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VANADIUM AVAILIBILTY TO MAIZE (*ZEA MAYS L.*) GROWN ON TWO CONTRASTING SOILS

By

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Declaration:

I, Jandre McCoy Bekker declare that the thesis, which I hereby submit for the degree MSc. Agric Soil Science at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

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DATE: 09/07/2014

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LIST OF ACRONYMS AND ABBREVIATIONS

AEC anion exchange capacity

BOF basic oxygen furnace slag

CCE calcium carbonate equivalent

CEC cation exchange capacity

ICP-AES inductively coupled plasma atomic emission spectrophotometer

ABSTRACT

Soils on the Eastern Highveld acidify naturally due to the high rainfall and the use of certain nitrogen fertilizers. Liming materials are used to ameliorate soil acidity. A large fraction of this liming material used is Basic oxygen furnace slag (BOF slag), a secondary by-product from the Iron and Steel industry, commercially known as Aglime. These slag contain various concentration of heavy metals, like vanadium.

No vanadium guidelines exist in South Africa. This study was done to determine the V threshold values where maize experienced reduced growth and to determine the V loading rate through slag application.

A pot trial was used to determine the concentrations where vanadium reduces plant growth, and to establish toxicity levels in maize. The pot trail was used to establish V threshold values with various indicators, like total V concentration in the soil, total V concentration in the plant, Bray 1 extractable V and ammonium acetate extractable V, where maize experienced reduced growth.

The threshold value where maize showed reduced growth in sandstone derived soils was at a total V concentration in the soil of 73.3 mg kg^{-1}. The Bray 1 extractable V at this threshold was 23.5 mg kg^{-1} and there was no V in the above ground plant material in the maize. The ammonium acetate extractability at this level was 1.68 mg kg^{-1}. V toxicity occurred at a total V concentration of 150 mg kg^{-1}, with Bray 1 extractable V at 77.6 mg kg^{-1} and total V in the maize plant 14.8 mg kg^{-1}

For the dolerite derived soil the threshold value was determined to be 235 mg kg^{-1} for the total V concentration in the soil. The Total V concentration in the plant was 0.5 mg kg^{-1} and the Bray 1 extractable V was 30.3 mg kg^{-1}. The ammonium acetate extractable V was 1.69 mg kg^{-1}.

A pot trail and field evaluation site was used to determine the V loading through slag application. Three slag where used containing different V concentrations, slag A containing the highest V (918 mg kg^{-1}) and B (153 mg kg^{-1}) and C (88.6 mg kg^{-1}) had

a lower V concentrations. Theoretical V loading values was determined for three different slags containing different V concentrations and by using the threshold V concentration generated in chapter 3, the period to reach the critical V threshold value for liming with slag A was determined. If all factors (V concentration and incorporation depth), were to be kept constant, it will take an estimated 186 years of liming with slag A for the sandstone derived soil to reach the threshold value of 100 mg kg^{-1} where V negatively affect the growth of maize plants. This period was calculated to be 472 years for the dolerite derived soil, due to the higher Fe content and finer textured soil, which increase the V sorption capacity of the soil. The safe period for the slag B and C in respect with V is much longer than slag A, but other heavy metal concentrations must be kept in mind for they too can accumulate in the soil and can influence the growth of maize negatively if certain threshold values are reached.The V concentration of all the parameters generated in the V toxicity pot trail was far below the threshold values of the slag pot trail and field evaluation site. This indicated that the slag use with high V concentration on the short term (10 years) is unlikely to negatively influence crop production.

CHAPTER 1: INTRODUCTION

1.1 Background

South Africa has limited agricultural resources and is classified as an arid country because the mean annual rainfall is 497 mm which is far less than the world average of 860 mm. The annual potential evaporation ranges from 1100 mm to 3000 mm (Huntley *et al.*, 1989). Only 14 % of the land is suitable for dry land production of which only 3 % is high potential (Scotney *et al.*, 1990). Mining activities on the Eastern Highveld have increased drastically over the last ten years and the impact on arable land is devastating, especially in areas where open cast mining is practiced, resulting in the loss of precious agricultural land. In most cases the most fertile land is removed for mining and so the land available for sustainable food production on the Eastern Highveld and has decreased. It is therefore of great importance that the fertile land that is left for crop production should be cultivated responsibly considering the fact that there is a world food shortage at hand (FAO, 2011). One of the most common soil degradation problems encountered in highly weathered soils under cultivation is soil acidification. Soil acidification significantly affects crop production and should be prevented to ensure sustainable crop production for the centuries to come.

Soils on the Eastern Highveld (Area include eastern part of Gauteng, Southern part of Mpumalanga and Northern part of the Free State in South Africa) acidify naturally due to the high rainfall (800 mm y^{-1}) and the use of certain nitrogen fertilizers, especially ammonium based fertilisers (Beukes, 1995). Most of these soils are predominantly derived from sandstone parent materials, which have a low buffer capacity and are sensitive to acidification (Fey & Dodds, 1998). Farmers on the Eastern Highveld use tons of liming material each year to ameliorate soil acidity aiming to maintain a soil pH (H_2O) range of between 6 and 6.5. This is the pH range where the essential elements for plant growth are readily available and where some elements like aluminium (Al), iron (Fe) and manganese (Mn) are unlikely to be toxic to plants. An estimated 4.7 million mega gram of lime are needed for the cultivated

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land in South Africa to ameliorate soil acidity and about 1 ton of lime is needed annually to prevent renewed acidification (DME, 2005).

A large fraction of this liming material used is BOF slag, a secondary by-product from the Iron and Steel industry, commercially known as Aglime. Slag contain various oxides, carbonates and silicates, and is sieved to micro fine particles (<0.25 mm), and therefore have a relative high acid neutralizing capacity. However, the disadvantage of slag is that it might contain heavy metals. Some slag used, for example, contains high levels of vanadium (V).

High levels of V can be toxic to certain plant species, which lead to an under developed root system and stunted growth. In animals the toxicity of V has been found to be high when it's been given parentally, low when it is orally administrated and moderate in the case of respiratory exposure. In humans both acute and chronic poisoning have been described in workers engaged in the industrial production and use of high levels of V. Most of the reported clinical symptoms reflect irritate effects of V on the respiratory (Vouk, 1979).

Vanadium has not been a specific research focus in South Africa and little work has been done to understand V dynamics in agriculture. Other heavy metals like lead (Pb), nickel (Ni), cadmium (Cd) and chromium (Cr) have been the main focus of various studies. Previous and current studies at the University of Pretoria focussed on slag use in agriculture, however V dynamics was not the main focus of this investigation (van der Waals, 2001).

No stipulated guidelines exist in South Africa governing heavy metal additions to soils through the application of slag. The proposed allowable heavy metal concentrations for fertilizers (Act No. 36 of 1947) do not include V. This is due to the fact that little research has been done on V and possibly also because V is not considered to be as environmentally detrimental as Pb and Cd. In this study the maximum permissible V concentration in soil and maize plant will be determined. There is no prescribe method to analyse plant available V, which is a more accurate

measurement to test for V toxicity in soils. Bray1 and ammonium acetate extraction methods will be tested as V extraction methods for soil to predict the level of V accumulation.

The risk posed by V as a result of agricultural slag use, is a function of 1) The V concentration in the slag; 2) The amount of slag added per unit area to ameliorate soil acidity; 3) Soil properties, (for example, clay mineralogy, clay content and exchangeable acidity) of the soil receiving the slag; 4) the incorporation depth of slag in the soil, 5) the type of crop to be planted on that soil, as well as the number of years that the slag was used.

Therefore, it is of vital importance to understand the dynamics of V in the soil system, to ensure the long-term sustainability of using slag in South African agricultural lands for food production.

1.2 Study aims

The overarching aim of this study was to gain insight into the dynamics of V in the plant- soil environment, focus on maize. The objectives were to:

a) Determine the threshold levels in two contrasting soils at which the growth of maize are influenced and / or toxic symptoms appear. It is hypothesised that the concentration where the growth of maize is negatively influenced will differ between soils with different V sorption capacities.

b) Evaluate the use of two extraction methods, to create threshold concentrations were V becomes toxic. It is hypothesised that Bray 1 would be a better extraction method compared to ammonium acetate because of the suggested analogy between phosphate and vanadate, and that vanadate is the dominate V state in oxidised conditions.

c) Determine the V loading rate through slag application and estimate the duration a specific slag can be used before plant growth is expected to be negatively impacted, and investigate the translocation of V in the maize plant. It is hypothesised that V loading over the short term (10 years) would not have a negative effect on the growth

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of maize plants, but might become a problem when V accumulation takes place over 100 years and longer.

CHAPTER 2: LITERATURE REVIEW

2.1 Soil acidity

Soil acidification is a natural process, which can be accelerated through the activity of plants, animals and humans or can be managed through good farming practises. Van Breemen (1991) describes soil acidification in several ways; an increase in soil acidity and / or a decrease in soil pH, a decrease in base saturation, an unbalanced availability of elements in the root environment, or a decrease of the acid neutralising capacity of the soil. An acid soil is a soil with a pH (H_2O) below 7 which might contain phytotoxic Al and Mn compounds at pH below 4 (Venter, 2004).

2.1.1 Origin of soil acidity

Acidification is the result of the addition, or generation of H^+ ions. The most common contributor of H^+ ions is when carbon dioxide dissolves in water to form carbonic acid. Carbonic acid dissociate releasing H^+ ions (Equation 2.1), but the contribution of H^+ ions is negligible when the pH is below 5.0. Another contributor is organic material that was subjected to microbial mediated oxidation. Humic substances formed, contain, for example, carboxylic functional groups (Equation 2.2) that can protonate and deprotonate depending on the pH. Decreasing the pH below the pKa value these functional groups will result in their protonation and increase in exchangeable or reserve acidity of the soil. An increase in pH will result in the release of the protons in the soil solution, increasing soluble acidity and buffering pH change. Dissolved organic substances can also form soluble complexes with basic cations (Ca^{2+} and Mg^{2+}) and facilitate the loss of these cations through leaching.

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightharpoons HCO_3^- + H^+ \quad pKa = 6.35 \tag{2.1}$$

$$[RCH_2OH\ldots] + O_2 + H_2O \leftrightharpoons RCOOH \leftrightarrow RCOO^- + H^+ \quad pKa = 3 \text{ to } 5 \tag{2.2}$$
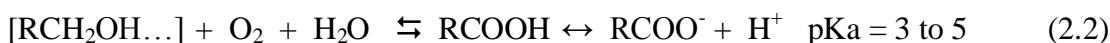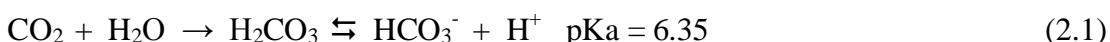
H^+ ions are generally produced during oxidation. During nitrification, ammonium ($NH_4^{+)}$ ions from organic matter or fertilizers are subjected to microbial oxidation and release two H^+ ions for each NH_4^+ ion oxidized (Equation 2.3).

$$NH_4^+ + 2O_2 \leftrightarrows H_2O + 2H^+ + NO_3^- \hfill (2.3)$$

Organic –SH groups and sulphur containing minerals like pyrite (FeS_2) can also be oxidised to form sulphuric acid (Equation 2.4). Pyrite is a mineral commonly associated with coal and is the main cause of acid mine drainage on the Eastern Highveld. When these acids dissociate in water, H^+ ions are produced. This is typically how acid rain is formed. Sulphur and nitrogen gasses from the combustion of fossil fuels, forest fires and lightning dissociate completely in rain drops because they are strong acids with low pKa values (Equation 2.5 & 2.6). Plants also contribute to H^+ ions to the soil. Plants must balance their cations and anions uptake. When a cation is taken up, the plant can take up an anion, or exude H^+ ions to maintain balance between positive and negative charges in the plant (Brady & Weil, 2003).

$$FeS_2 + 3^{1/2}O_2 + H_2O \leftrightarrows FeSO_4 + 2H^+ + SO_4^{2-} \hfill (2.4)$$

$$H_2SO_4 \leftrightarrows SO_4^{2-} + 2H^+ \hfill (2.5)$$

$$HNO_3 \leftrightarrows NO_3^- + H^+ \hfill (2.6)$$
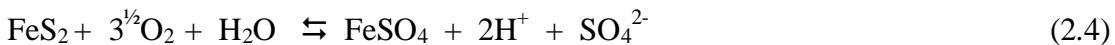
H^+ ions formation as a result of dissociation reactions (Brady & Weil, 2003).

Soils in high rainfall areas acidify naturally because of the leaching of basic cations (calsium (Ca), magnesium (Mg) and potassium (K)) in well drained soils. This happens in the case of N and S mineralization and oxidation of organic N and S when H^+ ions are produced. Protons will replace above mentioned basic cations and these cations in turn will leach with NO_3^- and SO_4^{2-} as charge balancing cation. The H^+ ions, however, remain behind in the topsoil, resulting in the acidification of the topsoil. This will lower soil pH in this layer and the pH buffer capacity (Bolan *et al.,* 2003). The intensity of acidification is dependent on the geology and topography of a specific area. This is a slow natural process (Helyar & Porter, 1989). Soils in the Highveld of the Mpumalanga Province are very sensitive to acidification because of

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high rainfall (800 mm year^{-1}) and the majority of these soils are sandier soils with poor buffering capacities (Fey & Dodds, 1998). This natural process can be accelerated by human activity such as inappropriate fertiliser use. Apart from acid rain, ammonium based nitrogen fertilisers and urea has been the main anthropogenic contributors to acidification of agricultural soils. With the addition of N fertilizers, nitrification produces H^+ and NO_3^-. These products from nitrification can leach below the root zone that can lead to subsoil acidity (Rowell & Wild, 1985; Bouman *et al*., 1995; Juo *et al*., 1995).

However, acidity is not only generated by oxidation reactions. Soluble mono calcium phosphate is the principal P component in superphosphate fertilizers. In the immediate vicinity of a superphosphate fertilizer granule, brushite ($CaHPO_4.2H_2O$) can precipitate. A mole of burshite precipitated will generate one mole of protons (Equation 2.7). With the dissolution of mono calcium phosphate, the formation of dicalsium phosphate accompanied with phosphoric acid which dissociates into phosphate and H^+ ions.

$$Ca^{2+} + H_2PO_4^- + 2H_2O \leftrightarrows CaHPO_4.2H_2O \text{ (brushite)} + H^+ \quad (2.7)$$

Phosphate ions are strongly adsorbed to most soils, where $H_2PO_4^-$ induced leaching of basic cations is unlikely to occur (Bolan *et al.,* 2003).

2.1.2 Effect of soil acidity on nutrient availability, and plant growth

Acidification influences the physical, chemical and biological characteristics of soils and therefore affects the transformation and biogeochemical cycling of both nutrients and heavy metals in soils. pH affect the surface charge and subsequent adsorption of solutes by variable charge soil components, such as layer silicate clays, organic matter, and oxides of Fe and Al (Adriano, 2001). pH affects the following: sorption of metal cations and anions in soil, metal speciation, complexation of metals with organic matter, precipitation/dissolution reactions, redox reactions, mobility and leaching, dispersion of colloids, and the bioavailability of nutrients and trace metals (Bolan *et al.,* 2003).

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Surface charge controls a number of physical and chemical properties of soil. Soil solution pH is one of the major factors controlling surface properties of variable charge components (Sposito, 1984; Barrow, 1985; Sparks, 1986). pH affects the surface charge through the supply of H^+ for adsorption onto metal oxides and the dissociation of the functional groups in the soil organic matter. An increase in pH increases the net negative charge or cation exchange capacity, and a decrease in pH increases the net positive charge or anion exchange capacity (Singh & Uehara, 1986).

The change in surface charge is the main reason for the effect of pH on anion and cation adsorption. Lower pH values increase the Al concentration in the soil solution, occupying a larger fraction of the cation exchange sites, and reducing base saturation (Ritchie, 1989).

Soil pH is one of the important factors that influence the availability of nutrients (Fölcher, 1975; Sumner, 1975; Sumner *et al.,* 1991). Acidification also leads to manganese (Mn) and iron (Fe) toxicities as well as deficiencies of phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K), sulphur (S), and molybdenum (Mo) (Ceballos *et al*., 1995; Zeigler *et al*., 1995).

Acidity influences the nitrification of N, which is reduced at pH of 6 and undetectable at pH lower than 4 (Alexander, 1977). Acidity also affect the solubility of soil P. Fe and Al concentrations are increased in the soil solution with a decrease in pH, increasing the adsorption/ precipitation of P. In variable charged soils, increasing acidity decreases the cation exchange capacity reducing the soil's ability to retain K, Ca and Mg, resulting in more K, Ca and Mg in the soil solution which is prone to leaching (Blue, 1986; Alibrahim, 1988).

Acidification affects the transformation of heavy metal ions through the altering of the surface charge in variable charged soils, altering the speciation of metals and influencing the reduction and oxidation reactions of metals. Thus, pH influences the pollution hazard of several heavy metals (Løbersli *et al*., 1991). Metals are more available in acid soil with the exception of a few metalloids like arsenate,

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molybdenate, selenate, vanadate and some valence state of chromium that is more available under alkaline conditions like chromate (Adriano, 1986).

Root growth restriction can occur in deep soil profiles due to subsoil acidity. Retarded root growth is the primarily effect of aluminium (Al) toxicity (Foy, 1974; Pinkerton & Simpson, 1986) and this affect the water uptake capability of roots which impact negatively on yield due to limited water uptake by the underdeveloped root system (Coventry *et al*., 1997).

2.2 Liming materials

The commonly used liming materials are dolomitic lime (≤ 15 mg kg^{-1} CaCO$_3$ and $\geq$ 70 mg kg^{-1} MgCO$_3$), calsitic lime (≥ 70 mg kg^{-1} CaCO$_3$ and ≤ 15 mg kg^{-1} MgCO$_3$), magnesite (containing ≥ 975 mg kg^{-1} MgCO$_3$ and ≤ 25 mg kg^{-1} CaCO$_3$) and BOF slags from the steel industry containing Ca and Mg alumino-silicates (Barber, 1967). The acid neutralizing value of liming materials is expressed in terms of calcium carbonate equivalent (CCE), which is the acid neutralizing capacity of a liming material expressed as a weight percentage of pure CaCO$_3$. The quantity of liming material required to ameliorate soil acidity depend on the reactivity which determine the neutralizing value of the liming material and the pH buffer capacity of the soil.

Venter (2004) mentions four approaches to ameliorate soil acidity which is used as lime recommendation guidelines in South Africa. The pH-texture method uses the clay content of soils and a specific target pH to determine the lime requirement. The SMP-buffer method implies the measurement of the change in pH of a buffer solution to which the test soil was added. Soils can be incubated with CaCO$_3$ to obtain a calibration curve. Lime requirement can be determined in terms of CaCO$_3$. The Eksteen method was developed by Eksteen (1969) for the winter rainfall region of South Africa, and is expressed as follows:

X = [RH − (Ca + Mg)] / (R + 1)

X = lime requirement in t ha^{-1} for a 0.15 m soil layer, R = the ratio of exchangeable Ca and Mg to exchangeable acidity to be achieved, H = exchangeable acidity measured in the soil, and (Ca + Mg) = HCl extractable Ca and Mg. The acid saturation method was developed for KwaZulu-Natal and soils are limed to an acceptable level of exchangeable acidity.

Bornman (1985) developed the Resin Suspension Method (RSM) to predict the reactivity of liming materials, compared to analytical grade $CaCO_3$. The SMP-buffer method in combination with the RSM method can be used to calculate the quantity of slag required to obtain the desired pH level in the soil.

Liming enhances the physical, chemical and biological characteristics of soil through the direct amelioration of soil acidity and through indirect effects on the mobilization of plant nutrients, immobilization of toxic heavy metals and the improvement of soil structure (Haynes & Naidu, 1998).

The calcium in liming materials helps with the formation of soil aggregates, improving soil structure. The lime induced improvement in aggregate stability is manifested through the effect of liming on dispersion and flocculation of soil particles (Chan & Heenan., 1998).

Acid soils are limed to overcome the chemical problems associated with acid soils like the high concentration of acid ions (H^+ and Al^{3+}) and toxic elements (Mn^{2+}), and low concentrations of basic cations (Ca and Mg) and other nutrients like P and Mo. The hydrolysis of the basic cations in lime produce OH^- ions which neutralize the H^+ ions, decreasing the activity and bioavailability of Al and Mn. Liming increase the solubility of P and Mo, increasing their availability. Lime also provides basic nutrient cations (Ca and Mg) and can be used to correct nutrient imbalances. The elevation in pH due to the addition of lime results in the precipitation of exchangeable Al and increase the negative charge or CEC (Bolan *et al.,* 2003).

Other liming materials include different slags derived from the processing of steel.

