INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Dissertation

Phosphorus Adsorption/Desorption of Water Treatment Residuals and Biosolids Co-Application Effects

Submitted by

James Anthony Ippolito

Department of Soil and Crop Sciences

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy
Colorado State University
Fall 2001

Colorado State University

October 1, 2001

WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY JAMES A. IPPOLITO ENTITLED PHOSPHORUS ADSORPTION/DESORPTION OF WATER TREATMENT RESIDUALS AND BIOSOLIDS CO-APPLICATION EFFECTS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Advisor

Department Head

ABSTRACT OF DISSERTATION

Phosphorus Adsorption/Desorption of Water Treatment Residuals and Biosolids Co-Application Effects

Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is commonly used in the municipal water treatment process to destabilize colloids for subsequent flocculation and water clarification. Water treatment residuals (WTR) can be classified as a waste material from these treatment plants. Concerns over land application of WTR are due to its postulated reduction of plant available P and potential plant Al toxicity with increasing WTR rates. Co-application of WTR with biosolids may benefit municipalities with biosolids inherently high in P concentrations and in terms of a cost savings by landfill avoidance. In a greenhouse study, I investigated the efficacy of co-application of WTR and biosolids to the native shortgrass steppe species blue grama (*Bouteloua gracilis* H.B.K. Lag) and western wheatgrass (*Pascopyrum smithii* (Rydb.) A. Love) using a factorial and a randomized complete block design. In a laboratory study, I studied the WTR's biosolids-borne P adsorbing capacity and the P adsorbing mechanism using batch studies, x-ray diffraction analysis (XRD), and electron microprobe analysis using wavelength dispersive spectroscopy (EMPA-WDS). The greenhouse factorial study showed that increasing WTR rate, averaged over biosolids rate, resulted in a decrease in blue grama P concentration, an increase in Al concentration, and a decrease in western wheatgrass P and Mo concentrations. Increasing biosolids rate, averaged over WTR rates, significantly affected most blue grama and western wheatgrass constituents. With only WTR addition (no biosolids), I observed an increase in blue grama Al concentration and uptake, a decrease in Mo concentration, and a decrease in western wheatgrass Mo concentration and uptake. The randomized complete block design greenhouse study showed a positive linear relationship between increasing WTR rate and yield and a negative linear relationship with shoot P and Al concentration with blue grama. With western wheatgrass, increasing WTR rate produced a negative quadratic effect on shoot Al concentration ($p<0.10$). The adsorption study indicated that co-mixing WTR and biosolids at ratios of 8:1 will adsorb all soluble biosolids P. The batch experiments suggested solid octacalcium phosphate formation as the P adsorbing mechanism. The XRD and EMPA-WDS results suggest that surface P chemisorption as an amorphous surface mineral phase might occur.

James A. Ippolito
Department of Soil and Crop Sciences
Colorado State University
Fort Collins, CO 80523-1170
Fall 2001

Acknowledgments

I would like to thank Dr. Ken Barbarick for his guidance, support, and friendship throughout the eight-year duration of this dissertation. Many thanks to my other committee members: Dr. Dean Heil, Dr. Ed Redente, and Dr. John Chandler for support, suggestions, and improvements. Also, my heartfelt gratitude to Colorado State University and their education benefit package for granting me the opportunity to attend classes while being a full-time employee.

I would also like to thank the Littleton/Englewood Wastewater Treatment Facility for supporting the Department of Soil and Crop Sciences biosolids research program over the past ten years. The continually renewed funding from the L/E WWTP has kept me employed while pursuing my Ph.D.

I could not have completed this manuscript without Dr. Susan Swapp in the Department of Geology and Geophysics at the University of Wyoming and her help with the electron microprobe analysis, Dr. Wendy Harrison in the Department of Geology and Geological Engineering at the Colorado School of Mines and her help with the x-ray diffraction analysis, and Ms. Colleen Green in the Department of Soil and Crop Sciences at Colorado State University and her help with the XRD interpretation.

In addition, there have been several students that have put their own time and effort in to this manuscript. Many thanks to Mr. Scott McFall, Mr. Alphonse Rideau, and Mr. Bill Crowder.

Finally, a heartfelt thanks to my wife, family, and friends who have finally seen my degree reach its fruition. Thanks for keeping me on the right track. Serenity Now!

Preface

The basis for this research began in the Summer of 1991. The city of Fort Collins, CO, purchased approximately 90,000 ha of land for the beneficial reuse of biosolids. In a pilot project, biosolids and water treatment residuals (WTR) were co-applied to study the effect on native rangeland soils and vegetation. The study, long since completed, has spurred several research projects included in this manuscript.

Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is commonly used in the municipal drinking water treatment process to destabilize colloids for subsequent flocculation and water clarification. Water treatment residuals are a waste material from these treatment plants. These residuals tend have a mineral form similar to amorphous aluminum hydroxide. Concerns over land application of WTR are due to its postulated reduction of plant available phosphorus (P) and potential plant aluminum (Al) toxicity. Land application of WTR, however, may benefit soils containing excess P concentrations. Understanding the initial process of WTR P adsorption is important for discerning where and how strongly P is being adsorbed. This information can ultimately aid in the understanding of which soil mineral phases are responsible for supplying the P needs to plants and crops.

