

BENEFICIAL USE OF DRINKING WATER
TREATMENT RESIDUALS

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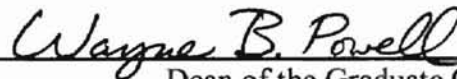
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CHAPTER I

CHARACTERIZATION OF DRINKING WATER TREATMENT RESIDUALS AS A SOIL SUBSTITUTE

ABSTRACT

The beneficial use of municipal or industrial residual materials as a soil substitute may be an economically viable source of needed topsoil for the reclamation of disturbed sites. The beneficial use of drinking water treatment residuals (WTR) as a soil substitute was evaluated in this study. Seventeen WTR were collected from municipalities in Oklahoma. Typical soil levels of selected soil quality parameters, pH, bulk density, electrical conductivity (EC), cation exchange capacity (CEC), plant available water (PAW) and total N levels were compared with WTR levels. Residual levels for pH (5.3 - 7.8), bulk density ($0.58 - 1.3 \text{ g cm}^{-3}$), EC ($0.22 - 1.1 \text{ ds m}^{-1}$), CEC ($14 - 57 \text{ cmol kg}^{-1}$) total N ($1.3 - 18.4 \text{ g kg}^{-1}$) and PAW ($26 - 416 \text{ g kg}^{-1}$) were generally similar to typical soil levels. Nutrients measured included inorganic WTR N ($28 - 263 \text{ mg kg}^{-1}$), Olsen extractable P ($4.0 - 49 \text{ mg kg}^{-1}$), Mehlich III (M III) K ($19 - 268 \text{ mg kg}^{-1}$), M III Ca ($0.178 - 21.1 \text{ g kg}^{-1}$), M III Mg ($8.0 - 1230 \text{ mg kg}^{-1}$), $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extractable SO_4 ($13 - 453 \text{ mg kg}^{-1}$), DTPA Fe ($7.6 - 231.4 \text{ mg L}^{-1}$), and Zn ($1.1 - 70.3 \text{ mg L}^{-1}$) were, generally, adequate for crop growth.. A subset of 14 WTR, ranging in chemical and physical properties and M III extractable P ($1.6 - 54.3 \text{ mg kg}^{-1}$) with adequate N and K, were selected for a tomato (*Lycopersicon esculentum*) bioassay. Mean vegetative yields ranged from 0.02 to 12.1 g pot⁻¹.

Tissue P ranged from 561 to 1840 mg kg⁻¹, below the sufficiency level of 2500 mg kg⁻¹. WTR from the tomato pots was sampled after 8 weeks growth and analyzed for water soluble cations and anions. Phytotoxic levels of NO₂-N (>10 mg kg⁻¹) were found in 5 of the 14 WTR. Tissue P or yield was not correlated with available WTR P, probably due to the toxic effect of the NO₂. The range of pH, EC, and CEC for the WTR were considered adequate for use as a soil substitute. None of the WTR were considered unsuitable as a soil substitute based on available nutrient status. Three WTR had total N levels of > 10 g kg⁻¹, which may present a NO₃ pollution hazard. Four WTR had bulk densities of < 0.75 g cm⁻³, which may be too porous for crop growth, 5 WTR had PAW values < 100 g kg⁻¹ and 5 WTR generated phytotoxic levels (> 10 mg kg⁻¹) NO₂-N, and so may not be suitable as soil substitutes. Based on the selected soil quality parameters and the generation of toxic levels of NO₂-N, 8 of the 17 WTR in this study show potential for use as a soil substitute.

INTRODUCTION

Topsoil is needed for the reclamation of disturbed sites, such as, abandoned strip mines, road construction sites or for landfill cover. Mining native topsoil for these purposes is environmentally unsound since it creates more disturbed sites. The beneficial use of municipal or industrial residual materials as a soil substitute is a potential source of topsoil and may provide an economical disposal option for the residual. In order for a residual material to be considered as a soil substitute it needs to be able to function like a soil. Brady and Weil (1996) suggest that a soil needs to be able to support plant growth, act as a filter to purify water, recycle plant and animal detritus and provide habitat for microscopic and macroscopic organisms. Soil quality has been defined as “the capacity of a soil to function, within ecosystem and land-use boundaries, to sustain biological productivity, maintain environmental quality and promote plant and animal health” (Doran and Parkin, 1994). Karlen et al. (1997) proposed that quantitative indicators should be used to determine the quality of a soil. In order to be useful, Karlen et al., (1997) suggest, these indicators should consider the soil’s function, be measurable relative to a standard and be sensitive enough to detect changes with time. Selected soil quality parameters included organic matter content, infiltration, aggregation, pH, microbial biomass, forms of N, bulk density, topsoil depth, salinity and available nutrients. Desirable levels of these parameters would be set based on the soil’s function. For example, soil quality parameters necessary for

semi-arid grazing land would differ from those for corn production. A soil substitute, suitable for plant growth, should have desirable chemical properties (e.g. pH 5 to 8, EC < 4 ds m⁻¹) and desirable physical properties (e.g. aeration, drainage, texture, structure, etc.). To be beneficial, a soil substitute should not have toxicity problems (e.g. excessive heavy metals).

Logan and Harrison (1995) and Logan and Lindsay (1996) measured chemical and physical properties of waste materials to characterize their potential suitability for use as a soil substitute. Characterization of alkaline stabilized municipal biosolids included measurements of pH, salinity, Bray P1 extractable P, water-soluble nitrate-N, and exchangeable Ca, Mg and K. Physical properties measured included percent solids, bulk density, particle density, total porosity, and available water. Currently, they are developing soil substitutes by blending residual materials. Residuals are, initially, screened individually, to determine their chemical and physical properties. Blends of residual materials (e.g. Alum WTR, alkaline stabilized biosolids) are intended to produce a soil substitute with an organic matter content between 3.5 to 5% by weight, electrical conductivity (EC) < 3ds m⁻¹, pH of between 6 and 8, total Kjeldahl nitrogen (TKN) level of < 1.1%, total phosphorus content < 3000 mg kg⁻¹, bulk density of 0.50 - 1.45 g cm⁻³, > 20% plant available water by volume, C:N ratio ranging from 10:1 to 25:1, solids content of > 50% and B levels as low as possible (Lindsay and Logan, 1998).

Residual materials from drinking water treatment have soil-like qualities and so may have the potential for utilization as a soil substitute. Drinking water treatment residuals (WTR) are a by-product of drinking water treatment. Alum, Al₂(SO₄)₃, or a

polymer (poly-aluminumchloride) are two coagulants used to remove turbidity color, taste and odor from raw water and to speed sedimentation. WTR contain suspended solids and organic material from the raw water, as well as the reaction product of coagulation, amorphous aluminum hydroxide, which accounts for approximately 50 to 150 g kg⁻¹, of the total residual (ASCE, 1996). Elliott and Dempsey (1991) reviewed the chemical and physical properties of WTR, using previous studies and found that WTR have a calcium carbonate equivalence (CCE) value in the range of 100 to 200 g kg⁻¹, and have little value as a liming material. Nutrient content tends to be low unless the raw water source is contaminated or nutrients are added during the treatment process. Total Kjeldahl nitrogen, typically, ranges from 4.4-10 g kg⁻¹ and the phosphorus content of WTR is typically low. Further, they warn that the P fixing capability of WTR can make soil P unavailable to plants. Total organic carbon is usually around 30 g kg⁻¹, which contributes to good aggregation and water holding capacity in soils amended with WTR. Aluminum and Fe oxides in the WTR also have a cementing effect, which contributes to soil aggregation.

WTR are currently disposed of in landfills, at great expense to municipalities, stored in on-site lagoons or discharged into sanitary sewer systems. Since WTR predominantly contain sediment, and humic substances from the raw water, they are similar to fine textured soils and may be suitable for use as a soil substitute (Elliott et al., 1988, 1990). The use of WTR as a soil substitute could be of economic benefit to municipalities, and provide economic and environmental benefits in the reclamation of disturbed sites.

Singly coordinated hydroxyl groups associated with Al and Fe oxides are extremely reactive to phosphate (Sparks, 1995; Sposito, 1989; Bohn et al., 1985). Materials rich in amorphous aluminum oxides, such as WTR, have the potential to adsorb labile P, making it unavailable to plants. The sorption mechanisms of phosphate and relative sorption capacity, by materials rich in Al oxides, have been the subject of research (Pardo and Guadalix, 1990; Parfitt, 1989; McLaughlin and Ryden, 1981). Phosphorus sorption was attributed to ligand exchange reactions on Al-OH functional groups. Results from P fractionation experiments, showed the addition of WTR to soil resulted in the labile P fraction decreasing while the less soluble chemisorbed Al and Fe bound P fraction increased (Cox et al., 1997; Jonasson, 1996).

Several studies have shown that, while improving soil properties, such as water retention or pH, WTR caused P deficiency and decreased yields that increased with WTR application rates. Bugbee and Frink (1985) used WTR, as an amendment to a potting media at rates of 0 to 670 g kg⁻¹, and found that addition of WTR resulted in reduced P availability and reduced lettuce (*Lactuca sativa*) yields, but increased water holding capacity in the growing media. Heil and Barbarick (1988) applied WTR at rates of from 0 to 25 g kg⁻¹, grew sorghum-sudangrass (*Sorghum bicolor sudanense*) and found decreased yields with WTR additions > 15 g kg⁻¹ due to P fixation by the WTR. Skene et al. (1995) experienced decreased growth of broad beans (*Vicia faba*) when WTR was spread in an even layer on the surface of sand, at rates of 20, 40, and 100 g kg⁻¹, with and without fertilizer addition. In a similar study, WTR was added at rates of 0.1 to 10 g kg⁻¹ to a growing media. Soil properties improved and yields of corn (*Zea mays*) increased in fertilized and unfertilized pots amended with WTR

(Rengasamy et al., 1980). At the high rate of application (10 g kg^{-1}), however, P uptake was reduced. Application of WTR at rates of 20 and 100 g kg^{-1} to a silt loam enhanced tomato growth (Elliott and Singer, 1988). The authors attributed the increased growth to reduced Al and Mn toxicity in the soil, due to an increase in pH of from 5.3 to 8.0 as a result of the WTR application. Additionally, heavy metal uptake in the plant shoots was reduced, due to soil fixation at the higher pH (Elliott and Singer, 1988). WTR has also been used as a soil amendment on field crops. WTR application rates $> 4.5 \text{ g kg}^{-1}$ decreased yields of wheat, even with P fertilizer additions (Cox et al., 1997). Alum and polymer WTR applied to forests at rates ranging from 0.8 to 2.5 g kg^{-1} had no effect on growth or nutrient content after, at least, one year (Novak et al., 1995; Bugbee and Frink, 1985). In general, high application rates of WTR ($> 10\%$) have caused P deficiency in crops. Little information is available on the use of 100% WTR as a soil substitute. The objectives of this work were determine the suitability of WTR as a soil substitute by (1) measuring the physical and chemical characteristics of a variety of drinking water treatment residuals and (2) conducting a bioassay using tomatoes.

MATERIALS AND METHODS

Seventeen WTR collected from municipalities across Oklahoma were used in this study. Fourteen were alum and 3 were polymer (poly-aluminumchloride) based. All WTR were air dried and crushed to $< 2.0 \text{ mm}$, unless otherwise stated.

WTR Chemical and Physical Characterization

WTR pH was determined in a 1:2 WTR:0.01 M CaCl₂ solution using a glass electrode (McLean, 1982). Cation exchange capacity (CEC) was determined by Na displacement (Rhoades, 1982). Electrical conductivity (EC) was measured in a 1:2 WTR: deionized water (Rhoades, 1982). Gravimetric water content was measured at 0.033, 0.5 and 1.5 M Pa in a pressure plate apparatus (Klute, 1986). Plant available water (PAW) was considered the water content between 0.033 and 1.5 M Pa. Bulk density was determined by measuring the dry weight of the WTR in the tomato pots followed by estimating volume by replacement of WTR with water (Blake and Hartge, 1986). Total nitrogen was determined by the Dumas method using a Carlo Erba 1500 series dry combustion analyzer (Bremner, 1996).

Nutrients

Using automated colorimetric analysis, NH₄-N was determined by the Indophenol-blue method and NO₃-N by the Griess-Ilosvay method (Mulvaney, 1996). Available P in WTR was measured using Mehlich III (M III) extraction (Mehlich, 1985) and by the Olsen method (Kuo, 1996) followed by inductively coupled plasma atomic emission spectroscopy (ICP). Water soluble P was determined by shaking 5 g WTR in 25 ml deionized water for 1 h and subsequent ICP analysis. Potassium, Ca and Mg were determined by M III extraction (Mehlich, 1985) followed by ICP analysis. Sulfate was determined by Ca(H₂PO₄)₂ extraction, followed by ICP analysis

(Tabatabai, 1982). Plant available Fe (Olson and Ellis, 1982) and Zn (Baker and Amacher, 1982) were determined by DTPA extraction, followed by ICP analysis.

Tomato Bioassay

A subset of, 14 WTR ranging in type (11 alum based or 3 polymer based) and M III extractable P (1.6 to 54.3 mg kg⁻¹) were selected for the tomato bioassay. WTR were air dried and crushed to pass a 6.25 mm mesh. Five tomato seeds were planted in 1 kg WTR and grown in a controlled environment growth chamber with daytime temperatures of 78° F and night temperatures of 74° F. Three replicates of each WTR were potted and, placed in a completely randomized block design. Nitrogen was added as KNO₃, so that each pot had ≥75 mg kg⁻¹ N. Plants were harvested after 8 weeks, foliage was washed with deionized water, and dried for 48 h in a forced air dryer at 75°C. The dried material was crushed and weighed, to determine yield. Foliage was digested in 10 mL of concentrated nitric acid at 90°C for 45 minutes (Zarcinas et al., 1987). Digests were evaporated to about 1 mL at 140°C, and then diluted to 50 mL. Solutions were analyzed for P by ICP.

Potential Toxicity

Heavy metals were extracted from WTR according to the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP; U.S. EPA, 1986). Soluble Al and NO₂-N were measured, by shaking 5 g WTR in 25 mL deionized water for 1 hr. Aluminum was determined by ICP analysis, NO₂ was determined by ion chromatography.

Nitrite-N measurements were confirmed by the Griess-Ilosvay method (Mulvaney, 1996).

RESULTS AND DISCUSSION

Chemical and Physical Characterization

Typical soil levels of selected soil quality parameters (Brady and Weil, 1996) were compared to WTR levels to determine how WTR chemical and physical properties are similar to or different from a “quality” soil (Table 1). The pH of WTR ranged from 5.3 to 7.8, with a median of 7.1 (Figure 1A), within the typical range of 5.0 to 8.0 adequate for plant growth (Bohn et al., 1985). Figure 2 is a key to the interpretation of the statistical box plots used to present data. The cation exchange capacity (CEC) of the WTR ranged from 13.6 to 56.5 cmol kg^{-1} with a median value of 30 cmol kg^{-1} (Figure 1B), generally higher than the typical soil range. The high CEC value may be a result of the variable charge on the amorphous Al oxide coupled with high pH and indicates an ability to retain nutrient cations. The EC of the WTR ranged from 0.22 to 1.1 ds m^{-1} (Figure 1C), well below the 4 ds m^{-1} associated with a saline soil. Bulk density of the WTR ranged from 0.58 to 1.3 g cm^{-3} , with a median of 0.9 g cm^{-3} (Figure 1D), lower than the typical range for soil of 1.0 to 1.55 g cm^{-3} . The gravimetric water holding capacity of the WTR measured at 0.033 M Pa ranged from 187 to 710 g kg^{-1} with a median of 400 g kg^{-1} (Figure 1E). PAW of the WTR was considered the difference between the water content at 0.033 and 1.5 M Pa and ranged from 26 to 416 g kg^{-1} , with a median value of 139 g kg^{-1} . While the median PAW is

within the typical range for soils (63 to 300 g kg⁻¹), some WTR values are much lower than typical soil values despite having much higher water holding capacities. For example, the four lowest PAW measurements were 26, 27, 67, and 71.8 g kg⁻¹, while the water holding capacities were 260, 280, 190, and 360 g kg⁻¹ respectively, indicating that, although a WTR may hold a significant amount of water, plant available water may be quite low. Total N levels ranged widely from 1.3 to 18.4 g kg⁻¹ in WTR, with a median value of 7.3 g kg⁻¹ (Figure 3A), higher than typical soil total N content of 0.2 to 5.0 g kg⁻¹. High total N levels in the WTR are likely caused by organic matter, removed from raw water, being concentrated in the WTR or the addition of N during the treatment process.