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The slag's composition differs due to different processes used in the processing of steel, therefore the neutralising reaction is not precisely known. It is not a pure carbonate but also contains Ca-silicate and could react (together with other constituents) in the following manner:

$$SiO_5Ca_3 + 6H^+ \Leftrightarrow 3Ca^{2+} + SiO_2 + 3H_2O \qquad (2.8)$$

$$SiO_4Ca_2 + 4H^+ \Leftrightarrow 2Ca^{2+} + SiO_2 + 2H_2O \qquad (2.9)$$

$$2CaO.Fe_2O_3 + 16H^+ \Leftrightarrow 2Ca^{2+} + 4Fe^{3+} + 8H_2O \qquad (2.10)$$

$$FeO.MnO + 4H^+ \Leftrightarrow Fe^{2+} + Mn^{2+} + 2H_2O \qquad (2.11)$$

$$CaO + H_2O \Leftrightarrow Ca(OH)_2 \qquad (2.12)$$

$$Ca(OH)_2 + 2H^+ \Leftrightarrow Ca^{2+} + 2H_2O \qquad (2.13)$$

$$MgO + 2H^+ \Leftrightarrow Mg^{2+} + H_2O \qquad (2.14)$$
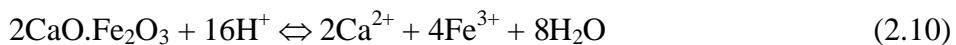
(After Vanacker, 1999).

Several types of slags are used as agricultural liming materials, such as blast furnace slag, open-hearth slag, and basic slag. These are all the by-products of steel processing plants and their composition depend on the raw material (ore), the specific process, and the product of the plant. Due to this, Ca and Mg aluminosilicates, Fe, Mn, phosphates, and other elements such as Cr, Ni, Co, Cd, Cu, Zn, Mo, and Ba may occur in differing quantities. Some of the elements can reach concentrations of several parts per thousand, which are then added to the soil.

Two main forms of slags are produced in and distributed from the heart of the Loskop Dam catchment area near Witbank and Middelburg (part of the Eastern Highveld). This is also the area in which soil acidification is reaching critical proportions in parts, and in which many soils are very sensitive to acidification (Fey & Dodds, 1998). The waste product, if finely ground, has a high Calcium Carbonate Equivalent (CCE) and is relatively cheap in comparison to other mined liming materials. Due to high transport costs and the proximity of the slags, large quantities are used in the area. As mentioned earlier, a source of concern is the fact that slags contain varying amounts of trace elements and heavy metals and that although most of the elements are not plant available at the pH levels in the soil after liming, the build-up of these elements

could be detrimental in the long-term. Slag use as a liming material serves as a waste management strategy for the Iron and Steel industry. In 2004 the total amount of lime used in RSA was 1.39 Mt tons, and 50.5 % was slag from the Iron and Steel industires. Table 2.1 gives an indication of the average composition of the slags.

TABLE 2.1. Average composition of slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).

Chemical Compound	Columbus Steel %	Highveld Steel %
Al_2O_3	2.3	1.3
CaO	49.5	55.4
Cr_2O_3	3.0	-
FeO	0.6	16.7
MgO	11.4	6.5
MnO	0.9	1.1
P	-	0.4
S	-	0.4
SiO_2	30.6	17.9
TiO_2	0.7	-
V_2O_5	-	1.6

After Van Der Waals, 2001.

2.3 Vanadium in the soil

2.3.1 Origin and concentration in soils

According to Nriagu (1998), the average concentration of V in the earth's crust is 100-150 mg kg^{-1}, which is almost the same as Ni, Zn and Pb. V is more abundant in mafic rocks (high in Fe and Mg) than in silicic rocks. Concentrations in gabbro and norite range between 200-300 mg kg^{-1}. The V concentration in silicic rocks like granite is about 80 mg kg^{-1}. In sandstone the V concentration is very low and has an average concentration of 12 mg kg^{-1}. V concentration in iron ores is in the range of 600 - 4100 mg kg^{-1} and in rock phosphates 10 - 1000 mg kg^{-1}. The production of

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super phosphate from V containing rock phosphate can further concentrate V to 50 - 2000 mg kg^{-1} (Evans & Landergen (1978) and ATSDR (1992).

The natural concentration of total V concentration in soil varies between 10 mg kg^{-1} and 220 mg kg^{-1} (Kabata-Pendias & Pendias, 1993). Panichev *et al*. (2006) however reported concentrations as high as 400 mg kg^{-1}. This variation is, however, a function of the parent material from which the soils are derived and other possible sources of contamination, including liming with materials having high levels of V.

The largest contributors of anthropogenic V are emission from the combustion of fossil fuels by power plants (USEPA, 1987). The average concentration of V in hard coals is 19 mg kg^{-1} (Yudovich, 1972). In 1972 oil combustion contributed 94.1% to the emissions of V into the atmosphere, coal contributed 4.5 % and metallurgical and other processes 1.2% (Van Zinderen Bakker & Jaworski, 1980). Other contributors are the emissions from petroleum refineries and metal plants (Kabata-Pendias, 1993) and in this study slag application to ameliorate soil acidity.

2.3.2 Vanadium dynamics in soil

There are about 80 different minerals containing V (Fleischer, 1987; Clark, 1990). These minerals are placed in four groups according to their crystal chemical structure. The groups are; sulfides, sulfosalts (derived from oxidized sulphide ores) of Pb, copper (Cu), Zn and Mn, silicates and oxides. There exist a group of minerals which contains pentavalent V in their structure occurring as isolated VO_4 tetrahedra which is the result of the oxidation of base metal sulfides (Evans & Landergen, 1978). A number of minerals in this group are isostructural with phosphates and vanadates like vanadinite ($Pb_5(VO_4)_3Cl$).

2.3.3 Speciation of vanadium

The speciation of an element is an important aspect to understand and determine the toxicity, bio-availability and its mobility in the environment (Bendito & Rubio, 1999; Ebdon *et al*., 2001; Sturgeon, 2000). The speciation of elements is influenced by pH

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and its oxidation state. V exist in the +3, +4 and +5 oxidations states in nature and below pH 8, the +4 and +5 states dominate under oxidising conditions (Peterson and Girling, 1981).

Mononuclear vanadate oxyanions ($H_2VO_4^-$ and HVO_4^{2-}) with a structural analogy like phosphate, are the dominant species of V(V) in dilute solutions (Wehrli & Stumm, 1989; Wanty & Goldhaber, 1992). In more concentrated solution (> 100 μmol L^{-1}) V might form polynuclear species (Cruywagen & Heyns, 1991) like decavanadate ($H_xV_{10}O_{28}^{x-6}$) and metavanadate (($VO_3)_x^{x-}$). Pyrovanadates ($V_2O_7^{4-}$) replace mononuclear oxyanions as the primary V(V) species at V concentrations higher than 0.1 mol L^{-1} (Baes & Mesmer, 1976). V (+4) and V (+5) are bound to oxygen to form oxyanions which tend to complex with ligands like phosphorous (P) and sulphur (S) (WHO, 1988).

The metavanadate (VO_3^-) anion can be reduced to the vanadyl (VO_2^+) cation, which may be an important form of V in soil according to Berrow *et al.* (1978). VO_2^+ is immobilized as humic acid complexes while the anions like orthovanadate (VO_4^{3-}) and metavanadate. (VO_3^-) are mobile in soils and potentially more toxic to soil micro biota (Goodman & Cheshire, 1975; Bloomfield, 1981). Little work has been done to establish methods to quantitatively separate the different species, which have different nutritional and toxicity properties (Mandiwana *et al.* 2005).

Poledniok and Buhl (2002) used the Tessier *et al.* (1979) extraction analysis procedure for heavy metals (Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn) to determine five fractions of V in two soils. The first is the exchangeable fraction, which contains metals adsorbed on the solid surface. The second fraction is metals bounded or precipitated by carbonates. The third fraction is metals adsorbed on surfaces of precipitating Fe, Al and Mn oxides and this is under oxidised conditions. The fourth fraction is metals adsorbed to the surface or bonded to organic matter. The fifth fraction comprises of metals built into the crystal lattice of primary and secondary minerals, which are not plant available. These authors reported that the exchangeable V was the same for both soils but not the total V concentration, which indicate that

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plant available V does not depend on total V concentration in the soil. The different concentrations of Fe, Mn and organic material determined the fraction of V held in that specific fraction. In both soils no V and carbonate compounds were found and this may indicate that V does not form compounds with carbonates.

2.3.4 Vanadium sorption

The aqueous chemistry of V is controlled by its redox state and sorption onto iron oxide and clay minerals (Trefry & Metz, 1989). Sorption onto minerals like goethite and hematite controls V concentration in groundwater (Breit & Goldhaber, 1989; Wanty & Goldhaber, 1992).

Keeney-Kennicutt & Morse (1984) suggested that VO_2^+ formed inner-sphere surface complexation at low pH. At higher pH, inner-sphere surface complexation was suggested through the adsorption of HVO_4^{2-}. The vanadate ion acts like phosphate and can adsorb through ligand exchange (Sigg & Stumm, 1980).

The V sorption capacity of soils directly influences the mobility and plant availability of V. If the structural analogy between vanadate ($H_2VO_4^-$) and phosphate ($H_2PO_4^-$) ions exist then it can be hypothesised that vanadate reacts like phosphate in the soil and the soil properties that influence P fixation will influence the V sorption and availability (Rehder, 1999; Crans, 1994). Common factors influencing phosphate availability are pH, AEC, Fe, Al, and Mn (oxy) hydroxides, the percentage carbon (C) and texture (Brady & Weil, 2002).

Wang and Lui (1999) determined the sorption capacity of two soils by shaking the soils with different concentrations of V. Different concentrations of NH_4VO_3 was added to two soils. The soil with the highest concentration of total Mn and Fe sorbed more V. pH also influenced the sorption of V. As the pH increased, the sorption capacity decreased and the plant availability of V increased.

2.3.5 Vanadium mobility

Vanadium (+5) is more soluble than V (+4) rendering it potentially more mobile and plant available and V (3+) is not found in oxidized conditions like oxidised soils (Van Zinderen Bakker & Jaworski, 1980). In neutral or alkaline soils V is more mobile relative to other heavy metals (Brooks, 1972). Martin and Kaplan (1996) found that V is not very mobile in the soil that they tested. In this study a V salt ($VOSO_4 \cdot H_2O$) was incorporated into the top 7.5 cm of the soil and samples were taken at various depths for 30 months. There was little increase in V concentration at a soil depth below 15 cm due to the presence of gibbsite and Fe oxide. One should mention that the V loading rate (5.6 kg ha^{-1}) was very low. It is not clear from the literature whether V, in the presence of Fe oxides, is removed from the aqueous phase as a precipitate, such as $Fe(VO_3)_2$, or sorbed onto the surfaces of Fe oxides (Rai & Zachara, 1984).

2.4 Vanadium in the plant

2.4.1 Concentration and toxicity

The question whether V is an essential nutrient for higher plants have not been answered (Morrell *et al.*, 1986; Kabata-Pendias & Pendias, 1992). According to Kabata-Pendias & Pendias (1993), V positively influence chlorophyll synthesis, potassium (K) consumption and nitrogen assimilation at concentrations lower than 2 ppm, while higher concentrations of V can be toxic and may cause sclerosis and limit plant growth. The concentration at which an element becomes toxic depends on the soil type and plant species. Plant species have different toxicity levels because some plants have developed mechanism to tolerate high heavy metals concentrations. An example of a V accumulator is *Astralgus confertifloris* with V concentration up to 144 mg kg^{-1}, growing in vanadium rich, sandstone derived soils in Utah, USA (Cannon, 1963).

Various symptoms were observed where plants were exposed to high concentrations of V. Somasundaram *et al.* (1994) found that V caused inhibition of chlorophyll biosynthesis, soluble protein and net photosynthesis of seedlings of rice (*Oryza sativa L.*). V can cause a decrease in Ca absorption by sorghum root tips (Wilkinson &

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Duncan, 1993), decrease phosphate uptake by maize roots (Sklenar *et al.*, 1994) and inhibit the growth of onion roots (Hidalgo *et al.*, 1988).

Nutrient solution studies are used to determine the essentiality or the toxicity of certain elements. It is also used to determine the factors that influence uptake like pH and other cations or anions in solution. Trails were conducted to determine the toxicity levels of V in a solution. V concentrations of 10 to 20 mg/l in nutrient solution were reported to be harmful to plants (Arnon & Wessel, 1953; Cannon, 1963). Welch (1973) found that $CaSO_4$ in solution enhanced the V uptake by roots and speculated that the V taken up by the plant cells accumulates within the interior of the cell and Ca is required for the retention of the absorbed V by the cells.

Wang and Liu (1999) conducted a greenhouse pot trial, to determine the V toxicity of soya bean seedlings in two soils. They applied NH_4VO_3 to the soil through seven V loading rates (0, 5, 10, 15 30, 50 and 75 mg kg^{-1}). They found that the toxicity levels in soil differ as a function of texture and Fe and Mn content. Soya bean seedlings in a sandy loam (20 % clay) soil with Fe concentrations of 22 000 mg kg^{-1} showed reduced growth at V loading rate of 30 mg kg^{-1} soil. In a sandy clay loam (32 % clay) soil with a Fe content of 46 000 mg kg^{-1} a V loading of 75 mg kg^{-1} did not affect the growth of soya bean plants negatively. This was due to a higher V fixation in the sandy clay loam. Neither plant tissue concentrations nor the plant available fraction of V were mentioned where toxicity occurred.

Kaplan *et al.* (1990) used $VOSO_4$ to determine V toxicity in collards (*Brassica oleracea*) in a sandy (6 % clay) and in a loamy sand (14 % clay) soil. The V loading rates were 0, 20, 40, 60, 80, and 100 mg kg^{-1}. Collards in the sandy soil with a V loading rate of 80 mg kg^{-1} showed a significant reduction in above ground biomass. This was at a higher V loading rate than the soya seedlings. This shows that different plant species have different threshold concentrations for V and that the mineralogy of the soil also influences V dynamics in the soil. The total V concentration in the plant at this loading rate was 10.3 mg kg^{-1}. Collards growing in the loamy sand with a higher Fe concentration, organic material and cation exchange capacity did not show

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a reduction in above ground biomass even at a V loading rate of 100 mg kg^{-1}. The total V concentration in these collard plants was 7.34 mg kg^{-1}.

2.4.2 Vanadium uptake and translocation in plants

Higher plants do not accumulate V and concentration is the highest in the roots where it is thought to precipitate out as calcium vanadate (Cannon, 1963; Hempill, 1972; Lepp, 1977; Wallace *et al.*, 1977. According to Peterson and Girling (1981) this might be a mechanism that the plant developed to tolerate high V concentrations. Kaplan *et al.*, (1989) confirmed that V accumulates in the roots which place V in a group of metals that is immobile in plants. When vanadate is taken up by the plant and translocated to the cells, it is easily reduced to vanadyl (VO^{2+}) (Crans & Tracey, 1998).

Martin and Kaplan (1996) planted bush beans (*Phaseolus vulgaris* L.) to determine the plant availability of V. Vanadyl sulfate ($VOSO_4$) was used as the V source and the loading rate was 5.6 kg ha^{-1}, which is a fairly low loading rate ($\pm$ 2.15 mg kg^{-1}) if the bulk density is taken as 1300 kg m^3 and the soil depth of 20 cm. The roots contained the highest concentration of V, which correlate with other literature. While the concentration in the above ground parts were appreciably low. V plant availability was drastically reduced as time progressed and the concentration was negligible after 18 months.

Welch (1973) found that V is passively absorbed by barley roots. The uptake was highly pH dependant and had a linear relationship with the concentration of V. The highest uptake was at pH 4, constant between pH 5-8, with VO_3^- the dominant specie, and decreased to very low at pH 10.

2.4.3 Vanadium interaction with other nutrients

According to Rehder (1999) and Crans (1994), there is a structural analogy between vanadate ($H_2VO_4^-$) and phosphate ($H_2PO_4^-$) ions. The accumulation of V by plants may reduce the uptake of P, which plays an important physiological role. Welch

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(1973) found that the anion that produced the greatest inhibition of V uptake was $H_2PO_4^{2-}$, but this inhibition was only 27% less than the control. Little inhibition of V uptake by roots occurred with anions like MoO_4^{3-}, BO_3^-, Cl^-, SeO_4^{2-}, CrO_4^{2-} and NO_3^-. This shows that V uptake is not greatly affected by other anions.

There is also a possibility that vanadyl, being a cation, can interact with calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Olness *et al.* 2001). This might indicate that before there is V toxicity, vanadium might influence plant nutrition to some extent.

2.5 Guidelines for vanadium and the use of slag

The Russians stipulate that 150 mg kg^{-1} is the maximum total V concentration allowed in soil (Ghost, 1985), but they do not mention the method of analysis. Canadian soil quality guideline for the protection of environmental and human health stipulates an upper limit of a total V concentration of 130 mg kg^{-1} in soil used for agriculture (Canadian Council. 1997). In South Africa no guidelines exist considering V concentration in ameliorants or in the environment.

Slag falls in the same category as fertilizers under Act No 36 of 1947. Guidelines exist for maximum allowable concentrations for some heavy metals but not V. Criteria used to evaluate slag are the fineness of the slag, which determines the reactivity and the Mg and Ca content, which will class it into calcitic or dolemitic "lime".

One of the remedies for heavy metal pollution is to apply slag to increase the pH and this will reduce the availability of most heavy metals (Logan, 1992; Hooda *et al*, 1997; Chaney *et al*, 2001). The problem with V is that it becomes more mobile and plant available as the pH increases (Adriano, 1986).

2.6 Extraction methods and analyses

Mandiwana *et al.* (2005) stated that there is little work done to quantitatively separate between different species of V so they experimented with a few methods. Mandiwana & Panichev (2004) determined 5 fractions of V using a sequential fractionation

procedure (and V determination with atomic absorption spectrometer). Firstly the water soluble fraction of V (V) was determined by shaking 0.25 g of soil with 25 ml de-ionised water for 24 h. The second was the determination of V (V) extracted with carbonated water. The soil was also shaken with deionised water before bubbling CO_2 through the suspension. The third method was to determine the V (V) extracted with 0.1 M sodium bicarbonate (Na_2CO_3). The precipitates of this method where ashed and then digested with HF and H_2SO_4 to determine V (IV). The total amount of V was determined by digesting 0.25 g of soil with HF and $HClO_4$. Mandiwana & Panichev (2004) found V (V) is easily leached from the soil by carbonated water. They also found that 50.8% of V present in polluted soils near a V mine, containing 7160 mg V kg^{-1} soil, was V (V). In another speciation analysis Mandiwana et al. (2005) used PO_4^{3-} instead of Na_2CO_3 to determine the V (V) fraction in the soil. They concluded that $(NH_4)_2HPO_4$ and Na_3PO_4 are excellent leaching agents, like Na_2CO_3, and that the use of P fertilizers will potentially increase the mobility of V (V) in the soil.

CHAPTER 3: VADADIUM TOXICITY THRESHOLD LEVELS FOR MAIZE: A POT TRIAL

3.1 Introduction

Greenhouse pot trials are commonly employed to study the uptake of elements and their effects on plant growth at various concentrations. The plant availability of V from slag was an important aspect that needed assessment. While field trials and field monitoring can give an indication of actual phyto-availability, too many variables exist that can complicate results and conclusion obtained. At field scale, for example, it is difficult to apply slag uniformly over large areas. Factors that can further exacerbate spatial variability are application history of fertilizer or liming material that could have contained V and natural variability of soil properties that can influence V plant availability (mineralogy, pH, texture etc.). Furthermore, especially under dryland conditions, any stress the crops experience can potentially alter the uptake of V and the uptake of essential elements. At greenhouse level many of these variables can be controlled and V uptake by crops can be investigated under more controlled conditions.

Subjecting crops to incrementally higher application levels of V, toxicity threshold levels for both the plant and soil type can be established. By doing this, lower limits for reduced growth and upper toxicity limits can be established. This, in turn, can be compared to typical V loading rates when BOF slag is used and thus enabling some predictive capability on the long term use of V containing slag in agriculture based on current application rates. At high loading rates the toxic concentration levels, as well as the visual symptoms of toxicity can be established. An analogue exists between the chemistry of orthovanadate and orthophosphate (Rheder, 1999; Crans, 1994). It is therefore hypothesised that extractants used to assess plant available P can also be used to determine plant available V.

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3.2 Aims

The aims of this chapter were to:

1) Establish V threshold concentrations where the growth of maize (*Zea mays L.*) is visibly influence;

2) Evaluate the ability of two commonly used soil extractants in agriculture (Bray 1 and Ammonium acetate) to predict plant available V.

