizer value of phosphate in SS-amended soil. Soil properties were the dominant factor determining plant available phosphate, where plant available phosphate decreased with increasing clay content, irrelevant of the type of treatment. There were, however, significant

differences between the chemical and biologically removed SS, where the biologically removed SS had higher plant available phosphate.

The RPFV % of the SS was comparable to MAP in terms of its plant availability. Wetting and drying cycles in the pot trial influenced the plant available phosphate from the SS, where the chemically treated sludge showed in general lower plant availability. The RPFV % of the biologically removed phosphate sludges was better than that of MAP and that of the chemically phosphate removed sludge were lower.

Application of all the different sludge types resulted in a positive reaction on plant available phosphate for all the soils. All the trials were conducted at pH of about 5.5. However, it is expected that biologically P removed sludge will perform better in acid soils. The reason being that ferric phosphate in the chemically treated sludge is less soluble under pH conditions lower than 5.5 than above it.

Keywords: Ammonium phosphate, Bray-1, incubation, municipal wastewater sludge, phosphate phyto-availability, relative phosphate fertilizer value %.

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Chapter 1

General background

1.1 Introduction

Phosphate (PO_4^{3-}) is a scarce natural resource. Phosphate reserves of the world were recently estimated to have a 90 year supply left at current rate of usage (Stewart *et al.*, 2005). This implies that alternative sources of phosphate should be searched for because the primary source of phosphate, namely apatite (rock phosphate), is finite (Brady & Weil, 2002). The second problem is the increase of sewage sludge (SS) around the world due to an increase in the world's population (US EPA, 1999). A growing population, urbanisation and an increase in the number of industries cause an increase in SS that needs to be either beneficially used or disposed of. The total daily wastewater inflow was estimated at 5400 MI d^{-1} in South Africa and Wastewater Care Works (WCW) are under pressure to dispose or utilize this sludge (Marx *et al.*, 2004).

Land application of sludge in the vicinity of WCW is a widely applied waste management strategy. Responsible land application is considered a beneficial use of sludge because it can improve soil quality, soil fertility, soil organic matter content, microbial activity and the residual N and P content (Stamatiadis *et al.*, 1999). Land application of sludge also has the advantage of increasing crop yields, and reducing fertilizer input (Magdoff & Amadon, 1980).

It is known that SS contains macronutrients and trace elements. The important macronutrients are nitrogen, phosphate, and potassium. SS can especially be used as a secondary source of phosphate, because of the limited quantities left of primary sources of phosphate, an appreciable high P concentration compared to cattle and chicken manure in SS and the increasing world SS production makes SS a viable source of phosphate (Brady & Weil, 2002). Land application of SS is a good way to recycle nutrients and organic matter, but there are potential health risks like pathogens, heavy metals and organic pollutants (Albiach *et al.*, 2001; Vasseur *et al.*, 2000). Heavy metals of concern that can be found in SS are As, Cd,

Cu, Pb, Hg, Mo, Ni, Se, Zn, and Cr. These elements are considered pollutants if they exceed the maximum concentration limits. Organic contaminants that can be found in SS include pesticides (chlordane and endrin), herbicides (2,4-D), volatiles (benzene and carbon tetrachloride), and semi-volatiles (O-Cresol) (US EPA, 1995). SS is a cheap source of plant nutrients, but its nutrient value varies considerably (Smith *et al.*, 1998; Petersen, 2003). The release rate of phosphate from SS (Stark *et al.*, 2005), plant available phosphate and the process (precipitation, solubilisation, mineralization and immobilization) involved are also of concern (Soon & Bates, 1982).

1.2 Phosphate recovery from sewage waste water

The quality and type of waste water treatment determines the quality of the SS produced (US EPA, 1999). Sewage sludge is treated by different stabilizing processes to control odour pathogens, biodegradable toxins, vectors and to bind heavy metals.

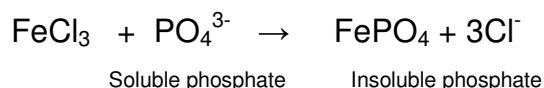
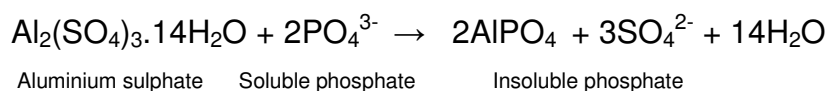
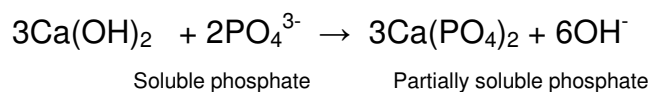
Phosphate recovery is a tertiary waste water treatment. Phosphate can also be removed from the sludge (US EPA, 1999). Because of the high volume of waste, the cost of disposal and the scarceness in the foreseeable future of phosphate, P source deposits induced a lot of studies to recover phosphate from dried sewage sludge and sewage sludge ash (Takashi *et al.*, 2001). Technology to reduce the mass and volume of sewage sludge to get a more concentrated usable product has gained interest. Incineration of sewage sludge is already practised around the world but new processes like supercritical water oxidation is starting to be implemented as an alternative treatment (Shanableh & Shimizu, 2000). Incineration and supercritical water oxidation can be used to remove all organic matter, including harmful organic substances, from sewage sludge to produce inorganic products so that phosphorus can be removed (Guibelin, 2004).

The orthophosphate anion (PO_4^{3-}) is the most common and abundant form of phosphorus. Phosphate is highly concentrated in sewage waste water compared to natural water bodies. Conventionally, phosphate is removed from sewage waste water by chemical precipitation and/or biological methods (NRC, 1996). The removed phosphate, being in an inorganic and/or organic

form, is concentrated in the sewage sludge leaving an almost phosphate-free waste water effluent that complies with standards of 1 ppm phosphate or less (Snyman & Herselman, 2006). This is done to prevent eutrophication downstream from the WCW.

1.2.1 Chemical precipitation

Phosphate can be removed by chemical precipitation from phosphate-rich sewage waste water and is normally done with ferric chloride, aluminium sulphate or calcium hydroxide (Equation 1.1) (Marx *et al.*, 2004). A method known and applied in practice is the Crystalactor process (Piekema & Giesen, 2001). Struvite formation is another method for phosphate precipitation with magnesium hydroxide and sodium hydroxide (Ueno & Fujii, 2001). Precipitation with lime produces a very fine precipitate in the form of calcium phosphate (Temmink *et al.*, 2002). Using aluminium salts or poly-aluminium chloride can cause co-precipitation of metals. This can also be expected when iron, as a metal salt, is used. Treatment with calcium hydroxide, aluminium sulphate or ferric chloride results in the precipitation of Ca-P, Al-P and Fe-P respectively (Equation 1.1). These are inorganic forms of phosphate. Phosphate equilibrium concentrations were the highest with Ca-P and Fe-P. Solubility of phosphate from Ca-P was decreased due to the formation of octacalcium phosphate.



Equation 1.1: Reactions of soluble phosphate with calcium hydroxide, aluminium sulphate and ferric chloride (Brady & Weil, 2002).

Sludge treated with ferric chloride decreases soil pH but this increases the solubility of Fe-P. Sludge treated with ferric chloride and aluminium sulphate and then applied to the soil increased the Fe- and Al-oxide content of the soil (Soon & Bates, 1982). Codling *et al.* (2000) found that SS that had been treated with ferric chloride or aluminium sulphate had less soluble phosphate than untreated SS. Using poly-aluminium chloride for the precipitation of phosphate causes the phosphate to be bound by the sludge (Steen, 1998).

1.2.2 Biological removal

Biological removal of phosphate from sewage waste water is done with bacteria known as phosphorus accumulating organisms (PAO). These bacteria are aerobic heterotrophs that only thrive in certain conditions. They are mainly filamentous bacteria (Wagner & Loy, 2002, Crocetti *et al.*, 2000, Hesselman *et al.*, 1999).

The availability of short chain volatile fatty acids let these organisms prevail (Marx *et al.*, 2004). The amount of phosphate removed from waste water is strongly correlated with the P concentration in the sewage waste water and the number of PAO probe-binding cells. Bacteria closely related to *Rhodocyclus*, *Acinetobacter* and *Propionibacter* are known as PAO in sewage waste water sludge. Biological phosphate removal in sewage waste water treatment was first observed in India (Srinath *et al.*, 1959). PAO have not been isolated and cultured as yet, however, biological phosphate removal is already done on full scale. The process has been developed out of an engineering perspective and not a microbiological perspective. Biological removal of phosphate is more beneficial from the perspective of effluent waste water salinization, rather than chemical removal by precipitation of phosphate, because there are no counter ions (like chloride) in the water that can increase salinity. Biological removal of phosphate can also be combined with chemical precipitation and nitrogen removal (Van Loosdrecht *et al.*, 1997).

1.3 Phosphate dynamics in the soil

In general, soil factors that influence phosphate fixation capacity of a soil are the presence of ferric, aluminium and manganese (oxy)hydroxides, soil pH,

cation exchange capacity (CEC), organic matter content and texture (Brady & Weil, 2002). Phosphate is not considered a mobile ion; however significant leaching can take place when the P fixation capacity is exceeded, or when bypass flow of phosphate occur through biological or physical macro pores in times of excessive leaching (Sims *et al.*, 1998).

Furthermore, it is essential for agronomic rate calculations to be able to quantify, with reasonable accuracy, the availability of nutrients from sludge. This is important in order to establish sustainable application rates and to minimize any potential environmental impact. Soil environmental conditions and soil properties control sludge mineralization and solubilisation through their effects on microbial and chemical activity (Leiros *et al.*, 1999; Metzger & Yaron, 1987).

1.3.1 Inorganic phosphate dynamics

Soil phosphate can be divided into four pools in terms of potential plant availability namely organic, in solution, labile and non-labile (Equation 1.2). The phosphate in solution can be replenished or decreased by organic phosphate (mineralization and immobilization) and by labile phosphate. Labile phosphate can also be increased by non-labile phosphate. The phosphate concentration of the soil solution is controlled by chemical and biological reactions of which chemical reactions are dominant (Brady & Weil, 2002).

Organic phosphate ↔ Phosphate in solution ↔ Labile phosphate ↔ Non-labile phosphate

Equation 1.2: Phosphate dynamics in soil

1.3.1.1 Inorganic phosphate in alkaline soils

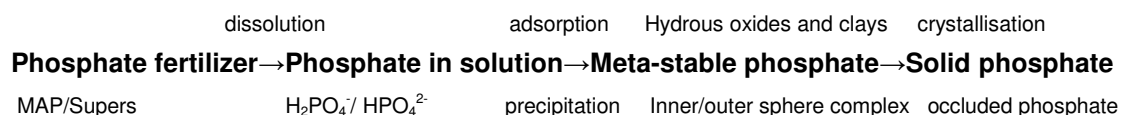
The availability of phosphate is determined by the solubility of various calcium phosphate compounds at high pH (pH \square 7) and calcareous soils. Different forms of apatite, like fluoroapatite, constitute the main phosphate mineral in calcareous and alkaline soils of arid and semi-arid regions. The proportion of Ca-phosphate increases with soil pH and Ca concentration in the soil (Mengel

& Kirkby, 2001). Small quantities of phosphate can exist in lattices of silicate minerals and as inclusions in minerals (Stevenson, 1982).

1.3.1.2 Inorganic phosphate in acidic soils

Phosphate from the soil solution is mainly made unavailable by precipitation and sorption by Fe (III) and Al (oxy)hydroxides. If the phosphate is not desorbed over time, the adsorbed phosphate will be changed into Al phosphate (variscite) and ferric phosphate (strengite). The variation in charge on the oxy-hydroxy surfaces plays an important role in phosphate sorption in soil. Because of association and dissociation of protons, a surface charge arises due to the pH and ionic strength of the soil solution.

The point of zero charge (pzc) of the surface is influenced by the hydration state, impurities, different coordination of hydroxyl groups to cations and specific adsorption of certain cations that change the pzc (White, 1980). Adsorption of phosphate to oxy-hydroxide surfaces occurs through specific and/or non-specific adsorption below the pzc of the mineral surface. Non-specific adsorption also occurs, where phosphate is negatively charged and binds to the protonated hydroxyl group on the clay mineral because of acidic conditions, indicating that non-specific adsorption is pH dependable (outer sphere complex). Specific adsorption of phosphate is done through ligand exchange where OH groups are replaced by phosphate groups (inner sphere complex). Phosphates that are adsorbed can also be integrated into the crystal structure to form solid phosphate that is not plant available (Equation 1.3).



Equation 1.3: Phosphate dynamics in acidic soil

Goethite (ferric oxy-hydroxides) and gibbsite are the most common surfaces where phosphate adsorption can occur in the soil. At pH below five adsorption of phosphate is mostly on goethite because it is much less soluble than gibbsite at low pH conditions. Below a pH of four, goethite play a more

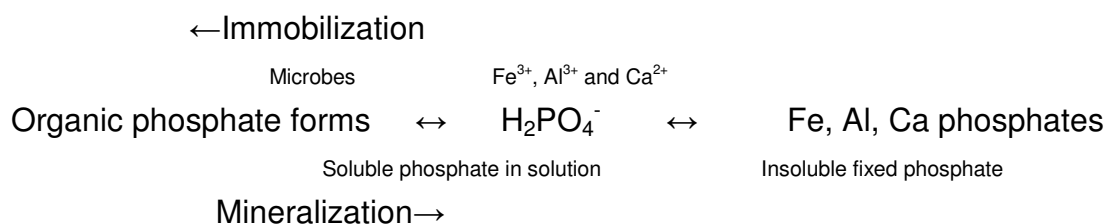
important role in sorption of phosphate since it is less soluble than gibbsite. At the pH above seven the main fraction is apatite in calcareous soils but at low pH phosphate is adsorbed and occluded (Brady & Weil, 2002). Drying is also known to decrease the availability of phosphate, and this is attributed to the precipitation of phosphate from the solution on mineral surfaces and the irreversible dehydration of sorbed phosphate and phosphate minerals (Fe, Al, Mn and Ca phosphates) (Wiklander & Koutler-Andersson, 1966). Phosphate sorption in the soil is also influenced by organic carbon when Al, and to a lesser extent Fe, is adsorbed by the organic colloids which are active in phosphate adsorption. These small amounts of Al and Fe found in natural acid peats and humic acids are almost completely hydrolysed and are therefore ineffective in adsorbing phosphate (White & Thomas, 1978).