Nutrients

To determine nutrient status, WTR nutrient levels were compared to adequate soil nutrient levels (Table 2)(Johnson et al., 1997). The WTR available inorganic N level ranged from 28 to 263 mg kg⁻¹, with a median of 79 mg kg⁻¹. Nitrate-N levels ranged from 5.31 – 123.3 mg kg⁻¹ with a median of 18.7 mg kg⁻¹ and NH₄-N levels ranged from 26.9 – 140 mg kg⁻¹ with a median of 51.2 mg kg⁻¹ (Figure 3B), within the adequate soil N range for most crops of 50 to 200 mg kg⁻¹. Olsen extractable WTR P levels ranged from 3.8 to 48.8, mg kg⁻¹, with a median of 13.1 mg kg⁻¹ (Figure 3D), slightly above the adequate level of 12 mg kg⁻¹ (Tisdale et al., 1985) for most crops. The WTR M III extractable P levels ranged from 1.6 to 54.3 mg kg⁻¹, with a median of 6.8 mg kg⁻¹ (Figure 3D), well below the 32.5 mg kg⁻¹ soil level considered adequate for most crops. Water soluble P levels ranged from 34 to 576 ug L⁻¹ with a median of

98 $\mu\text{g L}^{-1}$. Adequate water soluble P levels range from 50 to 200 $\mu\text{g L}^{-1}$ with an average of 125 $\mu\text{g L}^{-1}$ (Fohse et al., 1988). Mehlich III extractable WTR K levels ranged from 18.7 to 268 mg kg^{-1} , with a median of 78.5 mg kg^{-1} (Figure 3E). The median WTR value is slightly below the adequate soil K level of 125 mg kg^{-1} . Mehlich III WTR Ca levels ranged from 0.18 to 21.1 g kg^{-1} , with a median of 2.6 g kg^{-1} (Figure 4A), considerably higher than the adequate soil Ca value of 375 mg kg^{-1} . The high WTR Ca level is likely due to pH adjustment with lime during water treatment. The WTR SO_4 level ranged from 12.5 to 453 mg kg^{-1} , with a median of 138 mg kg^{-1} (Figure 4B), higher than the adequate soil SO_4 level of 14 mg kg^{-1} . Mehlich III extractable WTR Mg levels ranged from 8.0 to 1230 mg kg^{-1} , with a median of 117 mg kg^{-1} (Figure 4C), higher than the adequate soil Mg level of 50 mg kg^{-1} . The WTR DTPA extractable Fe levels ranged from 7.6 to 231 mg kg^{-1} , with a median of 60.4 mg kg^{-1} (Figure 5A), considerably higher than the adequate soil Fe value of 4.5 mg kg^{-1} . The WTR DTPA extractable Zn levels ranged from 1.1 to 70.3 mg kg^{-1} , with a median of 3.0 mg kg^{-1} (Figure 5B), higher than the adequate soil Zn level of 0.8 mg kg^{-1} . Of all the nutrient levels tested, only the median M III P levels were grossly deficient and this deficiency may be difficult to overcome due to the P adsorption capacity of the WTR. Added P can become fixed to Al-OH groups and be unavailable to plants (Cox et al., 1997; Jonasson, 1996). Individual deficiencies in other nutrients should be easily correctable with fertilizer.

Potential Toxicity

The Toxicity Characteristic Leaching Procedure (TCLP, U.S. EPA, 1986) is used to characterize municipal and industrial solid waste as hazardous or non-hazardous for the purpose of landfilling. All of the measured WTR heavy metal levels were well below the regulatory levels for the TCLP (Table 3) and so the WTR can be characterized as non-hazardous waste with respect to the metals tested, and can be disposed of in a non-hazardous landfill. The soluble Al levels ranged from 0.02 to 0.92 mg L⁻¹, with a median of 0.054 mg L⁻¹, below the level found to cause toxicity symptoms in soybeans (*Glycine max* (L.) Merr.) (1.8 mg L⁻¹) or corn (3.6 mg L⁻¹) (Sparks, 1995), so no Al toxicity problems are expected.

Tomato Bioassay

Despite having a broad range of M III P (1.6 to 54.3 mg kg⁻¹), with 1 WTR > the 32.5 mg kg⁻¹ considered adequate, a broad range of Olsen P (3.8 to 49 mg kg⁻¹), with 8 WTR > 12 mg kg⁻¹ considered adequate, and a broad range of ws P (34 – 576 ug L⁻¹) with 4 WTR > 125 ug L⁻¹ considered adequate, yields and tissue P were low. Average vegetation yield ranged from 0.017 to 12.8 g pot⁻¹, with a median of 0.052 g (Figure 6B). Tissue P ranged from 561 to 1840 mg kg⁻¹, with a median of 923 mg kg⁻¹ (Figure 6A). Sufficient tissue concentration at the early bloom stage is 2500 mg kg⁻¹, intermediate is 2000 mg kg⁻¹ while 1000mg kg⁻¹ is considered deficient (Geraldson et al., 1973). Because tissue P was so low and few plants had adequate yield, a reliable

correlation between either yield or tissue P with soil test P (M III, Olsen, or ws) was not obtained.

After 8 wks of growth the pots were sampled and the WTR soluble cations and anions were measured. High levels of $\text{NO}_2\text{-N}$ (35 to 402 mg kg^{-1}) were found in five of the 14 WTR. Black (1968) found $\text{NO}_2\text{-N}$ levels of $> 10 \text{ mg kg}^{-1}$ toxic to tomatoes. Conversion of NO_2 to NO_3 usually proceeds faster than conversion of NH_4 to NO_2 , in well aerated soils, so NO_2 does not accumulate. The activity of *Nitrobacter*, an NO_2 oxidizer, is inhibited by high pH and high NH_3 levels, more than NH_4 oxidizers and under these conditions NO_2 can accumulate (Haynes and Sherlock, 1986; Alexander, 1977). At a pH of 9.5, Alexander (1977) states that, $\text{NH}_4\text{-N}$ concentrations of 1.4 mg kg^{-1} can inhibit *Nitrobacter*, while having no effect on ammonium oxidizers and that it is the NH_3 , not the cationic NH_4 , that forms under high pH conditions that is toxic to the *Nitrobacter*.

Figure 7 illustrates the change in $\text{NO}_2\text{-N}$ concentrations in the five affected WTR before planting (week 0), during tomato growth (week 8) and two months after the conclusion of the bioassay (week 16). Nitrite-N levels though initially low, increased dramatically during the tomato study. Eight weeks after the conclusion of the tomato study, the $\text{NO}_2\text{-N}$ levels had decreased.

Figure 8 illustrates the trend between yield and tissue P concentrations and WTR P levels and WTR $\text{NO}_2\text{-N}$ levels. Data was transformed for use in this figure to adjust the scale as follows: average yield was multiplied by 10, with the exception of the average yield of WTR 14 was multiplied by 3. Water soluble P was divided by 10 and tissue P was divided by 100. The five WTR that had high $\text{NO}_2\text{-N}$ levels ($>10 \text{ mg kg}^{-1}$),

WTR 1 through 4 and 13, are presented on the graph by unfilled symbols. Only three WTR, (14, 8 and 16), had yields (12.8, 1.1 and 0.28 g, respectively) that separate them from the cluster of points around zero. These same three WTR, (14, 8 and 16), had the highest tissue P levels of (1770, 1840 and 1470 mg kg⁻¹), respectively. These same three WTR had the highest Olsen P levels, (47, 19, and 17.7 mg kg⁻¹), of the WTR not affected by NO₂-N (<10 mg kg⁻¹). This trend is repeated with ws P levels of 576 and 100 ug L⁻¹, in WTR 14 and 8, respectively and with M III P levels of 54.3 and 23.3 mg kg⁻¹, in WTR 14 and 16, respectively. Although WTR 1, 3, 4, and 13 were above the Olsen P sufficiency level of 12 mg kg⁻¹, with concentrations of 17, 25, 13, and 47 mg kg⁻¹, tomato growth was inhibited by toxic levels of NO₂. Tissue P did not appear to be affected as strongly as yield by NO₂.

CONCLUSION

In order for a WTR to be considered as a soil substitute, it needs to be able to function like a soil. For the purposes of this study the function is to support crop growth, while not being harmful to the environment. The selected soil quality parameters measured (Table 1), provide a measure of chemical and physical properties inherent in the WTR. The pH of the WTR is within the typical soil range of and should be adequate for crop growth. The EC of all the WTR studied were well below the 4.0 ds m⁻¹ associated with saline soils. The CEC of the WTR ranging from 13.6 to 56.5, indicates good nutrient holding capacity. Three of the WTR have total N levels > 10 g kg⁻¹, which may present a NO₃ pollution hazard. Assuming a 10% mineralization rate, a 1% total N level will release 2000 lbs ac⁻¹ of N. Five of the WTR

had PAW values $< 100 \text{ g kg}^{-1}$, which may make them inadequate as a soil substitute. Bulk density values $< 0.75 \text{ g cm}^{-3}$ may indicate the WTR is too porous to be suitable as a soil substitute. Bulk density affects PAW and WTR with low bulk densities are difficult to wet and dry too quickly. Four of the WTR had bulk densities $< 0.75 \text{ g cm}^{-3}$

None of the WTR were considered unsuitable as a soil substitute based on available nutrient levels (Table 2). Individual nutrient deficiencies can be corrected with fertilizers and the nutrient status of the WTR, is generally quite good. Inorganic N levels in 14 of the 17 WTR are $>$ than 50 mg kg^{-1} and 4 were $> 100 \text{ mg kg}^{-1}$. Olsen extractable P levels in 7 of the 17 WTR are greater than the adequate level of 12 mg kg^{-1} . Only 1 WTR has greater than the M III adequate P level of 32.5 mg kg^{-1} . Four of the 17 WTR have $> 125 \text{ ug L}^{-1}$ considered adequate w/s P. Seven of the 17 WTR have greater than the adequate level of 125 mg kg^{-1} M III K. Sixteen of the 17 WTR have greater than the adequate level of M III Ca of 375 mg kg^{-1} . Fourteen of the 17 WTR have greater than the adequate level of M III Mg of 50 mg kg^{-1} . Sixteen of the 17 WTR have greater than the adequate level of CaH_2PO_4 extractable SO_4 of 14 mg kg^{-1} . All of the WTR have greater than the adequate level of DTPA Fe of 4.5 mg kg^{-1} and of DTPA Zn of 0.8 mg kg^{-1} .

The generation of phytotoxic levels of $\text{NO}_2\text{-N}$ makes WTR unsuitable as a soil substitute. Five, of the 14 WTR used in the tomato bioassay, generated phytotoxic $\text{NO}_2\text{-N}$ levels $> 10 \text{ mg kg}^{-1}$. Further study of NO_2 generation is necessary to determine if it is a temporal problem or if it can be mitigated, by an adjustment of pH or nutrient status. There were no other toxicity problems evident in any of the WTR.

All of the TCLP metal contaminants were below the regulatory levels and water soluble Al $<1.0 \text{ mg L}^{-1}$.

Based on the selected soil quality parameters and the generation of toxic levels of $\text{NO}_2\text{-N}$ 8 of the 17 WTR in this study show potential for use as a soil substitute. Research is needed however, to evaluate the ability of soil chemical tests to accurately measure the adequacy of WTR nutrient status. Through a closer examination of WTR physical properties the PAW and bulk density of WTR may be improved.

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Table 1. Comparison of soil quality parameters for WTR with, typical soil levels for crop growth.

WTR	Type†	pH	Electrical conductivity	Cation exchange capacity	Total N	Plant available water‡	Bulk density
			ds m ⁻¹	cmol kg ⁻¹	g kg ⁻¹	g kg ⁻¹	g cm ⁻³
1	A	7.1	0.63	56.5	10.1	134	0.58
2	A	7.7	0.54	46.7	7.1	301	0.74
3	A	7.0	1.09	18.8	18.4	416	N/A
4	A	7.8	0.60	51.0	8.2	142	0.81
5	A	7.8	1.08	44.2	12.1	144	N/A
6	A	7.6	0.37	13.6	1.3	172	N/A
7	P	7.7	0.44	34.8	3.9	71.8	0.95
8	P	6.6	0.28	29.6	7.6	130	0.91
9	P	7.0	0.27	20.3	5.6	27.3	0.79
10	A	6.9	0.40	29.5	4.8	26.0	0.82
11	A	7.7	0.59	29.9	2.3	206	1.17
12	A	5.3	0.43	31.7	5.9	16.3	0.63
13	A	7.5	1.03	29.7	14.6	194	0.56
14	A	7.2	0.67	30.5	7.9	139	0.93
15	A	7.0	0.22	17.8	7.3	100	0.96
16	A	7.0	0.80	31.9	7.9	77	0.97
17	A	6.6	0.22	16.4	2.8	66.8	1.3
WTR Range		5.3 - 7.8	0.22 - 1.1	13.6 - 56.5	1.3 - 18.4	26 - 416	0.56 - 1.3
WTR Median		7.1	0.5	30.0	7.0	139	0.9
Soil Typical ¶		5.0 - 8.0#	< 4.0	3.5 - 35.6	0.2 - 5	63 - 300	1.0 - 1.55

† A = Alum WTR, P = Poly-aluminumchloride WTR

‡ Difference between gravimetric water content at 0.033 and 1.5 M Pa

¶ Typical soil levels (Brady and Weil, 1996)

Typical pH value (Bohn et al., 1985)

Table 2. Comparison of soil nutrient levels, adequate for most crop growth, with WTR levels.

Available Nutrients	Adequate Soil Level †	WTR Median	WTR Range	Method
----- mg kg ⁻¹ -----				
NO ₃ -N and NH ₄ -N	50 – 200	79.1	28 – 263	Automated colorimetric analysis
P‡	> 12	13.1	4.0 – 49	Olsen extractable
K	> 125	78.5	19 – 268	Mehlich III extractable
Ca	> 375	2630	178 – 21100	Mehlich III extractable
Mg	> 50	117	8.0 – 1231	Mehlich III extractable
SO ₄	> 14	138	13 – 453	Ca(H ₂ PO ₄) ₂ extractable
Fe	> 4.5	60.4	7.6 – 231	DTPA extractable
Zn	> 0.8	3.0	1.1 – 70.3	DTPA extractable

† Adequate soil nutrient levels from Johnson et al., 1997.

‡ Adequate Olsen P level from Tisdale et al., 1985.

Table 3. Contaminants measured by the Toxicity Characteristic Leaching Procedure and soluble Al levels in WTR.