3.3 Materials and methods

3.3.1 Soils used in this study

Two contrasting soils where chosen according to specific soil characteristics. The Nooit (Nooit) soil was a Clovelly soil from the Nooit experimental farm near Ermelo, with a textural class of a loamy sand (12% clay). Quartz (57%) dominated the clay fraction of the Nooit soil and also contained of 20% Mica, 20% kaolinite, and 5% Goethite. The main soil selection criteria was P adsorption capacity, would be a function of above mentioned mineralogy, and the abundance of these minerals would also be reflected by the total Al, Fe and Mn content of the soil. The Nooit soil has lower concentrations of total Al, Fe and Mn content (table 3.1) compared to the PPS soil, which lead to a low P adsorption capacity and because of the expected analogy between P and V, a low V adsorption capacity.

TABLE 3.1. The total concentrations of some of the elements in the two soils determined by a XRF scan.

	Al mg kg^{-1}	Si mg kg^{-1}	Fe mg kg^{-1}	Mn mg kg^{-1}
Nooit	14000	22670	16590	140
PPS	29100	17060	40980	270

The PPS soil was a topsoil sample collected from a Hutton soil form. This soil was a sandy clay loam (25% clay). The clay fraction of PPS is dominated by kaolinite (65%) and also contains 25% mica, 6% hematite and 4% smectite. PPS was collected

at the Hatfield experimental farm. The PPS soil also had a higher total Fe and Mn concentrations compared to the Nooit soil and expected higher V sorption capacity.

3.3.2 Vanadium content of mono ammonium phosphate

In this study mono-ammonium phosphate (MAP) was used as the P fertiliser. A XRF scan revealed that MAP contained 0.005 % V (50 mg kg^{-1}) (Fig 3.1). This is a relative low value and the V loading through the use of MAP as P fertilizer was expected to be negligible.

3.3.3 Liming, fertilization and vanadium loading

The soils used in this study were limed to a target pH(H$_2$O) of 6.5. The amount of lime required to reach this pH was estimated by establishing liming requirements for each soil.

Air-dried Nooit and PPS soil was passed through a 5 mm sieve and was weighed of in 4 kg pots. Analytical grade CaCO$_3$ was used as the liming material in the V toxicity trial. The Nooit soil received 4.00 g CaCO$_3$ per pot which was equivalent to 2.60 tons ha^{-1} and the PPS soil 6.40 g CaCO$_3$ per pot which was equivalent to 4.14 tons ha^{-1}. The bulk density of the soil was assumed to be 1300 kg m^{-3} and the incorporation depth taken as 0.2 m.

The soils were placed in a concrete mixer and the CaCO$_3$ was added and mixed for 5 minutes. The soils where subjected to wetting and drying and after six weeks the target pH was reached. After the incubation to correct the pH the soils were air dried. V was added to two soils, Nooit and PPS, to determine the V concentration in the soil where plant growth is affected negatively. The soils were treated with various levels of V. Ammonium metavanadate (NH$_4$VO$_3$), a V salt, was used for the different V loading rates. The different V loading rates were 0, 15, 30, 60, 100 and 250 mg kg^{-1} V. The respective treatments were separately mixed for the second time with a concrete mixer and transferred back to the pots. The loading range proved to be critical V loading rates that affect the growth of certain plant species as found in the literature (Wang & Liu, 1999; Kaplan *et al.*, 1990).

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The soils were also fertilized with mono ammonium phosphate (MAP), ammonium sulphate $(NH_4)_2SO_4$ and potassium chloride (KCl). The MAP was mixed into the soil together with the NH_4VO_3. The $(NH_4)_2SO_4$ and KCl were dissolved in water and then added to the pots after planting. The lower V loading rates received less N because NH_4VO_3 was the V source, $(NH_4)_2SO_4$ was used to ensure all the treatments received the same amount of N. Each pot received the equivalent of; 180 kg ha^{-1} N, 70 kg ha^{-1} P and 140 kg ha^{-1} K at planting. Each treatment was replicated four times, which gave a total of 48 pots for the V toxicity trial.

3.3.4 Planting and harvesting the maize in the vanadium toxicity trail

Maize was used as the test crop. Five maize plants were planted in each pot and were reduced to two plants per pot after emergence. After 6 weeks of growth the maize plants were pot bound and whole maize plants (above ground matter) were harvested. After harvest the plants were washed with deionised water, air dried at 60 ^{o}C for two days and weighed. The maize plants where milled and passed through a sieve. Representative air-dried soil samples were taken from each pot and passed through a 2 mm sieve.

Therefore to obtain a better picture of V uptake by maize, root analyses were performed. However, root analysis is often fraud with difficulties. Soil is often embedded in the roots and it is difficult to remove all the soil and completely eliminate soil contamination. Furthermore, precipitates of calcium, ferric and aluminium vanadate are expected to be sparingly soluble in water. Any precipitates on outer surfaces of roots would be difficult to rinse off with deionised water.

The ideal would have been to sample the roots of all the treatments, this was a shortcoming of this study. Only the roots of the control treatment and the 250 V loading rate of both soils were sampled and analysed. The highest application level for the Nooit soil resulted in underdeveloped roots and in order to obtain enough material to perform analysis, a composite sample were prepared from the different replicates. This means that no statistical analyses were possible for the root data.

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3.3.5 Chemical analysis

The soil pH was determined by weighing 20 g of soil in glass beakers and 50 ml deionised water was added (1:2.5 basis). The suspension was stirred and left for 1 hour and the pH reading was taken with a glass electrode pH meter. The soil pH was taken to ensure that all the pots where at the same pH level.

Bray 1 (0.03 M NH_4F + 0.025 M HCl) was used as an extractant for extractable PO_4^{-3} and presumably also VO_3^{-1} and/or VO_4^{3-}. Bray extractable phosphate has shown to be a good extractant to assess plant available P. It was therefore used as an extractant for V because of the analogy between orthovanadate and orthoposphate chemistry (Rheder, 1999; Crans, 1994). Eight grams of soil was weighed into Schott bottles and 60 ml of Bray 1 was added. The suspension was shaken for 60 seconds by hand and a drop of super flock was added. The suspension was filtrated through a 2 μm Whatman filter paper and analysed using an axially viewed Inductively Coupled Plasma Atomic Emission Spectrometer (ICP – AES).

Ammonium acetate was used to extract K^+, Ca^{2+}, Mg^{2+} Na^+ and presumably VO_2^+. Ammonium acetate extractable cations represent the soluble and exchangeable fractions of the elements in the soil and are generally considered to represent the plant available forms. Five grams of soil was weighed off in Schott bottles and 50 ml of ammonium acetate was added. The suspension was shaken for 30 min on a reciprocal shaker. The suspension was filtrated through a 2 μm Whatman filter paper and was analysed using an axially viewed ICP – AES.

The soil and plant samples were digested with a $HClO_4$:$2HNO_3$ digestion (ALASA, 1998) to determine the total concentrations of certain elements. For the $HClO_4$:$2HNO_3$ 0.5 g of the plant and soil samples was weighed of in 100 ml glass tubes and then 5 ml of the $HClO_4$:$2HNO_3$ solution was added. The samples were digested at 230 ^{o}C on the digestion block and then diluted to 100 ml with deionised water. Afterwards, the samples were analysed for V using an axially viewed ICP-AES.

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The V content of the soils was determined by means of three methods. The first was a XRF scan which is a qualitative- semi-quantitative powder scan. The second was a HNO_3 digestion (EPA 3050). The V in solution was determined by means of inductively coupled plasma mass spectrometry (ICP-MS). The third method was a $HClO_4$:$2HNO_3$ digestion (ALASA, 1998). The V concentration was determined by means of ICP-MS.

3.3.6 Statistical analysis

The statistical program SAS was used for statistical analyses of the data generated. The Tukey test was used to determine treatment effects at a probability level of ά = 0.05.

3.4 Results and discussion

After six weeks of growth the maize plants were all pot bounded. It was therefore reasonable to expect that good exploitation of the soil volume in the pots occurred. It is important to evaluate V uptake at various V loading rates. This will enable the establishment of lower limits where reduced growth will occur and upper levels where toxicity occur. With this established, predictions can be made on cumulative long term loading of V through slag application and management strategies can be developed to ensure long term slag use in agriculture.

3.4.1 Background concentrations of vanadium in soils

The background V concentration in soils over the world varies greatly, from 0-400 mg kg^{-1}. The V concentration in the control treatments of the two soils used in the pot trials was 26.4 (+/- 1.07) mg kg^{-1} for the sandstone derived Nooit soil and 56.0 (+/- 10.5) mg kg^{-1} for the dolerite derived PPS soil, determined by $HClO_4$:$2HNO_3$ digestion (ALASA, 1998). These background values were relatively low compared to concentrations found in the literature (Kabata-Pendias & Pendias, 1993; Panichev *et al.* 2006). The PPS 250 and Nooit 250 are the V concentrations in the soils after the V loading of 250 mg kg^{-1} in the toxicity trial. The XRF scan showed the highest V

concentration of the three methods for total V concentration, and the $HClO_4:2HNO_3$ the lowest (Fig 3.1).
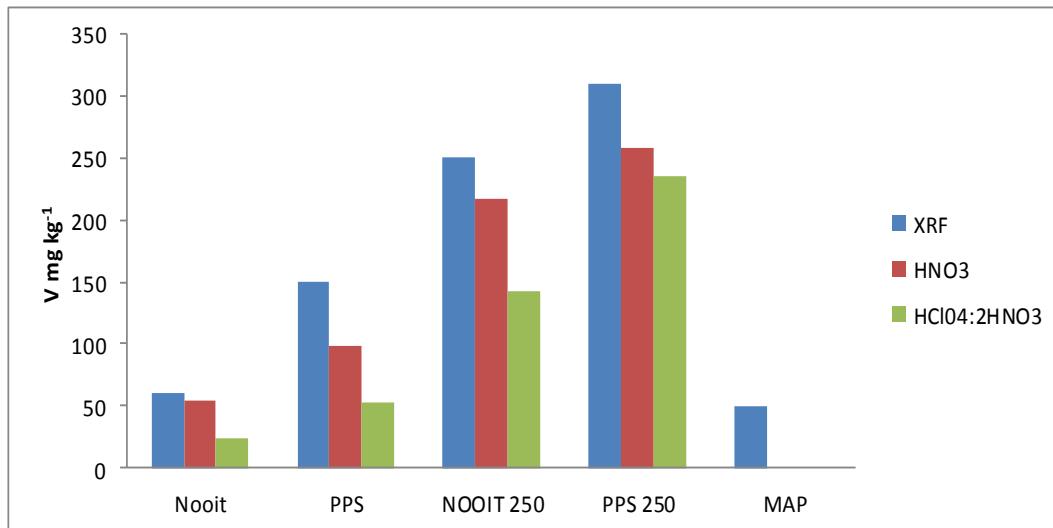
FIGURE 3.1 V concentrations in soils unamended with V compared to soils that received 250 mg kg^{-1} NH_4VO_3.

3.4.2 Effect of vanadium loading rates on dry matter yield

Fig 3.2 and Fig 3.3 illustrate the effect of high V concentrations on plant growth. In terms of loading rates, the Nooit soil showed reduced growth at the 100 mg kg^{-1} V (100 level) and stunted growth at the 250 mg kg^{-1} V loading rate (250 level) (Fig 3.2). According to Tukey's test, dry matter yield obtained from the 250 level was significantly lower than the other treatments. The 100 level was also significantly lower than the rest of the treatments except for the 60 mg kg^{-1} V loading rate. For the Nooit soil V loading rates greater than 60 mg kg^{-1} reduced biomass production and loading rates greater than 100 mg kg^{-1} was seemingly detrimental for plant growth. According to Kaplan *et al.* (1990) collards (*Brassica oleracea*) showed reduced biomass production at a V loading rate of 80 mg kg^{-1} in a 6 % clay soil. However Wang & Lui (1999) found that soya beans (*Glysine max*) showed reduced growth in a 20 % clay soil at a V loading rate of 30 mg kg^{-1}. This might be due to the fact that soya beans are more sensitive to V compared to other plants.

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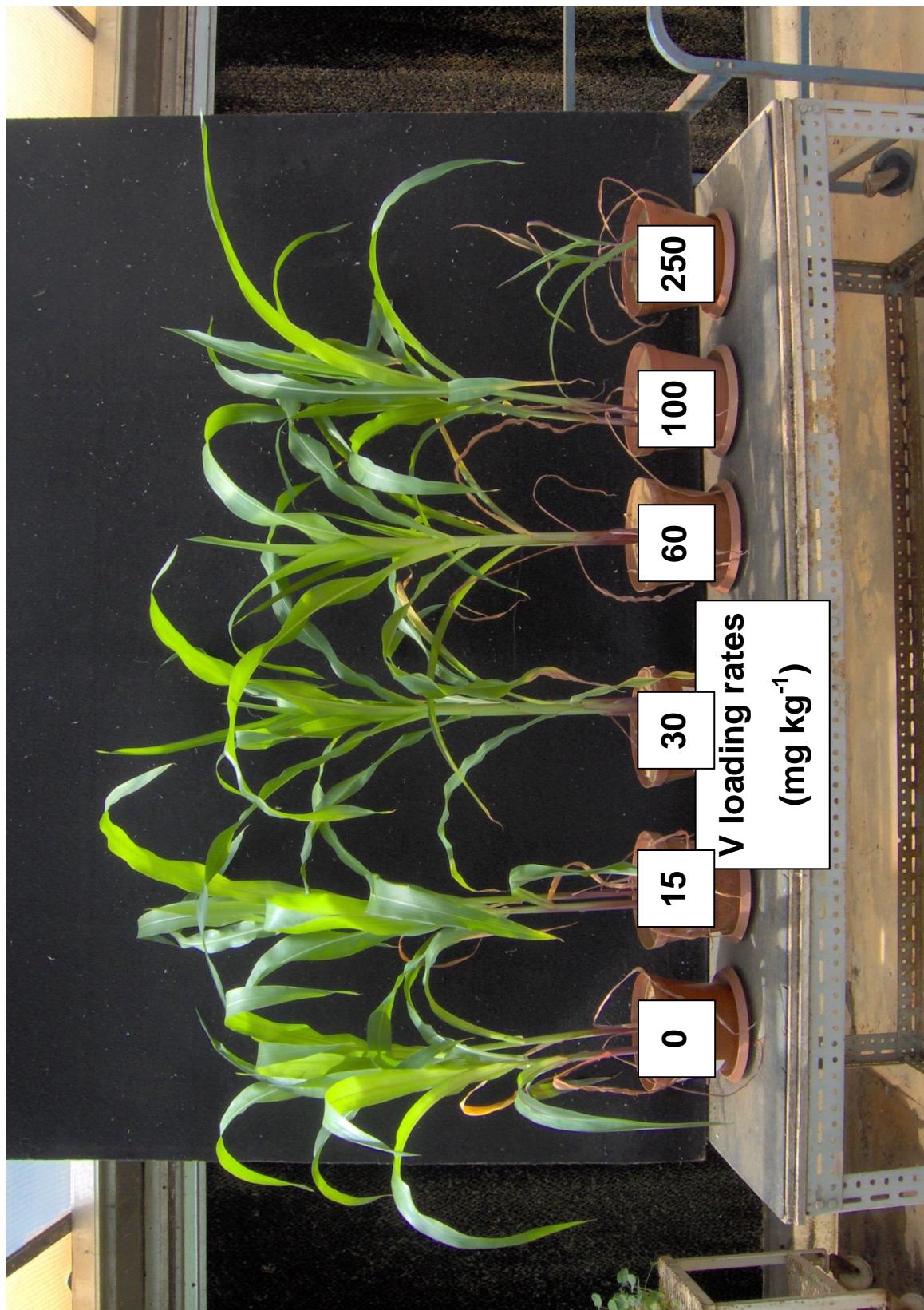
FIGURE 3.2 The effect of increasing V concentrations in on the growth of maize plants (Nooit soil).
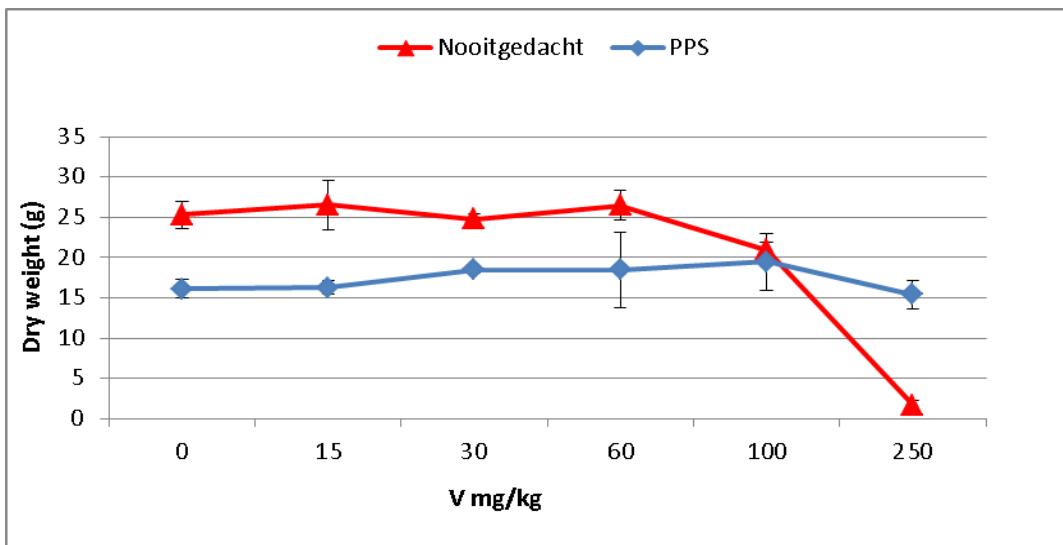
FIGURE 3.3 Aboveground biomass of maize plants (Dry mass) as affected by increased V loading rate.

Dry mass production did decrease for the PPS soil from a mean of 19.5 (+/- 3.49) grams per pot for the 100 level to about 15.4 (+/- 1.82) grams per pot for the 250 level but according to Tukey's test, this was not statistically significant at $\alpha = 0.05$.

There are a few reasons that can explain why the maize plants growing in the PPS soil did not show reduced growth or toxicity symptoms. Maize dry matter where not affected by the increasing V rates. The PPS was a dolerite derived soil with higher clay content than the Nooit soil. This suggests that the PPS most likely had a greater surface area available where V sorption could be facilitated compared to sandstone derived Nooit soil. The PPS soil also have a higher total concentration of Fe (40 980 mg kg^{-1}) compared to the Nooit soil (16 590 mg kg^{-1}). Ferric sesqui-oxides, for example, the ferric (oxy) hydroxides, goethite (α –FeOOH) and the ferric oxide hematite (α –Fe$_2$O$_3$) are known to almost irreversibly sorb phosphate and according to Sigg & Stumm (1980), vanadate sorption characterstics resembles that of phosphate. The PPS soil had 6% hematite while the Nooit soil only had 2% goethite. Vanadate is specifically sorbed and forms bi-nuclear bidentate innersphere complexes on goethite (Peacock & Sherman, 2006). It was therefore expected that the PPS soil would have a greater ability to attenuate V.

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3.4.3 Toxicity at total vanadium concentration in the soil and the plant

Table 3.2 summarise the values obtained through various V extractants (total V concentration and extractable V concentration) compared to V content in the plant material as well as dry mass production.

The average total V concentration at the 250 V loading rate in the Nooit soil was 150 (+/- 18.2) mg kg^{-1} and 14.8 (+/-1.24) mg kg^{-1} in the above ground plant tissue (dry mass) which is significantly different from the lower values. The V concentration in the lower loading rates is close to the detection limit and very low. This supports the fact that V is not tanslocated to the above ground parts of maize plants.

TABLE 3.2 A summary of the results from the V toxicity trail (total V concentrations, Bray 1 and ammonium acetate extractable).

Soil	V loading Rate	Total V soil	Total V Plant material (above ground mass)	V (Bray 1)	V (OAc)
			(mg kg^{-1})		
Nooit	0	26.4 (c)	0.18 (b)	0.12 (e)	0.00 (d)
	15	29.7 (c)	0.14 (b)	2.26 (de)	0.05 (d)
	30	37.4 (bc)	0.00 (b)	5.83 (d)	0.17 (d)
	60	48.0 (bc)	0.00 (b)	12.4 (c)	0.64 (c)
	100	73.3 (b)	0.00 (b)	23.5 (b)	1.68 (b)
	250	150 (a)	14.8 (c)	77.6 (a)	10.2 (a)
PPS	0	56.0 (c)	0.03 (b)	0.07 (c)	0.01 (c)
	15	62.1 (c)	0.05 (ab)	0.43 (c)	0.00 (c)
	30	64.8 (c)	0.07 (ab)	1.79 (c)	0.02 (c)
	60	79.4 (c)	0.14 (ab)	2.45 (c)	0.07 (c)
	100	112 (b)	0.10 (ab)	6.36 (b)	0.21 (b)
	250	235 (a)	0.50 (a)	30.2 (a)	1.69 (a)

- Total V soil – Pseudo total V concentration in the soil determined by the HClO$_4$:2HNO$_3$ digestion.
- Total V Plant (above ground) – V content in the plant determined by the HClO$_4$:2HNO$_3$ digestion.
- V (Bray 1) – Bray 1 extractable V determined by the Bray 1 extraction method
- V (AA) – Ammonium acetate extractable V determined by the ammonium acetate extraction method.
- (a) – Tukey's test for significant difference

The above ground plant tissue can be used to test for V toxicity. 14.8 mg kg^{-1} seems to be a threshold value for V in the above ground plant material of maize (Table 3.2).