1.3.2 Organic phosphate dynamics

Understanding the process of organic material breakdown and subsequent nutrient release is essential in both agricultural and environmental management, not only to ensure optimum nutrient supply to crops, but also to prevent environmental pollution. Decomposition and nutrient release depends on the quantity and quality of sludge added, transient soil environmental conditions like aeration, water potential and temperature, as well as soil properties such as texture, mineralogy, acidity and nutrient status of the soil (Parker & Sommers, 1983). Plants take up exclusively orthophosphate from the soil solution. Soil solution phosphate is mostly replenished by inorganic phosphate and not organic phosphate (Beck & Sanchez, 1994). Sewage sludge contains phosphate that is stored in the microbial biomass. Therefore, these organic phosphate fractions must first be mineralized before it can become soluble and plant available (Pietersen *et al.*, 2003). Soluble phosphate is assimilated/immobilized by microbes to organic phosphate forms that are not available to plants (Equation 1.4). The product of mineralization, (orthophosphate) is easily adsorbed to the soil, making it difficult to determine the net mineralization/immobilization rate (Brady & Weil, 2002).

Organic phosphate sources in the soil can be divided into three groups namely inositol phosphate, nucleic acids and phospholipids while SS contains

mainly inositol and phospholipids. Inositol phosphate is the most abundant organic phosphate making up to 10 to 50 % of the total organic phosphate content. It is quite stable and has a low solubility in acidic and basic conditions. Accumulation of inositol phosphate in the soil can be attributed to the formation of insoluble complexes of Al and Fe in acidic soils and insoluble complexes with Ca in basic soils.



Equation 1.4: Organic phosphate dynamics in soil

It was previously believed that phytin was the main source of inositol phosphate produced by plants, but it was found that micro-organisms synthesize inositol phosphate *in situ* (Stevenson, 1982). Nucleic acid comes from the degradation of plant and animal remains by micro-organisms and has low concentrations in the soil because of the ease of breakdown. Nucleic acid consists of RNA (ribonucleic acid) and DNA (deoxyribonucleic acid) which are important constituents of all living cells. Phospholipids are at very low concentrations in the soil and, together with nucleic acid, make up only 1 to 2% of the total organic fraction. Phospholipids are insoluble in water and originate from microbes which degrade lipids. Dissolved organic phosphorus originating from animal wastes is more mobile than soluble inorganic phosphate because it is not readily adsorbed by organic clay complex layers and CaCO₃ layers in the soil. By microbial breakdown of SS, phosphates are released at a slow rate and can be absorbed by plants before reaction with the soil occurs and before becoming insoluble and fixed. SS can form chelates with Al, Fe and Mn cations rendering them unavailable to bind with phosphate. This means phosphate is more plant available, since phosphate stays in the soil solution for longer (Brady & Weil, 2002).

Different enzymes, for example phosphatase and phytase, catalyse the mineralisation of organic phosphate in the soil, which transform it to plant

available inorganic phosphate forms (He & Honeycutt, 2001). Similar to N mineralisation, optimal phosphate mineralisation usually occurs when soil water content is at field capacity and declines as the soil dries (Cassman & Munns, 1980). Soil drying and rewetting influences soil phosphate availability and this influence can be divided into biological, chemical and physical effects (Nguyen & Marschner, 2005). Van Gestel *et al.* (1993) found that microbial mass can decrease with 58 % when a soil is dried and rewetted again. The phosphate mineralisation process will therefore be interrupted by a drying cycle. Upon rewetting, the microbial populations have to recover to optimum levels again before pre-drying mineralisation rates will be reached. Higher mineralisation is also associated with higher soil C content (Eghball *et al.*, 2005). The C/P ratio will determine net mineralisation which will occur at ratios of 200:1 or lower and net immobilization at 300:1 and higher ratios. At a C/P ratio of between 200:1 and 300:1 neither a gain nor loss of PO_4^{3-} is expected (Brady & Weil, 2002).

1.4 The phosphate fertilizer value of sludge

1.4.1 Sludge properties that influence the phosphate fertilizer value

The US EPA (1995) manual for land application of sewage and domestic septage reports that sewage sludge is 50 % as “effective” as inorganic phosphate fertilizer. However, this value has been a point of debate. Scientists have been highly critical of this sweeping generalisation of the phosphate fertilizer value of sludge because no literature is cited to support it (O’ Connor *et al.*, 2004). The phosphate availability from sludge is highly dependent on the waste water treatment. Phosphate removed by chemical precipitation in tertiary treatments using poly- aluminium salts, aluminium sulphate or ferric chloride results in the precipitation of sparingly soluble aluminium phosphates (Al-P) and ferric phosphates (Fe(III)-P). As a result, the phosphate in the sludge has low water extractability and plant availability and decreases the labile phosphate fraction. However, it also poses a low environmental risk (Maguire *et al.*, 2000b; Samie & Römer, 2001; Elloitt *et al.*, 2002; Hyde & Morris, 2004; O’ Connor *et al.*, 2004; Krogstad *et al.*, 2004;

Häni *et al.*, 1981; Kyle & McClintock, 1995). SS from waste water that underwent biological phosphate removal have a phosphate fertilizer value, in terms of plant availability, similar to that of manure and inorganic fertilizer (Stratful *et al.*, 1999; O' Connor *et al.*, 2004). Various sludge properties have been proposed as indicators to predict the phosphate fertilizer value of sludge. Elemental ratios, for example P:Fe ratio, have been proposed to evaluate and predict the phosphate fertilizer value of sludge (Samie & Römer, 2001). Samie & Römer (2001) recommended that sludge with a P:Fe ratio of 1:5 or higher, should not be considered for agricultural use. Water extractable phosphate (WEP), expressed as a percentage of the total phosphate (PWEF), is another useful indicator of both the potential environmental risk and the plant availability of phosphate (Elloitt & O' Connor, 2007).

Waste water treatment methods (aerobic or anaerobic digestion) and nutrient removal processes (chemical versus biological) influence the availability of phosphate (Frossard *et al.*, 1996; Maguire *et al.*, 2001; Penn & Sims, 2002; Pastene & Corey, 1980). The predominant form of phosphate in sludge that has undergone tertiary treatment is inorganic phosphate (McLaughlin, 1984). The application of lime to Fe or Fe+Al treated sludges, however, increases the concentration of the easily soluble phosphate fraction (Penn & Sims, 2002). Therefore, it is of the utmost importance to consider the type of sludge used when quantifying sludge application rates. This can help to optimize crop harvests and minimizing the environmental impact.

1.4.2 Approaches to quantify and express phosphate availability in soil

Many soil-based coefficients have been proposed to predict plant available phosphate. Acid oxalate extractable phosphate, expressed as a molar ratio of acid oxalate extractable Al and Fe, also known as the phosphate sorption index (PSI), is commonly used in Europe as a predictive tool to assess potential mobility and plant availability of phosphate. In America a similar index using Mehlich 1, the standard phosphate extractant used in the United States, has been developed (O' Connor *et al.*, 2004; Krogstad *et al.*, 2005). However, neither of these extractants is used nor found to be very successful

in South Africa. Bray-1 is the standardized phosphate extractant used for non-calcareous soils of the Eastern Highveld to assess plant available phosphate (Soil Science Society of South Africa, 1990).

The origin and treatment method of waste water determine the fertilizer value, so that the nutrient value of the sludge should be assessed before it is applied (Petersen, 2003). It is important to know how readily available phosphate is for plants when SS is incorporated into the soil. It is known that composted biosolids have a lower and steadier release rate than sewage sludge (USA EPA, 1999). Phosphate fixation occurs in the soil after application of freshly added phosphate. Both biological and chemical fixation occurs but chemical fixation is the most important. Chemical fixation is determined by the soil properties such as: pH, texture, %C, mineralogy and the phosphate sorption capacity (Brady & Weil, 2002). Chemical and biological reactions control the plant available phosphate concentrations in the soil, of which chemical reactions are the most important.

Sewage sludge can potentially be a valuable and economic source of phosphate. However, the availability of phosphate from sludge is variable and dependent on both soil and sludge properties. In general, the phosphate availability from sludge, and consequently its phosphate fertilizer value, is considered lower than that of, for example, chicken or cattle manure. However, depending on the phosphate fixing abilities of soil, phosphate availability from biologically phosphate removed sludge is reportedly similar to that of manure (Stratful *et al.*, 1999; O' Connor *et al.*, 2004.). On the other hand, it also has been reported that the application of Al/Fe-P-sludge can decrease the overall plant availability of phosphate in the soil (Hyde & Morris, 2004). Work done by Hons *et al.* (1990) found that Bray-1 best predicts wheat dry matter yields and estimated total P uptake by wheat, making it a good extractant with which to determine plant available phosphate. Chepkowny *et al.* (2001) also used Bray-1 to determine available phosphate in acidic soil when he investigated mineralization of soil organic phosphate in a pot trial.

Plant available phosphate is considered a functional concept rather than a measurable quantity. There is no simple and direct way to determine it. Plant available phosphate is defined as the total phosphate that a plant can extract during a growth cycle. Extraction methods are used to correlate with plant

uptake and growth response to determine the best extractant under certain soil conditions (Tiessen & Moir, 1993).

The influence of sludge properties on phosphate availability is more pronounced in soils with low phosphate fixing capacities. In soils with high phosphate fixing capacities, it seems that soil properties influencing phosphate availability dominates and the influences of sludge stabilisation is small (Elloitt & O' Connor, 2007).

Previous research by Pierzynski (1994), Peterson *et al.*, (1994) and Maguire *et al.*, (2000a,b) indicated that continuous sludge applications based on nitrogen demand will cause soil phosphate to accumulate to levels above those needed for optimum crop production.

1.5 Application

Application of SS in agriculture can be in a dried or liquid form. It can be spread on the soil surface, incorporated or injected in bands (US EPA, 1999). SS liquid can be applied by sprinkler irrigation (fertigation) where it is broadcasted on the soil as a percentage suspension. When placed in bands it is done at a depth of 0.1 m to 0.3 m; this reduces the run-off of sludge and odour problems (Brady & Weil, 2002). Surface application of liquid sludge is done by tractor drawn tank wagons, special applicator vehicles equipped with flotation tyres, or irrigation systems. It is usually restricted for use in areas with slopes less than 7%. The disadvantages of spraying liquid sludge on the surface are mainly potential odour problems and the reduction in the aesthetic value of the application site. To avoid the risk of runoff losses and excess leaching below the root zone, liquid sludge should preferably be applied in split rather than a single big application (Evanylo, 1999). Liquid sludge can also be injected below the soil surface. This method minimizes odour problems, reduces ammonia volatilization, minimizes runoff losses and can be used in areas with slopes of up to 15%. Liquid sludge injection can be conducted using tractor-drawn tank wagons with injection shanks or tank trucks fitted with flotation tyres and injection shanks.

Dewatered sludges are usually surface applied to crop lands using equipment similar to that used for applying limestone, or animal manures. The sludge is then incorporated into the soil by ploughing (Evanylo, 1999).

It is advisable to schedule sludge applications on agricultural lands around the time of tillage or planting. However, it depends on the type of soil, crop and climate. Correct sludge application timing is essential for efficient use of nutrients and to minimise possible pollution (Evanylo, 1999).

Apart from sludge and soil properties, sludge breakdown and nutrient release are also affected by soil management practises after sludge application. Soil disturbance, for example ploughing, usually increases mineralisation. Furthermore, incorporation of sludge is essential to ensure effective decomposition and nutrient release, because of the more favourable environment for microbial activity in the soil compared to the more extreme environmental conditions on the surface of the soil (Kandeler & Böhm, 1996).

1.6 Hypothesis

Plant available phosphate, extracted with Bray-1 from SS amended soil, will be determined by soil texture and SS properties influenced by the phosphate removal processes at the Wastewater Care Works (WCW) and when the fertilizer value is compared to mono ammonium phosphate (MAP). Biologically phosphate removed sludge will have an equal or better fertilizer value than MAP, while chemically phosphate removed sludge will have an equal or lower fertilizer value compared to MAP. Increasing clay content of soil will decrease plant available phosphate from SS.

1.7 Research questions

- Is there a difference in plant available phosphate from different SS because of different phosphate removal methods (chemical and/or biological) from the waste water?
- What is the phosphate fertilizer value of different SS compared to MAP commercial fertilizer?

- Does soil texture influence plant available phosphate from SS?

1.8 Study aims

To determine:

- The effect of different phosphate removal methods on plant available phosphate from SS in soils with contrasting phosphate sorption capacities.
- The effect of soil texture on the plant available phosphate from SS.
- A phosphate fertilizer value for SS with comparison to MAP.

1.9 Objectives

- An incubation study, pot trial and field trial will be done to determine the plant available phosphate from SS amended soils.
- This study will determine the plant available phosphate from different types of bio-solids.
- Phosphate Bray-1 extraction will be used to determine plant availability phosphate. The Bray-1 extractable phosphate of the sludge will be expressed as a percentage of Bray-1 extractable phosphate of commercial mono-ammonium phosphate (MAP) fertilizer; it will be referred to as the relative phosphate fertilizer value (RPFV).
- The soil properties and the sludge properties that affect the plant availability of phosphate will be investigated.
- An incubation study done under controlled conditions will be used to maintain optimal conditions for microbial and chemical activity in the soil. The pot trial will be done in a greenhouse and a field trial will be conducted to validate the results from the incubation study.

Chapter 2

Materials and Methods

2.1 Soil selection

Topsoils (0-20 cm) from the Eastern Highveld area in the Republic of South Africa were collected, air-dried and sieved (<2 mm) for subsequent analysis and screening. These soils were analysed for Bray-1 extractable phosphate, clay content, phosphate sorption capacity and pH. From these eleven soils, four were chosen (A, D, E and H) on the basis of clay content and phosphate sorption capacity (Table 2.1; Figure 2.1). Soil A, D and H refers to soil samples taken from the A horizon of a Clovelly soil form and soil E was soil samples taken from the A horizon of the Shortlands form (Soil Classification Working Group, 1991).