WTR	Contaminants						Soluble Al
	As	Ba	Cd	Cr	Pb	Se	
	----- mg L ⁻¹ -----						
1	0.015	4.65	0.014	0.197	0.00	0.089	0.32
2	0.000	2.01	0.003	0.007	0.036	0.039	0.33
3	0.009	2.19	0.012	0.034	0.000	0.015	0.92
4	0.000	3.62	0.002	0.009	0.001	0.014	0.12
5	0.000	4.40	0.000	0.012	0.000	0.025	0.35
6	0.000	3.04	0.000	0.014	0.001	0.000	0.03
7	0.000	6.90	0.000	0.016	0.000	0.000	0.05
8	0.001	2.20	0.004	0.010	0.004	0.001	0.02
9	0.000	4.86	0.001	0.008	0.000	0.015	0.02
10	0.022	1.78	0.011	0.023	0.000	0.028	0.02
11	0.000	2.97	0.000	0.006	0.000	0.006	0.04
12	0.003	0.30	0.001	0.008	0.001	0.003	0.11
13	0.000	1.82	0.000	0.007	0.000	0.007	0.05
14	0.001	2.96	0.011	0.005	0.006	0.007	0.09
15	0.000	2.94	0.001	0.020	0.000	0.019	0.41
16	0.000	2.93	0.005	0.008	0.000	0.021	0.02
17	0.001	1.25	0.002	0.030	0.000	0.006	0.19
Regulatory level	5	100	1	5	5	1	N/A

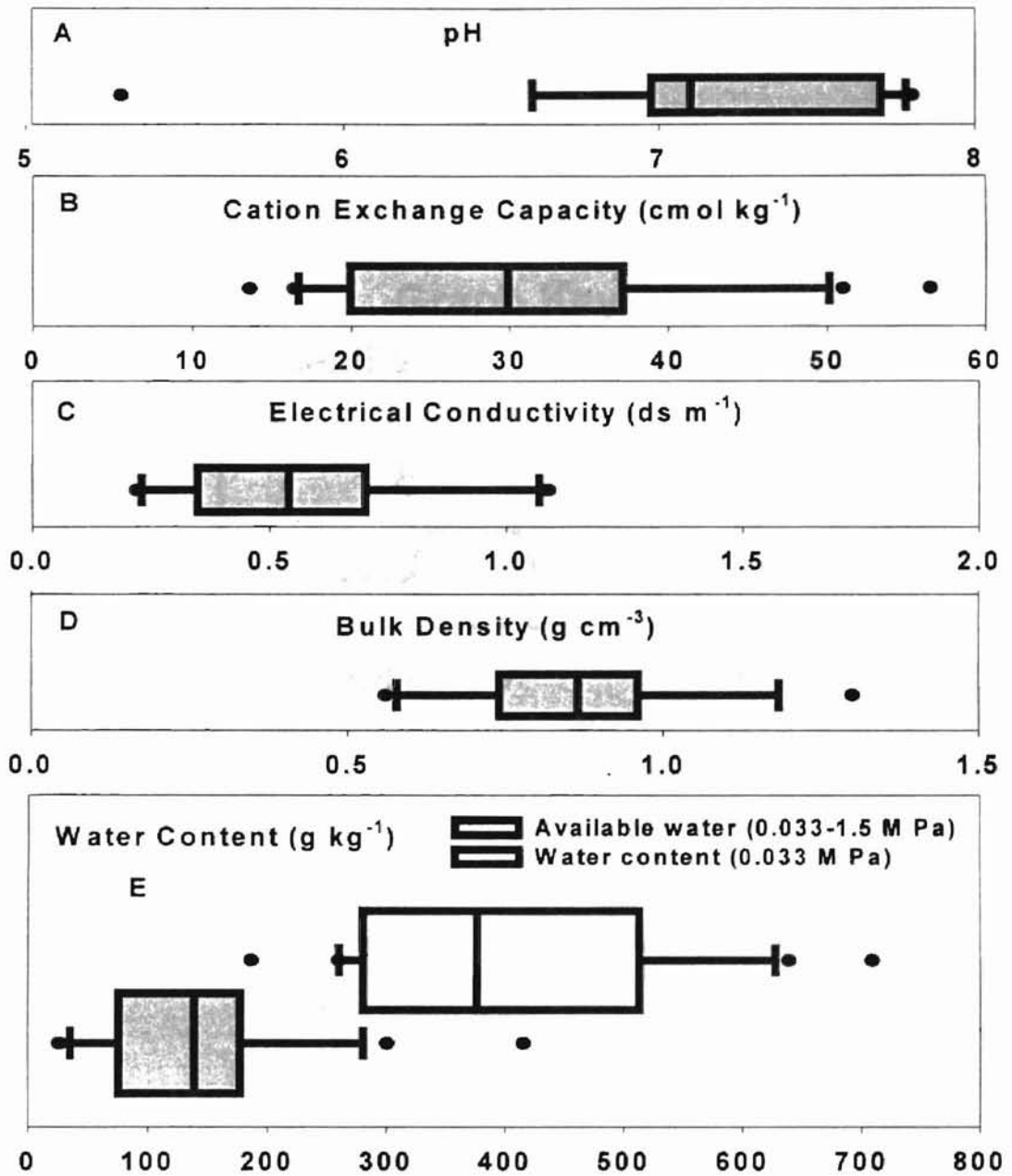


Figure 1. Statistical summary of selected soil quality parameters, (A) pH, (B) cation exchange capacity, (C) electrical conductivity, (D) bulk density and, (E) water holding capacity (0.033 M Pa) and plant available water (difference between water content at 0.033 and 1.5 M Pa), of WTR.

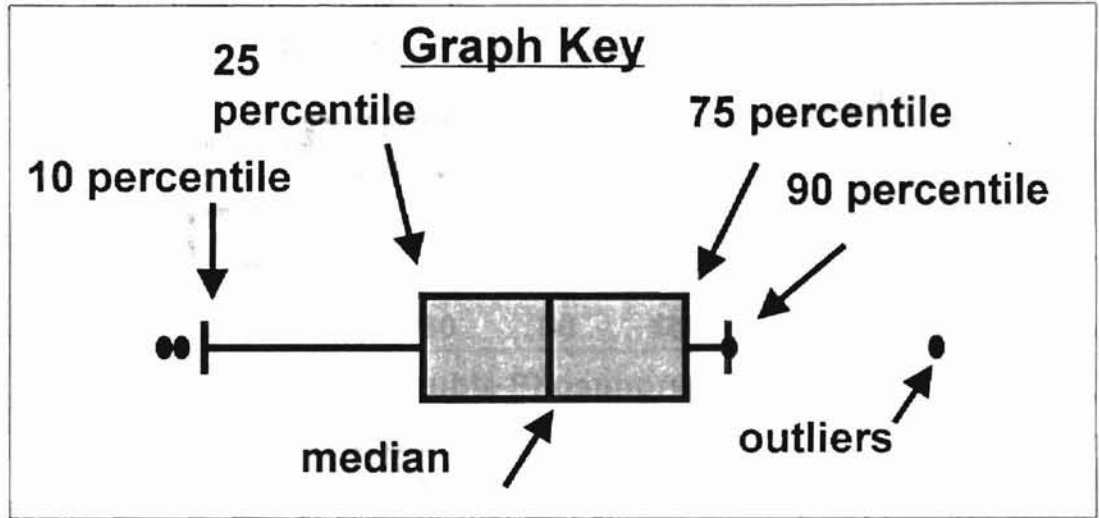


Figure 2. Key to the interpretation of statistical box plots used in Figure 1 and Figures 3-6.

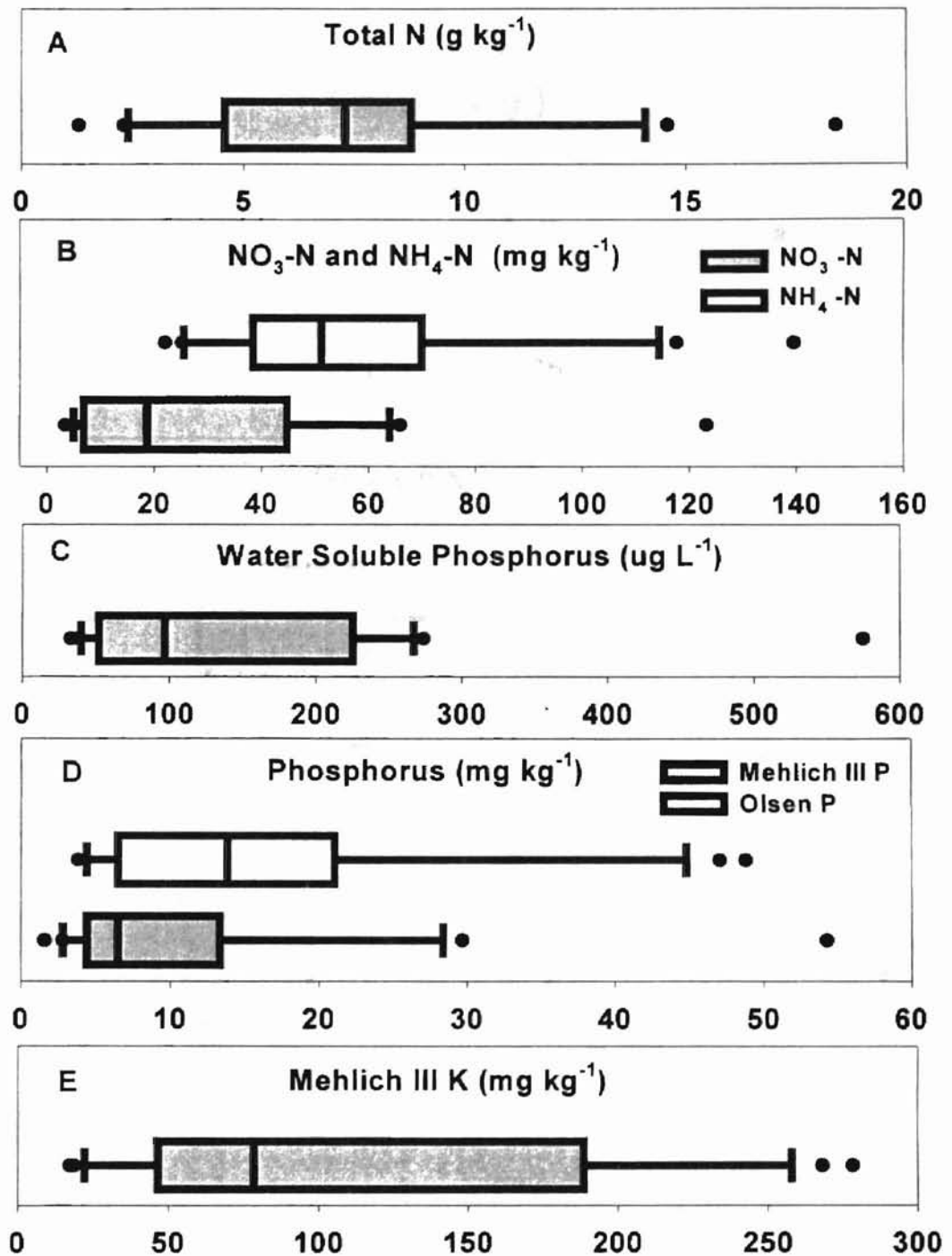


Figure 3. Statistical summary of (A) total N, (B) available inorganic $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, (C) Water soluble P, (D) Mehlich III and Olsen extractable P and (E) Mehlich III extractable K levels in WTR.

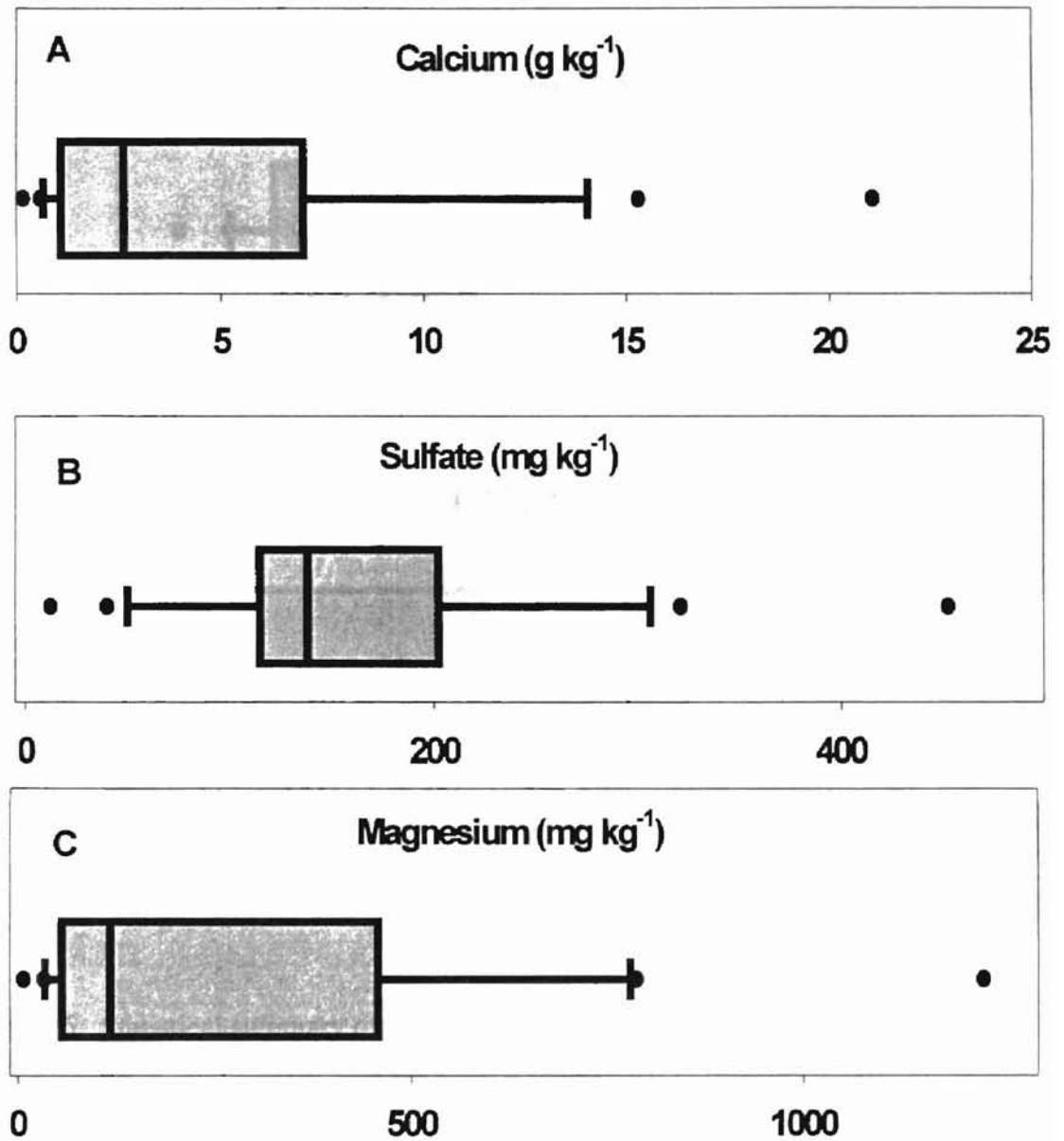


Figure 4. Statistical summary of (A) calcium, (B) sulfate, and (C) magnesium levels in WTR.

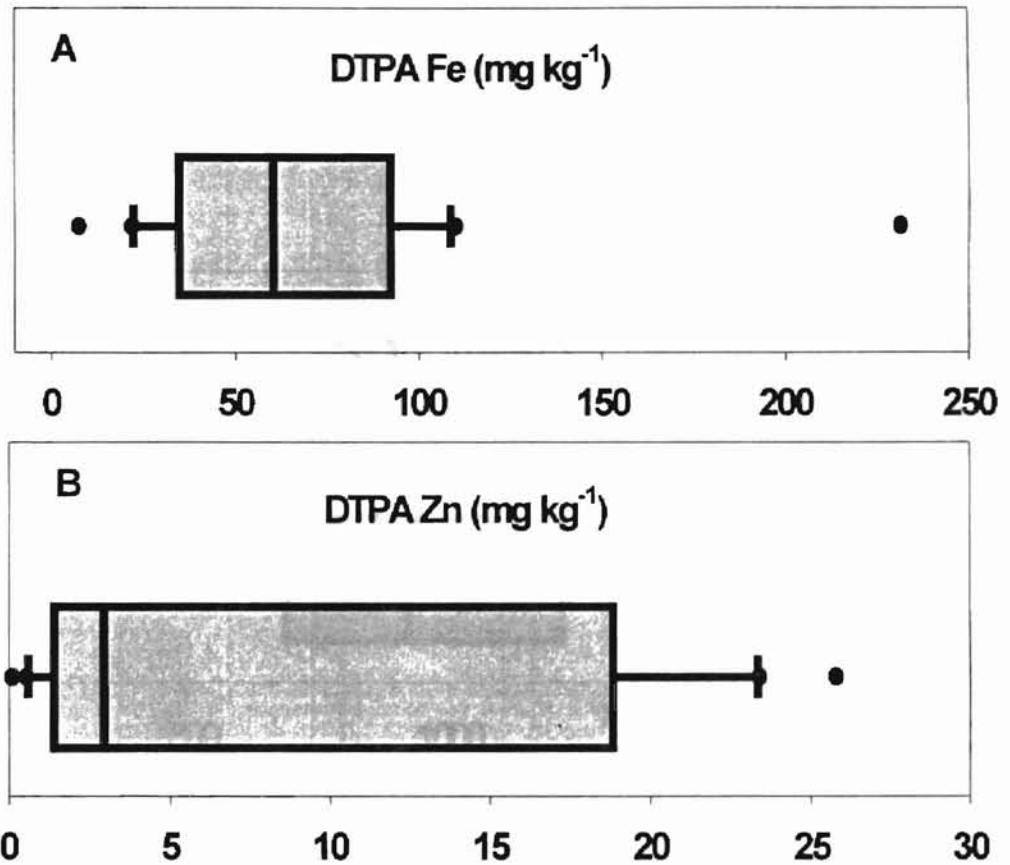


Figure 5. Statistical summary of WTR levels of DTPA extractable (A) Fe, and (B) Zn.