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14.8 mg kg^{-1} might be a threshold value for maize but will differ for different plant species. According to Kaplan *et al.* (1990) collards (*Brassica oleracea*) showed reduced biomass production at a V loading rate of 80 mg kg^{-1} and had a total V concentration in the plant of 10.32 mg kg^{-1} and 11.80 mg kg^{-1} at a V loading rate of 100 mg kg^{-1}. Currently no basic guidelines on critical threshold levels exist in South Africa. This value can be used as the upper limit for V in above ground material for maize.

The pseudo total V concentration at the 250 V loading rate for the PPS soil was 235 (+/- 22.0) mg kg^{-1} and 0.50 (+/- 0.30) mg kg^{-1} in the above ground plant tissue (dry mass). The V levels in the above ground material for the 250 level in the PPS soil was far less than the V levels in the Nooit soil. This again indicates the low plant availability of V in the PPS soil which has a significant V fixing ability.

3.4.4 Toxicity symptoms

The V toxicity symptoms were stunted growth with sclerosis on the older leaves (Fig 3.4) and a small, underdeveloped root system. This correlates with the findings of Wang and Lui (1999), who described V toxicity in soya beans with stunted growth, yellow and withered foliage and small roots showing sign of senesces.

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FIGURE 3.4 A maize plant showing stunted growth at the highest V loading rate (250 mg kg^{-1}) in the Nooit soil after six weeks.

3.4.5 The extractability of vanadium; comparing Bray 1 and ammonium acetate

The Bray 1 extractable V for the Nooit soil at the 0 level was 0.12 (+/- 0.02) and increased to 23.5 (+/- 0.98) mg kg^{-1} at the 100 level and 77.6 (+/- 4.00) mg kg^{-1} at the 250 level. The Bray 1 extractable V for the PPS soil at the 0 V loading rate was 0.07 (+/- 0.04) mg/kg and increased to 30.2 (+/- 2.77) mg kg^{-1} at the 250 V loading rate. For the highest V application level, the Bray 1 extractable fraction represented 12.1 % of the total V. This shows that the Bray 1 extractable V increased as the V concentration in the soil increased (Fig 3.5).
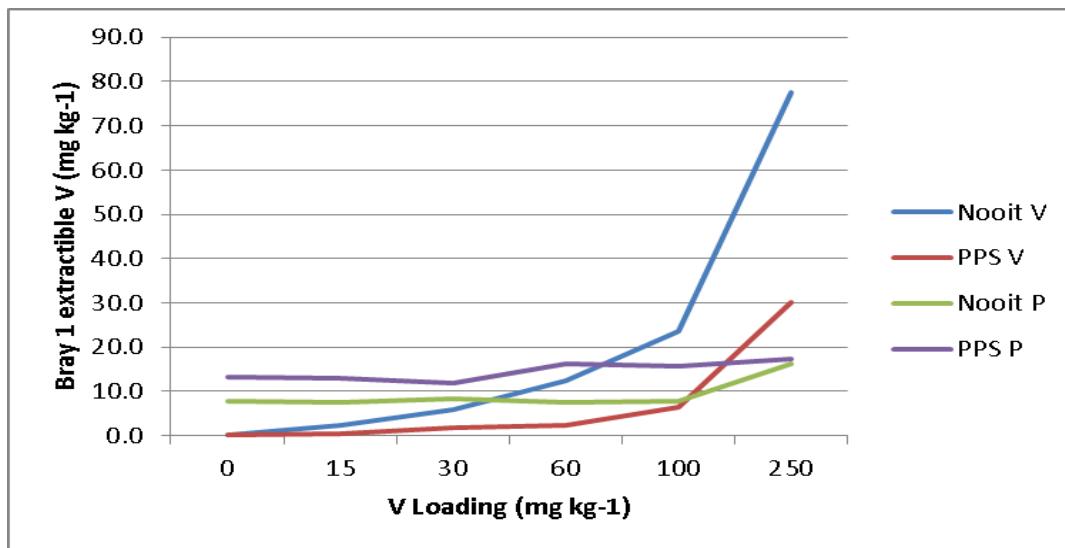
FIGURE 3.5 The Bray 1 extractable V and P as influenced by the increasing V loading rates.

It was suspected that the increased V concentration would have an effect on the Bray 1 extractable P. However, the Tukey test only showed a significant increase in the P extractability for the Nooit soil as the V loading rate increased. One of the reasons for the increase in V extractability might be due to exchange reaction between the two anions: orthovanadate ($H_2VO_4^-$) and orthophosphate ($H_2PO_4^-$) in the Nooit soil. The Bray 1 extractable P in the Nooit soil at the 0 V level was 5.93 (+/- 3.30) mg kg^{-1} and increased to 16.8 (+/- 3.33) mg kg^{-1} for the 250 V level, almost three times higher than the control. The Bray 1 extractable P for the PPS soil at the 0 V loading rate was 13.1 (+/- 1.26) mg kg^{-1} increased slightly to 17.3 (+/- 4.98) mg kg^{-1} at the 250 V level. This represented an increase of 32% but was not statistically significant. The lesser effect on Bray 1 extractability P in the case of the PPS could have been the result of less competition and enough surface area and sorption sites for both vanadate and phosphate.

The sandier Nooit soil probably had less sorption sites for vanadate and phosphate. This could have resulted in more competitive sorption between V and P. The ammonium acetate extractable V in the Nooit soil at the 0 level was 0 (+/- 0.02) mg kg^{-1} and 10.2 (+/- 0.41) mg kg^{-1} at the 250 level.

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The ammonium acetate extractable V at the 0 V loading rate for the PPS soil was 0.01 (+/- 0.01) mg kg^{-1} which is almost zero and the highest V concentration extracted with ammonium acetate for the PPS soil was 1.69 (+/- 0.12) mg kg^{-1} at the 250 V loading rate.

Ammonium acetate was in general a poorer extractant for V compared to Bray 1. NH$_4$OAc is a weaker extractant and is buffered at pH = 7. The acetate did not displace the vanadate. In these oxic soils it was suspected that the applied V (V) was not reduced to vanadyl. Bray 1 is a stronger extractant (pH = 3) and the F$^-$ could easily displace the sorbed V. Because of the suspected structural analogy between vanadate (H$_2$VO$_4^-$) and phosphate (H$_2$PO$_4^-$) ions (Rheder, 1999; Crans, 1994), Bray 1 might be more appropriate to use when testing for the extractability of V compared with ammonium acetate, which represents the cationic form of V (VO$_2^+$). A good extraction method to predict plant available V should not only correlate well with the plant availability of an element but must also be in range with the actual quantity taken up by the plant.

As discussed previously growth reduction occurred at the highest V application levels (100 and 250 mg kg^{-1}). The corresponding Bray 1 extractable V levels for the 100 and the 250 levels were 23.5 and 77.6 mg kg^{-1}, respectively. The data therefore suggested a Bray threshold level of 23.5 (< 24 mg kg^{-1} if rounded up) for sandstone derived soils which is arguable for the most common soils used for maize production on the Eastern Highveld. The results of the PPS soils, suggested that dolerite derived soils would sorb V, lowering vanadium's plant availability even at high V application levels.

3.4.6 Root analysis

The values obtained through the Bray 1 extraction method did not correlate well with the total V taken up by the plant. A possible explanation for this was that much of the V taken up by the plants was immobilised in the roots through the precipitate of, for example, calcium vanadate (Cannon, 1963; Hempill, 1972; Lepp, 1977; Wallace *et al*., 1977).

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The V content of the roots (dry mass) at the 0 V level for the Nooit soil was 4.51 mg kg^{-1} and the Bray 1 extractable V was 0.12 (+/- 0.09) mg kg^{-1}. The V concentration in the roots increased to 158 mg kg^{-1} for the 250 V level. The corresponding Bray 1 extractable V at this level was 77.6 (+/- 3.97) mg kg^{-1} which was about half of the V taken up by the maize roots. The total V concentration in the above ground plant material at the 250 level was 14.8 mg kg^{-1}.

In the PPS soil the V content in the roots at the 0 V level was 3.04 mg kg^{-1} which was similar to the V concentration in the roots in the Nooit soil. The Bray 1 extractability was 0.07 (+/- 0.04) mg kg^{-1}. The total V content of the roots in the PPS soil, at the 250 level, was 25.2 mg kg^{-1} which correlate better with the Bray 1 extractable V of 30.2 (+/- 2.77) mg kg^{-1} for this loading rate. The total V concentration in the above ground plant material was 0.5 mg kg^{-1}. This also showed that for the PPS soil, substantial V immobilisation occurred in the soil itself and the low V levels in above ground material was not only the result of poor translocation of V in the plant

3.4.7 Vanadium interaction with other nutrients

There are a few researchers that suggested that V might have an influence on the uptake of other nutrients. Vanadate might influence phosphate uptake, and vanadyl might influence cations like Ca and Mg (Rehder, 1999; Crans, 1994 & Welch, 1973).

An increase in K extractability was observed (Fig. 3.6), as the V concentration increased in the soil. The ammonium acetate extractable K in the Nooit soil, at the 0 V level, was 26.1 (+/- 4.12) mg kg^{-1} and increased to 44.0 (+/- 4.29) mg kg^{-1} for the 250 V loading rate. This represented an increase by 69%, which was statistically significant according to the Tukey's test ($\alpha = 0.05$).

The ammonium acetate extractable K in the PPS soil at the 0 V level was 23.2 (+/- 4.34) mg kg^{-1} and increased to 29.5 (+/- 6.42) mg kg^{-1} for the 250 V loading rate, which is a statistically insignificant increase of 27%.

The highest V treatment for the Nooit soil showed an ammonium acetate extractable V level of 10.2 mg kg^{-1}.
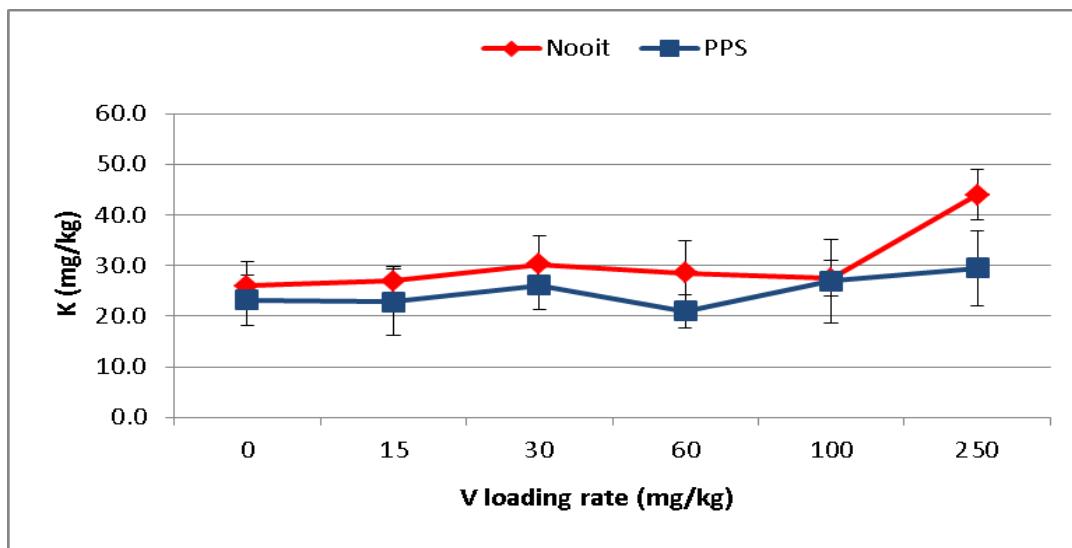
FIGURE 3.6 The ammonium acetate extractable K at different V loading rates.

The plant analysis did not show any increase in P and K levels for the highest V treatments. This was most likely because sufficient amounts of K and P were supplied to the plants. The plants would only have responded if they were stressed with respect to K and P. Under field conditions this might not manifest as theorised. The reason for this is that at these high levels of V, the maize plant experienced reduced growth and poorly developed roots, therefore, on a whole, the plant might not benefit from the greater availability of these nutrients. The poor root development will reduce the yield of maize plants.

3.5 Conclusion

The threshold value where maize showed reduced growth in the Nooit soil was at a total V concentration in the soil of 73.3 mg kg^{-1}. The Bray 1 extractable V concentration at this threshold was 23.5 mg kg^{-1} and there was no V in the above ground plant material in the maize. The ammonium acetate extractability at this level was 1.68 mg kg^{-1}.

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For the PPS soil the threshold value was observed at a total soil V concentration of 235 mg kg^{-1}. The Total V concentration in the plant was 0.5 mg kg^{-1} and the Bray 1 extractable V was 30.3 mg kg^{-1}. The ammonium acetate extractable V was 1.69 mg kg^{-1}. The V concentration in the roots for the 250 level was 158 mg kg^{-1} for the Nooit soil and 25.2 mg kg^{-1} for the PPS soil.

V availability is highly dependent on soil characteristics and differed between the two contrasting soils used in this study. The results indicated that the factors affecting P plant availability can possibly be extrapolated to V in typical oxic soil environments. It is reasonable to expect that soil properties known to influence P sorption, for example texture, clay mineralogy and the abundance of Fe (oxy) hydroxides, can be used to predict V plant availability and mobility. Soils with finer texture means that a larger surface area is available for V sorption that could facilitate V sorption compared to coarse textured soils. It is suspected that red soils derived from mafic igneous rock like dolerite, diabase, norite and basalt, with a relative high kaolinite clay fraction would all behave like the PPS soil and would have higher V sorption capacities. Fine textured soils with red apedal B horizons like Hutton and Shortland soil forms will have a higher V tolerance.

No significant reduction in growth or any V toxicity was induced in the high P fixing PPS soil. This dolerite derived soil exhibited relatively low V plant availability compared to the Nooit soil even at the highest V loading. Clear threshold levels were established for the sandstone derived Nooit soil. The maize grown in Nooit soil showed reduced growth at a V loading rate of 100 mg kg^{-1} and showed toxicity symptoms (stunted growth and sclerosis on older leaves) at a V loading rate of 250 mg kg^{-1}. Based on these results sandstone (coarse textured) derived soil will exhibit a higher V plant availability than a dolerite (fine textured) derived soil with higher concentrations of Fe.

In terms of V content of above ground material, levels greater than 10 mg kg^{-1} severely influenced the growth of maize plants. The pot trial also indicated that Bray 1 levels of higher than 23.5 mg kg^{-1} negatively impacted plant growth. Therefore,

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Bray 1 can be used as an extractant to predict V plant availability and possible V toxicity.

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CHAPTER 4: PHYTO-AVAILABILITY OF VANADIUM FROM BASIC OXYGEN FURNACE SLAG USED IN AGRICULTURE

4.1 Introduction

Soils acidify on the Eastern Highveld. BOF slag is used to rectify acidification. The reason is that most of the BOF slag is generated at steel plants much closer than natural lime sources, rendering it more economically viable as transport costs keep on escalating. Although these BOF slag has the same neutralizing capabilities compared to natural lime source, it contains more impurities like heavy metals, depending on the steel plant proses. Some of these slags contained various concentrations of different heavy metals. This study focused on slag containing different concentrations of V.

It seems that higher plants like maize are not likely not accumulate V under natural conditions (low V concentration) in the above ground parts as seen in the toxicity pot trial (chapter 3). Usually the V concentration is the highest in the roots where it is thought to precipitate out possible as calcium vanadate (Cannon, (1963), Hempill, (1972), Lepp, (1977), Wallace *et al*., (1977)) Kaplan *et el*., (1989) place V in a group of metals that is immobile in plants, V is taken up and accumulates in the roots, but minimum translocation to other plant parts take place. Higher V concentrations reduced plant growth and had a negative effect on the dry matter of maize. It is therefore important to determine the V loading rate through different liming rates.

The field evaluation was done to investigate actual V loading under normal agricultural practises and to determine the distribution and variation of V under field conditions and to see if there was any translocation to the different above ground plant parts. The fields chosen had a six year liming history with a V containing slag. One

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field was located near Delmas (S 26 09.612 E 28 44.903) (Appendix A, Fig A1) and the other near Ogies (S26 03.332 E 29 06.934) (Appendix A, Fig A2), both located on the Eastern Highveld.

As already mentioned slag is used as an alternative liming material, because it is the closest liming material source for farmers on the Highveld, making it cheaper due to lower transport cost. The toxicity of V is however a reality and if these concentration of V are reached in soil, as determined in chapter 3, the consequences are fatal. It is therefore important to study the V loading through liming with a V containing slag.

4.2 Aims

The aim of the slag pot trial was to determine the plant availability of V from slag under realistic agronomical slag application rates. The aim for the field monitoring was to determine the plant availability of V under field conditions and to determine the translocation of V in mature maize plants.

4.3 Materials and methods

4.3.1 Slag trial

Three slag where used in the slag pot trial. The four liming material was analytical grade $CaCO_3$. Slag A was a V rich basic oxygen furnace (BOF) slag and has the highest V concentration and is commercially, slag B was a stainless steel plant slag, with an intermediate V concentration. Slag C was a steel plant slag with a low V concentration. The V content of the three slags used in this study was also determined with the same three methods used for the soils. Slag A had the highest V concentration followed by slag B and then C (Fig 4.1). The HNO_3 acid digestion and XRF scan methods showed higher V concentration than the $HClO_4$:HNO_3 acid digestion.
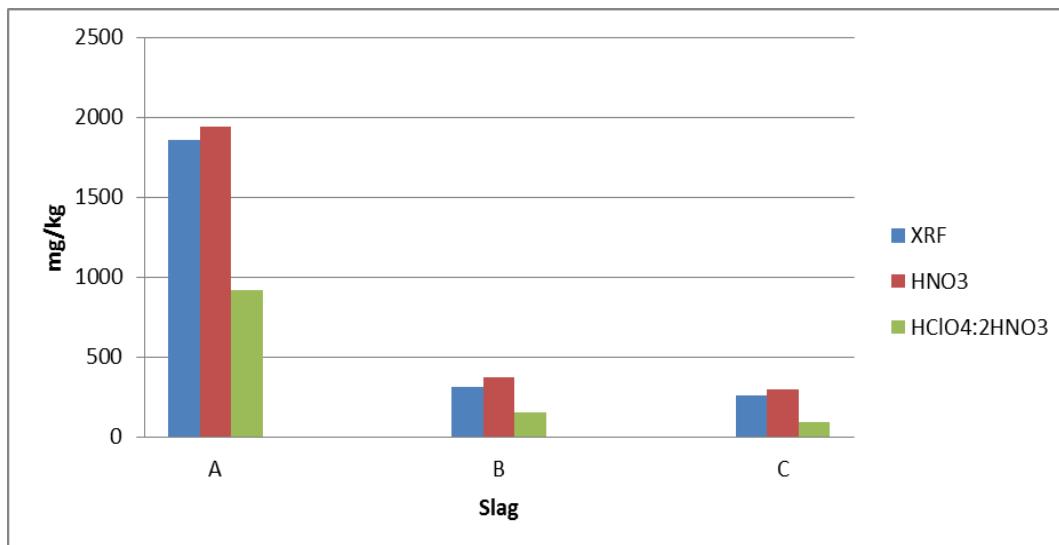
FIGURE 4.1. The V concentrations of the three slags as determined by various methods.

Fig 4.2. shows the concentrations of V, relative to Cr and Ni (as determined by a XRF scan and a $HClO_4:2HNO_3$ acid digestion). Slag A contained the most V and low levels of Cr. Slag C, on the other hand, contained the most Cr .
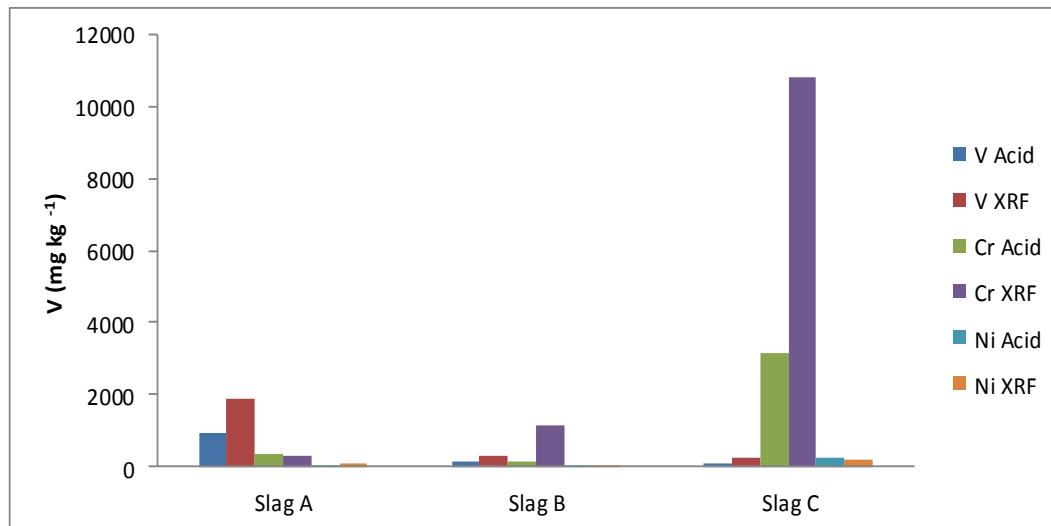
FIGURE 4.2. The vanadium, chromium and nickel content of the three slags used as determined by XRF and $HClO_4:2HNO_3$ acid digestion.