The soils chosen had low Bray-1 extractable phosphate concentrations (≤ 15 mg phosphate kg^{-1}) and showed a gradient in phosphate sorption capacity for the equilibrium phosphorus concentration method (EPC) when 300 mg phosphate kg^{-1} was added to the soil (Table 2.1). All four the soils had a similar pH (H_2O and KCl) (Table 2.1). The four soils were collected in bulk samples of 50 kg each, air-dried and sieved (< 2 mm) for subsequent chemical analysis (Table 2.1). The total P of these soils were determined by digestion in a nitric acid-perchloric acid mixture (Olsen & Sommers, 1982). The water content at field capacity was determined with the use of pressure membrane apparatus where soils are subjected to different matric potentials (-10 to 30 kPa) and then soil water content was determined gravimetrically (Table 2.2). The chemical properties and texture (sieving and pipette method) of the soils were determined according to the methods described in the Handbook of Standard Soil Testing Methods for Advisory Purpose (Soil Science Society of South Africa, 1990). Exchangeable cations and CEC were determined with ammonium acetate solution buffered at pH 7.

Clay mineralogy was determined with the use of X-ray-diffraction (XRD). The mineralogy of the soils varies considerably and it is one of the factors that determine phosphate fixation in soil (Table 2. 3).

Table 2.1: Selected chemical properties of soils used in the study

Soil	A	D	E	H	Unit
pH (H ₂ O)	5.5	5.4	5.8	5.8	
pH (KCl)	4.4	4.4	5.1	5	
P (Bray 1)	6	15	2	12	mg kg ⁻¹
P (Ambic)	23	28	2	16	mg kg ⁻¹
K	233	559	37	112	mg kg ⁻¹
Ca	258	904	390	245	mg kg ⁻¹
Mg	78	269	361	89	mg kg ⁻¹
Na	0	1	16	0	mg kg ⁻¹
CEC	5.5	8.1	9.5	4.2	cmol ₍₊₎ kg ⁻¹
C content	1.1	2.2	0.6	0.6	%
P fixation capacity (EPC)	30	6	143	1	mg phosphate kg ⁻¹
Total P	295	439	240	203	mg kg ⁻¹

Soil minerals responsible for the phosphate fixation capacity of soil in order of decreasing degree of fixation are:

Amorphous Al-, Fe-, Mn-oxides, allophane > crystalline Al-, Fe-, Mn-oxides > 1:1 clays > 2:1 clays (Sanchez *et al.*, 1991). Goethite and hematite are (oxy)hydroxides of Fe while kaolinite is a 1:1 clay. Illite is a 2:1 clay (Brady & Weil, 2002). Soils containing predominantly 1:1 type clays (highly weathered red and yellow brown soils) have a much higher phosphate sorption capacity than soils with predominantly 2:1 type clays soils if they have the same clay content (Johnson *et al.*, 1991). This is because of the larger surface areas of exposed Al-OH groups in 1:1 type clays (Stevenson, 1982). Soil A and H had low phosphate fixation capacity while soil D had a medium and soil E has a high phosphate fixation capacity relative to each other. Soil E has a high kaolinite and clay content (Table 2.2) that favours phosphate fixation while soil D and H have relatively the same % kaolinite, but soil H has a significant lower clay content (7 %) than soil D (30 %) (Table 2.2). Soil A, D and H have a high quartz content (Table 2.2), but quartz has a very low affinity for phosphate. The soils used in the experiment had a pH (H₂O) between 5.4 and 5.8. By using soils with more or less the same pH helped to reduce the effect

Table 2.2: Selected physical properties of used soils in the study

Soil	Munsell Colour (Wet)	Sand (%)	Silt (%)	Clay (%)	Density (g cm ⁻³)	Water content at field capacity (%)	Texture
A	Brown 7.5 YR 5/2	76	12	12	1.2	17	Sandy loam
D	Dusky red 2.5 YR 3/2	48	22	30	1.0	33	Sandy clay loam
E	Red 10 R 4/6	25	30	45	1.0	35	Clay
H	Reddish brown 5 YR 4/3	83	10	7	1.3	13	Loamy sand

Table 2.3: Mineralogy of the clay fractions of the four soils

Soil	% Quartz	% Illite	% Kaolinite	% Goethite	% Hematite
A	58	28	14	0	0
D	54	14	32	0	0
E	14	7	75	0	5
H	39	29	29	3	0

of pH on phosphate sorption capacity and its influence on the study.

A strong linear correlation was obtained between phosphate sorption capacity and clay content where phosphate sorption increased with clay content (Figure 2.1). The deviation from this linear correlation can be attributed to the mineralogy of the soil, that resulted in considerable variations in sorption capacities between soils with the same clay content (Johnson *et al.*, 1991).

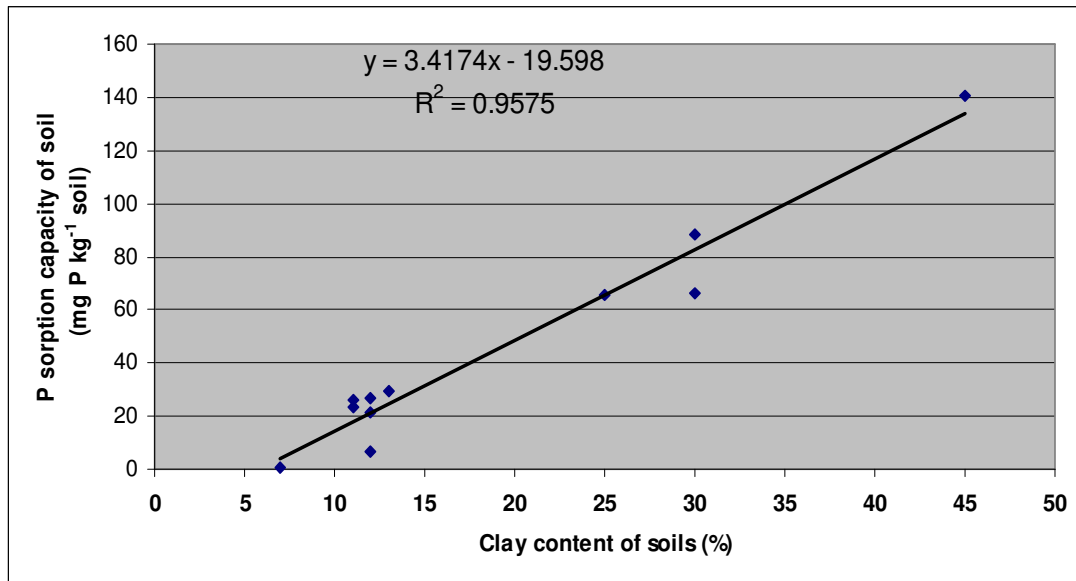


Figure 2.1: Relationship between clay content and phosphate-sorption capacity for 11 soils.

2.2 Description of the sludges used

The various sludges used in the study were:

- ASP (Activated Sludge Pasteurization): Organic fertilizer (granular) from Daspoort WCW. The ASP product is manufactured by injecting anhydrous ammonia and phosphoric acid into SS, with a water content of between 11 – 18 %, and dried to a solid content of 93 %. The granules have a diameter of between 3 and 5mm after the product is dried in a mixer. It is sold as a commercial product that contains equal amounts of nitrogen and phosphorus of 11 % (Table 2.4). Both N and P are mainly in inorganic form.
- Sasol (SAS): Biological petrochemical sludge from Secunda. Aerobic activated biosolid that is thickened and incinerated which is costly and has a negative environmental impact.
- Agriman (AGR): Commercial bio-solid product from Sutherlandridge WCW. This is waste activated sewage sludge that is dewatered, dried and granularized and sold commercially. The phosphate is biologically removed from the waste water .

- Vlakplaas (VLAK): An anaerobic and aerobic dry bed sludge that comes from Vlakplaas WCW. Phosphate was chemically removed by precipitation with ferric chloride from the waste water.
- Daspoort (DAS): An anaerobic and activated dry bed sludge that comes from Daspoort WCW where the phosphate is biologically as well as chemically removed from the waste water.

2.3 Sludge properties

For this study the plant availability of phosphate was determined for five sludges from different WCW, where phosphate was removed from the waste water by chemical, biological or both methods. Sludge samples were collected in a sealed container. The water content of each sample was determined as the main difference between air dried and collected sample, expressed as a percentage of the collected sample. Results are presented in Table 2.4.

Sub-samples of the air dried sludge were taken and analysed according to the following methods (results are presented in Table 2.4): Total analysis with the use of microwave assisted digestion was done on the five sludges that were used in the study. The sludge were characterised in terms of:

- pH was determined in suspension of solid: solution = 1:5.
- Total nitrogen (N) was determined by a semimicro-Kjeldahl procedure (Bremmer & Mulvaney, 1982).
- Total carbon (C) content was measured with a LECO CHN-1000 apparatus.
- The total P of these sludges was determined by digestion in a nitric acid-perchloric acid mixture (Olsen & Sommers, 1982).
- Ca, Mg, Na, K, Na, Fe, Cu, Mn, Zn, S and Al content were determined by means of microwave assisted acid digestion and quantitatively elemental analysis of the solution with ICP-MS.
- Water extractable P and Cl was determined by extraction with water in the ratio solid: solution = 1:20.
- Solids were determined by deducting moisture content.

- Ash was determined by incineration at 550 °C for 1 hour in an oven and organic matter was determined from the difference between ash and solid content.

These sludges will be discussed in Chapter 3.

Table 2.4: Sludge analyses

	Agrimán	Daspoort	Vlakplaas	Sasol	ASP	KH ₂ PO ₄	MAP	Units
Moisture	8.9	5.6	5.4	6.6	9.5	0.1	2.1	%
pH (Water)	7.1	6.5	7.0	6.0	7.7	4.7	4.7	
Solids	91.1	94.5	94.6	93.4	90.5	99.9	97.9	%
Ash	39.6	44.5	42.4	8.5	41.4	86.8	36.9	%
Organic Matter	51.5	50.0	52.2	84.9	49.1	BDL	BDL	%
Tot. N	4.0	3.0	3.1	7.5	10.7	3.3	11.0	%
Tot. C	27.5	26.3	26.5	45.5	20.5	n/a	1.1	%
C/N Ratio	6.8	8.9	8.5	6.1	1.9	n/a	0.1	
Ca	3.2	3.1	2.9	0.6	1.2	n/a	0.5	%
Mg	0.8	0.3	0.3	0.2	0.9	n/a	0.8	%
Tot. P	3.7	3.7	2.9	0.8	11.2	22.8	23.5	%
K	0.5	0.1	0.2	0.3	0.2	28.7	0.1	%
Na	0.1	0.1	0.2	0.1	0.0	n/a	0.1	%
Fe	4.6	10.1	11.6	0.7	1.6	n/a	0.6	%
Cu	901.6	446.2	640.0	35.5	306.5	n/a	77.3	mg kg ⁻¹
Mn	698.4	369.5	2517.0	144.8	305.4	n/a	386.5	mg kg ⁻¹
Zn	1212.0	1408.0	4139.0	226.0	757.3	n/a	6458.0	mg kg ⁻¹
S	0.9	0.9	2.8	1.1	0.7	n/a	2.6	%
Al	1209.0	5849.0	9186.0	2238.0	5430.0	n/a	1214.0	mg kg ⁻¹
Water Soluble Cl	0.3	0.2	0.4	0.2	0.4	n/a	1.8	%
Water Soluble P (WEP)	2.2	0.1	BDL	1.9	83.3	222.2	227.9	g kg ⁻¹
Water extractable P (PWEPP)	5.9	0.3	BDL	23.7	74.3	100	96.9	%

BDL = Below detection limit

n/a = not applicable

2.4 Experimental layout

To determine the phyto-availability and fertilizer value of different sludges, an incubation study, a pot and field trial with maize (*Zea mays* L cv. K₂-Agri Sahara) was conducted. The incubation study consisted of four soils (A, D, E and H), five sludge treatments (ASP, Sasol, Agriman, Vlakplaas and Daspoort), two fertilizer treatments (MAP and KH₂PO₄) and a control where no sludge or fertilizer was added to the soil. Soil A was used for the pot and field trial. The P added to the incubation study, pot trial and field trial was at the same application rate (280 kg P ha⁻¹).

2.4.1 Incubation trial

Forty grams of air dried samples from each soil type (A, D, E and H) was weighed into separate 500 ml plastic bottles. Four replicates of the following P treatments were prepared: ASP, SAS, AGR, VLAK, DAS, MAP and KH₂PO₄, all applied at 72 mg total P kg⁻¹ dry soil and an un-amended control. This amount of P was derived from the sludge guidelines (Guidelines for utilisation and disposal of wastewater sludge, 1999) which is based on the current upper limit of 10 ton dry sludge ha⁻¹. Assuming the sludge has an average total P concentration of 2.8%, an incorporation depth of 0.3 m and dry bulk density is 1300 kg m⁻³, this equates to 72 mg total P kg⁻¹ dry soil. The sludge contained different amounts of P and in order to apply the same amount of P various rates of sludge were applied. Sufficient samples were prepared for each treatment to allow destructive sampling at 0, 1, 3, 7, 14, 21, 28, 35, 42, 84 and 168 days after amendment. This was repeated for the four soils: A, D, E and H. and resulted in eight P treatments, eleven sampling dates, four soils and four replications - a total of 1408 experimental units.

The dry soil and P treatments were thoroughly mixed. Each experimental unit's soil water was adjusted to field capacity with deionised water, capped and incubated in the dark at 25° C (+ or - 2° C) constant temperature under aerobic conditions. Soil water was not adjusted during the incubation period because the plastic bottles were waterproof, but the head space was sufficient for aerobic conditions to prevail (large air volume to soil ratio). Bottles for day 84 and 168 were opened every 42 days for air exchange. Sub-samples were

extracted with Bray-1 at the different sampling dates. The sampling units were not dried before analysis but water content of soil was taken into account when analysed with Bray-1 so that the soil/extractant ratio remained 1:7.5. Additional calculations were made to compensate for soil water content of the sampling units at the time of analysis. Sampling units were not dried because drying is also known to decrease the availability of phosphate, and this causes the precipitation of phosphate out of solution on mineral surfaces, and the irreversible dehydration of sorbed phosphate and phosphate minerals (Fe, Al, Mn and Ca phosphates) (Wilklander & Koutler-Anderson, 1966).