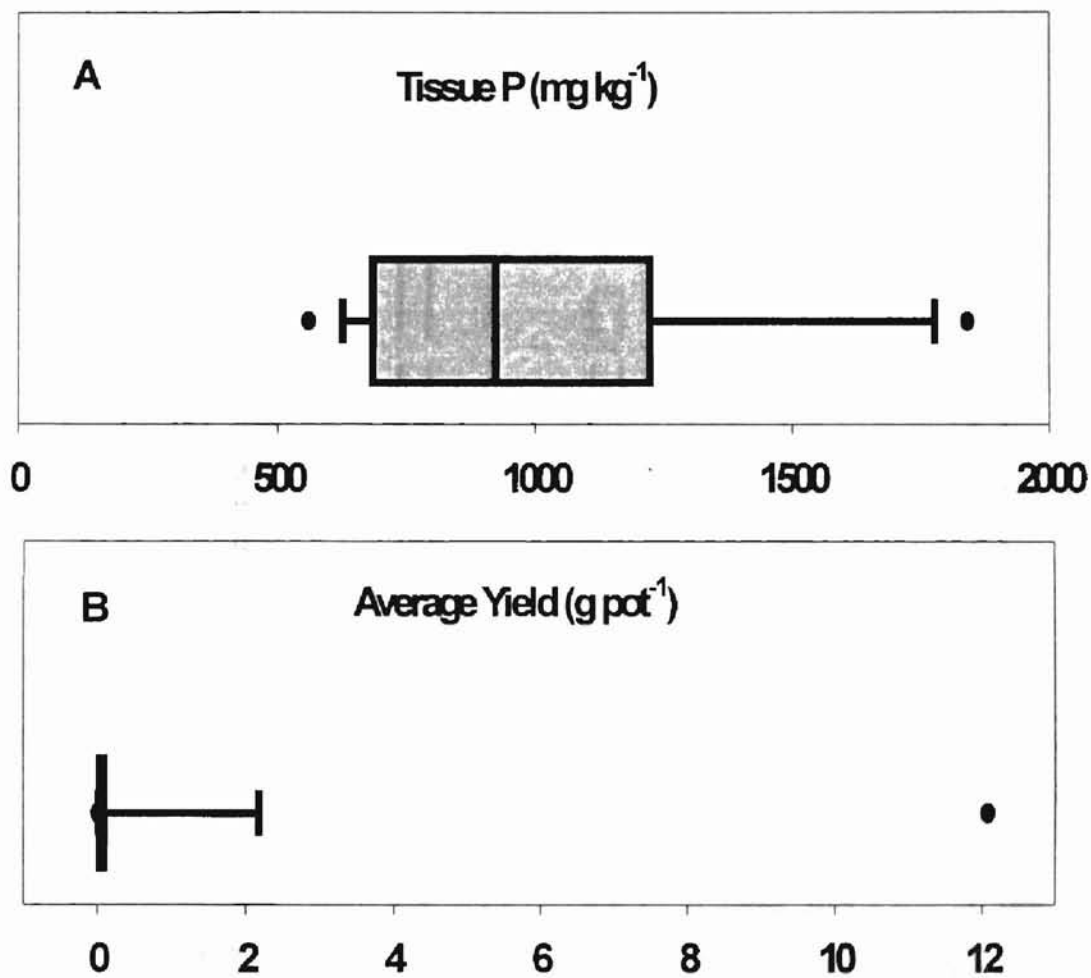


Figure 6. Statistical summary of tomato bioassay levels of (A) tissue P and, (B) average vegetative yield per pot.

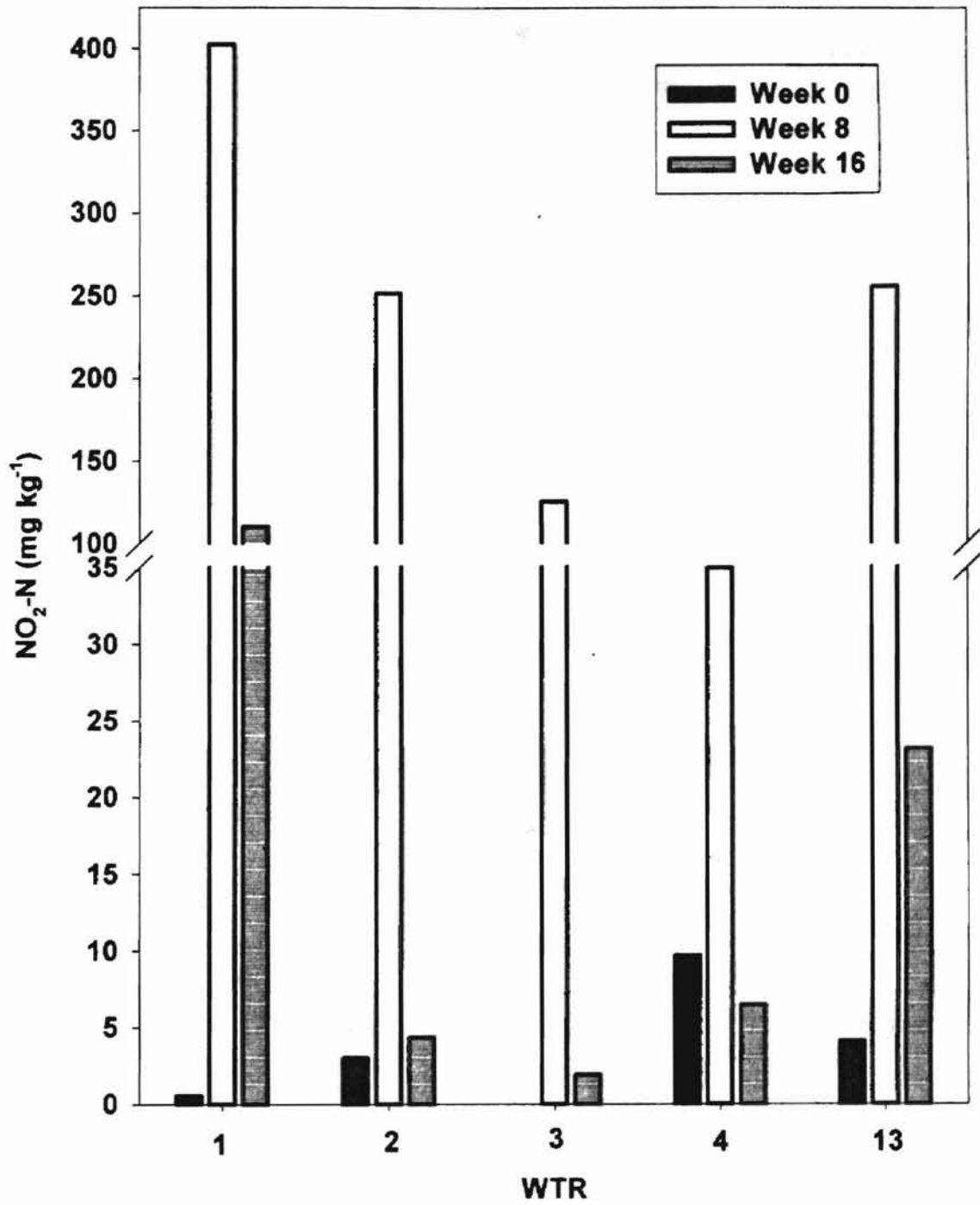


Figure 7. Water soluble NO₂-N levels of WTR 1, 2, 3, 4 and 13, in tomato pots, from tomato bioassay at, 0, 8 and 16 weeks.

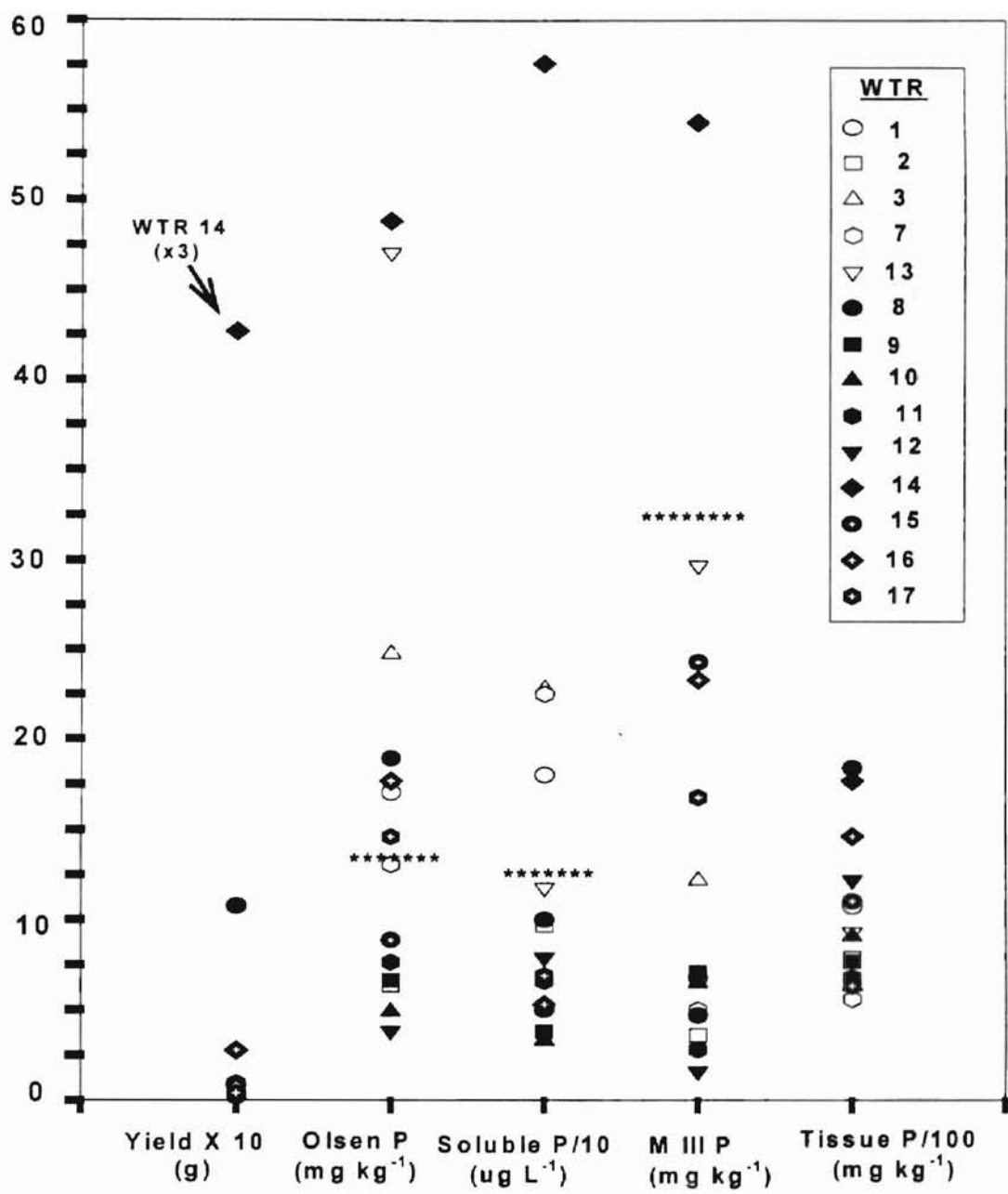


Figure 8. Average tomato vegetative yield per pot, Olsen extractable P, water soluble P (divided by 10), Mehlich III extractable P, and tomato tissue P (divided by 100), for WTR. ***** indicates adequate level for P. Unfilled symbols denote WTR with toxic (> 10 mg kg⁻¹ NO₂-N).

CHAPTER II

PHOSPHORUS SORPTION CAPACITY OF DRINKING WATER TREATMENT RESIDUALS FOR POTENTIAL USE AS A P SORBENT TO PROTECT WATER QUALITY

ABSTRACT

Land application of manure is an economically viable disposal option for animal producers. However, when P application rates exceed crop requirements manure application can become an environmental problem, threatening water quality. Land application of drinking water treatment residuals (WTR) as a P sorbent is one potential strategy to protect water quality. The objectives of this work were to (1) determine the P sorption capacity of a variety of WTR and (2) determine WTR components or chemical processes (precipitation, adsorption) responsible for the P sorption capacity. Eighteen WTR from municipalities in Oklahoma and nine non-calcareous soils, used for comparison with the WTR, were studied. Chemical properties and components related to P sorption were measured in WTR and soil. Amorphous Al and Fe (Al_{ox} and Fe_{ox}) and water soluble Ca (ws Ca), were used as potential indices of P sorption. Phosphorus sorption isotherms were generated by batch equilibration. Using the batch equilibration data the linearized Langmuir P adsorption maxima (P max), the non-

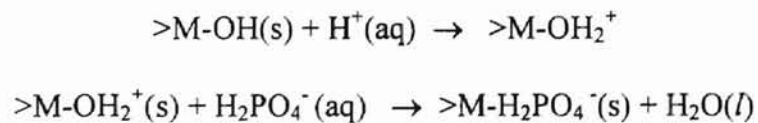
linear Freundlich distribution coefficient ($P K_d$) were determined to examine P sorption. Using the Al_{ox} and Fe_{ox} levels, a third model was used to examine the P sorption capacity (PSC). MINTEQA2, a geochemical speciation model, was used to determine potential phosphate mineral precipitation during the batch equilibration. The median P max of the WTR was 6.7 times greater than that of the soil, 1.0 and 0.15 $g\ kg^{-1}$, respectively. The median $P K_d$ of the WTR was 24 times greater than that of the soil, 236 and 9.72 $L\ kg^{-1}$, respectively. The median WTR PSC was 35 times greater than for the soil, 20 and 0.57 $g\ kg^{-1}$ respectively. The correlation of WTR P max and $P K_d$ with Al_{ox} and ($Al_{ox} + Fe_{ox}$) were significant ($P < 0.01$). Neither WTR P max or $P K_d$ were significantly correlated with Fe_{ox} . MINTEQA2 was configured to consider only precipitation and not adsorption during the simulations. The results showed positive saturation indices (SI) for 0, 4, 10, and 14 of the 18 WTR for equilibration of WTR with 4, 8, 16, or 32 $mg\ L^{-1}$ P solutions, respectively. Positive SI values indicate super saturation of the WTR solution with respect to calcium phosphate solid phases considered, and potential precipitation of these solid phases. Precipitation of calcium phosphate minerals would entail concurrent losses of P and Ca from solution. The batch equilibration data showed that dissolved P decreased but dissolved Ca did not decrease. Therefore, P adsorption and not precipitation is likely the predominant mechanism for P sorption by WTR during the batch equilibration.

Introduction

Soluble P in runoff water, or eroded soil can threaten surface water quality. Land application of manure is an economically viable disposal option for animal producers and has other benefits, including, soil organic matter and plant of nutrients. When P application rates exceed crop requirements, however, manure application can become an environmental problem. The role of P runoff from agricultural land in the eutrophication of surface water has been well documented (Sharpley et al., 1994; Daniel et al., 1998; Correll, 1998). Excessive soil P levels, as a result of poultry production, has been implicated in the degradation of water quality in the Chesapeake Bay and its tributaries (Sims and Price, 1998). As a result of increased concern, many states are developing manure application limits based on water quality. The Oklahoma Natural Resources Conservation Service (NRCS) Conservation Practice Standard Waste Utilization Code 633 proposed guidelines for land application of waste (NRCS, 1995). In an effort to protect water quality in P-sensitive watersheds, USEPA Region VI CAFO regulations (Smolen and Caldwell, 1994) and the Oklahoma Feed Yard Act have adopted the NRCS guidelines to limit the application of animal manure to land with excessively high soil P. The state of Maryland is requiring nutrient users, both agricultural and non-agricultural, to implement N and P based management plans (Sims et al., 1999). Where water quality standards are not being met, states must develop total maximum daily load limits (TMDL) to determine new point source permit limits. Currently, there are over 20 lawsuits pending against the USEPA for failing to develop TMDL in areas where water quality continues to be degraded (Parry, 1998). A lawsuit filed by environmental groups in Delaware, resulted in a

Total Maximum Daily Load Agreement between the state of Delaware and the USEPA which requires the state to set limits on the amount of pollutants, including nutrients, that can be discharged into water by point and non-point sources and to develop strategies to reduce pollutant levels (Sims et al., 1999). Often land application rates for manure and biosolids are based on crop N requirements resulting in a two to threefold excess P application (Parry, 1998). Current strategies used to reduce the transport of P to surface waters include the use of conservation tillage, crop residue management, cover crops, buffer strips, contour tillage, runoff water impoundments and terracing. However, these strategies are more efficient at controlling particulate P in runoff than dissolved P (Sharpley et al., 1994; Daniel et al., 1998). In order to achieve reductions in P transport to surface water, new best management practices (BMP) need to be developed and implemented to control soluble P (Sims et al., 1999).