The Calcium carbonate equivalent (CCE) values were determined for the slags using the Soil Suspension Method (Bornman 1985). This was to predict the reactivity of the

slag and to apply the correct quantity of the slag to reach the specific target pH values. 50 mg of liming material was added to 50 g of soil. 125 ml of deionised water was added and the soil suspension was stirred and left to equilibrate over 24 hours. The soil suspension was stirred thoroughly before the pH reading was taken. The CCE-RS value relative to analytical grade $CaCO_3$ was determined as follows:

$$\frac{\Delta pH\ (slag)}{\Delta pH\ (CaCO3)} \times 100$$

Table 4.1 summarise the CCE-RS values for the three slags in the Nooit and PPS soils. Slag C had the highest CCE-RS values so less quantities of this slag is necessary to obtain a certain pH compared to the other slag. Slag A had the lowest CCE-RS and has the lowest acid neutralising ability, thus a larger quantity of slag A is necessary to obtain the desired pH.

TABLE 4.1. The calcium carbonate equivalent (CCE) values for the three slags in the two soils

	CCE values %	
	Nooit	**PPS**
Slag A	44	54
Slag B	59	60
Slag C	68	75

Fig 4.3 shows the pH values obtained after liming in the Nooit and PPS soils with the different liming materials in the slag pot trial (Chapter 4). The different target pH values was chosen to accomplish 4 different application rates (Target pH 4, 6, 6.5 & 7).The Nooit soil target pH of 4 could not be reached because the Nooit soils initial pH was 4.7. The pH of the Nooit soil limed with analytical grade $CaCO_3$ was about 0.5 a unit below the target pH value and about 1 unit below the target pH in the PPS soil. This shows a slight error in the buffer curve measurement where $Ca(OH)_2$ was used and which is a stronger base compared to $CaCO_3$. The pH values obtained with Slag A was near the target pH value in the Nooit soil but not in the PPS soil. This can also be attributed to the error with the buffer curve. The pH of the soils limed with

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slag B and C correlated well with the target pH values. Taking into account the error with the buffer curve, then the actual CCE values were slightly higher for slag B and C than initially estimated.
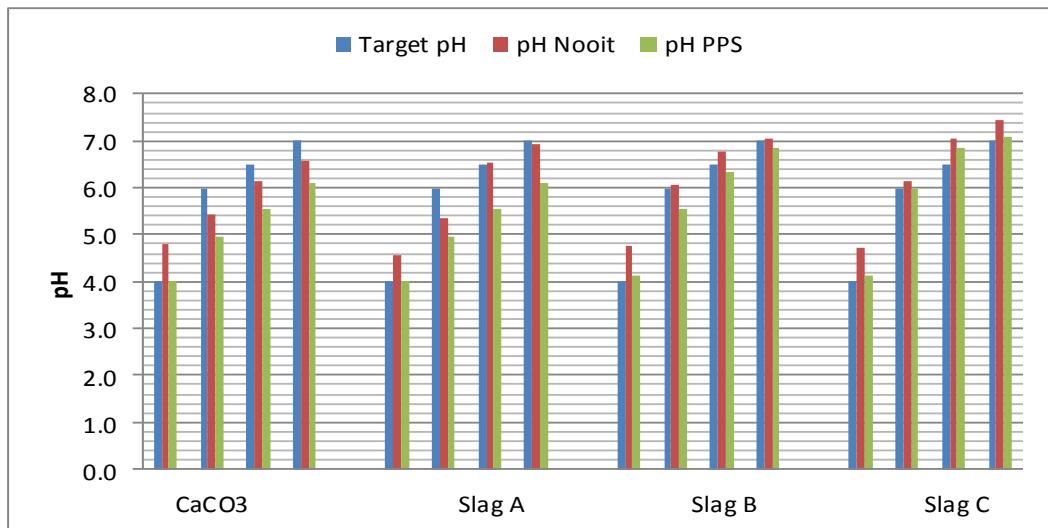
FIGURE 4.3. The pH values of the soil solution after the two soils were limed with the various liming material.

A greenhouse pot trial and field monitoring were used to gain better understanding of V release and V plant availability in soils amended with V containing slag. It was also done to determine the short term risk posed by the use of slag under natural conditions and to determine the actual V field loading rate through slag application. The V loading rates used in the pot trial and at the field evaluation site are typical of a six year liming period on the Eastern Highveld, which will represent short term reactions in the soil and relatively low cumulative V loading rates. With the V loading rate calculated, one can make predictions on the sustainability on the use of V containing slag as a liming material.

The V status of the soil at the field monitoring sites and the slag pot trial will be investigated on hand with parameters, generated from the V toxicity pot trial. These parameters are; total V concentration in the soil and in the maize plant and Bray 1 and ammonium acetate extractable V.

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The two soils for the slag trial were the same than that used in Chapter 3 (toxicity pot trial), (Nooit and PPS). The soils chosen, represented typical soil conditions that requires liming. The soil properties are reported in Chapter 3. The slag trial had 4 pH target levels; 4.0, 6.0, 6.5 and 7.0. These different target pH levels resulted in four liming rates simulating a low to high liming rate for one season. Four different liming materials were used according to the difference in V concentrations; slag A, B and C and $CaCO_3$. These slags are commonly used as liming materials by farmers on the Eastern Highveld. Analytical grade $CaCO_3$ was the fourth liming material and was used for the control, containing no V.

Buffer curves for both soils were determined, using the addition of saturated $Ca(OH)_2$ solution to 50 g of soil with a solution ratio of 1:1. The solution was left to equilibrate for 24 hours, after which the pH was determined. The concentration of the saturated $Ca(OH)_2$ solution was determined by titrating with a 0.01M HCl solution. The moles of $Ca(OH)_2$ needed per mass of soil to reach this target pH were then converted to an equivalent amount of pure $CaCO_3$, by multiplying it to the molar mass of $CaCO_3$, taking into consideration account the difference in molecular weight between the hydroxyl and carbonate groups.

The Nooit and PPS soils were passed through a 5 mm sieve and placed in 4kg pots. The different liming materials were weighed, together with the P fertilizer in the form of MAP. A summary of the quantities of the lime added to each pot is given in Table 4.2. The four replications were mixed together in a concrete mixer for 5 min to ensure that the soil and the liming materials were mixed thoroughly. The pots were filled with 4 kg of soil. There were three wet and dry cycles over a six week period to ensure enough reaction time for the liming materials and to ensure that the target pH values were reached. Two maize plants was plant in every pot. The maize plants received the same fertiliser and were sampled like the maize in the toxicity pot trail (Chapter 3). The maize plants were harvested after six weeks of growth, and the above ground plant material was dried and sampled according the different treatments.

TABLE 4.2. The liming rates for the different soils and the different liming materials

Soil	Liming mat. (CCE)	Target pH	g/pot	ton/ha	pH after liming
Nooit	**CaCO3**	4.00	0.00	0.00	4.8
		6.00	2.60	1.69	5.4
		6.50	4.00	2.60	6.1
		7.00	4.60	2.99	6.6
	Slag A (0.44)	4.00	0.00	0.00	4.6
		6.00	5.91	3.84	5.3
		6.50	9.09	5.91	6.5
		7.00	10.45	6.80	6.9
	Slag B (0.59)	4.00	0.00	0.00	4.8
		6.00	4.41	2.86	6.1
		6.50	6.78	4.41	6.8
		7.00	7.80	5.07	7.0
	Slag C (0.68)	4.00	0.00	0.00	4.7
		6.00	3.82	2.49	6.2
		6.50	5.88	3.82	7.0
		7.00	6.76	4.40	7.4
PPS	**CaCO3**	4.00	0.00	0.00	4.0
		6.00	4.40	2.86	5.5
		6.50	6.40	4.16	5.5
		7.00	8.00	5.20	6.1
	Slag A (0.54)	4.00	0.00	0.00	4.0
		6.00	8.15	5.30	5.0
		6.50	11.85	7.70	5.5
		7.00	14.81	9.63	6.1
	Slag B (0.6)	4.00	0.00	0.00	4.1
		6.00	7.33	4.77	5.5
		6.50	10.67	6.93	6.3
		7.00	13.33	8.67	6.8
	Slag C (0.75)	4.00	0.00	0.00	4.1
		6.00	5.87	3.81	6.0
		6.50	8.53	5.55	6.9
		7.00	10.67	6.93	7.1

4.3.2 Field evaluation

Two sites were identified; a 20 ha field under irrigation near Delmas ("Delmas site") and 40 ha under dry land production near Ogies ("Ogies site"). These sites were chosen to investigate the mobility of V, under irrigation compared to dry land maize production. The soils at the Delmas site consisted of deep (> 1.2 m deep) Hutton and

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Clovelly soil forms. The Ogies soils consisted mainly of deep Clovelly soil forms. The soil texture at these sites range from sandy to sandy loam soils (9 - 18% clay). The texture of the soils from these sites was similar than that of the Nooit soil used in the pot trials.

Samples were taken on a 100 m grid, which means one sample per hectare. These sites were chosen because they were limed with Slag A which had the highest total V concentration (918 mg kg^{-1}). According to the agronomists that advised the farmers these two sites had a six year liming history, and each received about 6 tons of slag A over this period, 3 tons/ha every third year.

Soil and plant samples were taken six weeks (42 days) after emergence and 17 weeks (120 days) after emergence. The samples were taken on a 100 m grid which was logged as waypoints using the Global Positioning System (GPS) so that the second sampling could be done near the point from the first sampling. The samples taken after six weeks were to compare the field evaluation site's result with the pot trial's results. The second sampling was done to determine the V translocation in the mature maize plant.

With the 120 days sampling, the different plant parts, the cob, upper leaves and lower leaves, were cut with a pruning shear and sampled separately. The soil samples were collected at two depth intervals, 0–30cm and 30–60 cm with a Johnson soil auger, to determine the concentration of V in different horizons and to investigate if there was any accumulation or removal of V at these two soil depths. Soil samples were also taken from natural soils nearest to the fields. These natural soils did not receive any slag at all, and served as the control samples. Samples marked K1 – K4 is the control waypoints of the Ogies site and samples K5 – K7 was the control samples for the Delmas site, as seen on the two Google Earth Maps (Appendix A1 & A2).

The plant samples were washed and then oven dried at 60 °C for two days and sieved. The soils samples were air dried and passed through a 2 mm sieve.

4.3.3 Soil and plant analysis

The soil and plant analysis performed for the slag pot trial and field evaluation were the same as in chapter 3.

4.3.4 Statistical analysis

The statistical program SAS was used for statistical analyses of the data generated from the aglime pot trial. The Tukey test was used to determine significant difference at a significance level of $\alpha = 0.05$ between the different treatments. Means with the same letter are not significantly different. Population statistics was done on the field samples using Microsoft Excel. The frequency distribution and cumulative normal distribution curves were drawn for the different data sets. A one-tailed T test with unequal variance was used to determine whether the control samples outside the field were significantly lower than the soil samples inside the field.

4.4 Results and discussion

4.4.1 Biomass production of maize as influenced by soil acidity and liming

The importance of liming was illustrated in the liming pot trail. Both the controls of the Nooit and PPS soil received no lime and had very low pH values. The Nooit soil control had a $pH(H_2O)$ of 4.7, however, it showed no reduced growth compared to the other pots, which received lime and slag (data not shown). Tukey's test also showed no significant difference in the above ground dry mass of maize plants growing in soils with different pH values in the Nooit soil, which had low exchangeable acidity.

In the case of the PPS soil, a Tukey's test showed a significant difference between the dry mass of maize plants that was limed and maize plants that received no liming material (Fig. 4.4). The maize plants growing in the PPS soil which received no liming material, showed reduced and stunted growth as a result of an under developed root system, although it received the same amount of fertilizer and water as the other treatments. This is probably due to the fact that the pH (H_2O) of 4 is very low and the exchangeable acidity was higher compared to the exchangeable acidity of the Nooit

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soil. At pH 4(H_2O) Al is more soluble and can lead to Al toxicities or deficiencies of P, Ca, Mg, K, S, and Mo (Ceballos *et al.*, 1995; Zeigler *et al.*, 1995). As the pH increased, the maize growth was normal.
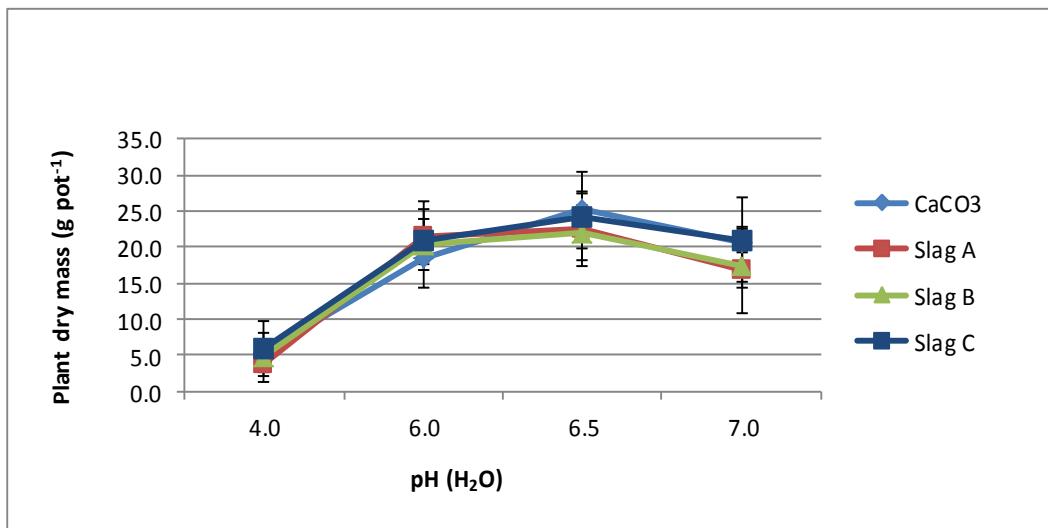

FIGURE 4.4 The dry mass of the maize plants (above ground biomass) grown in the PPS soil at the various target pH levels achieved with different liming rates.

4.4.2 Estimating vanadium loading rates for the slag pot trail

There are various factors that influence the V loading rates of soils through liming. The factors include; V content of slag, slag reactivity, which in turn will influence quantity of slag added to ameliorate soil acidity, and the incorporation depth in the soil. It is also difficult to apply liming material homogeneously over a field, as wind direction and particle size of the liming material play a huge role. A soil depth of 20 cm for slag incorporation was used in this study for all the calculations. This is a more realistic incorporation depth, because slag are more commonly incorporated and mixed in the soil with a disc harrow which have an average incorporation depth of 20 cm.

Van der Waals & Claassens (unpublished report) made an estimate of the V loading through slag application based on a V content of 1500 mg kg^{-1} slag. According to these authors, V concentration in the soil after 100 years would be 50 mg kg^{-1} if V

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background levels were negligible and the slag applied at 1.5 tons/ha/year. Other assumptions were an incorporation depth of 30 cm and bulk density of 1500 kg m^3.

Slag A originated from the same steel plant than that used by Van der Waals & Claassens, however, this time around the V content was lower. The total V concentration for slag A, B and C was 918 (+/- 116), 153 (+/- 50.56) and 88.6 (+/- 9.10) mg kg^{-1} respectively. Based on this V content the V loading rates for slag A, B and were calculated at 0.35, 0.06 and 0.03 mg kg^{-1} year^{-1} respectively (Table 4.2). This was based on an incorporation depth of 0.2 m and a bulk density of 1300 kg m^{-3} and assuming no V losses occur through erosion or leaching. Table 4.2 summarises the theoretical long term accumulation of V if this yearly loading rate is consistently applied and the V content of the slags stays constant. A slag incorporation depth of 20 and 30 cm were taken to establish an upper and lower limited to allow for the variability that can occur because of different means of incorporation. As mentioned previously 20 cm represent the average depth for disc harrow while 30 cm can be viewed as a limit for conventional (mouldboard) ploughing. In chapter 3 the threshold V concentration where maize exhibited reduced growth was determined at 100 mg kg^{-1} for the sandier Nooit soil. This threshold value was used as a reference to estimate the years it will take to reach critical V level. The Nooit soil is a sandstone derived soil, commonly cultivated on the Highveld. While the dolerite derived soils like the PPS soil occurs as dyke intrusions and is less common on the Eastern Highveld.

Depending on the incorporation depth it was estimated that it would take between 189 – 283 years to reach the V threshold value of 100 mg kg^{-1} where the growth of maize is influenced negatively. It would take an estimated 470 -700 years to reach the 250 mg kg^{-1} level for the PPS soil, if all of the parameters that influence V accumulation are kept constant as assessed in this study. The Russian guideline stipulate a total V concentration of 150 mg kg^{-1} and the Canadian threshold V concentration is 130 mg kg^{-1} but the type of soil or crop are not mentioned in these guidelines. It would take 343 years to reach the Canadian V threshold concentration and 428 years for the suggested Russian V concentration. As time progress, it is possible that V could transform to more stable forms on mineral surfaces, rendering it unavailable for plants. This could increase the years that V containing liming material could be used

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before the critical V levels are reached. Further research is necessary to study the long term availability of V in the soil applied through slag application.

Slag B and C contained lower V compared to slag A, and had lower V accumulation rates (Table 4.3.) The safe period for these slags in respect with V is much longer but other heavy metal concentrations must also be kept in mind. Slag containing lower V concentrations must be used on V sensitive soils like the Nooit soil as an alternative liming material.

TABLE 4.3 The predicted V accumulation rates and the years to reach the V threshold level for the sandstone derived Nooit soil (100 mg kg^{-1}) and Canadian regulatory level (130 mg kg^{-1}) for various incorporation depths and at agronomic slag application rates

Slag	V content of slag	V loading per year (mg kg^{-1} a^{-1})[#]		Years to reach:			
				100 mg kg^{-1}		130 mg kg^{-1}	
	mg kg^{-1}	Incorporation depth					
		20 cm	30 cm	20 cm	30 cm	20 cm	30 cm
Slag A	919	0.35	0.24	189	283	246	368
Slag B	154	0.06	0.04	1127	1690	1465	2197
Slag C	88.6	0.03	0.02	1956	2934	2543	3814

Based on an annual application rate of 2 ton ha^{-1}

Total V analysis was done on the slag amended soils with the aim to corroborate the calculated V loading rates. However, the liming rates and subsequent V loading rates were too low to establish measurable differences between the control and slag treatments (Figures 4.5 & 4.6). A Tukey's test showed no significant difference between the total V concentration ($HClO_4$:$2HNO_3$ digestion) of the $CaCO_3$ and slag treatments for both soils (ALASA, 1998).