2.4.2 Pot trial

2.4.2.1 Site description

The same soil type, soil A, that was used in the incubation study was also used in the glasshouse pot trial at the Hatfield Experimental Farm of the University of Pretoria.

2.4.2.2 Experimental design

The same application rate of 280 kg P ha⁻¹ was used as in the incubation study. The same eight treatments from the incubation study were used and also replicated four times. Pots containing 4 kg of soil were placed on a rotating table to minimize spatial effects between pots. The soil was mixed thoroughly before and after incorporating the 8 treatments, with some treatments getting additional N and K fertiliser (KNO₃) to compensate for non-sludge treatments with low N and K value.

The trial was duplicated so that one trial had crops planted and the other was free from crops to determine phosphate uptake. Maize (*Zea mays* L cv. K₂-Agri Sahara) was planted in the pots at four seeds per pot at a depth of 3 cm and watered to field capacity. After germination the seedlings were thinned out to 2 per pot. After 42 days the maize plants (stems and leaves) were harvested before plants became pot bound.



Figure 2.2: Pot trial layout in greenhouse.

2.4.2.3 Sampling and analysis

The plants (above ground) were weighed to determine wet mass and dried at 60° C and reweighed to determine dry mass. Plants were then ground (<0.25 mm) and digested using nitric and perchloric acid and analyzed for total P. The soils in the pots were air dried and sieved (< 2mm) and analysed with Bray-1 to determine plant available phosphate. The same analysis methods were used as for the incubation study (Section 2.4.1).

2.4.3 Field trial

2.4.3.1 Site description

A previously uncultivated site was selected in the Leandra district, Mpumalanga, South Africa on the farm Springboklaagte (26 °18'26.1" S, 28 ° 53'25.9" E). This site is situated at an altitude of 1602 m above sea level and has a temperate, summer rainfall climate with an average annual rainfall of 684 mm. The recorded on site rainfall for the 2009/2010 rainfall season was 810 mm.

Refer to Table 2.1-2.3 for details on chemical, physical and mineralogical properties of soil A (profile depth of 1.2 m) used in the study. From the soil analysis it can be seen that Soil A had sufficient levels of macronutrients

except phosphate. The pH of the soil was in an adequate range for plant growth (Table 2.1).

2.4.3.2 Experimental design

The experiment consists of two sludge treatments namely Agriman and ASP, one fertilizer treatment (MAP) and a control where no sludge or P fertilizer were applied ($0 \text{ kg ha}^{-1} \text{ P}$) at $280 \text{ kg total P ha}^{-1}$ (the same rate that was applied in the incubation study and the pot trial) and a control with no added phosphate. All treatments were replicated four times. Additional N was applied to the treatments so that nitrogen was not a limiting factor and that all plots contained the same N level. Thus the experiment consisted of 4 treatment combinations of 16 plots with a size of 20 m by 20 m per plot in a complete randomized block design.

The amount of sludge and fertilizer applied were equivalent to $280 \text{ kg total P ha}^{-1}$, basically simulating a phosphate based land application strategy using sludge as a phosphate fertilizer at an application rate of 10 ton dried sludge ha^{-1} .

The plot area was sub-soiled to a depth of 700 mm with an implement that has a tine spacing of 600 mm. The sludges were applied evenly by hand to each plot and then incorporated to 100 mm with a disc harrow followed by ploughing to a depth of 300 mm to ensure good incorporation. The field was harrowed and planted with maize (*Zea mays* L cv. K₂-Agri Sahara) at a plant density of 28000 plants ha^{-1} with an inter-row spacing of 910 mm in mid-November 2009. The experimental plots were sprayed with a pre emergence herbicides Diamant 700 (1 l ha^{-1}) and Caballo (1 l ha^{-1}) and an insecticide Lambda EC (70 ml ha^{-1}). Six weeks after plant, post emergence herbicides Crocodile (1 l ha^{-1}) and Caballo (1 l ha^{-1}) and an insecticide Lambda EC (120 ml ha^{-1}) were applied to all the plots.

2.4.3.3 Sampling and analysis

Soil samples were taken from each plot at the start of the trial before the sludge and fertilizer were applied (day 0) and at day 14, 42, 65, 94, 142 and

195 after application. Application of treatments and planting were completed on the same day. Soil samples were taken from the top 300 mm of the soil at three random positions within each plot and pooled together. The soil samples were air dried and sieved through a 2 mm sieve and analysed for extractable phosphate using the Bray-1 method (Soil Science Society of South Africa, 1990). Grain yield with a corrected moisture content of 12 % was determined from four 10 m rows in each plot and grain from each plot was sampled at three random positions within each plot. The grain samples from each plot were pooled and mixed. The grain was milled and digested for total P determination concentration by means of an $\text{HClO}_4/\text{HNO}_3$ digestion for plant materials as prescribed by ALASA (1998). Phosphate in solution was determined by analysis with an Inductively Coupled Atomic Emission Spectrometry (ICP-AES).

2.5 Statistical analysis

Statistical analysis of the data was done with SAS program (SAS Institute, 1999) using the Student t Test (LSD).

Chapter 3

Results and Discussions

3.1 Introduction

Phosphate is highly concentrated in sewage waste water and can be removed by chemical precipitation and/or biological methods from the waste water (NRC, 1996). The removed phosphate, being in inorganic and/or organic form is concentrated in the sewage sludge, leaving an almost phosphate free waste water.

The plant available phosphate and phosphate fertilizer value of different SS in soils is compared to MAP in an incubation study, pot and field trial. In an incubation study the plant available phosphate and phosphate fertilizer value of different SS mixed with four different soils and were compared with that of MAP. The plant available phosphate was determined using Bray-1 extract. Bray-1 was used in the study to determine if plant available phosphate from SS is influenced by clay content and mineralogy of the soil and the method of phosphate removed from the waste water at the WCW.

Pot and field trials were conducted with maize to determine plant available phosphate to determine crop uptake and growth as influenced by different waste water treatments and to validate the incubation study under varying conditions of the pot and field trial. Phosphate availability from sludge amended soils, however, depends on the type of treatment and processes which the waste water went through at the WCW (Kyle & McClintock, 1995; Maguire *et al.*, 2001; Soon *et al.*, 1978). This was confirmed by Penn & Sims (2002) who observed a greater increase in the labile phosphate fraction in soils that received sludge from waste water where phosphate was biologically removed compared with soils receiving Fe and lime treated sludges. Studies conducted by Kirkham, (1982), McCoy *et al.*, (1986), and Frossard *et al.*, (1996) also confirmed that phosphate from sludge is often less soluble and plant available due to the addition of chemicals, such as metal salts and/or lime at the WCW. The phosphate availability from sludge is highly dependent on the treatment it underwent. Phosphate removed by chemical precipitation

using poly-aluminium salts, aluminium sulphate or ferric chloride results in the precipitation of sparingly soluble, aluminium phosphates (Al-P) and ferric phosphates (Fe(III)-P). As a result, the phosphate in the sludge has low water extractability and plant availability. However, it also poses a low environmental risk (Maguire *et al.*, 2000; Samie & Römer, 2001; Elloitt *et al.*, 2002; Hyde & Morris, 2004; O' Connor *et al.*, 2004; Krogstad *et al.*, 2005).

Decomposition and nutrient release of sludge depend on both the quantity and quality of sludge added, transient soil environmental conditions like aeration, water potential and temperature as well as soil properties such as texture, mineralogy, acidity and nutrient status of the soil (Parker & Sommers, 1983). Soil factors that influence the phosphate fixation capacity of a soil are the presence of ferric, aluminium and manganese (oxy) hydroxides, soil pH, cation exchange capacity (CEC), organic matter content and texture (Brady & Weil, 2002). Phosphate is not considered a mobile ion, however, significant phosphate leaching can take place when the phosphate fixation capacity is exceeded, or when bypass flow of phosphate occur through biological or physical macropores in times of excessive leaching (Sims *et al.*, 1998). Waste water that underwent biological phosphate removal has a phosphate fertilizer value, in terms of plant availability, similar to that of manure and inorganic fertilizer (Stratful *et al.*, 1999; O' Connor *et al.*, 2004). Various sludge properties have been proposed as indicators to predict the phosphate fertilizer value of sludge. Of these, total P concentration and water soluble phosphate are of most importance.

With this study a relative phosphate fertilizer value was determined with the comparison of different sludge with MAP. Of the soil factors, the most important is clay content because it is a physical property and not a chemical characteristic that can be altered. The incubation study was validated under field conditions with pot and field trials because the incubation study was performed under controlled conditions.

3.2 Incubation study

3.2.1. Relative Phosphate Fertilizer Value (RPFV)

Data from the incubation study was used to calculate a relative phosphate fertilizer value for the different sludges, which was taken as the Bray-1 extractability of phosphate from a sludge amended soil, expressed as a percentage of the Bray-1 extractability of the MAP treatment of the same soil after 168 days (Figure 3.1). KH_2PO_4 had a higher RPFV than MAP due to its higher water solubility seen in Table 2.4. Using the RPFV approach isolates the sludge effect from the soil effect and helps to directly compare the phosphate fertilizer value of the sludge to the phosphate fertilizer value of commercial fertilizer, like MAP, which is commonly used.

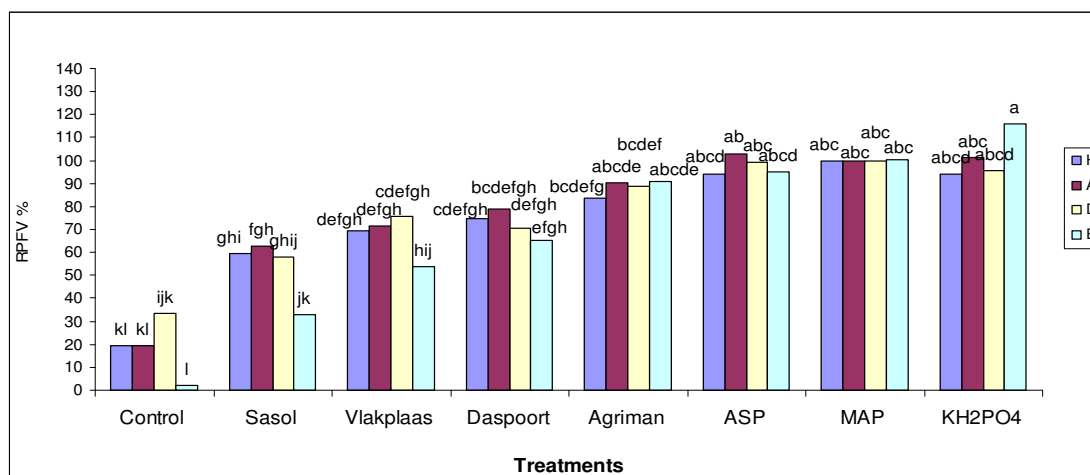


Figure 3.1: Relative phosphate fertilizer value of sludge compared to MAP after 168 days of incubation in soil (A, D, E and H). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

Agriman has a high RPFV percentage (83-91 %) because the phosphate is biologically removed from the waste water in this sludge. ASP also had a high fraction of soluble phosphate (94-100 %) because of its manufacturing process where phosphoric acid was injected into the sludge. Daspoort (65-75 %), Vlakplaas (54-76 %) and Sasol (33-63 %) had low RPFV values because the inorganic phosphate fraction is not plant available because the phosphate is bonded to a metal such as Fe, Al and/or Ca. Daspoort and Vlakplaas were

treated with ferric chloride therefore the inorganic phosphate fraction is bonded to Fe which has a low plant availability. The difference in RPFV percentages between Daspoort and Vlakplaas was a result of the amount of ferric chloride added to the sludge as well as the higher content of Zn, Mn and Al that can complex phosphate and decrease its RPFV percentage (Table 2.4).

Sewage sludge treatment methods (aerobic or anaerobic digestion) and nutrient removal processes (chemical versus biological) influence the availability of phosphate (Frossard *et al.*, 1996; Maguire *et al.*, 2001; Penn & Sims, 2002; Pastene & Corey, 1980) as seen in Figure 3.1 where the Agriman and ASP differ significantly from Vlakplaas in some of the different soil treatments. The predominant form of P in sludges that have undergone tertiary treatment is inorganic phosphate (Mclaughlin, 1984). Chemicals used in tertiary treatments such as Al or Fe salts decrease the labile phosphate fraction in the sludge (Elliott *et al.*, 2002; Häni *et al.*, 1981; Kyle & McClintock, 1995). The percentage of total P found in the easily soluble fraction is higher in sludges not treated with Fe or Fe + Al (Penn & Sims, 2002) and this can be seen in Figure 3.1 where the biologically removed phosphate sludge like Agriman had a higher extractability of phosphate using Bray 1 than the chemically removed phosphate sludge like Daspoort and Vlakplaas.

3.2.2 Soil properties

In the incubation study four soils were used and the data for each soil was graphically illustrated to show the difference in plant available phosphate determined by Bray-1 (Figure 3.2-3.5). The soils with high phosphate fixing capacity and high clay content (soil D and E) exhibited the lowest potential plant available of phosphate and the soils with a low phosphate fixing capacity and low clay content (soil A and H) had the highest, irrespective of the sludge source being chemically or biologically removed. Therefore soil properties seem to be more dominant than sludge properties to determine the plant available phosphate using Bray-1.

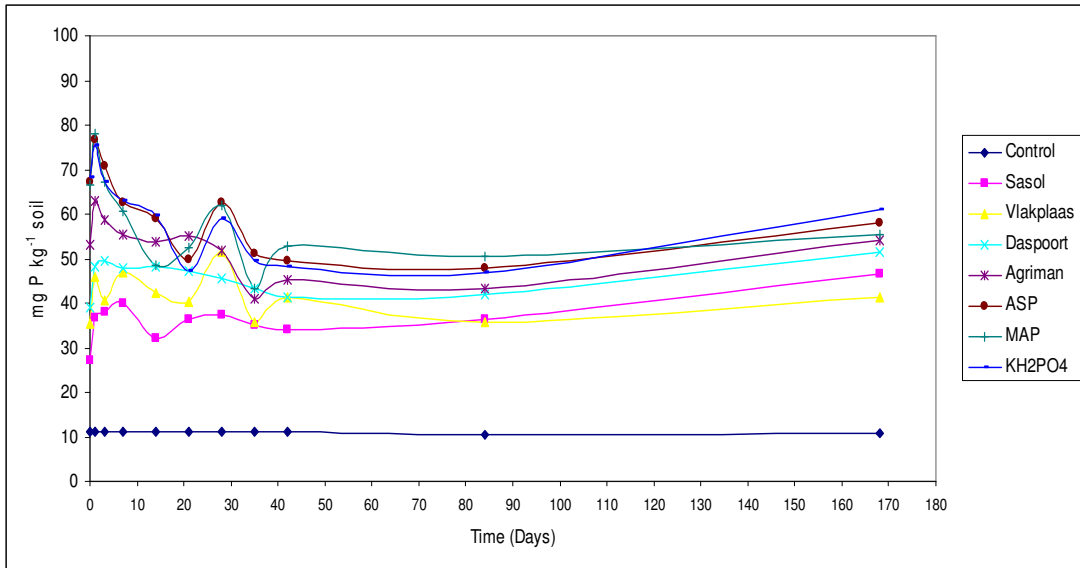


Figure 3.2: Change in Bray-1 extractable P over time for the sludge amended soil A compared to fertilizer treatments MAP and KH_2PO_4 .