One possible BMP is to render P insoluble, either by ligand exchange through the addition of Al or Fe oxides, or precipitation reactions, through the application of Ca containing materials as a strategy to protect surface water quality. Hydroxyl groups associated with the surfaces of Al and Fe oxides, hydroxides and oxyhydroxides (hydrous oxides) are a major source of P sorption capacity in soil and form insoluble surface complexes when they react with P from the soil solution (Sparks, 1995; Sposito, 1989; Bohn et al., 1985; McBride, 1994). Phosphate is adsorbed onto hydrous metal oxides through the following ligand exchange reaction:



M is usually Al or Fe. The covalent bond formed between the hydrous oxide and phosphate is very stable (Sposito, 1989).

Precipitation of soluble P as a phosphate mineral is another potential mechanism to remove P from solution. Materials that contain high levels of calcium and have a pH near 7.0 favor the formation of calcium phosphates, while Al or Fe phosphates are more stable in highly acid soils (Lindsay, 1979). Increases in the calcium phosphate mineral P fraction was found after incubating soils with KH_2PO_4 or manure leachate for 24 hours (Robinson and Sharpley, 1996). Adsorption and precipitation reactions can occur consecutively or simultaneously and it is difficult to distinguish which mechanisms are operating. Some degree of super-saturation of an ion needs to occur, however, in order for precipitation to commence (McBride, 1994).

Due to their high P fixing ability, Al and Fe containing materials and waste materials have been studied as P sorbents in soils with excessive P levels. Phosphorus fixation, by bauxite mining residuals (red mud), which are rich in Fe oxides has been studied. Red mud has been investigated as a soil amendment to reduce P runoff and leaching, in an effort to protect groundwater quality (Barrow, 1981; Ward and Summers, 1993; Vlahos et al., 1989; Peters and Basta, 1996). Alum, $(\text{Al}_2(\text{SO}_4)_3$, (not precipitated as in WTR) has been used as an amendment in poultry litter to decrease water-soluble P levels (Moore & Miller, 1994; Shreve et al., 1995). The mechanisms of P sorption, by Al and Fe containing materials, have been the subject of study. The relative sorption capacities of freshly prepared allophane, a disordered aluminosilicate, Al gel, aged Al gel, and gibbsite were investigated by McLaughlin et al., (1981). The P sorbed by these components decreased in the order allophane > fresh Al

gel > aged Al gel > gibbsite. The authors attributed the differences in P sorption to the number of functional Al-OH groups available. The relative P sorption capacity of natural samples of allophane, ferrihydrite, hematite and goethite were determined by Parfitt, 1989. The relative amount of P sorbed after 10 days of incubation was allophane > ferrihydrite > goethite > hematite. The authors attributed the P sorption to a ligand exchange reaction. Similarly, P reaction mechanisms were studied in three Andosols, rich in allophane (Pardo and Guadalix, 1990). They found that as more P was sorbed increased displacement of OH was also observed.

Drinking water treatment residuals (WTR) are the by-product of the drinking water treatment process where coagulation is used to remove turbidity, color, odor and taste from raw water and to speed sedimentation. Residuals generated using, Alum, $\text{Al}_2(\text{SO}_4)_3$, or a polymer (poly-aluminumchloride) as a coagulant, are investigated in this work. WTR contain suspended solids and organic material from the raw water, as well 50 – 150 g kg^{-1} amorphous aluminum hydroxide, the reaction product of coagulation (ASCE, 1996). In this work the P sorbing capacity of drinking water treatment residuals (WTR) will be examined.

WTR has been used to reduce soluble P in soils that have excessive amounts of bioavailable P from manure application (Peters & Basta, 1996). Application of WTR in a buffer strip, reduced soluble P in runoff water from 22.3 to 4.93 mg L^{-1} . Surface application of WTR as a buffer strip, to pasture treated with poultry litter, reduced soluble P from 15 mg L^{-1} to 8.1 mg L^{-1} (Gallimore et al., in press). Large differences in sorption capacity were found between the two WTR used in these studies. In another study, WTR was applied to plots planted in fescue. After 4 months, at the

high rate of WTR application, 18 Mg ha⁻¹, dissolved P in runoff water was reduced from 1.08 to 0.43 mg L⁻¹ (Daniel et al., 1999). Transformations of P in soils amended with alum WTR have also been investigated. Results of P fractionation experiments showed that levels of labile P decreased while the less soluble chemisorbed Al and Fe and Ca-bound fractions of P increased with the addition of the WTR (Jonasson, 1996; Cox et al., 1997).

The objectives of this work were to (1) determine the P sorption capacity of a variety of WTR and (2) to determine WTR components or chemical processes (precipitation, adsorption) responsible for the P sorption capacity.

MATERIALS AND METHODS

Fifteen alum and 3 polymer (poly-aluminumchloride) based, for a total of 18 WTR, were collected from municipal drinking water treatment plants across Oklahoma. Nine non-calcareous Oklahoma Benchmark Soils with textures ranging from clay to loamy fine sand were used for comparison with the WTR. All materials were air-dried and crushed to < 2.0 mm.

Chemical Characterization

Chemical properties and components related to P sorption were measured in WTR and soil. Amorphous Al and Fe (Al_{ox} and Fe_{ox}), and water-soluble Ca (ws Ca), were used as potential indices of P sorption. Amorphous Al and Fe in WTR and soil were determined by acid ammonium oxalate extraction (McKeague and Day, 1966) followed by inductively coupled plasma atomic emission spectroscopy (ICP) analysis.

Water soluble Ca was measured by shaking 5 g WTR with 25 mL deionized water for 1 hr followed by ICP analysis. WTR and soil pH were determined in a 1:2 WTR:0.01M CaCl₂ solution (McLean, 1982).

Phosphorus Sorption

Phosphorus sorption isotherms were generated by batch equilibration by shaking 1g WTR:25 mL of 0, 4, 8, 16, or 32 mg L⁻¹ P solutions, prepared from NaH₂PO₄, for 15 hr. Solution P was measured by the modified Murphy-Riley colorimetric method (Murphy and Riley, 1962), and sorbed P was determined by difference. The linearized Langmuir P sorption maxima (P max) and the non-linear Freundlich distribution coefficient (P K_d) were determined as two measures of P sorption by WTR and soil. The linearized Langmuir equation used was

$$c/x/m = 1/kb + c/b$$

where c = the equilibrium solution P concentration in mg L⁻¹, x/m = the amount of P sorbed in mg kg⁻¹, k = the bonding energy coefficient, and b = P adsorption maxima in mg kg⁻¹. The non-linear Freundlich equation used is

$$q = K_d C^{1/n}$$

where q = the amount of P sorbed in mmol kg⁻¹, K_d = a distribution coefficient in L kg⁻¹, C = equilibrium P concentration in mmol L⁻¹, and n = a correction factor (Sparks, 1995). A third measure of P sorption capacity (PSC) considered in this study and one that has gained acceptance in the Netherlands is

$$PSC = 0.5 (Al_{ox} + Fe_{ox})$$

Where Al_{ox} and Fe_{ox} are acid ammonium oxalate extractable Al and Fe in $mmol\ kg^{-1}$ (Van der Zee, 1988). This model is used for non-calcareous soils and assumes that the mechanism of P sorption is chemisorption on amorphous Al and Fe oxides (Schoumans, 1998).

Potential Precipitation

The geochemical assessment model MINTEQA2 (ver.3.11) was used to determine potential phosphate mineral precipitation during the generation of the P adsorption isotherms. A modified thermodynamic database, was used in the model (Lindsay, 1993). Dissolved cations and anions in WTR were determined by shaking five g WTR with 25 mL of de-ionized water for one hour, solutions were filtered through 0.45 μm membrane filters, cations were measured by (ICP), and anions by ion chromatography (IC). Dissolved concentrations of Al^{+3} , Ca^{+2} , Cl^{-} , K^{+} , Mg^{+2} , Mn^{+2} , Na^{+} , NO_3^{-} , NO_2^{-} , SO_4^{-2} , Zn^{+2} and pH (1:2, WTR:0.01M $CaCl_2$) were input data for MINTEQA2. Saturation indices were calculated by MINTEQA2. Phosphorus solid phases were calculated using initial dissolved P concentrations of 0, 4, 8, 16 Or 32 $mg\ L^{-1}$ from the batch equilibration study. The saturation index (SI) is defined as

$$SI = \log IAP/K_f$$

where, IAP is the ion activity product of the appropriate chemical species and K_f is the formation constant of the possible solid phase. An $SI > 0$ indicates super-saturation while an $SI < 0$ indicates under-saturation of the soil solution, with respect to a specific mineral. As the dissolution-precipitation reaction nears equilibrium, the SI value approaches zero (Allison et al., 1991). The calcium phosphate possible solids in

the thermodynamic database used included brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), monetite (CaHPO_4), octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 2.5\text{H}_2\text{O}$), whitlockite ($B\text{-Ca}_3(\text{PO}_4)_2$), and hydroxapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). The saturation indices of the possible solid phases were used to determine if precipitation of phosphate minerals could be occurring during the batch equilibration.

Results and Discussion

Phosphorus Sorption

The amount of P sorbed by the WTR, during the batch equilibration, was substantially greater than the mean P sorbed by the soils (Figure 1). There is a tremendous range in adsorption capacity among the WTR but a trend for WTR type (alum/polymer) and P sorption capacity was not apparent. Three models of P sorption were used to further examine batch equilibration data (Figure 2). The median Langmuir P sorption maxima (P max) of the WTR (1.0 g kg^{-1}) is 6.7 times higher than that of the soil (0.15 g kg^{-1}). The WTR P max ranged from 0.53 to 1.2 g kg^{-1} while the soil P max ranged from 0.035 to 0.18 g kg^{-1} (Figure 2A). Figure 3 is a key for the interpretation of the statistical box plots used to present data in Figure 2 and 4. The linearized Langmuir adsorption isotherm model, was first applied to describe P sorption in soil by Fried and Shapiro (1956) and Olsen and Watanabe (1957). The Langmuir equation was originally developed to describe adsorption of gas molecules on planar surfaces. Due to the heterogeneous nature of soils, the Langmuir isotherm can be used qualitatively to describe adsorption phenomena, but it can also describe

precipitation (Veith and Sposito, 1977) and so should not be used to make mechanistic determinations. So although the WTR data conformed well to the Langmuir adsorption model ($r^2 > 0.90$, $P < 0.01$), adsorption and/or precipitation may have occurred. While not resolving mechanistic questions, the Langmuir adsorption isotherm has the distinct advantage of providing a calculated sorption maxima (P_{max}), which allows the sorption capacity of a material to be determined. The second sorption model used was the non-linear Freundlich equation ($P K_d$), a strictly empirical sorption model, commonly used to describe adsorption and/or precipitation phenomena (Figure 2B). The WTR batch equilibration data fit the Freundlich equation well ($r^2 > 0.95$, $p < 0.01$), with derived values of n ranging from 0.33 to 0.71. The median $P K_d$ of the WTR (236 L kg^{-1}) is 24 times greater than that of the soil (9.72 L kg^{-1}). The $P K_d$ term relates to the affinity of a material for P. For similar values of n , the $P K_d$ can be used to compare the amount of P sorbed by different materials relative to each other but does not provide a sorption maxima. The WTR $P K_d$ values ranged from 35 to 1317 L kg^{-1} . This broad range indicates a wide variation in affinity for P by different WTR. The third P sorption model used has gained wide acceptance in the Netherlands and is used to determine the P sorption capacity (PSC) of non-calcareous soils. The PSC model assumes adsorption of P occurs only on amorphous Al and Fe oxides (Figure 2C). The median PSC of the WTR is 35 times greater than for the soil, with 20 g kg^{-1} for WTR and 0.57 g kg^{-1} for soil. The large variability in P sorption capacities of the WTR (Figures 1 and 2) is most likely attributable to differences in the water treatment process (i.e. how much coagulant is used) and to differences in the

sediment content of the raw source water. For example, the Al_{ox} content of the WTR ranged from 1.0 to 67 $g\ kg^{-1}$.

The chemical properties and components that effect P sorption for WTR and soil are shown in Tables 1 and 2, respectively. The WTR contain substantially greater amounts of amorphous Al oxides than soil. Adsorption of P in soil is related to hydrous metal oxide content (Sparks, 1995; Sposito, 1989; Bohn et al., 1985; McBride, 1994). The median WTR Al_{ox} content is 32.0 $g\ kg^{-1}$ vs 0.74 $g\ kg^{-1}$ for the soil and the median WTR Fe_{ox} content is 4.9 $g\ kg^{-1}$ vs. 0.81 $g\ kg^{-1}$ for the soil (Figure 4). Having 43 times as much Al_{ox} and 6 times as much Fe_{ox} as the soil, WTR has much greater sorption capacities than soil. The ratio of $Al_{ox}:Fe_{ox}$ for the WTR is 6.6, while for the soil is 0.91. The disproportionately high $Al_{ox}:Fe_{ox}$ content in WTR compared to soil is the result of the Al oxide generated from coagulation.

The correlation of the P max and P K_d with the chemical properties and components related to P sorption (Al_{ox} and Fe_{ox}) for WTR and soil were determined. The WTR and soil P max and P K_d are significantly correlated ($P < 0.01$) with Al_{ox} and $Al_{ox} + Fe_{ox}$ (Table 3). Statistical analysis of linear regression parameters showed all slopes were different from zero. Figures 5 and 6 illustrate the relationship of WTR and soil P max with Al_{ox} , for WTR and soil respectively. Neither the P max or P K_d of the WTR was significantly correlated with Fe_{ox} . It is possible that the disproportionately large $Al_{ox}:Fe_{ox}$ prevented a correlation between P max or P K_d and Fe_{ox} . If the coagulant used was an Fe salt, such as $Fe_2(SO_4)_3$ or $FeCl_3$, a significant correlation between P sorption and Fe_{ox} may have been obtained. There was no significant correlation between WTR P max or P K_d with water-soluble Ca. This lack

of correlation does not rule out the possibility of calcium-phosphate precipitation because, the preponderance of Al_{ox} may be masking P precipitation. Significant regressions ($r^2 > 0.85$) between P sorption parameters (EPC and PBC) and amorphous Al, measured using citrate dithionate bicarbonate extraction, were found in soils amended with alum WTR (Elliott et al., 1990). Because soils were amended with alum WTR at $\leq 100 \text{ g kg}^{-1}$, it is likely that P sorption was influenced by both soil and alum WTR properties. The soil P max and P K_d were, significantly correlated ($P < 0.01$) with Al_{ox} and $Al_{ox} + Fe_{ox}$, and were also significant ($P < 0.1$) with Fe_{ox} . To our knowledge, no information on the correlation of P sorption with Al_{ox} or Fe_{ox} in WTR is reported in the literature.