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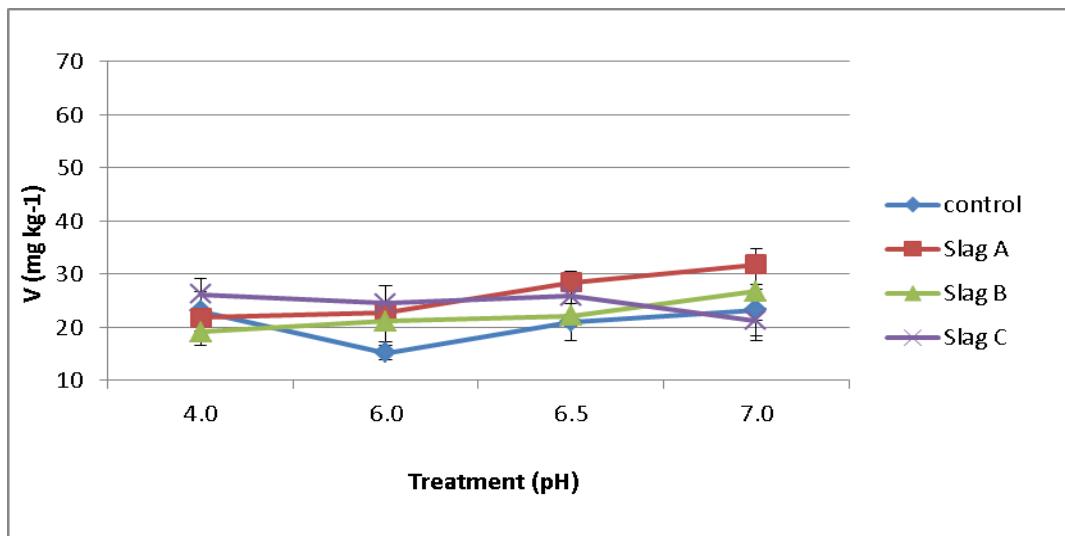
FIGURE 4.5 The total V concentrations in the Nooit soil after the different liming treatments.
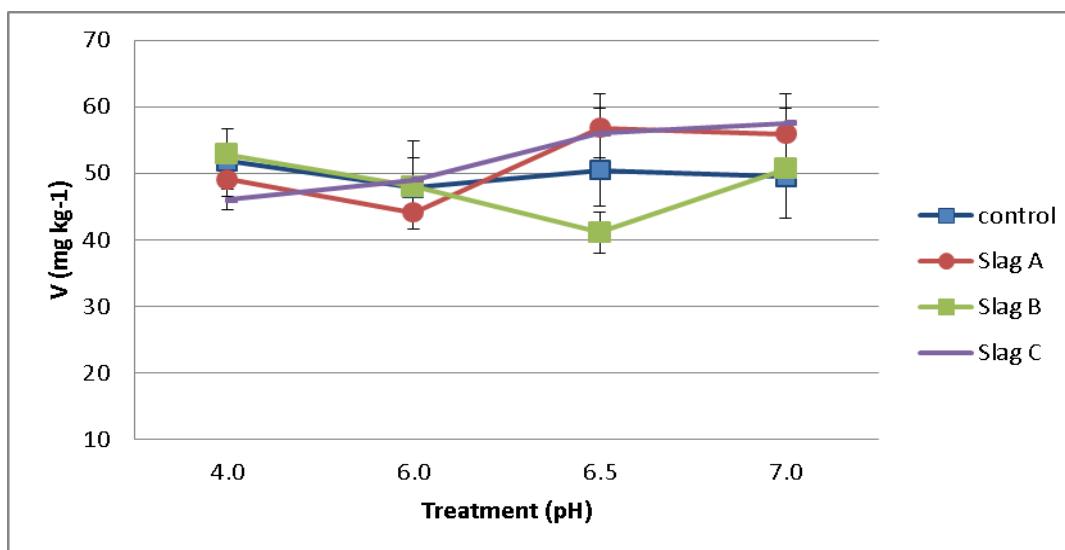

FIGURE 4.6 The total V concentrations in the PPS soil after the different liming treatments.

4.4.3 Vanadium plant availability and plant uptake for the slag pot trial

According to literature and the V toxicity trail, the V concentrations in above ground plant parts are very low under normal V concentration in soils. Vanadium is immobilised in the roots, or precipitate on the root surface (Cannon, 1963; Hempill, 1972; Lepp, 1977; Wallace *et al*., 1977).

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The threshold V concentration in the above ground dry mass of maize plants was determined in the V toxicity trial to be 14.8 mg kg^{-1} (Chapter 3). In the slag pot trial the highest V concentration in the above ground mass of the maize plants was 0.21 mg kg^{-1}, with all the other treatments lower than 0.21 mg kg^{-1}. This shows that V is not translocated and does not accumulate in the above ground plant part of the maize plant under low V loading rates.

4.4.4 Vanadium translocation in the maize plant in the pot trail

Plants did not reach maturity in the pot trial, therefore, to study the translocation of V in the plant, mature plants were sampled, where different plant parts were sampled separately under field conditions. A total of eight mature maize plants were sampled at each site. The different plant parts collected were; leaves and stem underneath the cob, the cob, and leaves and stem above the cob. The plant analyses from the slag pot trial and the first field evaluation sampling showed that V isn't readily taken up by the maize plant. So only some of the samples were taken for the second field evaluation to test this hypothesis.

4.4.5 Influence of vanadium loading through slag application on its Bray 1 extractability of vanadium in the pot trail

In the slag pot trial vanadium's Bray 1 extractability increased as the quantity of Slag A increased, in both soils (Red line Fig. 4.7 & 4.8). The control and other slag treatments did not show an increase in Bray 1 extractable V due to an increase in slag application rate. The Bray 1 extractable V at the 0 treatment in the Nooit soil was 0.28 (+/- 0.07) mg kg^{-1} and 1.55 (+/- 0.06) mg kg^{-1} at the pH 7 treatment, a 453 % increase. In the PPS soil the Bray 1 extractable V at the 0 treatment was 0.13 (+/- 0.04) mg kg^{-1} and 0.65 (+/- 0.05) at the pH 7 treatment, a 400 % increase. This means that if more slag A is applied, the Bray 1 extractability of V increases.
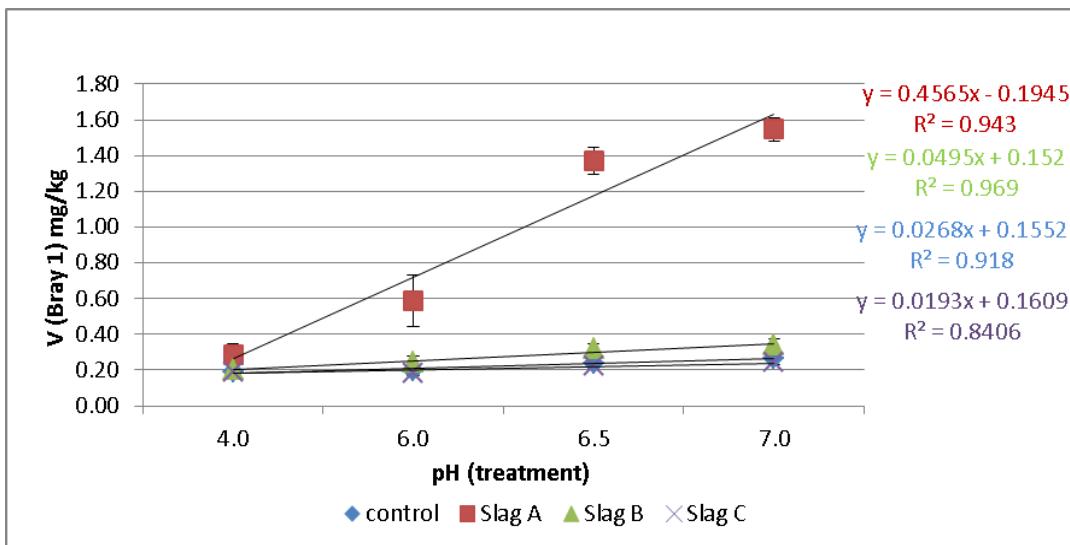
FIGURE 4.7 The Bray 1 extractable V in the Nooit soil as influenced by the different lime treatments.
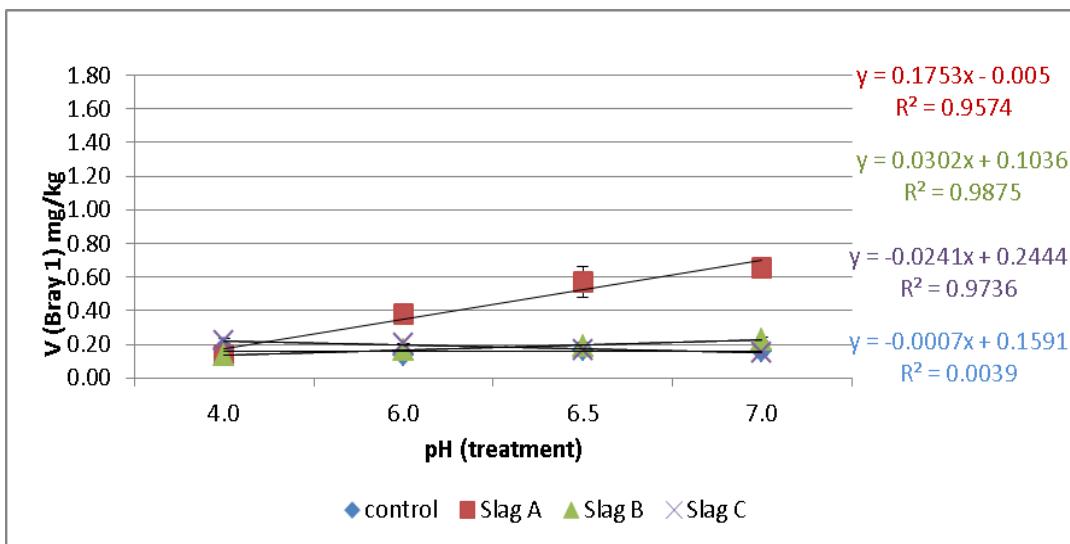

FIGURE 4.8 The Bray 1 extractable V in the PPS soil as influenced by the different lime treatments.

4.4.6 Influence of vanadium loading through slag application on its ammonium acetate extractability in the pot trail

The ammonium acetate extractable V in both soils was about 0.18 mg kg^{-1} for all the treatment levels, which indicate that the dominant available fraction of V in the slag is

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vanadate or that the V in slag is oxidised to vanadate in a well-drained soil or that ammonium acetate is a poor V extractant.

4.4.7 Estimating vanadium loading rates for the field evaluation sites

The background V concentrations of the Ogies and Delmas control samples (8.4 & 19.1 mg kg^{-1}) were lower than the Nooit (26.4 mg kg^{-1}) and PPS (49.9 mg kg^{-1}) soils. These values were also relatively low compared to the natural V concentrations for soils found in the literature, which ranges between 10 mg kg^{-1} and 220 mg kg^{-1} (Kabata-Pendias & Pendias, 1993; Panichev *et al.* 2006). The theoretical increase of V over the six year period with slag A should have been 2.1 mg kg^{-1}. The variation for the top 30 cm at the Delmas site, as shown in the frequency distribution graph (Fig 4.9), however, was too high and it was impossible to detect any increase in V.
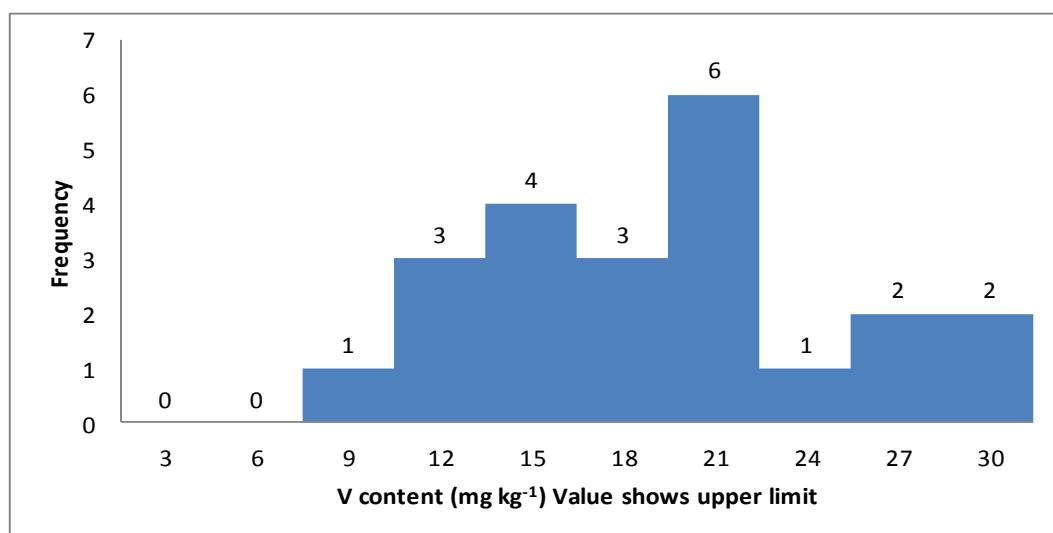

FIGURE 4.9 The frequency distribution for the total V concentrations of the 0-30 cm soil samples at the Delmas site, (control samples omitted)

The 95 % confidence interval for a normal distribution population of total V concentration ranged from 10.1 to 31.4 mg kg^{-1} for the top 30 cm at the Delmas site. The total V concentration frequency distribution for the 30-60 cm soil depth samples was similar to the 0-30 cm soil depth samples (Appendixes B, Fig B1). In the 30-60 cm soil depth the range (with a 95 % confidence interval), for total V concentration

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was 8.9 – 26.4 mg kg^{-1}. According to a one-tailed T-test with unequal variance there were no difference between the total V concentration of the 0-30 cm and 30-60 cm soil samples. This indicated that there was no significant or measureable removal from the topsoil or significant accumulation of V in the subsoil. A cumulative normal distribution was drawn for the top 30 cm (Fig 4.10, 0-60 cm soil depth in Appendix B, Fig B2.) to compare the V content of the control soils (red data points) relative to that collected at the slag amended Delmas site. The orange data point is the mean of the outside samples. The control samples were located almost at the median (0.5) of the population, for these samples to suggest a significant difference, it should have been located in the lower 5% (<0.05) of the distribution. An one-tailed T-test with unequal variance on the same samples also showed that the controls did not differ significantly from samples collected at the slag amended Delmas site (P= 0.054 for 0-30cm and P=0.34 for 30-60cm). This corroborated the findings of the cumulative normal distribution approach (Fig 4.10)
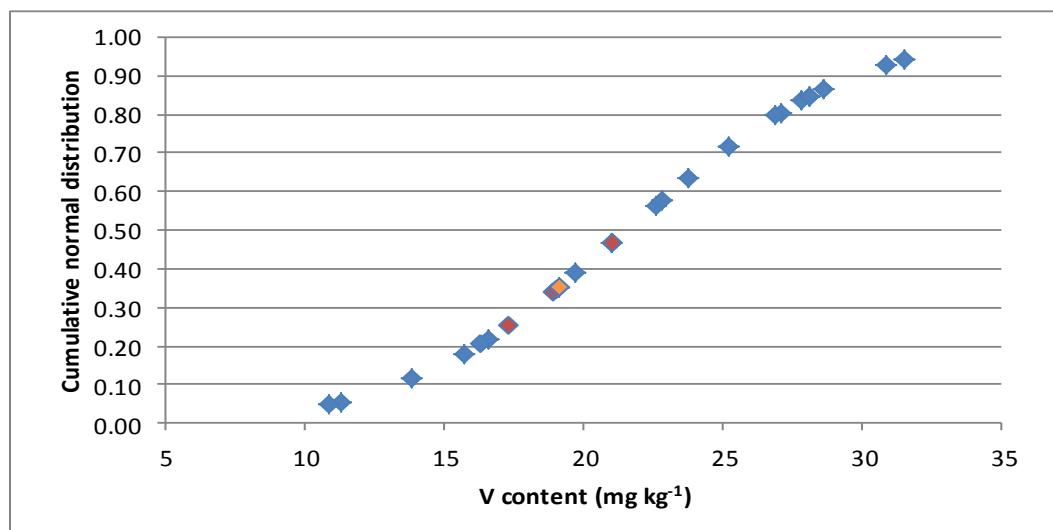

FIGURE 4.10 The total V cumulative normal distribution curve for the 0-30 cm soil samples of the Delmas site. The red data points represent the samples collected outside the field. The orange data point is the average of the outside samples.

For the Ogies site, the 95 % confidence interval of total V concentration for the top 30 cm ranged from 8.4 to 21.1 mg kg^{-1}. The frequency distribution figure for the total V

concentration for the top 30 cm at the Ogies was closer to a normal distribution compared to the Delmas population site (Fig 4.11),. The frequency distribution for the 30-60 cm soil depth samples (Appendixes B, Fig B3) looks similar to the 0-30 cm soil depth samples. In the 30-60 cm soil depth the total V concentration range was 5.50 – 20.0 mg kg^{-1} for a 95 % confidence interval.
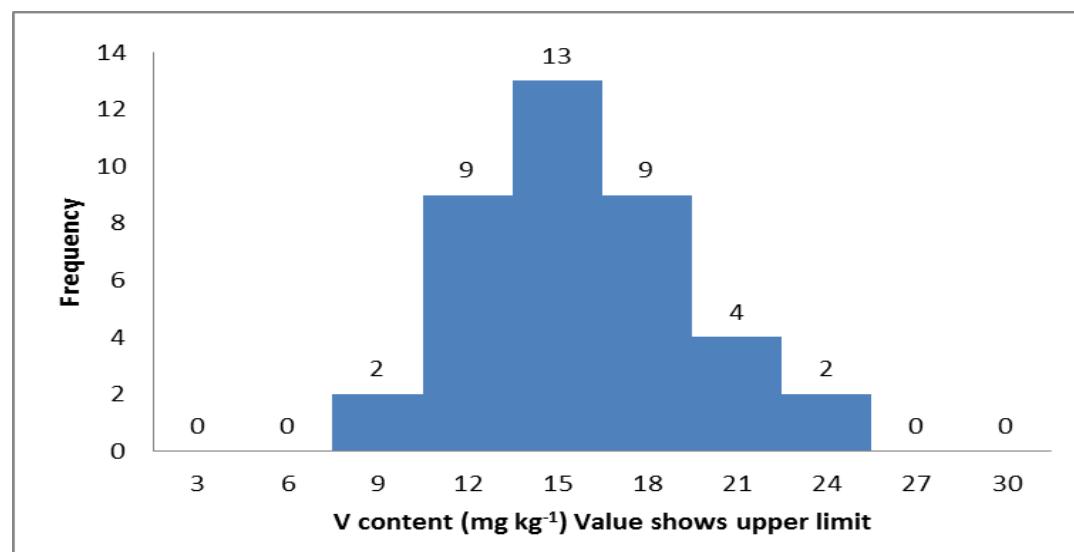

FIGURE 4.11 The total V concentration frequency distribution of the 0-30 cm soil samples at the Ogies site, (control samples omitted).

The cumulative normal distribution curve for the 0-30 cm soil depth of the Ogies soil samples are illustrated in Fig 4.12 and the 30-60 cm in Appendix B, Fig B4. These data points for the samples collected outside the field were clearly located in the lower tail of the distribution, showing a clearer separation from the amended soils and therefore stronger evidence of some vanadium enrichment in the cultivated fields The amount of samples were small and arguably would have been better described by a T distribution. An simple one tailed T test with unequal variance seemed to support the fact that the total V concentration of the control population for the Ogies site differed significantly from the population of the field samples in the field for the 0-30 cm (P = 0.0002) and 30-60cm (P = 0.0009). Therefore, a measurable effect of the use of V containing slag was detected for the Ogies site. The two-tailed T-test, however, showed no difference in the total V concentrations between the 0-30 cm and 30-60 cm

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soil depth, again showing no measurable removal or accumulation took place from either soil depth.
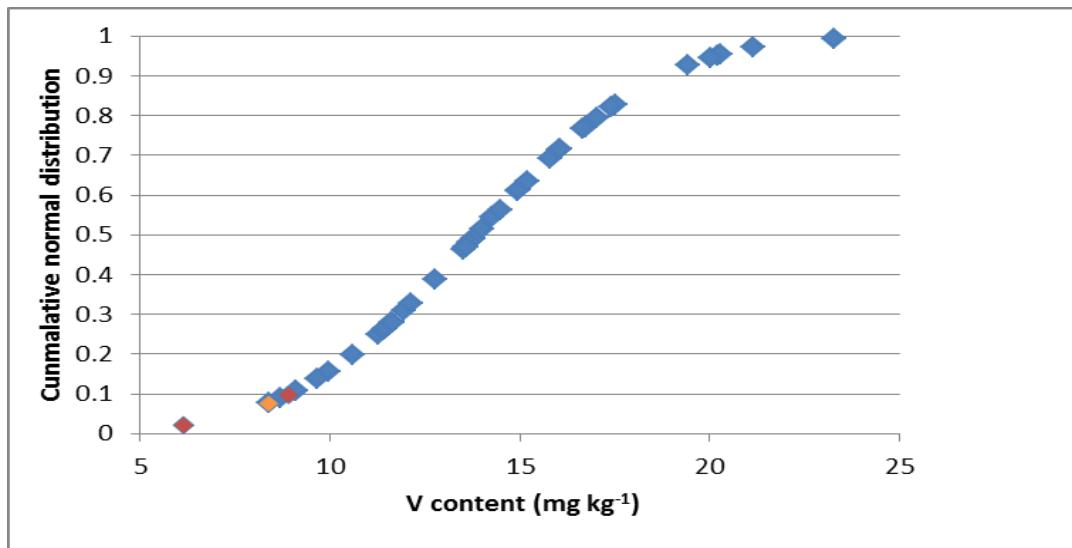

FIGURE 4.12 The cumulative normal distribution curve for the 0-30 cm soil samples of the Ogies site. The red data points represent the samples collected outside the field. The orange data point is the average of the outside samples.

Although the population statistic showed a difference in V concentration between the control and the field samples, the variability of V in the fields made it difficult to determine a loading rate in the soils with a short liming history (six years). Another problem is that the liming history before the six years of precision farming at these two sites was unknown.