Application of chemically treated sludge (Vlakplaas and Daspoort) did not decrease P availability in the soil, because of the unavailability of Fe in an adequately limed soil application of chemically treated sludge with a high Fe (Table 2.4) content resulted in a slow but positive phosphate reaction where phosphate became plant available using Bray-1 extract (Figures 3.2, 3.4 and 3.5).

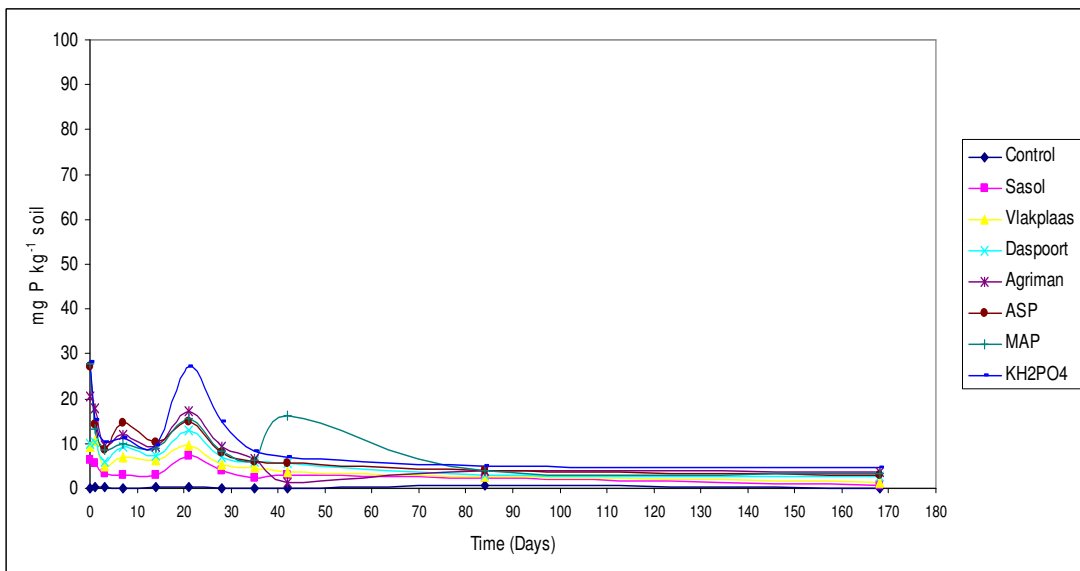


Figure 3.3: Change in Bray-1 extractable phosphate over time for the sludge amended soil E compared to fertilizer treatments MAP and KH_2PO_4 .

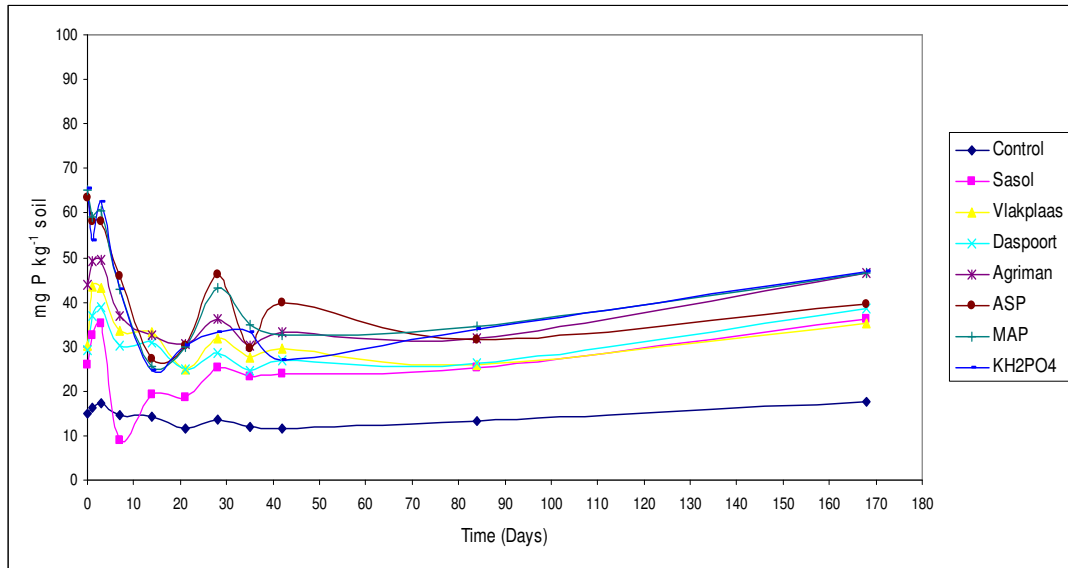


Figure 3.4: Change in Bray-1 extractable phosphate over time for the sludge amended soil D compared to fertilizer treatments MAP and KH_2PO_4 .

In acid soils the effect of Fe in sludge was unfavourable because ferric phosphate is expected to be the most stable at low pH and therefore show low plant phosphate availability (Jansson, 1972). Therefore it is very important to use a well-limed soil when applying chemically treated sludge to prevent a decrease in the availability of phosphate in the soil. Under acidic soil conditions (less than pH 5) the aluminium and iron from the sludge will be in solution and will then precipitate the phosphate making it unavailable to plants (Figure 3.3).

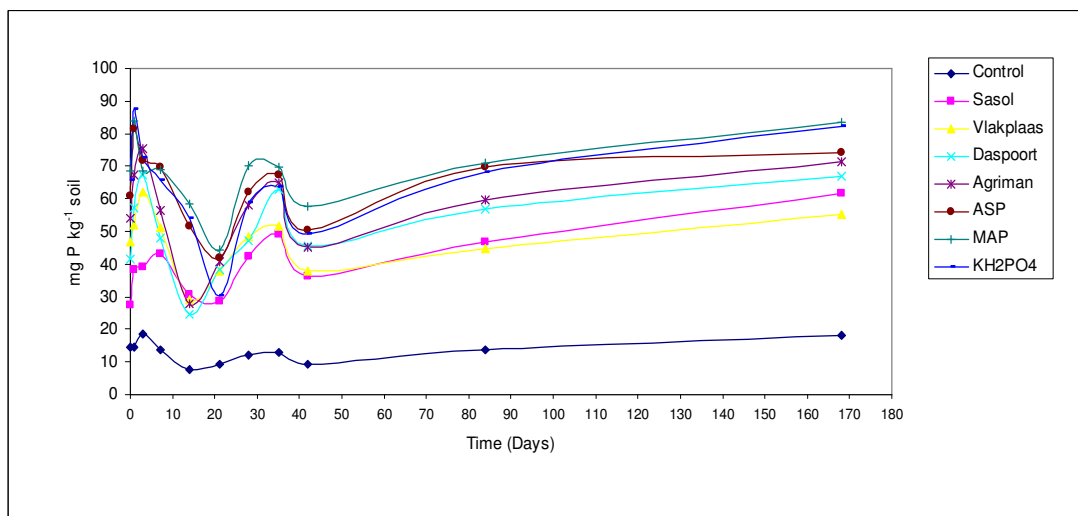


Figure 3.5: Change in Bray-1 extractable phosphate over time for the sludge amended soil H compared to fertilizer treatments MAP and KH_2PO_4 .

Under neutral conditions (higher than pH 6) the iron and aluminium in solution will be less and therefore not be able to fix phosphate. Under alkaline conditions the calcium will be in solution and precipitate phosphate from solution but will be more soluble than iron and aluminium phosphate precipitate.

3.2.3 Sludge properties

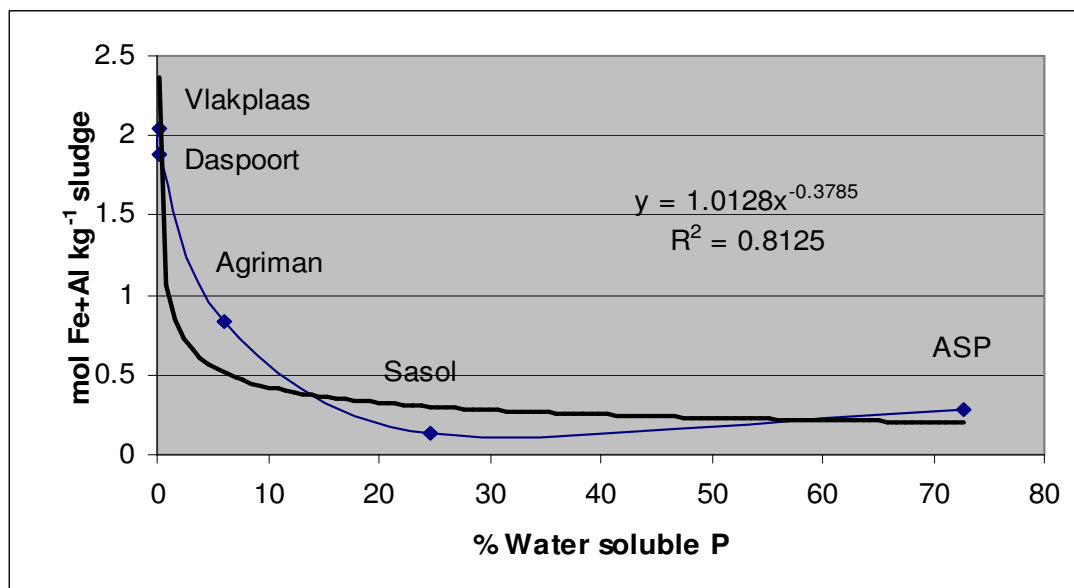


Figure 3.6: Relationship between water soluble phosphate and iron content of the sludge.

The total P content of the three sludges namely Agriman, Daspoort and Vlakplaas was between 3 % and 4 %. However, their water soluble phosphate differs immensely and when comparing their Fe and Al content, it was clear what great influence their concentration has on the availability of phosphate. The differences in Fe concentrations in the soils are due to the phosphate removal process used by each WCW (Table 2.4).

The effect of Fe and Al on the water extractability of phosphate from sludge was also evident in this study and in accordance with the literature on phosphate release from sludge (Maguire *et al.*, 2000; Samie & Römer, 2001; Elloitt *et al.*, 2002; Hyde & Morris, 2004; O' Connor *et al.*, 2004; Krogstad *et al.*, 2005). Vlakplaas sludge had the highest Fe and Al content and exhibited a

water extractable phosphate below the method detection limit. Sasol sludge, on the other hand, had the second highest water extractable phosphate (23.8 %), after the enriched ASP sludge (74.4 %) and was in the same range than that reported for chicken manure (Elloitt & O' Connor, 2007). The water extractable phosphate of MAP was 97.0 %. However, Sasol sludge is considered a poor phosphate source because of its low total P content. Hence water extractable phosphate, on its own, is not an adequate parameter to measure the phosphate fertilizer value of sludge.

The Fe content of the sludge was compared to their water soluble phosphate in Figure 3.6 with Vlakplaas having the lowest water soluble phosphate but the highest Fe content and Sasol the highest water soluble phosphate but the lowest Fe content. There is a direct relationship between the Fe content and the water soluble phosphate in the sludge. The Fe content can be ascribed to the extraction method of the waste water plant but the source of the waste water can also be a factor, depending on it being from a domestic or industrial area. Comparing Al and Fe on a molar basis, it can be seen that the Al concentration is significantly lower than the Fe concentration. Elemental ratios, for example P:Fe ratio, have been proposed to evaluate and predict the value of sludge as a phosphate fertilizer (Samie & Römer, 2001). Samie & Römer (2001) recommended that sludge with a P:Fe ratio of 1:5 or higher, should not be considered for agricultural use. All of the sludges complied with the elemental ratio with Vlakplaas having the highest ratio of 1:2.2 and the rest of the sludge having a ratio 1:1 and less, making all of them suitable for agricultural use. Water extractable phosphate (WEP), expressed as a percentage of the total phosphate (PWEP), is another useful indicator of both the potential environmental risk and the plant availability of phosphate in sludge (Elloitt & O' Connor, 2007). From Table 2.2 it can be seen that the WEP % for the Vlakplaas and Daspoort sludges is low but that Agriman, Sasol, ASP and MAP is increasingly higher as the Fe content is lower in the sludge. According to Jansson (1972), excess metal hydroxide in chemically treated sludge can react with the phosphate in the soil solution and make it less available. Changes were observed in Bray-1 extractable phosphate over all the sample dates of the incubation for the sludge amended soils (A, D, E

and H) compared to fertilizer treatments with MAP and KH_2PO_4 , as can be seen in Figures 3.2-3.5.

The Bray-1 extractable phosphate for the four soils amended with the specific sludge treatment show the influence of excess Fe in sludge on the availability of phosphate from the sludge (Figure 3.5) where this is more evident in soil H with the lowest phosphate fixation capacity. This is evident in the Vlakplaas and Daspoort treatments, which is the lowest for the four soils than the Agriman treatment on day 0. Soil H on each treatment isolates the influence of the soil properties, showing the direct effect of sludge properties on Bray-1 extractability over time. A study by Barrow (1979) comparing long (62-240 days) and short (1 hour-20 days) incubations found that desorbing phosphate was increased rapidly at first but then net re-adsorption occurred in short incubations, while in long incubations there was a slower desorption and no net re-adsorption in the soil when comparing day 0 and 21 and comparing day 42 and 168 in Figure 3.5 with soil H .