Potential Precipitation

The Langmuir and the Freundlich model cannot be used to determine sorption mechanisms, because both adsorption and/or precipitation data often fit both models. Therefore, it is possible that the WTR P sorption mechanism may be adsorption and/or precipitation. In an attempt to determine the P sorption mechanism(s), precipitation was investigated by applying MINTEQA2 (a geochemical equilibrium model) to investigate the potential precipitation of monetite or brushite in the batch equilibration study used to generate the P max and P K_d values. The MINTEQA2 model considers both precipitation and adsorption processes, but was configured, in this study, to consider only precipitation and not adsorption. MINTEQA2 simulations showed positive saturation indices (SI) for 0, 4, 10 and 14 of the 18 WTR for equilibration of WTR with 4, 8, 16 or 32 mg L^{-1} P solutions, respectively. Positive SI values indicate

super saturation of the WTR solution with respect to calcium phosphate solid phases considered (brushite and monetite), and potential precipitation of these solid phases. However precipitation may not have occurred because, competing adsorption processes not considered by MINTEQA2, may have reduced solution P concentrations to undersaturated levels for the formation of the calcium phosphate solid phases. Also, MINTEQA2 is an equilibrium model that relies solely on thermodynamic data and does not consider chemical kinetics (Allison et al., 1991). The formation of calcium phosphate minerals other than monetite and brushite was considered too slow to have been a factor in the 15 hr batch equilibration study (Lindsay, 1979; Sposito, 1989). Precipitation of calcium phosphate minerals would entail concurrent losses of P and Ca from solution. The highest P solution concentration used in the batch equilibration was 1.0 mM and Ca concentration ranged from 0.18 to 2.1 mM with an average of 0.84 mM. The batch equilibration data showed that dissolved P decreased but dissolved Ca did not decrease. Thus, P adsorption and not precipitation was likely the predominant mechanism for P sorption by WTR during the 15 hr batch equilibration.

Conclusions

While generally considerably higher than soils, the WTR examined in this study exhibited a wide range of adsorption capacities. Before a WTR is used as a P sorbent, the adsorption capacity should be tested, to determine if it will perform adequately. This study suggests that there is an empirical relationship between Alox and P sorption capacity. While no Ca precipitation occurred during the 15 hr batch equilibration

study, Ca precipitation may be a significant source of P sorbtion in the long term. Long term sorption and desorption studies in the lab and in the field, using a broad range of WTR will aid in the effective use of WTR as a P sorbent in the short-term and long-term protection of surface water quality.

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Table 1. Chemical properties, related to P sorption, of drinking water treatment residuals.

Material	Type†	pH	Al _{ox} ‡	Fe _{ox} ‡	ws Ca‡
			-----g kg ⁻¹ -----		
Bartlesville	A	7.1	41.4	2.17	0.46
Broken Bow	A	7.0	45.4	7.53	0.05
Claremore	A	7.7	38.0	5.40	0.36
Chickasha	A	7.8	44.2	1.78	0.63
Clinton	A	7.7	30.6	2.64	0.41
Comanche	A	7.6	1.05	1.44	0.18
Draper Lake	P	7.7	7.31	5.44	0.28
Henryetta	P	6.6	2.55	13.0	0.16
Hugo	P	7.0	34.0	10.3	0.14
Idabel	A	6.9	49.5	15.1	0.28
Lawton	A	7.7	22.9	1.77	0.25
McAlester	A	5.3	67.2	1.79	0.14
Mohawk	A	7.5	27.9	5.82	0.74
Muskogee	A	7.2	26.8	6.36	0.51
Sallisaw	A	7.8	24.0	5.14	0.34
Sand Springs	A	7.0	45.9	4.30	0.12
Wagoner	A	7.0	45.9	4.74	0.37
Wister	A	6.6	9.70	3.52	0.11
Average		7.2	32.3	5.26	0.30
Median		7.4	34.0	4.74	0.28

† A = alum WTR, P = polymer WTR,

‡ Al_{ox} & Fe_{ox} = acid ammonium oxalate extractable Al & Fe,
ws Ca = water soluble Ca.

Table 2. Selected chemical properties of soils.

Soil Series	Texture	pH	Al _{ox} †	Fe _{ox} †
			----- g kg ⁻¹ -----	
Bernow	Fine sandy loam	3.8	0.21	0.74
Clarksville	gravely silt loam	4.7	1.18	1.40
Dougherty	Loamy fine sand	4.3	0.29	0.28
Durant	Loam	6.4	0.78	2.33
Kirkland	Silt loam	4.8	0.78	1.42
Lebron	Clay	7.4	1.12	1.30
Mansic	Clay loam	7.7	0.74	0.34
Pratt	Loamy fine sand	5.7	0.12	0.15
Tillman	Silty clay loam	5.4	0.59	0.81
Average		5.6	0.65	0.97
Median		5.4	0.74	0.81

†Al_{ox} and Fe_{ox} = acid ammonium oxalate extractable

Table 3. Correlation coefficients of P sorption indices with P sorption capacities for WTR and soils.

P Sorption Capacities	Chemical Properties		
	Al _{ox} §	Fe _{ox} §	Al + Fe _{ox} §
WTR P max†	0.66**	-0.33	0.62**
WTR P K _d ‡	0.69**	-0.17	0.65**
Soil P max†	0.93**	0.69*	0.85**
Soil P K _d ‡	0.82**	0.77*	0.87**

† P max = Langmuir P adsorption maxima

‡ K_d = non-linear Freundlich distribution coefficient

§ Acid ammonium oxalate extractable

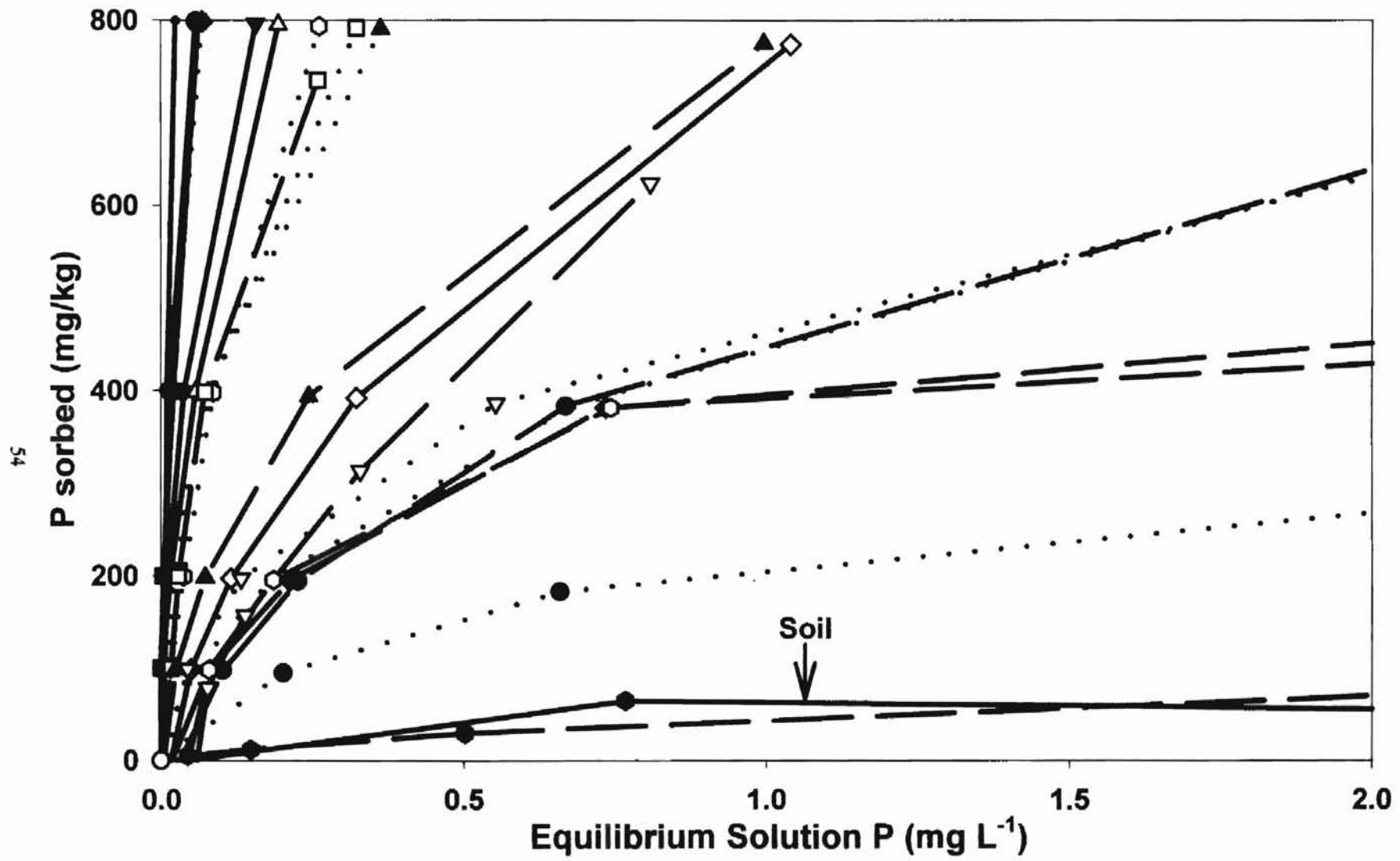


Figure 1. Comparison of phosphorus sorption isotherms of WTR with mean sorption isotherm values of soil.

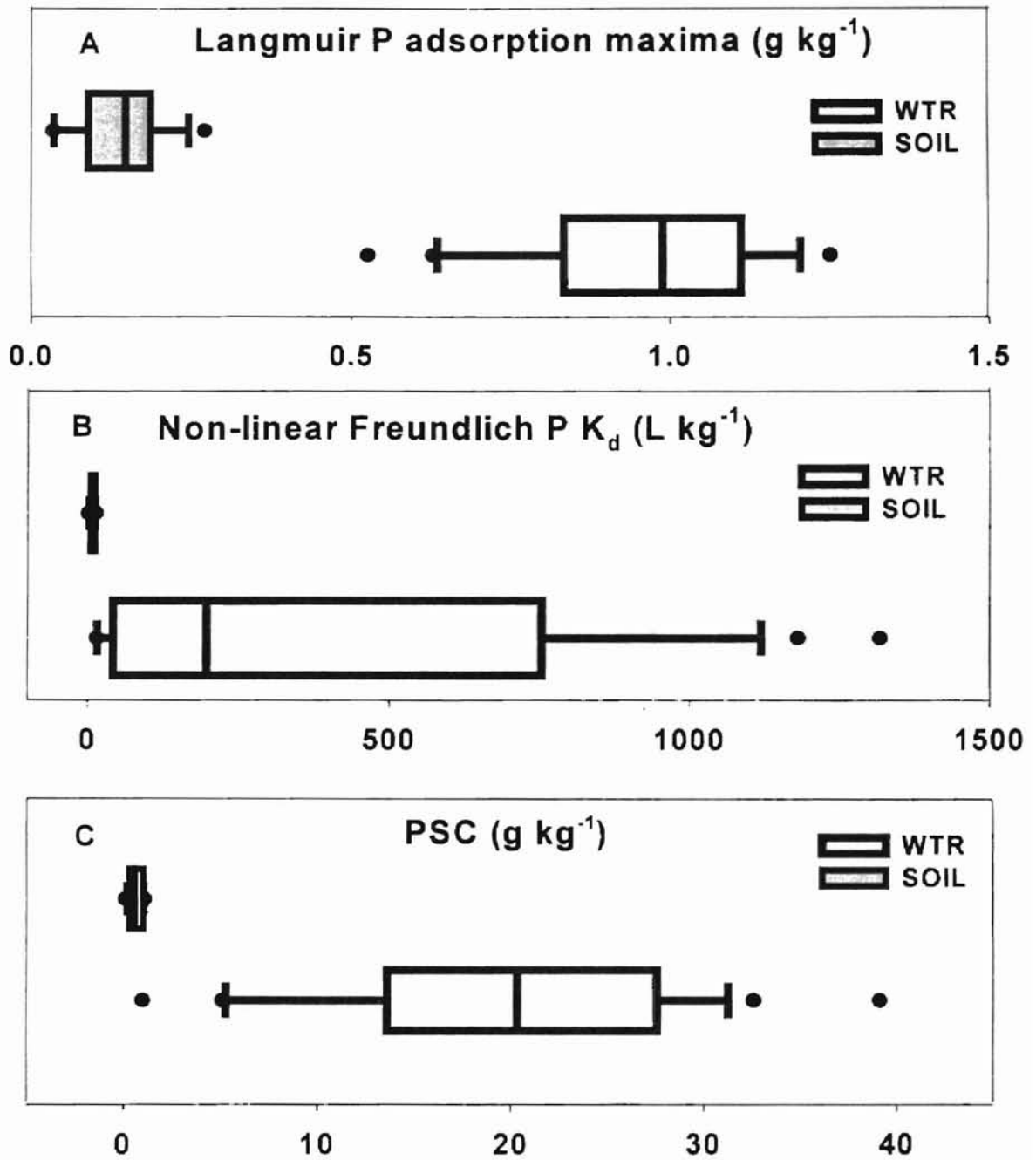
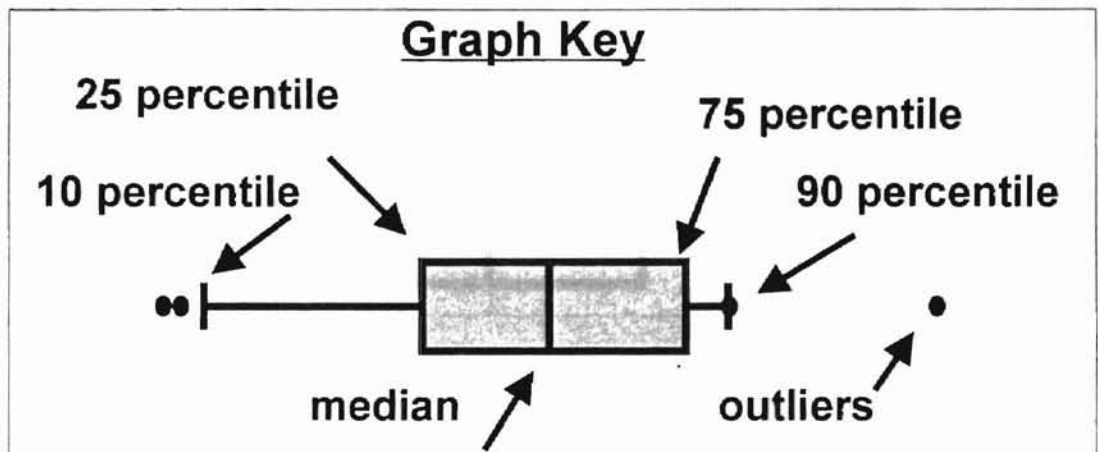


Figure 2. Statistical summary and comparison of WTR and Soil (A) Langmuir P adsorption maxima, (B) non-linear Freundlich P K_d and (C) Phosphorus sorption capacity (PSC).

Figure 3. Key to interpretation of the statistical box plots used in Figures 2 and 4.