4.4.8 Vanadium plant availability and plant uptake in the field evaluation site

In the field evaluation site the average total V concentration in the maize plant was 0.13 mg kg^{-1} with a maximum of 0.18 mg kg^{-1} for the Delmas site and an average of 0.19 mg kg^{-1} and maximum of 0.31 mg kg^{-1} for the Ogies site. These values were below the estimated total V concentration of 10 mg kg^{-1} (chapter 3) where reduced growth can be expected.

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4.4.9 Vanadium translocation in the maize plant from the field evaluation sites

Kaplan *et al*., (1989) confirmed that V accumulates in the roots which place V in a group of metals that is immobile in plants. There is minimum translocation of V in the maize plant and the concentration decreased as the distance from the roots increase (Fig. 4.13). For the Delmas site the leaves below the cob had the highest V concentration (0.45 +/- 0.08 mg kg^{-1}), then the leaves above the cob (0.04 +/- 0.11 mg kg^{-1}). The cob itself had no V, and this supports Kaplan's theory that there is a minimum transport of V in the plant. The total V concentration in the maize plants growing at the Ogies site was 0.76 +/- 0.08 mg kg^{-1} for the leaves and stem underneath the cob, 0.41 +/- 0.15 mg kg^{-1} for leaves and stem above the cob and 0.03 +/- 0.08 mg kg^{-1} in the cob.
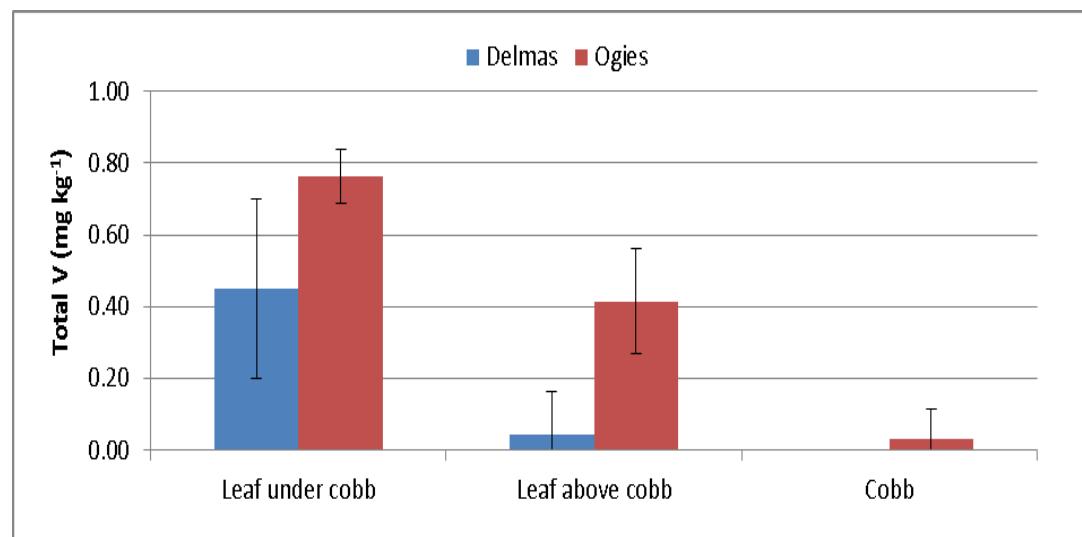

FIGURE 4.13 The V concentrations in the above ground maize plant at the two field evaluation sites at 120 days of growth.

4.4.10 Influence of vanadium loading through slag application on Bray 1 extractability of vanadium at the field evaluation site

The 95 % confidence interval for Bray 1 extractable V ranged from 0.11 to 0.28 mg kg^{-1} for the top 30 cm of soil of the Delmas field evaluation site (Fig 4.14). The frequency distribution for the 30-60 cm soil depth was similar to the 0-30 cm soil

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depth. In the 30-60 cm soil depth (Appendixes B, Fig B5) the range was 0.11 to 0.19 mg kg^{-1}. The Bray 1 extractable V cumulative normal distribution curve for the 0-30 cm soil depth of the Delmas soil samples are illustrated in Fig 4.15 and for the 30-60 cm soil depth in Appendix B, Fig B6. The red data points represent the samples collected outside the field. The orange data point is the average of the outside samples. According to a one tailed T test with unequal variance showed that the Bray 1 extractable V control population of the Delmas did not differ significantly from the population of the samples in the field for the 0-30 and 30-60 cm soil depth (P= 0.4 & 0.07).
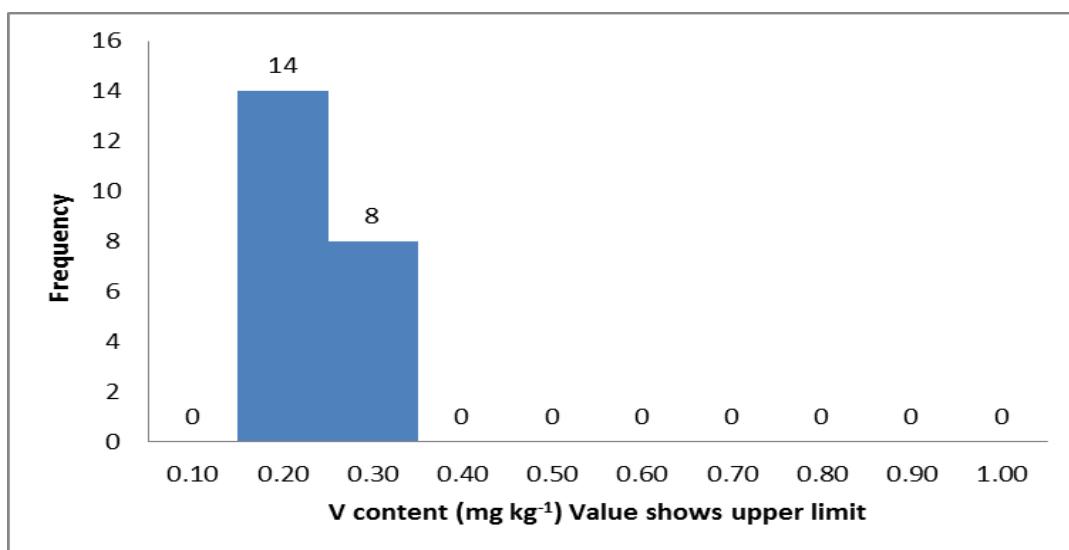

FIGURE 4.14 The Bray 1 extractable V frequency distribution of the 0-30 cm soil samples at the Delmas site, without the control samples.
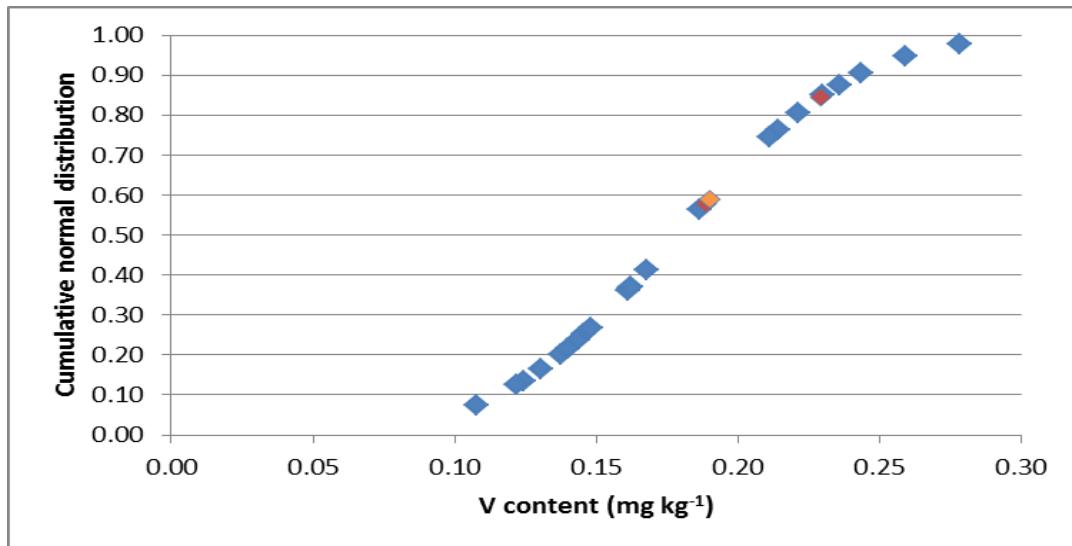
FIGURE 4.15 The cumulative normal distribution curve for the Bray 1 extractable V of the 0-30 cm soil samples of the Delmas site.

The 95 % confidence interval for Bray 1 extractable V ranged from 0.13 to 0.95 mg kg^{-1} for the top 30 cm of soil of the Ogies field evaluation site (Fig 4.16).
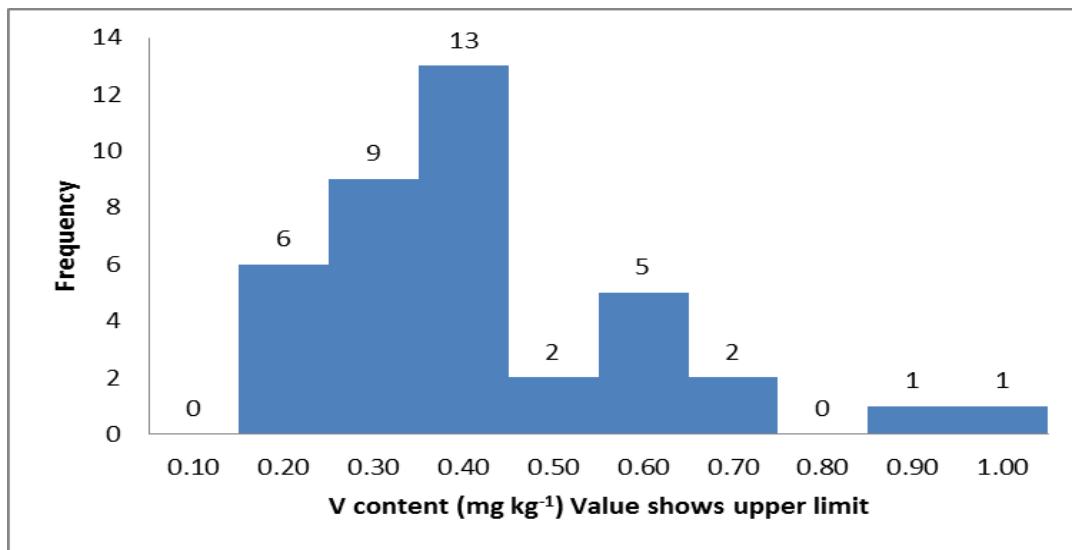

FIGURE 4.16 The Bray 1 extractable V frequency distribution of the 0-30 cm soil samples at the Ogies site, without the control samples.

The frequency distribution for the 30-60 cm soil depth looks similar to the 0-30 cm soil depth. In the 30-60 cm soil depth (Appendix B, Fig B7) the range was 0.11 to 0.37 mg kg^{-1}. The cumulative normal distribution curve for the 0-30 cm soil depth of

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the Ogies soil samples are illustrated in Fig 4.17 and for the 30-60 cm soil depth in Appendix B, Fig B8. The red data points represent the samples collected outside the field. The orange data point is the average of the outside samples. According to a one tailed T test with unequal variance showed that the Bray 1 extractable V control population of the Ogies site did not differ significantly from the population of the field samples in the field for the 0-30 and 30-60 cm soil depth (P= 0.15 & 0.18). A one tailed T test with unequal variance showed a significant difference between the samples in the field at the two soil depths. The 0-30 cm soil samples had a higher Bray 1 extractable V compared to the 30 – 60cm soil samples.
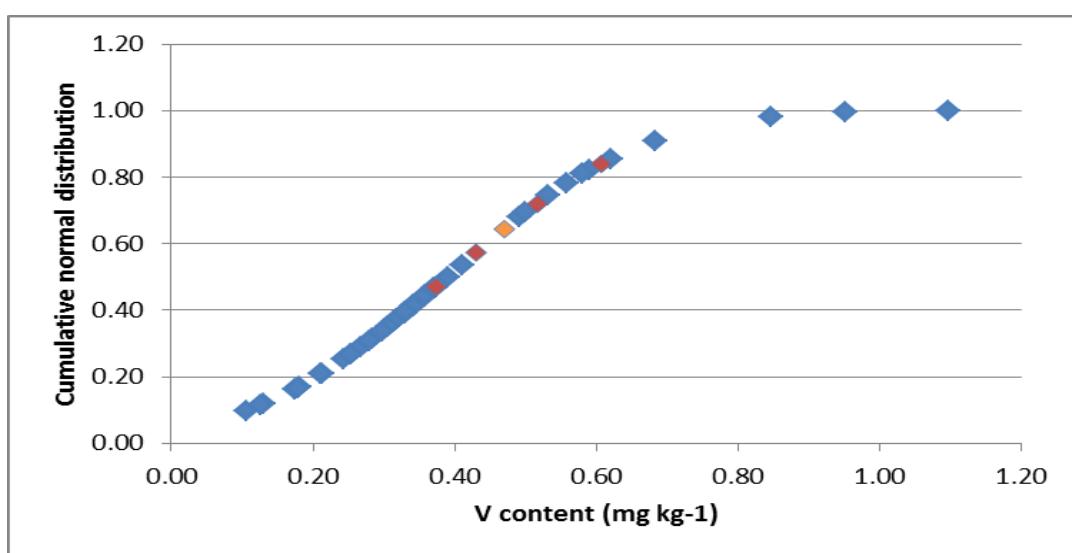
FIGURE 4.17 The cumulative normal distribution curve for the Bray 1 extractable V of the 0-30 cm soil samples of the Ogies site

The data from the field evaluation site for Bray 1 extractable V was lower compare to the data obtained from the slag pot trail. This suggests that the Bray 1 extractability of V decrease over time. This happens when V is sorbed to Fe mineral surface like goethite and a further study should be done to investigate the long term reactions of V in soils. All the field evaluation site soil samples is far below the Bray 1 extractable V concentration of 23.6 mg kg^{-1} soil (chapter 3) where V influence the plant growth of maize negatively.

4.4.11 Influence of vanadium loading through slag application on acetate extractability of Vanadium at the field evaluation site

The ammonium acetate extractable V in the Delmas and Ogies soils showed no difference between the control samples and the samples in the field. The Delmas soil ranged from 0.05 to 0.09 mg kg^{-1} for the 0-30 cm soil depth and 0.05 to 0.1 mg kg^{-1} for the 30-60 cm soil depth. The Ogies 0-30 cm samples ranged from 0.06 to 0.17 mg kg^{-1} and from 0.05 to 0.14 mg kg^{-1} for the 30-60 cm soil depth.

4.5 Conclusion

The slag pot trial showed the effect of soil acidity and the importance of liming. The maize growing in the PPS soil showed reduced growth in the untreated pH(H$_2$O) = 4 soil. This shows the necessity to lime soils that has acidified to a pH below 4, even with slag that contain various concentrations of heavy metals. If these concentrations are determined, the loading rates can be used to manage these limes as sustainable liming materials.

By using the same theoretical approach as Van der Waals & Claassens to calculate V accumulation and by using the threshold V concentration generated in chapter 3, the period to reach the critical V threshold value for liming with slag A was determined. If all factors (V concentration and incorporation depth), were to be kept constant, it will take an estimated 186 years of liming with slag a in the Nooit soil to reach the threshold value of 100 mg kg^{-1} where V will negatively affect the growth of maize plants. This period was calculated to be 472 years for the PPS soil, due to the higher Fe content and finer textured soil, which increase the V sorption capacity of the soil. The safe period for the slag B and C in respect with V is much longer than slag A, but other heavy metal concentrations must be kept in mind for they too can accumulate in the soil and can influence the growth of maize negatively if certain threshold values are reached.

The plant availability of V under the low V loading rates was low. All the V concentration in the above ground plant parts of the maize plants were far below the threshold value for total V (14.8 mg kg^{-1}) in the plant as determined in chapter 3. As the application rate in the pot trail with slag A increased, the Bray 1 extractable V increased. The Bray 1 data from slag A showed that Bray 1 can be used as a method to predict the V status in a certain soil.

The second sampling of the maize plant parts confirmed that minimum V was translocated to the above ground plant part, especially to the cob, which V concentration was close to zero. This shows that it is safe to use the maize after harvest in respect with V concentration.

To determine the actual total V loading rate proved to be a difficult task, the main reason being the low loading rate applied to the pots over the simulated 6 year period. The data from the field evaluation showed an increase in the V content in the field samples of the Ogies evaluation site compared to the control samples outside the field, but the loading rates could not be quantified. The reason for this was the variance of all the soil samples. A long term evaluation site with an accurate slag history and well defined control sites at the border of the field, where slag A is applied as liming material, should be identified and monitored.

The total V concentrations in the plants were also close to zero which supports the fact that V is not translocated in the plant under natural V concentration. All these results of the V toxicity pot trail and the slag pot trial shows that the use of slag that contains high concentrations of slag is save over the short period (10 years) and even longer if the sites are monitored and managed.

The Bray 1 extractability of V increased as the pH of the soil increased and when slag A was used as a liming material. All the Bray 1 extraction values for V in the pot trial and at the field evaluation site were well below the threshold value of 30 mg kg^{-1}.

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CHAPTER 5: SUMMARY AND CONCLUSION

Soil acidification is a wide spread problem especially on the Eastern Highveld. Slag is used to rectify soil acidification, but can contain various levels of heavy metals like vanadium. A toxicity pot trial was used to determine the level where V becomes toxic to maize plants in two soils, Nooit and PPS. The toxicity pot trail was used to establish V threshold values with various indicators, like total V concentration in the soil, total V concentration in the plant, Bray 1 extractable V and ammonium acetate extractable V.

The threshold value where maize showed reduced growth in the Nooit soil was at a total V concentration in the soil of 73.3 mg kg^{-1}. The Bray 1 extractable V at this threshold was 23.5 mg kg^{-1} and there was no V in the above ground plant material in the maize. The ammonium acetate extractability at this level was 1.68 mg kg^{-1}. V toxicity occurred (stunted growth and sclerosis on older leaves) at a total V concentration of 150 mg kg^{-1}, with Bray 1 extractable V at 77.6 mg kg^{-1} and total V concentration in the maize plant of 14.8 mg kg^{-1}.

For the PPS soil, a dolerite soil with a larger V sorption capacity compared to the Nooit soil, the threshold value was determined to be 235 mg kg^{-1} for the total V concentration in the soil. The Total V concentration in the plant was 0.5 mg kg^{-1} and the Bray 1 extractable V was 30.3 mg kg^{-1}. The ammonium acetate extractable V was 1.69 mg kg^{-1}. The Russian guideline stipulate that 150 mg kg^{-1} is the maximum total V concentration allowed in soil (Ghost, 1985) and the Canadian soil quality guideline 130 mg kg^{-1} in soil used for agriculture (Canadian Council. 1997). Although both of these guidelines do not distinguish between soil types, however, these values correspond with the values obtained for the Nooit soil. At the moment there are no V guidelines in South Africa, therefore from a regulatory point of view it seems that both the Canadian and Russian guidelines would be reasonable to use..

V availability is highly dependent on soil characteristics as was evident from the slag en toxicity pot trail. The results indicated that the factors affecting phosphate plant availability can possibly be extrapolated to vanadate for oxic soil environments

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(where V is in the +5 oxidation state). It is reasonable to expect that soil properties known to influence P sorption, for example texture, clay mineralogy and the abundance of Fe (oxy) hydroxides, can be used to predict V plant availability and mobility. Soils with finer texture means that a larger surface area is available for V sorption that could facilitate V sorption compared to coarse textured soils. Red coloured soils derived from mafic rocks, with a relative high kaolinite clay fraction and high P fixing capacity (which the PPS soil represented) is expected to also have higher V sorption capacities. Fine textured soils with red apedal B horizons like Hutton and Shortland soil forms will have a higher V tolerance.

Theoretical V loading rates were calculated for three different slags containing different V concentrations and by using the threshold V concentration generated in chapter 3, the period to reach the critical V threshold value for liming with slag A was determined. If all factors (V concentration, incorporation depth and no erosion), were to be kept constant, it will take an estimated 186 years of liming with slag A in the Nooit soil to reach the threshold value of 100 mg kg^{-1} where V will negatively affect the growth of maize. This period was calculated to be 472 years for the PPS soil, due to the higher Fe content and finer textured soil, which increase the V sorption capacity of the soil. The safe period for the slag B and C in respect with V is much longer than slag A, but other heavy metal concentrations can be limiting and influence the growth of maize negatively if certain threshold values are reached.