In soil E (Figure 3.3), all the phosphate had been fixated by day 168, regardless of the phosphate source, due to the high fixation capacity that soil E showed over time.

A similar trend (the WEP % for the Vlakplaas and Daspoort sludges is low but that Agriman, Sasol, ASP and MAP is increasingly higher as the Fe content is lower in the sludge) was seen over time (Figure 3.2-3.5) Soil H shows the highest availability of phosphate and soil E the lowest phosphate availability when comparing the four soils A, D, E and H. As mentioned before, soil H had the lowest clay content (7 %) and soil E the highest (45 %), while the clay content of soil A and D were 12 % and 30 % respectively. For Sasol there was a general increase of phosphate availability over time, as well as in Daspoort and Vlakplaas because phosphate in the sludge was in an unavailable form and then solubilised over time. However for MAP, ASP, Agriman and KH_2PO_4 there was an initial high amount of available phosphate and then a lowering of availability and thereafter a steady increase in phosphate availability as extracted by Bray-1. MAP, ASP and KH_2PO_4 are all inorganic phosphate forms that contain high percentages water soluble phosphate. It can be seen that there was not a big difference between availability of phosphate from the different sludge sources, being either chemically removed phosphate or

biologically removed phosphate sludge and that the soil properties namely clay content determines the availability of phosphate.

3.3 Pot trial

The uptake of inorganic elements by plants from the soil is the best indicator of plant available nutrients (Chambell, 1978). That is why plants are used to validate chemical methods of extraction of plant available nutrients in the soil. Decomposition, nutrient release and availability of nutrients from SS depend on both the quantity and quality of sludge added, temporary soil environmental conditions like aeration, water potential and temperature, as well as soil properties that include texture, mineralogy, acidity and nutrient status of the soil (Parker & Sommers, 1983). Furthermore, it is essential for agronomic rate calculations to be able to quantify, with reasonable accuracy, the availability of nutrients from SS. ASP is enriched with N and P to have the same N concentrations as MAP, Sasol had a higher N content relative to the other sludges, closer to that of MAP, but with a very low P content. Agriman has N and P concentrations close to that of other WCW sludge, this can be seen in Table 2.4. These attributes will influence the total fertilizer value of the sludge and in the end determine the sludges viability as a secondary fertilizer source.

3.3.1 Wet and dry mass of plants

The wet biomass of the Sasol treatment was significantly higher than the other treatments (Figure 3.7). This was due to the inherent high N (7.5 %) content of the Sasol sludge. It should be mentioned that a germination problem occurred with the Sasol treatment and seedlings were replanted in the Sasol pots so that each pot had 2 seedlings. All the pots received equivalent amounts of N, except for the Sasol treatment because of the high N:P ratio ($\pm 9:1$) compared to the other sludges ($\pm 1:1$), sludge was applied on P basis causing germination problems due to the high salt concentration in the soil caused by high N levels ($2600 \text{ kg N ha}^{-1}$) of Sasol sludge treatment.

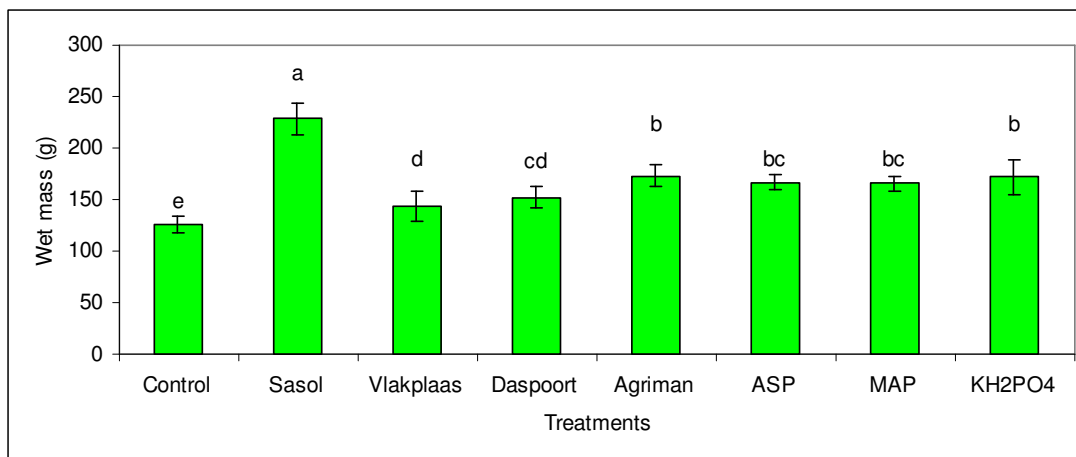


Figure 3.7: Wet biomass production in the pot trial for the different sludge and fertilizer treatments. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

There were no significant differences in availability of phosphate between the Agriman, ASP, MAP and KH_2PO_4 , making Agriman just as effective as the other inorganic treatments which are used commercially. There was, however, a significant difference between Vlakplaas and Agriman. Agriman and Daspoort showed a difference in availability as influenced by the different phosphate removal sludge treatments (Figure 3.7). The dry mass of the different treatments is similar to the wet mass of the treatments (Figure 3.8). There was a significant difference in dry matter production between the Control, Sasol, Vlakplaas and Agriman treatments and this is similar to the Bray-1 extractable phosphate levels of the different treatments in Figure 3.9. There was no significant difference between Agriman, ASP, MAP and KH_2PO_4 . It was therefore concluded that these treatments had the same amount of available phosphate, while there was no significant difference between the Vlakplaas and Daspoort treatment.

3.3.2 P concentration of maize plants

When considering the P content of the plants of the different treatments (Figure 3.9) with the dry mass of the plants (Figures 3.8) for the various treatments dry matter production increase as the P content increases (Figure 3.9). This suggested that a higher N content in the sludge (Table 2.4) did not

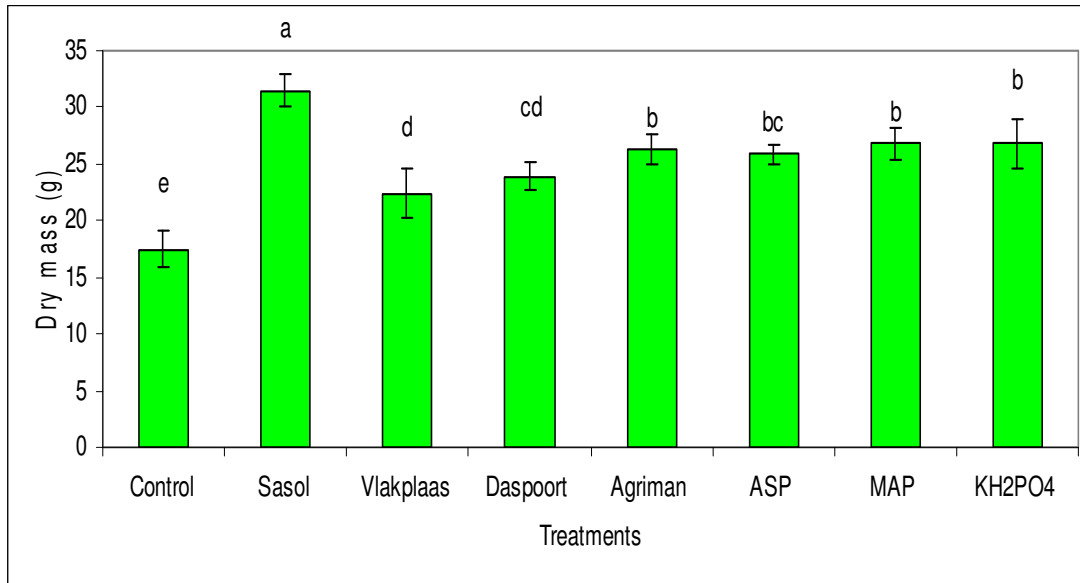


Figure 3.8: Dry biomass production in the pot trial for the different sludge and fertilizer treatments. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

influence the phosphate uptake by the plants and it was predominantly a P effect.

There were significant differences between the biologically phosphate removed sludge treatment and chemically removed phosphate sludges. However, there were no significant differences between the inorganic treatments and Agriman. This indicated that Agriman and MAP performed equally well as phosphate source. In a study conducted in the USA, sludge application correlated with increased P content of maize while the control plot had 0.27 % in the leaves and the P content of maize leaves for the sludge treatments was 0.56 % P, with normal ranges being between 0.2-0.4 % for leaves (Chapman, 1973). This supports the results from the present study that biologically removed phosphate sludges can elevate P levels in plants like fertilizer treatments.

3.3.3 Bray-1 extractability of phosphate

There were significant differences between the Bray-1 extractable phosphate from soil of pots with maize and the soil of pots with no maize for the following treatments: Sasol, Vlakplaas, Daspoort and Agriman, but for the ASP, MAP

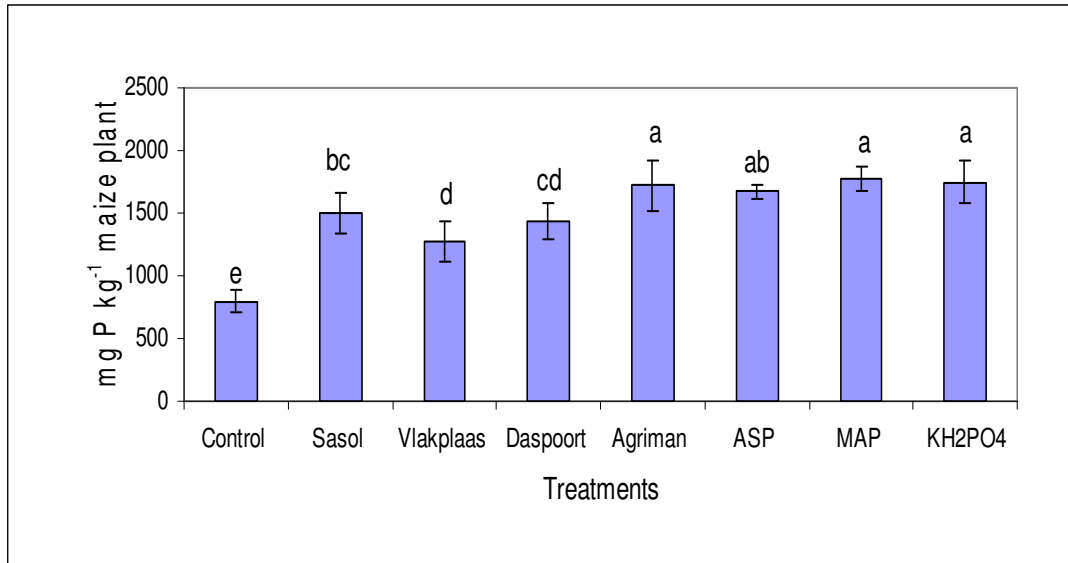


Figure 3.9: The influence of different SS and fertilizer treatments on the P concentrations of the maize plants (dry mass) in the pot trial. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

and KH_2PO_4 there were no significant differences among them. This can be attributed to the difference in the initial availability from the sludge compared to the inorganic sources that are more soluble. The low Bray-1 extractability of phosphate from the KH_2PO_4 treatment can be attributed to its high solubility (Table 2.4) and subsequent fixation by the soil during the alternating wetting and drying cycles (Figure 3.10). Drying and rewetting influences soil phosphate availability and this influence can be divided into biological, chemical and physical effects (Nguyen & Marschner, 2005). Van Gestel *et al.* (1993) found that microbial mass can decrease with 58 % when a soil is dried and rewetted again. The phosphate mineralisation process will, therefore, be interrupted by a drying cycle. Upon rewetting, the microbial populations have to recover to optimum levels again before pre-drying mineralisation rates will be reached again. Drying is also known to decrease the availability of phosphate and this is attributed to the precipitation of phosphate on mineral surfaces, and the irreversible dehydration of sorbed phosphate and phosphate minerals (Fe, Al, Mn and Ca phosphates) (Wiklander & Koutler-Andersson, 1966).

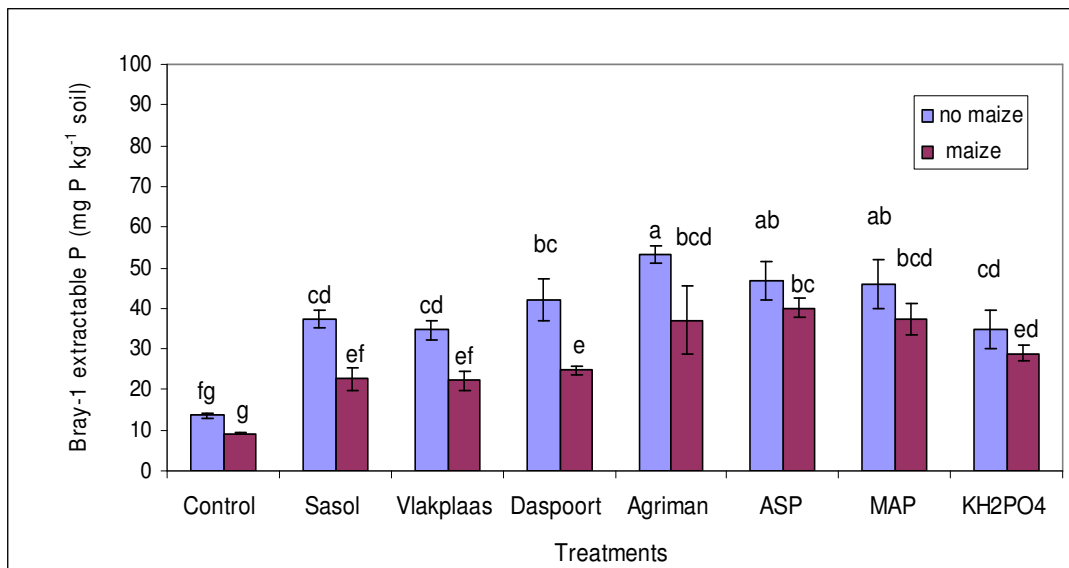


Figure 3.10: A comparison of Bray-1 extractable phosphate of sludge amended soils in planted and unplanted pots. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

Plant uptake of phosphate for all treatments resulted in a measurable decrease in Bray-1 extractable phosphate of the soil. The biomass production did not show differences between sludges and fertilizer (Figure 3.8). However, the sludge treatments showed a statistically significant decrease in Bray-1 extractability of phosphate. It can be seen that the pots without maize had a higher Bray-1 extractable phosphate concentration than the soil from the pots with maize (maize plants extracted phosphate from soil from the pots). Agriman, ASP and MAP treatments had higher phosphate values than the Sasol, Vlakplaas and Daspoort treatments. There was no significant difference between the maize and no maize for the treatments ASP, KH₂PO₄ and MAP. However, there was a significant difference between the maize and no maize treatments for Agriman, Sasol, Vlakplaas and Daspoort showing that they have a lower plant available phosphate. Based on a two-year greenhouse study, using 12 different types of sludges, that realistically can be used in agriculture, and bahiagrass (*Paspalum notatum* Flugge) as a test plant, O' Connor *et al.*, (2004) proposed three general phytoavailability classes relative to triple super phosphate (TSP). The proposed classes are: high (> 75 % of TSP), moderate (25–75 %) and low (< 25 % of TSP). Results

from this study showed that sludge from biologically phosphate removed waste water fell in the high category. However, all types of Al/Fe-P-sludge were in the moderate to low category. Sludges with total Fe and Al content $> 50 \text{ g kg}^{-1}$ like Daspoort (107 g kg^{-1}) and Vlakplaas (125 g kg^{-1}) and sludges processed to a high solid content ($> 60 \%$) were all in the lowest class (Table 2.4). In this study mono ammonium phosphate (MAP) was used instead of TSP.