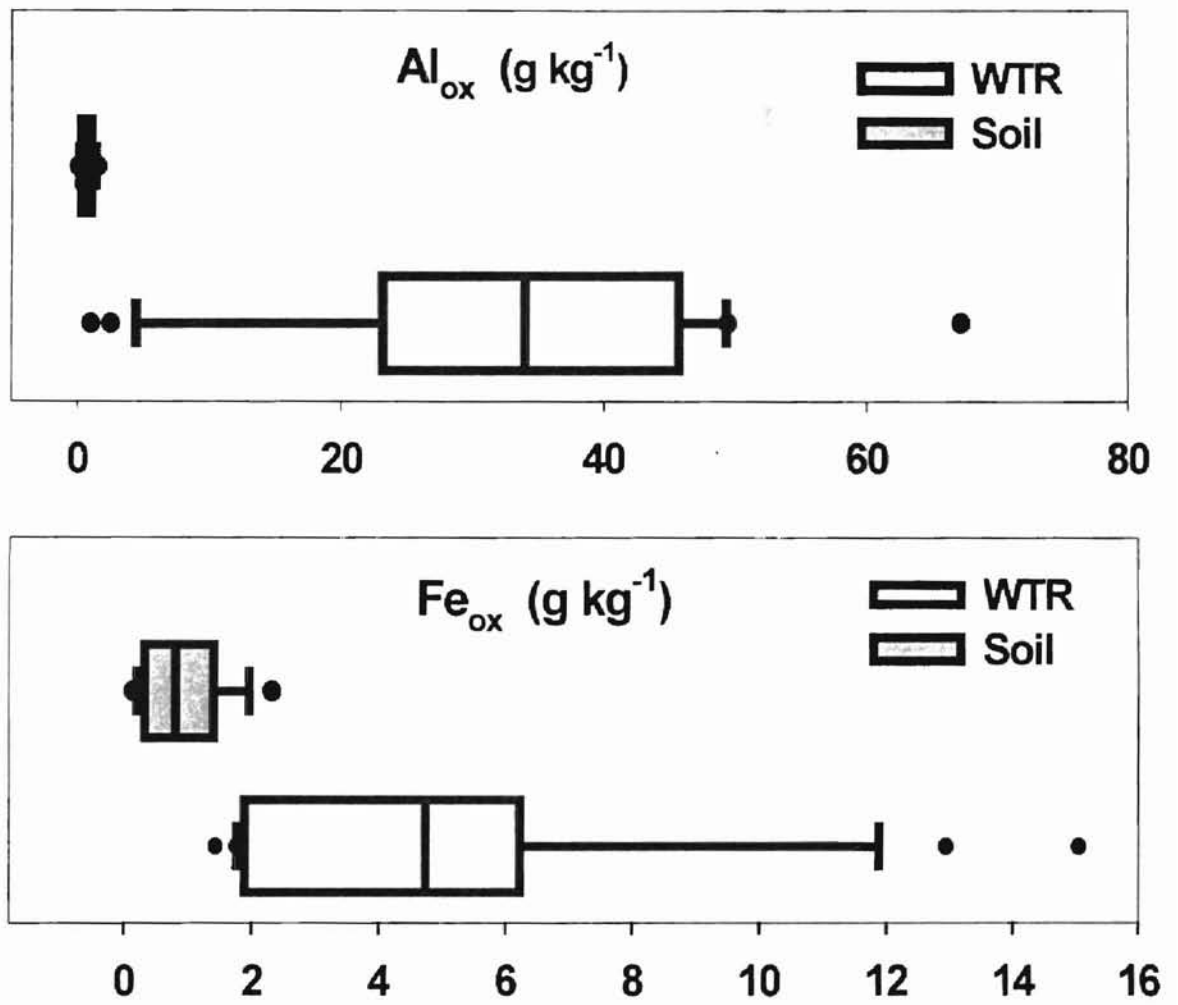


Figure 4. Statistical summary and comparison of WTR and soil levels of acid ammonium oxalate extractable (A) Al, and (B) Fe.

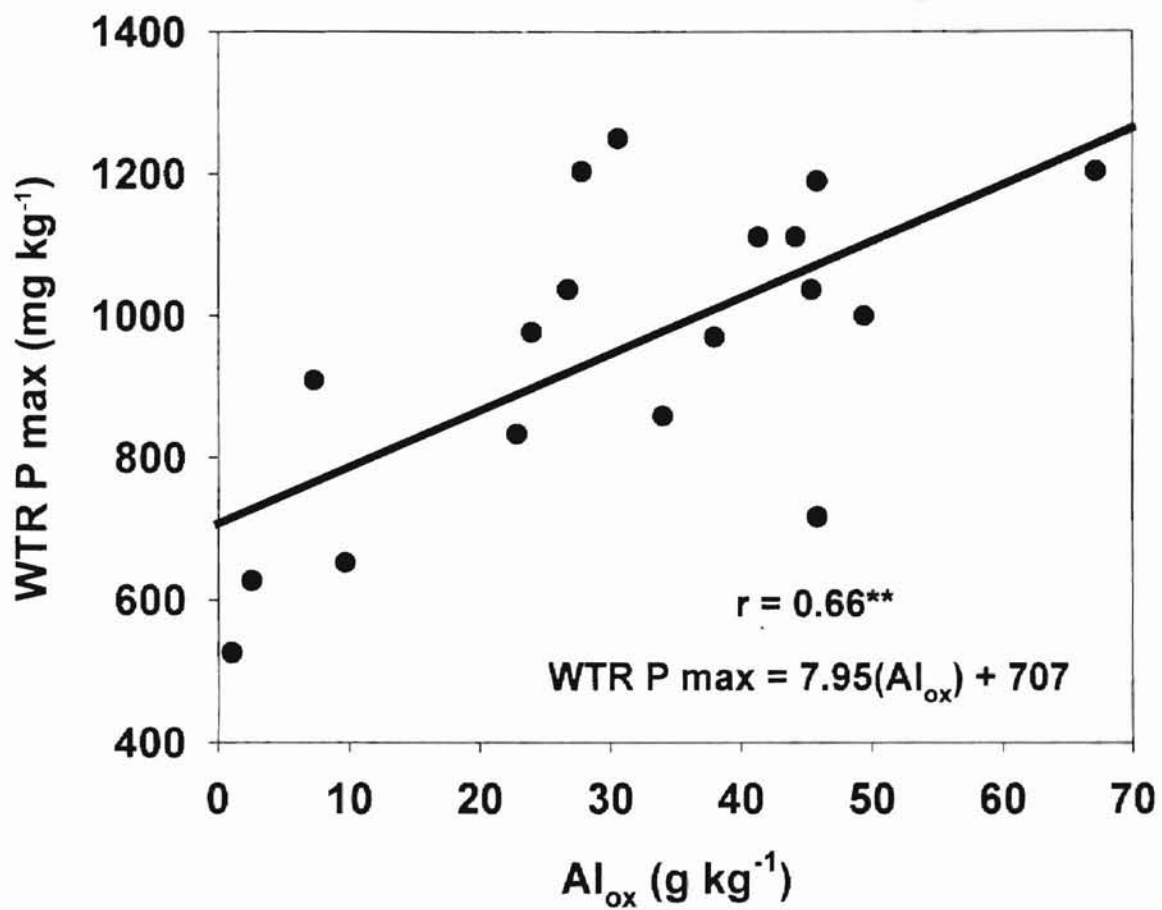


Figure 5. WTR Langmuir P sorption maxima vs acid ammonium oxalate extractable Al (Al_{ox}).

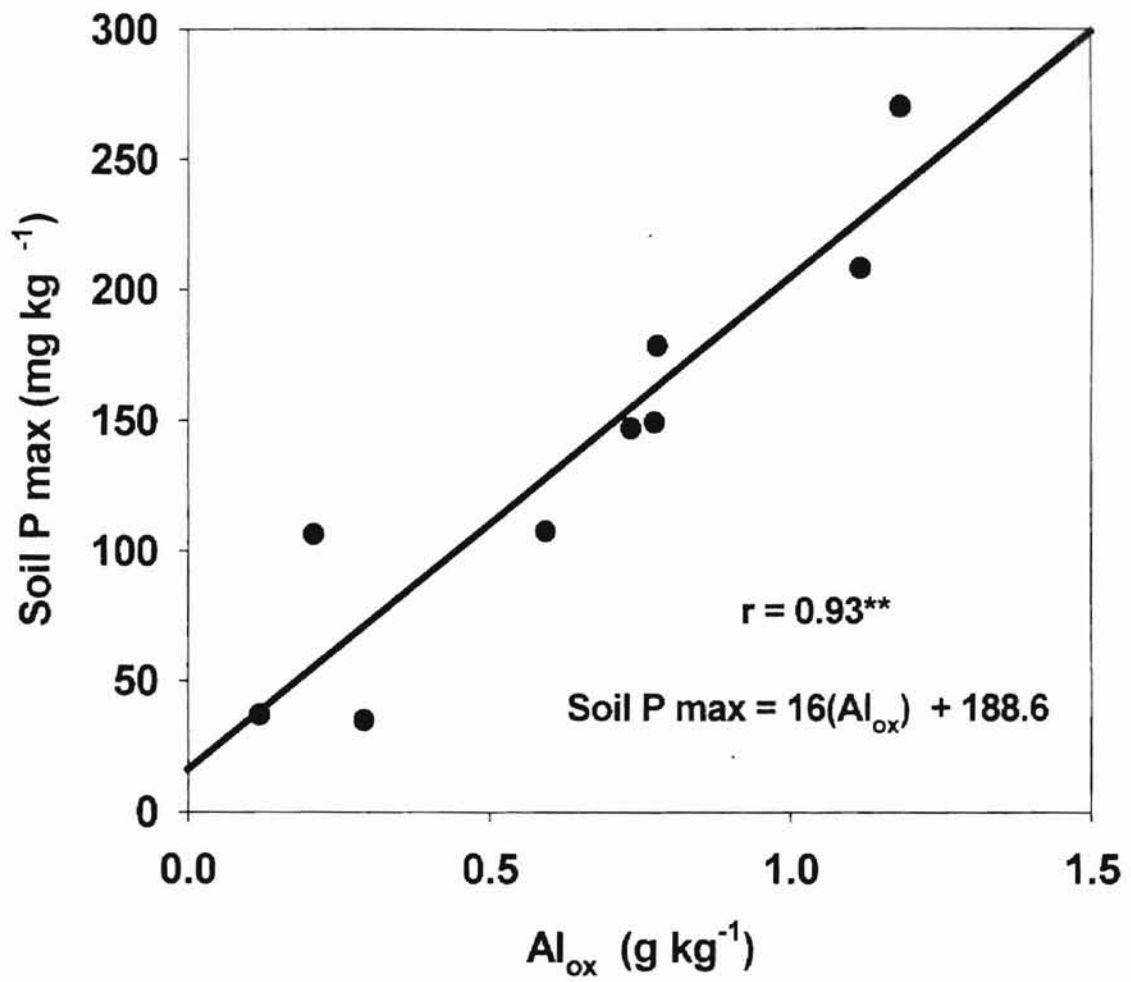


Figure 6. Soil Langmuir P sorption maxima vs acid ammonium oxalate extractable Al (Al_{ox}).

APPENDIX OF DATA

WTR Properties

WTR	rep	pH	CEC	EC	Total N	Gravimetric Water content		
						0.33 M Pa	0.5 M Pa	1.5 M Pa
			cmol kg ⁻¹	ds m ⁻¹	%			
1	1	7.11	56.0	0.63	1.06	45.0	48.0	39.4
1	2	.	57.1	.	.	55.1	49.2	33.9
2	1	7.10	47.3	0.54	0.71	55.7	38.6	.
2	2	.	46.2	.	.	55.0	38.8	25.3
3	1	7.01	13.0	1.09	1.84	70.9	42.6	34.8
3	2	.	24.6	.	.	70.9	41.4	47.5
4	1	7.75	51.0	0.60	0.82	28.6	29.9	30.2
4	2	.	51.0	.	.	28.6	29.7	14.5
5	1	7.77	44.1	1.08	1.21	48.4	38.5	41.9
5	2	.	44.4	.	.	48.1	38.9	25.9
6	1	7.59	18.2	0.37	0.13	26.5	14.3	10.6
6	2	.	9.1	.	.	25.7	13.9	7.1
7	1	7.65	37.3	0.44	0.39	36.3	33.1	29.7
7	2	.	32.3	.	.	35.5	34.6	.
8	1	6.56	22.5	0.28	0.76	42.5	37.3	24.6
8	2	.	36.7	.	.	42.6	28.2	34.4
9	1	7.00	18.3	0.27	0.56	29.9	28.1	24.8
9	2	.	22.4	.	.	25.2	26.6	24.8
10	1	6.94	31.1	0.40	0.48	26.1	26.6	23.3
10	2	.	27.8	.	.	26.0	25.8	23.6
11	1	7.70	30.8	0.59	0.23	43.5	26.3	23.0
11	2	.	29.1	.	.	43.3	28.4	22.6
12	1	5.29	39.4	0.43	0.59	62.2	52.3	47.8
12	2	.	24.0	.	.	65.6	52.4	47.3
13	1	7.53	29.7	1.03	1.46	65.4	51.0	38.6
13	2	50.9	51.2	38.9
14	1	7.23	34.0	0.67	0.79	37.7	27.5	23.5
14	2	.	27.1	.	.	37.6	33.2	24.0
15	1	7.03	16.4	0.22	0.73	28.6	21.9	17.8
15	2	.	19.1	.	.	28.0	22.9	18.7
16	1	7.02	31.7	0.80	0.79	32.9	29.0	25.2
16	2	.	32.1	.	.	33.1	29.2	25.4
17	1	6.64	18.5	0.22	0.28	17.4	18.4	11.4
17	2	.	14.2	.	.	20.0	19.8	12.6

WTR Nutrients

WTR	rep	NH ₄ -N mg kg ⁻¹	NO ₃ -N mg kg ⁻¹	Olsen P mg kg ⁻¹	MIII P mg kg ⁻¹	M III K mg kg ⁻¹
1	1	71.9	19.1	17.3	7.61	188
1	2	70.4	18.3	16.8	6.01	206
2	1	72.8	70.5	6.46	4.05	78
2	2	63.6	61.4	6.25	3.08	79
3	1	56.6	4.9	9.82	6.08	38
3	2	54.9	5.7	7.29	5.69	47
4	1	67.5	7.5	24.5	13.1	77.1
4	2	72.0	7.1	25.0	11.3	75
5	1	106	64.7	24.7	9.34	198
5	2	97.3	47.5	21.8	10.5	174
6	1	22.8	5.7	4.30	6.6	218
6	2	21.4	5.6	4.44	6.5	215
7	1	50.8	4.9	.	4.9	284
7	2	51.7	5.0	13.1	5.1	253
8	1	42.7	43.9	19.2	4.8	286
8	2	47.5	42.5	18.6	4.6	271
9	1	31.7	31.1	6.73	7.4	158
9	2	32.1	31.2	6.56	6.7	189
10	1	52.4	3.1	5.03	7.1	90
10	2	42.4	4.0	4.77	5.91	98
11	1	26.9	41.3	7.60	2.38	164
11	2	23.5	29.3	7.71	3.20	159
12	1	113	14.6	3.80	1.63	55.1
12	2	123	9.1	3.86	1.49	60.7
13	1	143	126.0	46.8	30.1	80.0
13	2	136	120.6	47.3	29.4	56.7
14	1	40.9	50.3	45.3	56.0	202
14	2	40.3	49.7	52.3	52.7	211
15	1	41.6	42.3	8.65	24.5	80.9
15	2	41.4	40.3	9.09	24.1	81.3
16	1	63.7	12.1	18.3	22.1	103
16	2	62.5	19.9	17.0	24.4	102
17	1	27.6	14.1	15.3	.	.
17	2	26.2	13.8	14.6	16.8	187

WTR Nutrients

WTR	rep	MIII Mg mg kg ⁻¹	MIII Ca mg kg ⁻¹	SO ₄ -S mg kg ⁻¹	Fe ppm	Zn ppm
1	1	50.1	2302	12.5	7.6	0.55
1	2	62.3	2957	.	.	.
2	1	327	19310	121	50.1	5.2
2	2	356	22820	.	.	.
3	1	96	626	94.5	85.9	70.3
3	2	110	568.2	.	.	.
4	1	258	2962	322	61.5	1.5
4	2	248	2648	.	.	.
5	1	456	7067	188	110.3	3
5	2	420	7389	.	.	.
6	1	754	5408	138	56.2	1.1
6	2	746	4457	.	.	.
7	1	1209	6746	89.5	69	22.9
7	2	1252	7197	.	.	.
8	1	531	1734	129	231	25.8
8	2	503	1755	.	.	.
9	1	86	862.6	122	103	2.3
9	2	116	1147	.	.	.
10	1	39	2249	212	60.4	2.3
10	2	41	2249	.	.	.
11	1	796	15770	154	23.4	17.9
11	2	780	14850	.	.	.
12	1	9	191.8	453	34.8	0.12
12	2	7	164.4	.	.	.
13	1	58.5	9209	122	58.8	1.3
13	2	53.4	8893	.	.	.
14	1	273	3129	247	101	19.8
14	2	285	3860	.	.	.
15	1	35	1862	40	34.3	2.9
15	2	32	1668	.	.	.
16	1	84	978.3	199	22	23.4
16	2	94	1133	.	.	.
17	1	117	1100	165	89.8	4
17	2					