The V concentration of the slag pot trail and field evaluation site was far below the threshold values compared to the V threshold values generated in the V toxicity pot trail. Minimal V translocation occured to above ground material in the maize under conditions of low V loading simulated in the pot trail and in the field evaluation site was not taken up by the plant and that was harvested at the field evaluation site. This indicated that the slag use with high V concentration in the short term (< 10 years) is unlikely to negatively influence crop production because of the low V loading rate to the soil (0.35 mg kg^{-1}) and little transfer of V to above ground parts of maize.

More information is needed to predict the long term use of slag containing high V concentrations. Sandy soils with long term application rates and control sites, which received no slag application, should be established and then monitored. If other slag is available, slag A should not be used for long periods on the same soils, especially if it is a sandy soil. A long term application site with a detailed slag application history with numerous control sites which received no slag might give a more accurate V loading rate.

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APPENDIX A: Google maps of the Ogies and Delmas evaluation sites
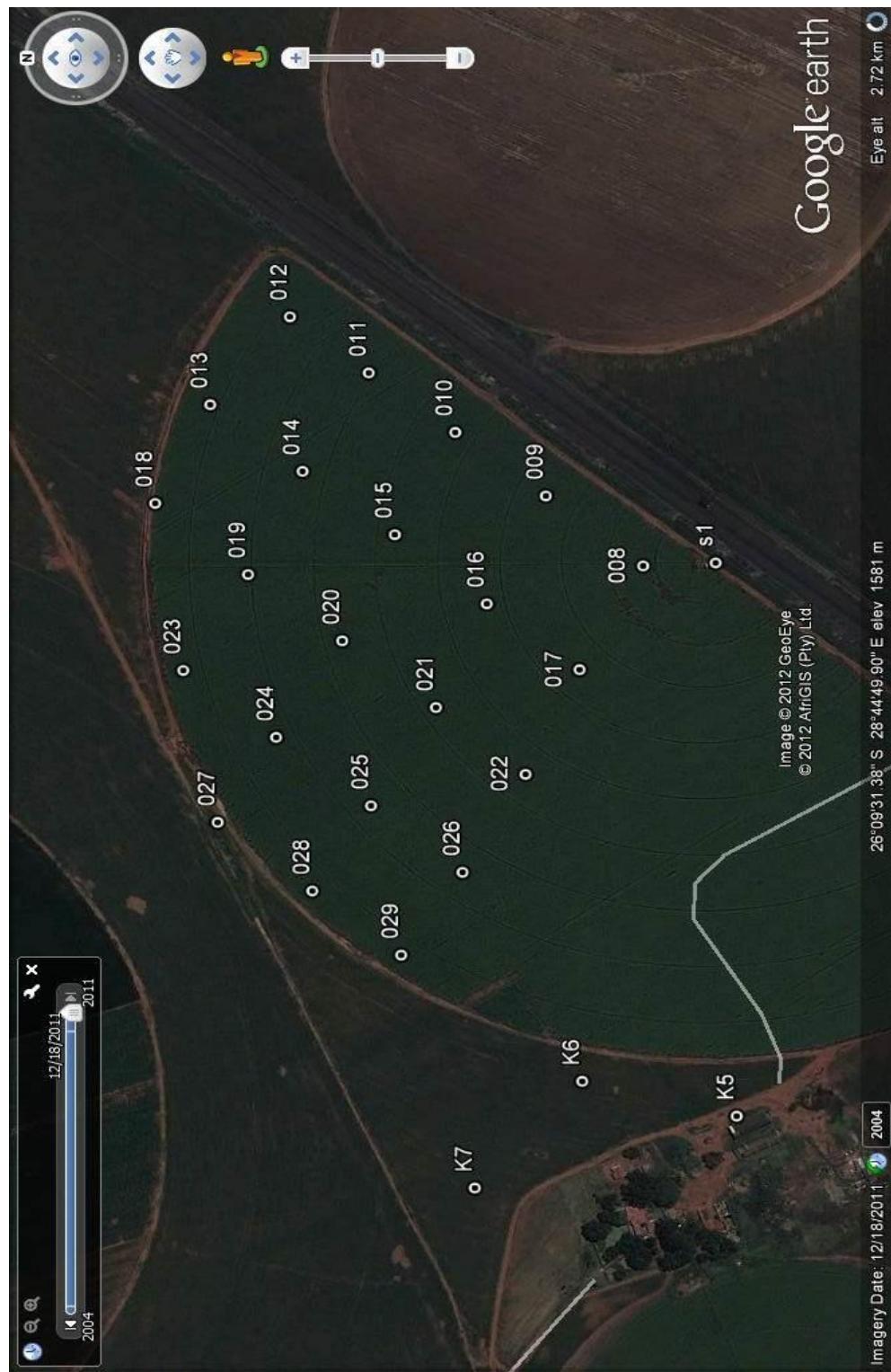
FIGURE A.1. A Google Map of the Delmas field evaluation site

FIGURE A.2. A Google Map of the Ogies field evaluation site

APPENDIX B: The frequency distribution and cumulative normal distribution curves for the different soil and soil depths.
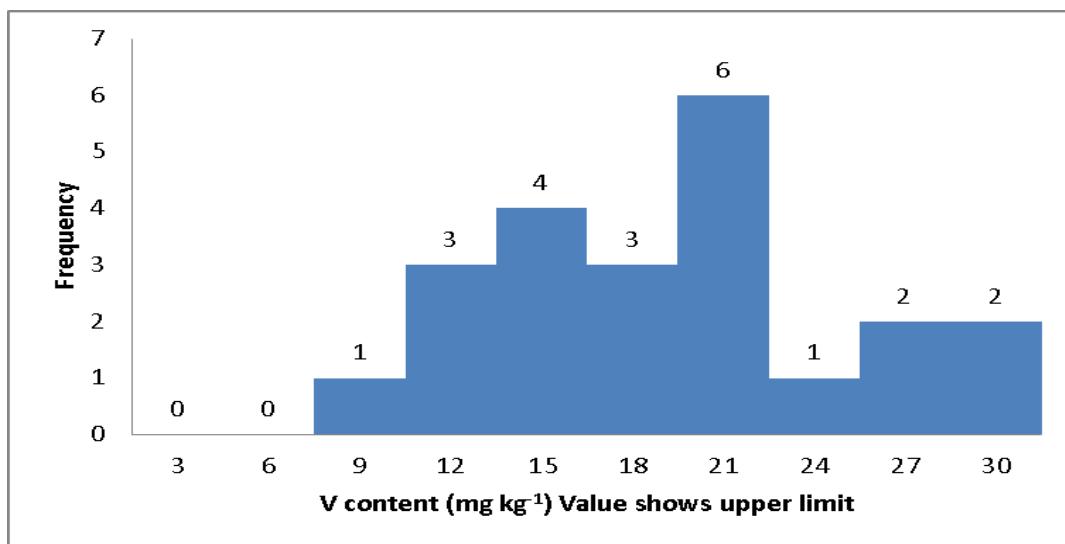

FIGURE B1: The total V concentration frequency distribution of the 30-60 cm soil samples at the Delmas site, without the control samples
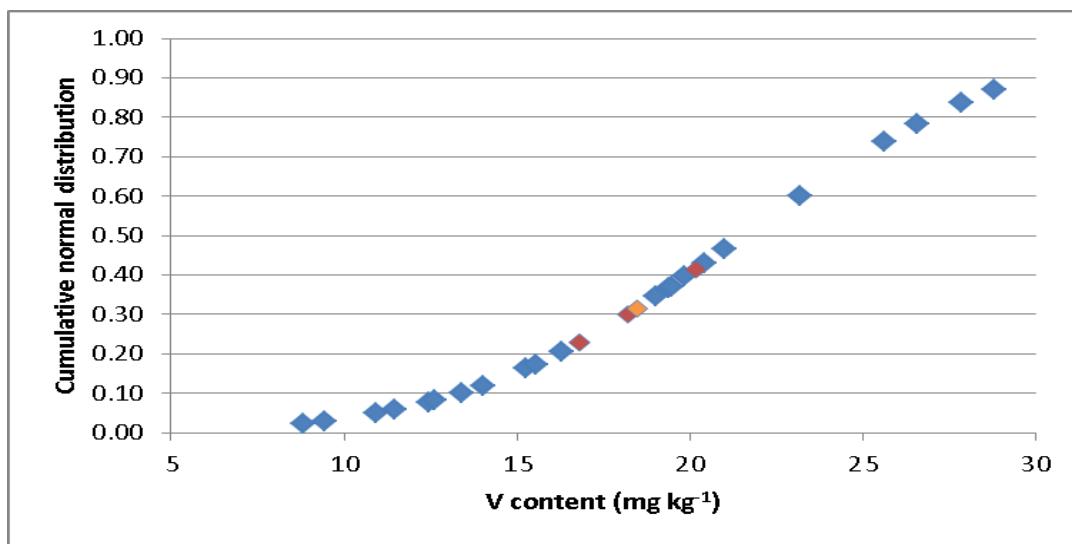

FIGURE B2. The total V cumulative normal distribution curve for the 30-60 cm soil samples of the Delmas site.
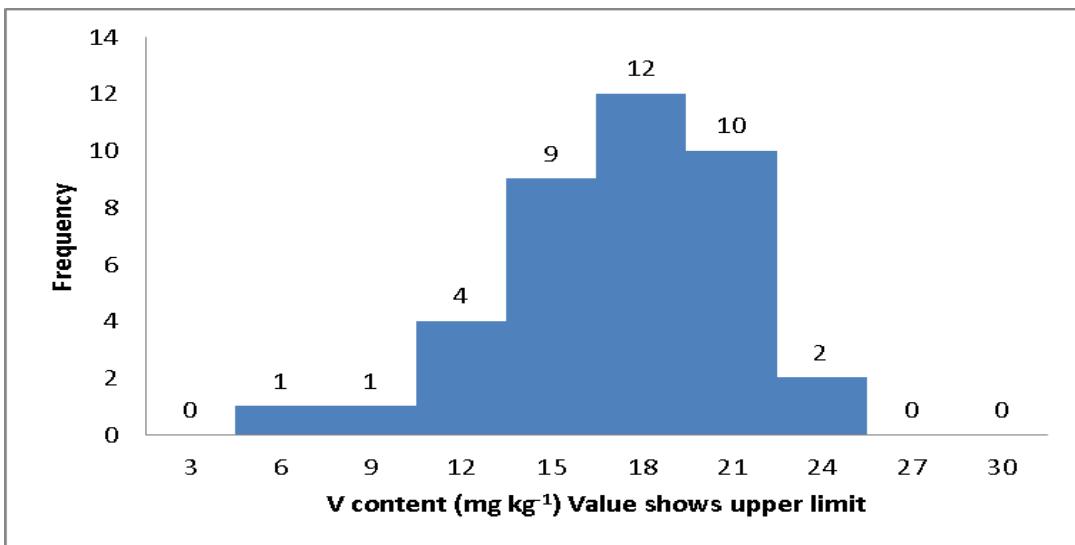
FIGURE B3. The total V concentration frequency distribution of the 30-60 cm soil samples at the Ogies site, without the control samples
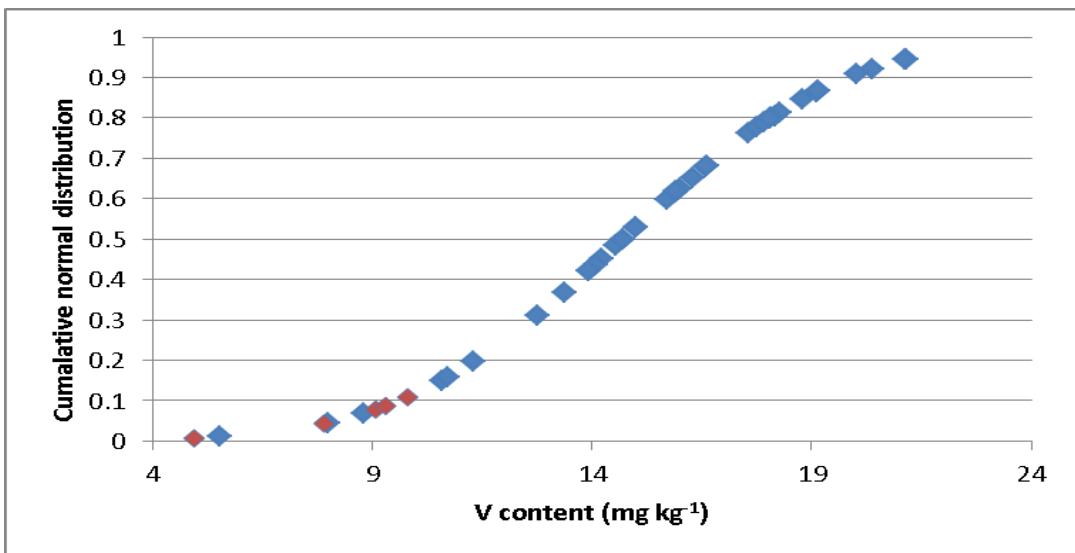
FIGURE B4. The total V cumulative normal distribution curve for the 30-60 cm soil samples of the Ogies site.

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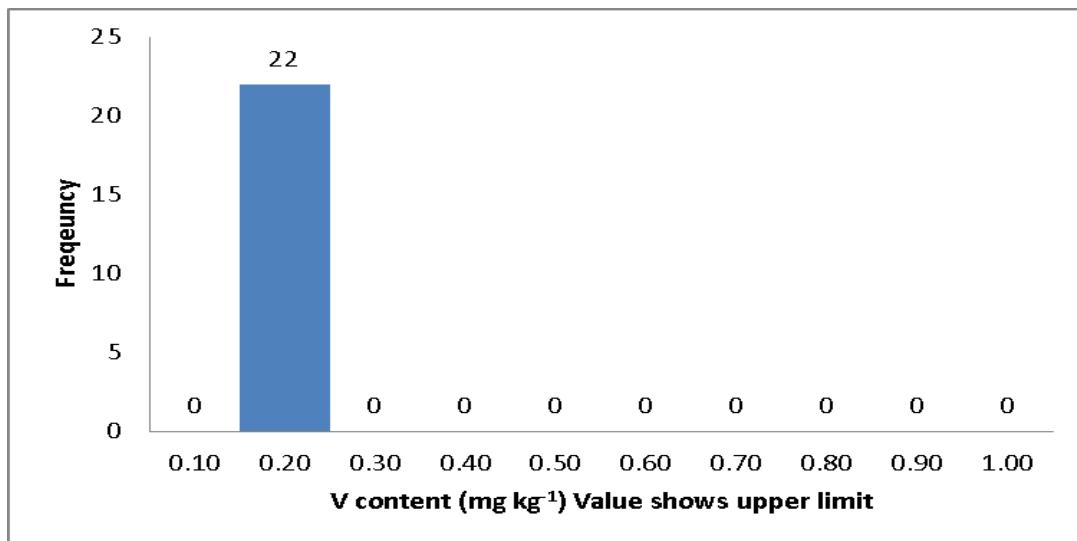
FIGURE B5. The Bray 1 extractable V frequency distribution of the 30-60 cm soil samples at the Delmas site, without the control samples.
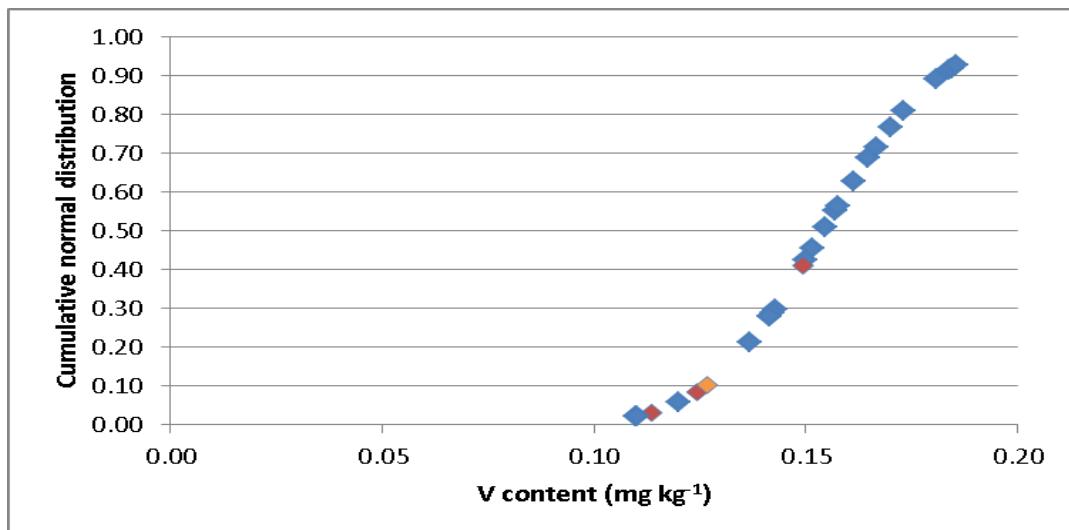

FIGURE B6. The Bray 1 extractable V cumulative normal distribution curve for the 30-60 cm soil samples of the Delmas site.
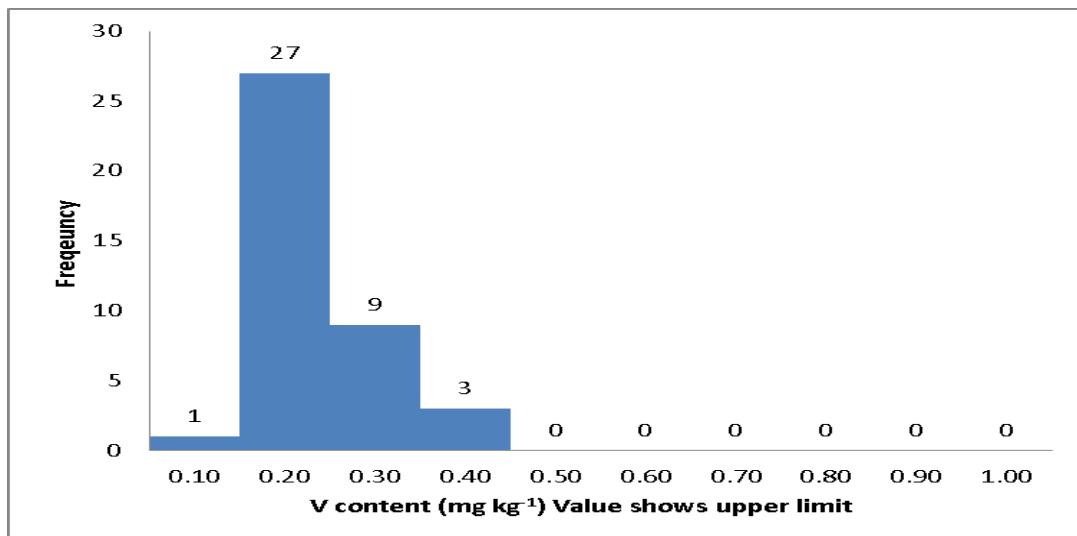
FIGURE B7. The Bray 1 extractable V frequency distribution of the 30-60 cm soil samples at the Ogies site, without the control samples.
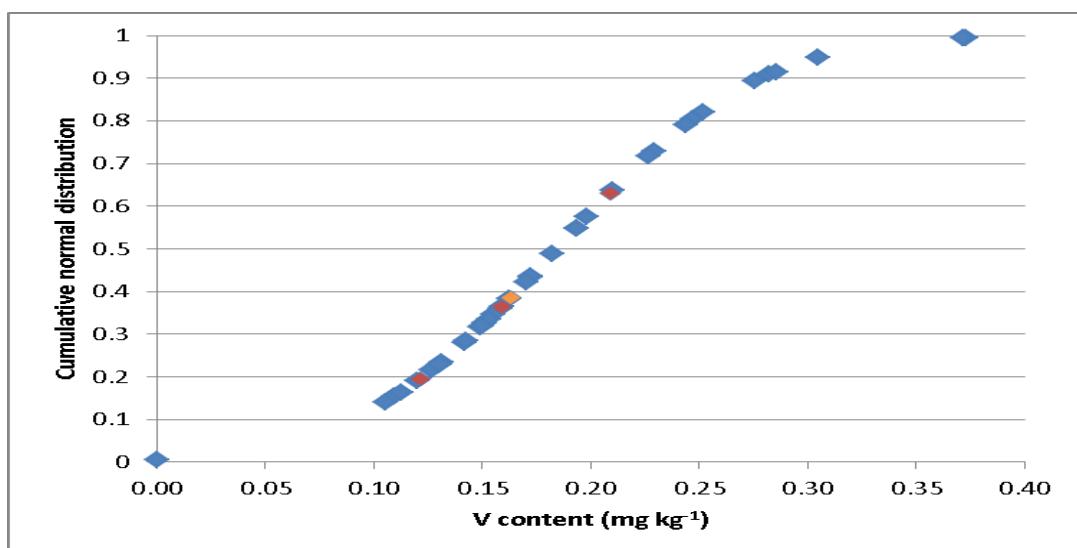

FIGURE B8. The Bray 1 extractable V cumulative normal distribution curve for the 30-60 cm soil samples of the Ogies site

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