Figure 3.11 shows a definitive trend between the plant uptake and the Bray-1 extracted phosphate comparing the sludges (Agriman, Daspoort, Vlakplaas and Sasol) and the other phosphate sources (MAP, ASP and KH_2PO_4). The sludge treatments showed lower plant uptake than the amount of phosphate in soil from unplanted pots while the inorganic phosphate source treatments had a higher plant uptake than phosphate removed from the soil. This can be attributed to the organic carbon content of the sludge treatments causing a decrease in fixation. Daspoort and Vlakplaas had the lowest plant uptake, and even though the inorganic treatments had a lower soil phosphate, it still had high plant uptake and was not a limiting factor.

This can be due to the fixation of phosphate from the soil solution, but the soil solution was replenished from the non-labile pool to restore equilibrium as the soil solution was lowered because of plant uptake. The reduction of phosphate sorption capacity of a soil caused by organic fertilization like SS is because of the change in chemical properties like an increase in pH, exchangeable Fe and Al and complexation of phosphate sorption sites at the reactive surfaces in the soil (Iyamuremye *et al.*, 1996). This may cause the organic treatments to have a higher soil phosphate Bray-1 than the inorganic treatments.

3.3.4 Relative phosphate fertilizer value

Agriman and ASP had a higher RPFV % than MAP and this was due to the fact that MAP is fixed more by the soil (Figure 3.12). It was even more pronounced with KH_2PO_4 , which is a pure and soluble form of P and was fixed much quicker and easily while ASP and Agriman contains more organic phosphate and organic compounds that decreases the fixation capacity of the

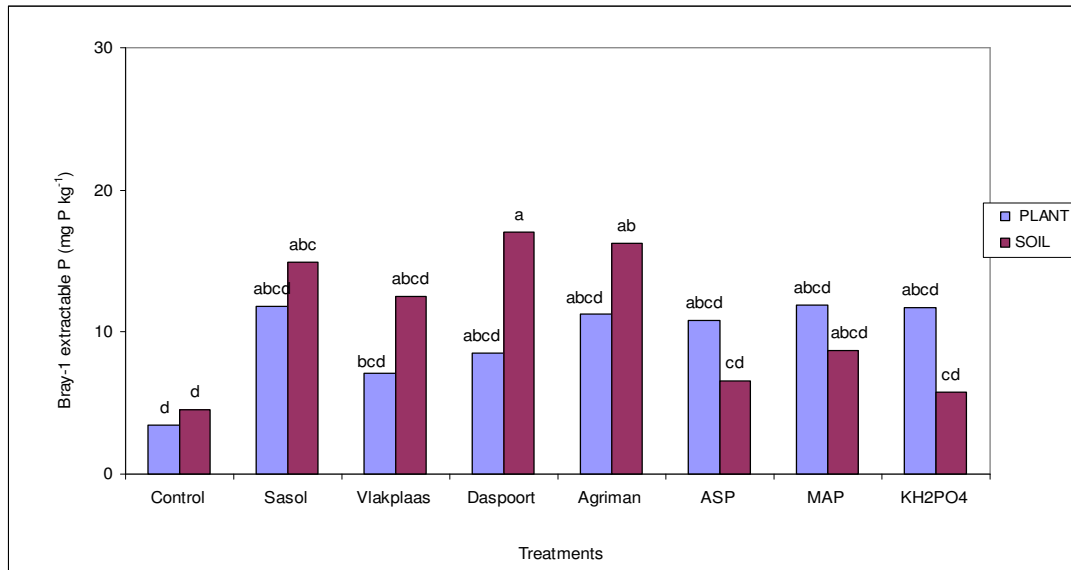


Figure 3.11: The influence of different SS treatments on the phosphate Bray-1 concentration in the soil extracted by the maize plants (by subtracting phosphate of unplanted pots from planted pots), compared to total P concentration of the maize plants. (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

soil. Because of the wetting and drying cycles in the pot trial, the effect of phosphate fixation is elevated for the inorganic phosphate sources. Drying is also known to decrease the availability of phosphate, and this is attributed to the precipitation of phosphate from solution on mineral surfaces, and the irreversible dehydration of sorbed phosphate and phosphate minerals (Fe, Al, Mn and Ca phosphates) (Wilklander & Koutler-Andersson, 1966). Phosphate sorption in the soil is influenced by organic carbon when Al, and to a lesser extent Fe, is adsorbed by the organic colloids which are active in phosphate adsorption. These small amounts of Al and Fe held by natural acid peats and humic acid are almost completely hydrolysed and are therefore ineffective in adsorbing phosphate (White & Thomas, 1978).

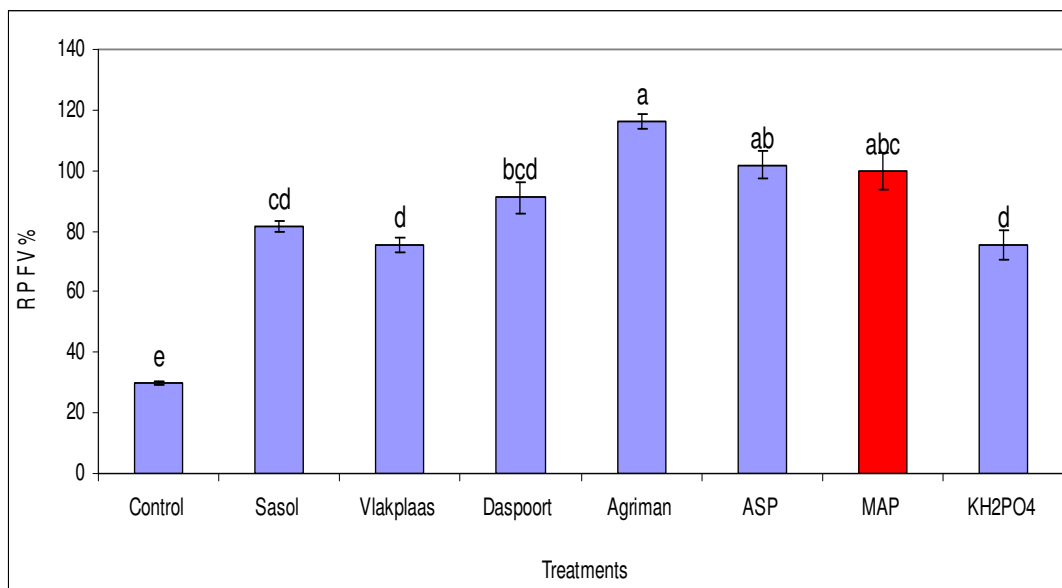


Figure 3.12: The relative phosphate fertilizer value percentage (RPFV %) of the different treatments (compared to MAP commercial fertilizer) after 42 days of the pot trial. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

3.4 Field trial

Field trials are necessary to validate incubation studies and pot trials and obtain a more realistic assessment of phosphate fertilizer value under varying environmental conditions. Wetting - drying cycles are also known to increase mineralisation. This is the result of the sudden bloom of micro organisms, called a microbial flush, upon the rewetting of dry soils (Rey *et al.*, 2005) but this can increase the phosphate fixation rate by the soil. The phosphate that is released through mineralization is more than the plant needs and the difference is mineralized.

Furthermore, the phosphate availability and the phosphate fertilizer value of sludge are not only functions of sludge properties. The influence of sludge properties on phosphate availability is more pronounced in soils with low phosphate fixing capacities. In soils with high phosphate fixing capacities, it seems that soil properties influencing phosphate availability dominate and the influences of sludge stabilisation is small (Elloitt & O' Connor, 2007).

Some of the SS that were used in the incubation study were also used in the field trial, namely ASP and Agriman, MAP and a control (no phosphate added). These SS treatments are the only ones that are commercially available hence they are the only ones used in a field scale trial.

3.4.1 Bray-1 extractability of soil phosphate for the field trial

There was no significant difference between ASP and MAP, but both differed significantly from the control and Agriman (Table 3.1). This was attributed to the fact that ASP and MAP were both inorganic forms of phosphate containing ammonium. The availability of the phosphate in Agriman is lower than that of ASP and MAP due to the organic nature of the phosphate in the Agriman (see Table 2.4). This is in accordance with a statement from Beck & Sanchez, (1994) who stated that soil solution phosphate is mostly replenished by inorganic phosphate and not organic phosphate. In sewage sludge a large fraction of phosphate is stored in microbial biomass but these phosphate fractions first need to be mineralized before it can become plant available. Soluble phosphate in SS is immobilized by microbes into organic phosphate forms that are not available to plants, but organic phosphate can be mineralized to soluble phosphate so that it is plant available (Pietersen *et al.*, 2003). The large variation within treatments over time can be attributed to the ploughing action which incorporated the phosphate into the soil and because phosphate is not mobile in the soil which caused that there is an uneven distribution of phosphate in the soil profile.

3.4.2 Maize grain yield

There was no significant difference in P content of the maize grain between any of the treatments including the control (Figure 3.13). This can be ascribed to the natural sufficient occurrence of phosphate in the soil at 6 mg kg^{-1} using Bray-1 extractant. This was still sufficient for a 6500 kg ha^{-1} yield, indicating that phosphate was not a limiting factor regardless of the low soil phosphate concentration in the control. Although a difference can be seen, it was not significant.

Table 3.1: Bray-1 extractable phosphate for the different treatments at different sampling times for the field trial. (Different letters x, y, z show significant difference between treatments while a, b, c, d and e show significant differences over sampling times at $\alpha=0.05$).

Day	Control (mg phosphate kg ⁻¹) ^x	Agriman (mg phosphate kg ⁻¹) ^y	ASP (mg phosphate kg ⁻¹) ^z	MAP (mg phosphate kg ⁻¹) ^z
0 ^a	16	16	18	15
14 ^{bc}	16	35	16	16
42 ^d	14	38	29	24
65 ^{cd}	9	20	21	43
94 ^{ab}	8	39	13	12
142 ^{ab}	11	14	22	31

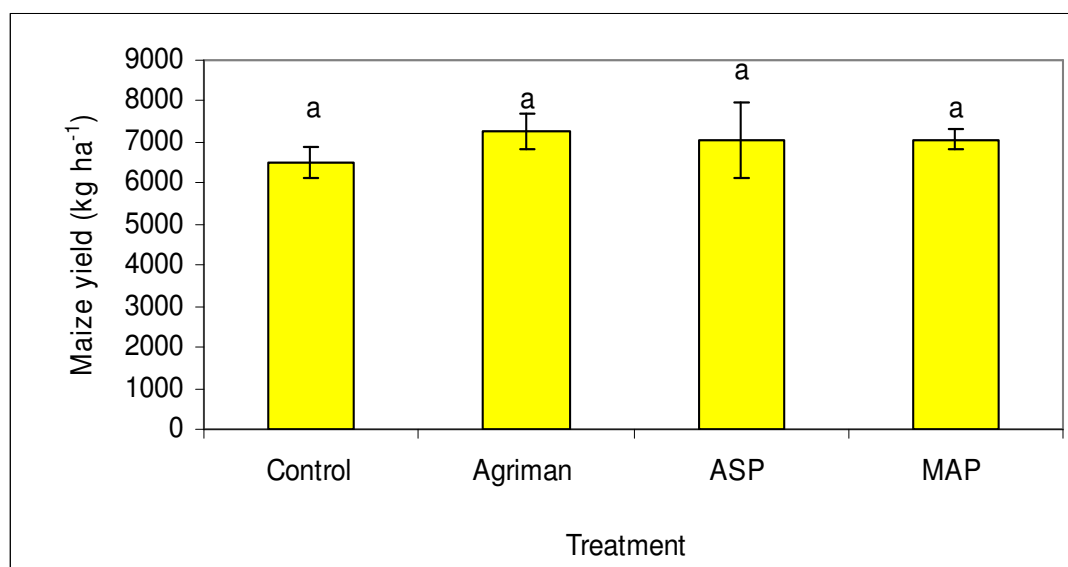


Figure 3.13: The influence of different treatments on the mean maize yield of the field trial. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

3.4.3 P content of maize grain

Considering the P content of the grain, there was a significant difference between the control and the other treatments (Figure 3.14). The P content increased due to the application of ASP, MAP and Agriman treatments. These

findings compare well with the results of Jones (1967) who found elevated levels of total P in the grain of sludge treatments compared to the control, but all levels for maize plants for all the treatments were in the normal ranges as stipulated in the Fertilizer Handbook (2003). Organic fertilizer like SS can have an equivalent or even better effect on yield than phosphate from inorganic sources (Sharpley, 1996). The reason for this is a wider impact on chemical and physical properties. Organic fertilizers can increase the availability of phosphate in the soil because it influences the biological, physical and chemical properties of the soil (Gerke, 1994).