Toxicity Characteristic Leaching Procedure

WTR	rep	As	Ba	Cd	Cr	Pb	Se
				mg L ⁻¹			
1	1	0.027	4.6	0.025	0.199	0	.
1	2	0.004	4.7	0.003	0.194	0	0.089
2	1	0.000	2.0	0.003	0.012	0.04	0.064
2	2	0.000	2.0	0.003	0.002	0.00	0.015
3	1	0.009	2.2	0.013	0.039	0.00	0.016
3	2	0.008	2.2	0.012	0.029	0.00	0.013
4	1	0.000	3.6	0.002	0.012	0.00	0.008
4	2	0.000	3.7	0.002	0.006	0.00	0.019
5	1	0.000	4.2	0.002	0.016	0.00	0.025
5	2	0.000	4.6	0.002	0.009	0.00	0
6	1	0.000	3.1	0.002	0.008	0.00	0
6	2	0.000	3.0	0.002	0.020	0.00	0
7	1	0.000	6.9	0.002	0.011	0.00	0
7	2	0.000	6.9	0.002	0.020	0.00	0
8	1	0.001	2.2	0.004	0.010	0.00	0
8	2	0.001	2.2	0.004	0.009	0.00	0.001
9	1	0.001	4.8	0.001	0.011	0.00	0
9	2	0.001	4.9	0.001	0.005	0.00	0.015
10	1	0.022	1.8	0.021	0.027	0.00	0.017
10	2	0.022	1.7	0.002	0.019	0.00	0.039
11	1	0.022	2.9	0.001	0.004	0.00	0.009
11	2	0.022	3.0	0.000	0.009	0.00	0.002
12	1	0.022	0.3	0.001	0.006	0.00	0.003
12	2	0.022	0.3	0.001	0.010	0.00	0.004
13	1	0.022	1.8	0.001	0.009	0.00	0.000
13	2	0.022	1.8	0.001	0.006	0.00	0.014
14	1	0.000	3.0	0.012	0.003	0.00	0.01
14	2	0.001	3.0	0.011	0.008	0.01	0.01
15	1	0.001	3.0	0.001	0.019	0.00	0.01
15	2	0.001	2.9	0.001	0.022	0.00	0.03
16	1	0.001	3.0	0.006	0.009	0.00	0.03
16	2	0.001	2.9	0.005	0.008	0.00	0.01
17	1	0.001	1.3	0.000	0.032	0.00	0.01
17	2	0.001	1.2	0.003	0.028	0.00	0.00

Tomato Bioassay Data

WTR	rep	Mean Foliage P mg kg ⁻¹	Mean Yield g pot ⁻¹	Bulk Density g cm ⁻³
1	1	1032	0.02	0.52
1	2	899	0.02	0.63
1	3	1299	0.02	.
2	1	768	0.05	0.74
2	2	818	0.03	0.75
2	3	783	0.04	0.72
4	1	978	0.03	0.77
4	2	821	0.04	0.83
4	3	109	0.03	0.82
7	1	746	0.07	0.93
7	2	490	0.10	0.98
7	3	446	0.11	0.93
8	1	1558	0.50	0.93
8	2	1648	1.66	0.96
8	3	2316	1.07	0.84
9	1	917	0.05	0.76
9	2	741	0.04	0.77
9	3	654	0.05	0.84
10	1	1117	0.09	0.84
10	2	848	0.06	0.82
10	3	768	0.08	0.81
11	1	894	0.06	1.19
11	2	461	0.01	1.20
11	3	695	0.05	1.13
12	1	1309	0.02	0.61
12	2	1316	0.01	0.64
12	3	1046	0.02	0.63
13	1	1058	0.05	0.58
13	2	988	0.06	0.54
13	3	757	0.06	0.57
14	1	1884	11.5	0.94
14	2	1890	11.4	0.90
14	3	1533	10.64	0.96

Tomato Bioassay Data

WTR	rep	Mean Foliage P	Mean Yield	Bulk Density
		mg kg ⁻¹	g pot ⁻¹	g cm ⁻³
15	1	904	0.09	0.93
15	2	.	.	0.94
15	3	1309	0.08	0.99
16	3	1214	0.18	1.07
17	1	721	0.03	1.19
17	2	.	.	.
17	3	606	0.06	1.34

Tomato Bioassay Nitrite Levels

WTR	rep	0 wks mg kg ⁻¹	8 wks mg kg ⁻¹	16 wks mg kg ⁻¹
1	1	1.05	414	93.2
1	2	0.00	390	127
2	1	2.89	237	4.7
2	2	3.09	264	4.0
4	1	0.00	97.0	0.0
4	2	0.00	153	3.8
7	1	10.03	19.9	7.7
7	2	9.23	50.0	5.3
8	1	0.00	1.32	0.0
8	2	0.00	0.00	0.0
9	1	1.57	14.3	0.0
9	2	1.61	1.93	0.0
10	1	0.00	0.00	0.0
10	2	0.00	0.00	0.0
11	1	4.74	0.00	0.0
11	2	0.00	0.00	0.0
12	1	0.00	2.69	0.0
12	2	0.00	0.00	0.0
13	1	3.14	211	28.5
13	2	5.05	299	17.8
14	1	0.00	2.30	0.0
14	2	0.00	11.2	0.0
15	1	5.31	1.28	0.0
15	2	7.33	1.35	0.0
16	1	0.00	0.00	0.0
16	2	0.00	0.00	0.0
17	1	0.00	0.00	0.0
17	2	0.00	.	0.0

WTR Sorption Capacity Data

WTR	rep	Al _{ox} mg kg ⁻¹	Fe _{ox} mg kg ⁻¹	P max g kg ⁻¹	PSC g kg ⁻¹	P K _d L kg ⁻¹
Bartlesville	1	44520	2253	1.11	24.4	773
Bartlesville	2	38304	2093			
Broken Bow	1	47000	8008	1.04	28.2	1317
Broken Bow	2	43880	7048			
Claremore	1	37496	5324	0.97	23.3	517
Claremore	2	38500	5476			
Chickasha	1	47280	1864	1.11	25.9	579
Chickasha	2	41160	1689			
Clinton	1	33036	2805	1.25	18.3	236
Clinton	2	28240	2466			
Comanche	1	1290	1574	0.53	1.0	14.6
Comanche	2	808	1303			
Draper Lake	1	8880	6492	0.91	5.7	86.1
Draper Lake	2	5740	4380			
Henryetta	1	2913	13708	0.63	5.1	17.1
Henryetta	2	2188	12188			
Hugo	1	37612	11004	0.86	22.4	157
Hugo	2	30436	9616			
Idabel	1	66360	19656	1.00	32.6	267
Idabel	2	32548	10464			
Lawton	1	29248	2198	0.83	13.6	15
Lawton	2	16480	1333			
McAlester	1	78840	2010	1.20	39.1	1180
McAlester	2	55600	1575			
Mohawk	1	34104	6668	1.20	17.6	754
Mohawk	2	21616	4980			
Muskogee	1	31812	7116	1.04	17.2	105
Muskogee	2	21764	5608			
Sallisaw	1	26232	5524	0.98	15.2	157
Sallisaw	2	21776	4748			
Sand Springs	1	51440	4612	1.19	27.6	977
Sand Springs	2	40440	3990			
Wagoner	1	54960	5384	0.72	27.7	42.0
Wagoner	2	36740	4092			
Wister	1	10784	3613	0.65	6.6	35.3
Wister	2	8628	3433			

Soil Sorption Capacity Data

Soil Series	Al _{ox} mg kg ⁻¹	Fe _{ox} mg kg ⁻¹	pH	P max g kg ⁻¹	PSC g kg ⁻¹	P K _d L kg ⁻¹
Bernow	168	722	3.8	0.11	0.32	6.65
Bernow	249	754				
Clarksville	1209	1418	4.7	0.27	1.07	13.2
Clarksville	1158	1383				
Dougherty	220	279	4.3	0.03	0.25	2.82
Dougherty	363	281				
Durant	724	2305	6.4	0.18	1.09	13.9
Durant	838	2350				
Kirkland	852	1578	4.8	0.15	0.84	11.1
Kirkland	699	1268				
Lebron	1142	1292	7.4	0.21	1.00	9.72
Lebron	1094	1310				
Mansic	774	344	7.7	0.15	0.52	11.7
Mansic	698	328				
Pratt	130	163	5.7	0.04	0.11	1.69
Pratt	108	145				
Tillman	662	846	5.4	0.11	0.57	6.89
Tillman	525	782				

MINTEQA2 INPUT DATA

Water Soluble Cations

WTR	rep	Al	Ca	K	Mg	Mn	Na	Zn
				mg L ⁻¹				
Bartlesville	1	0.32	92.9	9.5	5.49	1.01	15.6	0.03
Bartlesville	2	0.33	90.3	8.7	5.01	0.99	14.0	0.01
Broken Bow	1	0.96	9.6	9.3	3.38	0.87	7.8	0.03
Broken Bow	2	0.89	10.3	8.7	3.43	1.10	6.9	0.03
Claremore	1	0.11	68.8	7.7	13.3	0.32	24.6	0.07
Claremore	2	0.12	75.3	7.3	12.6	0.34	21.5	0.06
Chickasha	1	0.28	125	19.3	19.5	0.20	83.1	0.00
Chickasha	2	0.41	128	19.7	20.2	0.21	87.4	0.03
Clinton	1	0.19	84.4	5.0	7.56	0.02	7.1	0.01
Clinton	2	0.16	79.3	4.7	7.08	0.02	6.2	0.01
Comanche	1	0.03	35.2	5.7	11.5	0.15	24.5	0.04
Comanche	2	0.03	36.1	5.8	11.8	0.15	27.9	0.01
Draper Lake	1	0.05	57.5	8.9	15.8	0.08	9.8	0.01
Draper Lake	2	0.04	52.6	8.8	15.0	0.12	9.0	0.01
Henryetta	1	0.02	30.7	6.8	9.4	0.41	7.4	0.00
Henryetta	2	0.03	34.5	7.3	11.0	0.56	8.2	0.01
Hugo	1	0.02	26.9	5.1	4.0	1.25	16.7	0.01
Hugo	2	0.01	28.6	5.4	4.2	1.25	17.2	0.04
Idabel	1	0.03	63.3	6.1	0.7	0.52	6.3	0.00
Idabel	2	0.02	50.1	11.2	0.8	0.62	14.8	0.03
Lawton	1	0.04	50.1	4.0	9.2	0.05	71.7	0.01
Lawton	2	0.04	50.2	4.0	9.2	0.05	71.8	0.01
McAlester	1	0.15	26.2	4.3	1.5	5.23	43.2	0.02
McAlester	2	0.08	31.7	4.4	1.8	5.48	44.5	0.03
Mohawk	1	0.07	114	7.5	1.1	0.07	6.5	0.04
Mohawk	2	0.04	184	4.0	1.7	0.03	16.6	0.01
Muskogee	1	0.02	101	9.7	9.3	1.62	18.6	0.04
Muskogee	2	0.02	103	9.4	9.4	1.72	16.9	0.01
Sallisaw	1	0.06	66.7	14.5	13.3	0.17	37.2	0.03
Sallisaw	2	0.08	67.6	14.2	13.2	0.16	38.8	0.07
Sand Springs	1	0.38	23.4	3.5	0.6	4.11	3.0	0.01
Sand Springs	2	0.44	23.5	3.5	0.6	3.99	2.7	0.00
Wagoner	1	0.02	75.7	7.3	7.6	2.27	8.9	0.01
Wagoner	2	0.01	74.1	7.1	7.2	1.59	9.1	0.01
Wister	1	0.23	20.8	3.7	4.2	1.13	7.7	0.00
Wister	2	0.14	21.8	3.8	5.4	2.37	9.8	0.00

MINTEQA2 INPUT DATA

Water Soluble Anions

WTR	rep	PO ₄	Cl	NO ₂	NO ₃	SO ₄
			mg L ⁻¹			
Bartlesville	1	0.32	24.1	1.90	52.1	37.9
Bartlesville	2	0.27	20.5	2.03	54.9	34.7
Broken Bow	1	0.72	97.9	0.00	3.13	111
Broken Bow	2	0.76	99.8	0.00	2.97	111
Claremore	1	0.59	39.3	0.00	3.38	63.6
Claremore	2	0.80	37.9	0.00	3.42	70.0
Chickasha	1	0.82	155	8.71	39.6	147
Chickasha	2	0.86	170	8.99	40.3	152
Clinton	1	1.10	5.42	3.70	80.2	54.6
Clinton	2	1.02	6.16	3.67	86.1	61.2
Comanche	1	0.14	19.7	0.00	6.53	60.1
Comanche	2	0.15	18.6	0.00	6.46	58.5
Draper Lake	1	0.72	46.4	6.59	6.18	21.4
Draper Lake	2	0.65	44.4	6.07	6.28	20.0
Henryetta	1	0.25	5.84	0.00	28.1	34.0
Henryetta	2	0.35	6.21	0.00	35.1	41.9
Hugo	1	0.11	9.45	1.03	39.5	25.8
Hugo	2	0.11	10.6	1.06	36.2	25.4
Idabel	1	0.10	14.8	0.00	6.49	74.5
Idabel	2	0.11	25.8	0.00	7.94	60.6
Lawton	1	0.21	83.7	3.12	56.3	44.7
Lawton	2	0.20	84.1	0.00	55.4	43.5
McAlester	1	0.24	44.3	0.00	5.38	67.7
McAlester	2	0.25	46.7	0.00	6.79	76.6
Mohawk	1	0.38	29.7	2.06	461	60.9
Mohawk	2	0.34	38.9	3.32	582	71.7
Muskogee	1	1.71	36.8	0.00	5.48	115
Muskogee	2	1.81	37.0	0.00	6.84	117
Sallisaw	1	0.15	54.9	8.26	114	46.1
Sallisaw	2	0.15	55.7	6.31	113	45.6
Sand Springs	1	0.15	4.09	3.49	29.1	7.2
Sand Springs	2	0.16	3.38	4.82	29.0	7.7
Wagoner	1	0.17	123	0.00	5.29	37.3
Wagoner	2	0.16	121	0.00	4.91	39.9
Wister	1	0.19	5.15	0.00	7.26	37.0
Wister	2	0.23	4.97	0.00	11.8	37.4

Phosphorus Sorption Isotherm Data

	Equilibrium P	P Sorbed
	mg L ⁻¹	mg kg ⁻¹
AB Jewell	0	0
	0	100
	0.009	200
	0.009	400
	0.024	799
Bartlesville	0	0
	0.002	100
	0.005	200
	0.013	400
	0.057	799
Broken Bow	0.002	0
	0.000	100
	0.003	200
	0.021	399
	0.062	798
Claremore	0.004	0
	0.002	100
	0.016	200
	0.057	399
	0.194	795
Chickasha	0.003	0
	0.006	100
	0.011	200
	0.038	399
	0.156	796
Clinton	0.016	0
	0.050	99
	0.116	197
	0.323	392
	1.041	774
Comanche	0.034	-1
	0.767	65
	7.06	19
	6.83	183
	17.70	286

Phosphorus Sorption Data

	Equilibrium P	P Sorbed
	mg L ⁻¹	mg kg ⁻¹
Draper Lake	0.004	0
	0.054	99
	0.181	195
	0.678	383
	2.526	737
Henryetta	-0.005	0
	0.202	95
	0.66	183
	2.89	324
	10.1	534
Hugo	0.001	0
	0.002	100
	0.008	200
	0.082	398
	0.323	792
Idabel	0.003	0
	0.010	100
	0.02	199
	0.08	398
	0.36	791
Lawton	0.00	0
	0.04	99
	0.13	197
	0.55	386
	2.60	735
McAlester	0.002	0
	0.003	100
	0.006	200
	0.017	400
	0.068	798
Mohawk	0.004	0
	0.016	100
	0.04	199
	0.09	398
	0.26	793

Phosphorus Sorption Data

	Equilibrium P mg L ⁻¹	P Sorbed mg kg ⁻¹
Muskogee	0.03	-1
	0.10	97
	0.23	194
	0.67	383
	2.5	737
Okmulgee	0.01	0
	0.02	100
	0.03	199
	0.07	398
	0.26	735
Sallisaw	0.00	0
	0.02	99
	0.07	198
	0.24	394
	1.00	775
Sand Springs	0.01	-0.24
	0.02	99.5
	0.04	199
	0.09	397
	0.20	795
Wagoner	0.04	-1
	0.08	98
	0.21	195
	0.73	382
	7.13	622
Wister	0.02	0
	0.08	98
	0.19	195
	0.74	381
	5.69	658
Mean Of Soil	0.02	-1
	0.04	5
	0.15	12
	0.50	29
	2.52	84

VITA²

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