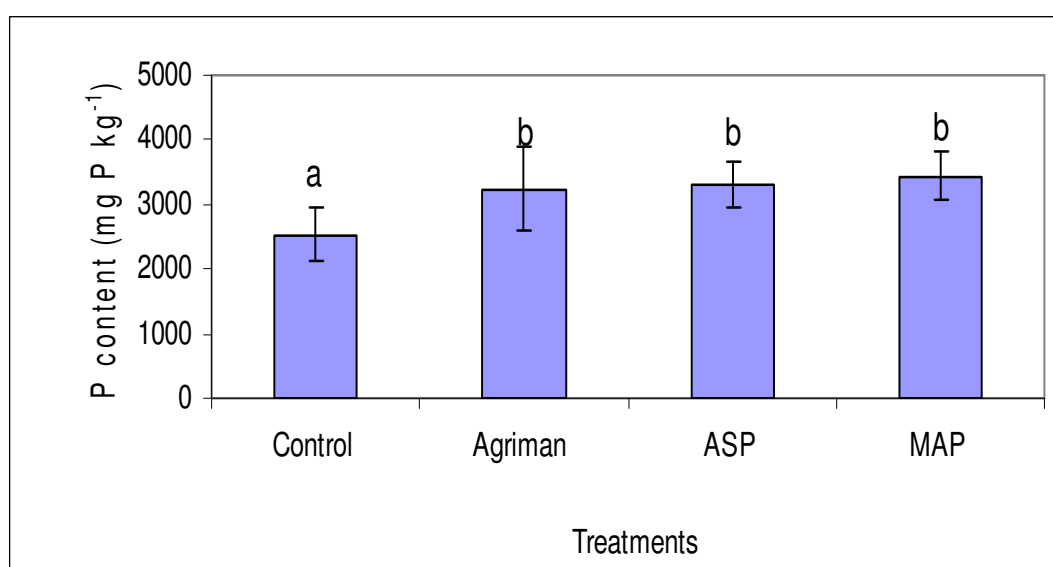


Figure 3.14: The influence of different treatments on P content of the maize grain. (Error bars represent the standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

3.5 Comparisons of Bray-1 extractable phosphate for incubations, pot and field trials

A comparison was made at day 42 because this was the last day before the maize plants from the pot trial were harvested. The influence of drying on Bray-1 extractable phosphate was also assessed. This was done by comparing Bray-1 extractability of the incubation trial with the same soil and sludge treatment of the pot trial where the incubation treatments were dried before it was analysed (incubation dry) and not dried (wet incubation) (Figure

3.15). There was no significant difference between the control treatments from the pot trial and incubation study, and also no significant difference between the MAP treatments from the pot trial and incubation study. There was a significant difference between the KH_2PO_4 treatment of the pot trial and the incubation. This difference can be ascribed to the wetting and drying cycles causing an increase in phosphate fixation because of the adsorption and precipitation of the water soluble phosphate from the soluble KH_2PO_4 and MAP. Drying is known to decrease the availability of phosphate, and this is attributed to the precipitation of phosphate on mineral surfaces, and the irreversible dehydration of sorbed phosphate and phosphate minerals (Fe, Al, Mn and Ca phosphates) (Wiklander & Koutler-Andersson, 1966).

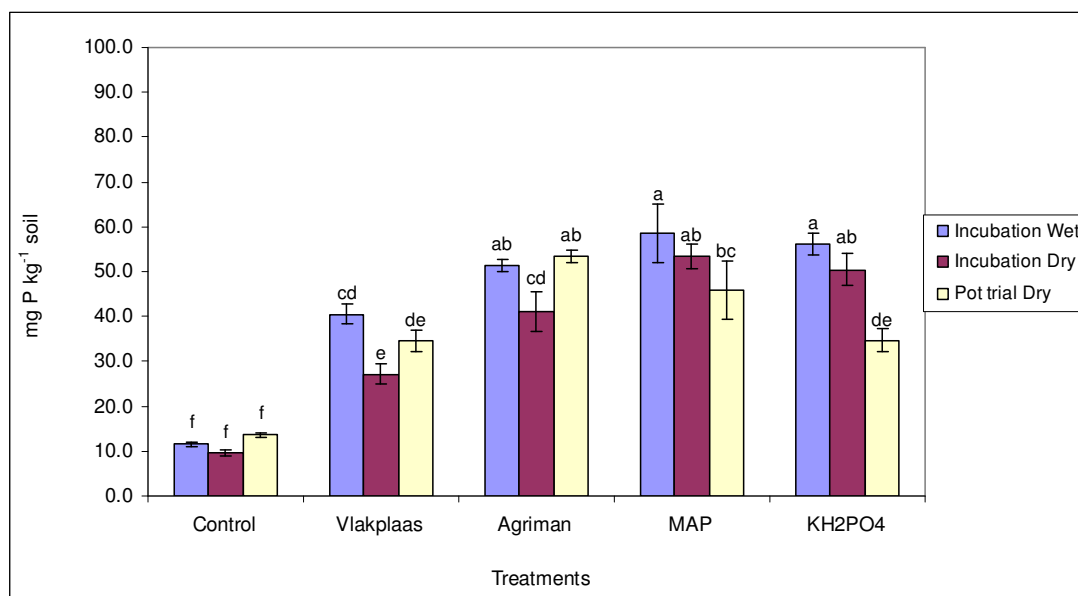


Figure 3.15: Comparing Bray-1 extractable phosphate from the pot trial with the wet and dried soil analysis of the incubation study at 42 days. (Error bars show standard deviation). (Treatments with the same letter/s do not differ significantly at $\alpha=0.05$).

There was a significant difference between the pot trial and the incubation study for the Agriman treatment. This can be due to the microbial flush that is created with the wetting and drying cycles. Van Gestel *et al.* (1993) found that microbial mass can decrease by 58 % when a soil is dried and rewetted again. The phosphate mineralisation process will, therefore, be interrupted by

a drying cycle. Upon rewetting the microbial populations have to recover to optimum levels before pre-drying mineralisation rates will be reached again.

There was a significant difference between the wet incubation and dried incubation sample units of Vlakplaas, however, no significant difference was observed between the dried incubated samples and pot trial for Vlakplaas (Figure 3.15). This can be attributed to the high Fe content of the sludge (Table 2.4) that caused partial fixation of the high inorganic phosphate fraction and upon drying these minerals were dehydrated and decreased its solubility, which was not Bray-1 extractable. The drying of the incubated samples from Vlakplaas resulted in a statistically significant decrease in the Bray-1 extractability, which was not evident for the control, MAP and KH_2PO_4 .

There was a significant difference between the field trial, incubation and pot trial for the MAP and ASP treatment which both are of inorganic origin (Figure 3.16). This can be attributed to the continuous wetting and drying cycles experienced under field conditions, which were more severe than in the pot trial. It is therefore interesting to note that Agriman's phosphate availability is less affected by drying. There was no significant difference between the incubation study and the field trial for the Agriman treatment. This may be due to continuous changes in soil conditions creating microbial flushes and releasing phosphate at a slower rate. In the ASP and MAP treatments, the inorganic phosphate is soluble and directly released in solution, causing it to be fixated more readily. It can be noted that incubation study alone is not a reliable indicator of the RPFV as seen in Figure 3.16 as there is a lot of variation between the incubation study and the plant available study.

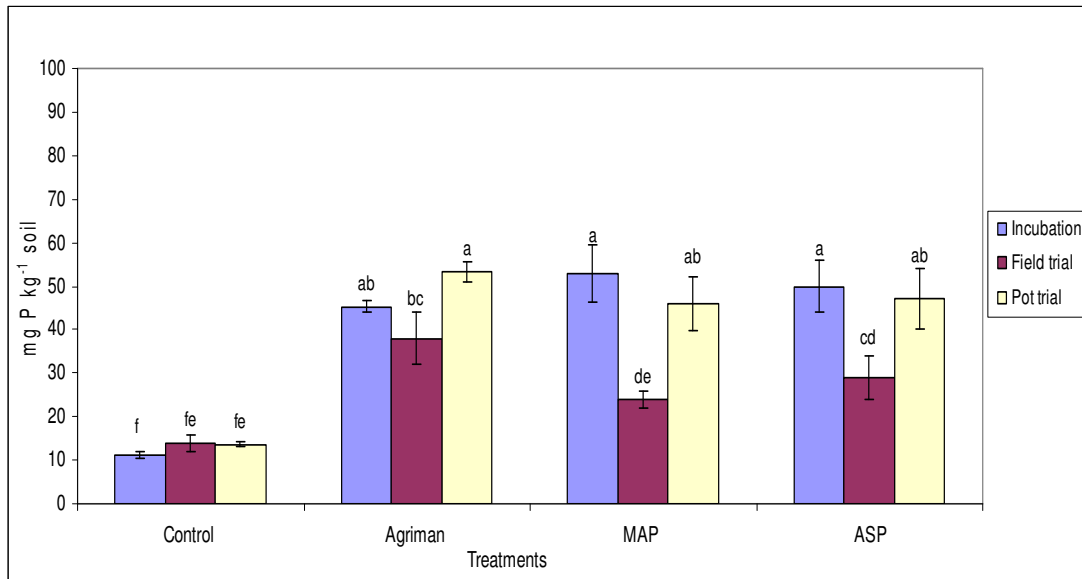


Figure 3.16: Comparing Bray-1 extractable phosphate of the field trial with the incubation study and pot trial at 42 days. (Error bars show standard deviation).

Chapter 4

Summary and general conclusion

The effect of the soils clay content and mineralogy on plant available phosphate were determined and it was concluded that soils with a high clay content decreased the plant available phosphate from the phosphate source regardless of the source type (being either commercial fertilizer or sludge), meaning that soil properties dominate at higher clay content. At high loading rates the plant available phosphate was determined by the sludge characteristics because the soils phosphate fixing capacity is exceeded but at low quantities the soil will play the determining role. In the study the phosphate fertilizer value of the sludge expressed as a percentage of MAP was used to determine the fertilizer value of the sludge. Results from this study showed that sludge from biologically phosphate removed waste water (Agriman) fell in the high category. However, all types of Al/Fe-P-sludge (Daspoort and Vlakplaas) were in the moderate to low category of phosphate plant availability according to O' Connor *et al.*, (2004).

Bray-1 extractable phosphate from sludge amended soils in the incubation study suggested that different waste water treatments had an effect on plant available phosphate but these levels were still optimal for plants even for the Fe treated sludge. This study supported global research findings that the chemical (ferric chloride reactant) removal of phosphate from waste water decreased the potential plant availability, examples are Daspoort and Vlakplaas. While with biological phosphate removal, the potential plant available phosphate was higher compared to chemically removed phosphate as in the case of Agriman.

When conducting incubation studies on the availability of phosphate from sewage sludge in soil it is best to do it in a soil with a low phosphate fixation capacity and low clay content like soil H, but the RPFV concept addresses this challenge efficiently. The reason is to better isolate sludge effects from soil effects on phosphate fixation. This may aid in better quantification of mineralization and solubilisation of phosphate from a sludge amended soil.

Soil properties, however, play an important role in the availability of phosphate.

In the pot trial Bray-1 extraction underestimates plant available phosphate from sewage sludge, but overestimates plant available phosphate from inorganic fertilizer. Bray-1 extracts Al and Fe phosphates from soil. Inorganic fertilizers are very soluble and the % phosphate from sewage sludge is less available than from inorganic fertilizers. But phosphate Bray-1 extracts organic phosphate and inorganic phosphate from soil in variable ratios; that is why Bray-1 underestimates plant available phosphate from sewage sludge. Wetting and drying cycles in the pot trial caused an increase in phosphate fixation for the inorganic treatments compared to the incubation study where the soil was kept at field capacity.

In the field trial it was concluded that sludge applied at the same P rates is just as effective as commercial fertilizer and the phosphate is just as plant available in terms of total grain yield and total P content of grain. It can therefore be concluded that sludge is a viable phosphate source for fertilizer if the maize production site is nearby a WCW. However, each scenario will be unique and various factors, such as the sludge phosphate removal treatment, total P content, the soil and the quantity of sludge required must be considered. If the sludge's total phosphate concentration, water soluble phosphate, Fe and Al content as well as the treatment type is known it is possible to determine the phosphate fertilizer value and the plant availability of phosphate from the sludge.

There was a definite increase in the plant availability of phosphate after application, especially for the MAP and ASP treatments in the field trial. The reason for this is that phosphate is in a soluble form, consequently being immediately available, while the phosphate in Agriman is initially less plant available because it has a higher organic phosphate content and had to be mineralised first giving Agriman slower phosphate release properties than MAP and ASP over time. Comparing the P content of the grain from the MAP, ASP and Agriman treatments, there was no significant difference between the treatments, because P content of maize grain is to a large extent genetically determined and vegetative plant part may have been a better indicator of the phosphate fertilizer value of the different sludge treatments. There was a

distinct difference between the control and the sludge treatments, however, the data on hand suggested that the differences was not statistically significant. When the mean values are compared it seems that, for the one season considered, the two agricultural sludge products are as good as inorganic fertilizer in delivering enough phosphate for plant growth, but there are still practical issues involved like esthetical issues and the spread-ability. The yield determinations also showed that there were differences in yields between the treatments with Agriman having the highest yield and the control the lowest although these treatments did not differ significantly. The P content of the grain showed a significant difference between the treatments and the control but no significant difference between treatments.

Soil properties are the main determining factors of phosphate availability from SS sources and SS has a minimal effect on availability of phosphate if the pH of the soil is kept neutral because in low pH soils the Fe from chemically treated sludge will be soluble and precipitate phosphate from the sludge as well as phosphate from the soil solution if Fe is in excess. So if soil pH is kept neutral, any type of sludge can be applied to soil to increase plant available phosphate but if SS will be applied to acidic soils, it will be better to apply BPR sludge because it has a low Fe content. At low pH microbial activity will be low and the mineralisation rate of organic phosphate will be slower.

The RPFV of the different sludge compared to MAP gives an estimate of the value of the sludge in terms of its phosphate value and with the nature of the sludge it can now be determined what the fertilizer value will be of each sludge type. Wetting and drying cycles in the pot trial lowered the RPFV of the chemical sludge but increased the RPFV of the biological sludge. The incubation study overestimates the RPFV, while the pot trial is a more true reflection of the RPFV of the sludge because it simulates field conditions.

In future studies there should be focused on other commercially available sludge products, their Fe content and total P concentration as a benchmark of their phosphate fertilizer value. Biologically removed phosphate sludges like Agriman hold advantages over chemically removed sludges like Vlakplaas.

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