Co-application of WTR with biosolids may benefit municipalities with biosolids inherently high in P concentrations and in terms of a cost savings by landfill avoidance. Determining proper ratios of co-application are necessary in order to ensure proper plant P nutrition without over application or subsequent P deficiency symptoms.

TABLE OF CONTENTS

TABLES

TABLES

FIGURES

TABLES

Chapter 1

Factorial Co-Application of WTR and Biosolids to Blue Grama and Western Wheatgrass

Accepted for publication in the Communications in Soil Science and Plant Analysis, 2002.

ABSTRACT

The beneficial reuse of water treatment plant residuals (WTR) and biosolids via land co-application is of concern since the WTR is postulated to greatly reduce plant P availability and, along with biosolids, possibly provide an additional source of trace metals to soil. Potential plant Al toxicity with increasing WTR rates, because of the Al content of WTR [$Al_2(SO_4)_3 \bullet 14H_2O$], has also been speculated. In a greenhouse study I investigated the efficacy of co-application of WTR and biosolids to the native shortgrass steppe species blue grama (*Bouteloua gracilis* H.B.K. Lag) and western wheatgrass (*Agropyron smithii* (Rydb.) A. Love). Co-application rates were a factorial combination of 0, 2.5, 5, 7.5, and 10 g kg^{-1} of WTR and 0, 2.5, 5, 7.5, and 10 g kg^{-1} of biosolids. Increasing WTR rate, averaged over biosolids rate, resulted in a decrease ($p<0.10$) in blue grama P concentration and an increase in Al concentration. Increasing biosolids rate, averaged over WTR rates, significantly affected most constituents. With only WTR addition (no biosolids) to blue grama, I observed an increase in plant Al concentration and uptake, and a decrease in plant Mo concentration. Increasing WTR rate, averaged over biosolids rate, produced a significant decrease in western wheatgrass P and Mo concentrations. Increasing biosolids rate, averaged over WTR rates, again affected most constituents studied. With only WTR addition (no biosolids) to western wheatgrass, I observed a decrease in plant Mo concentration and uptake. In both studies no significant WTR-biosolids interactions were observed. My results indicate WTR could reduce P availability even when co-applied with biosolids. Co-application can aid municipalities dealing with excessive biosolids-borne P and Mo application associated with an

agronomic (nitrogen) biosolids application rate. However, high application rates of WTR should be avoided due to its adverse effect on P availability to plants, unless a supplemental P source is supplied.

ABBREVIATIONS

EC, electrical conductivity

ICP-AES, inductively coupled plasma-atomic emission spectroscopy

p, probability level

USEPA, US Environmental Protection Agency

WTR, water treatment residuals

INTRODUCTION

Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is commonly used in the municipal drinking water treatment process to destabilize colloids for subsequent flocculation and water clarification. Water treatment residuals (WTR) can be classified as a waste material from municipal drinking water treatment plants, whereas biosolids are a by-product of wastewater treatment plants. Biosolids have been proven effective soil amendments, whereas research of WTR soil addition is still in its infancy.

Most WTR generated via water treatment plants is currently discharged to sanitary sewers, lagooned, or dewatered and disposed of in landfills (Elliott et al., 1990). Current environmental concerns over WTR discharge to receiving waters has resulted in this practice being discouraged in many locales (Lucas et al., 1994). Although no federal guidelines exist for water treatment plant effluents, US Environmental Protection Agency (USEPA) regions or individual states can prohibit direct discharge (AWWA, 1987).

In the past, the potential benefits of WTR to the soil have generally been considered limited. Cornell and Westerhoff (1981) state "attempts to use coagulation sludges as soil conditioners or stabilizers have had little success." Rengasamy et al. (1980), Dempsey et al. (1989), and Lin (1988), however, report significant levels of nitrogen (N) in WTR, which may benefit the soil condition.

The organic matter content of WTR is variable and their addition may or may not benefit the soil. Reports of 3 to 35 % average total organic content have been reported for WTR (Elliott et al., 1990; Bugbee and Frink, 1985).

Rengasamy et al. (1980) found that adding wet WTR markedly altered the mechanical properties of soils, increasing aggregation and decreasing the modulus of rupture of molded soil briquettes. Scambilis (1977) reported increased soil cohesion by alum- and softening-sludge additions.

Changes in soil moisture properties have also been documented. Bugbee and Frink (1985) found that improvements in soil moisture holding capacity and aeration from WTR additions were sufficient to offset induced P deficiencies. Rengasamy et al. (1980) found that WTR addition increased water retention. Scambilis (1977) found that both alum and softening sludges modestly increased soil drainage ability.

Recent investigation into the use of alum as a poultry litter amendment have been documented. Shreve et al. (1995) examined the effects of alum addition to poultry litter on phosphorus (P) concentrations and load in runoff to evaluate the effects of amended litter on forage (fescue) production. They observed decreased P runoff loss and increased forage yields with alum-amended litter compared to non-amended poultry litter. Their results indicated alum-amended litter can be a poultry manure management tool for limiting P inputs into surface waters, while increasing forage yields and fertilizer value of litter and economically benefitting poultry producers.

In a separate study, Moore et al. (1995) showed addition of alum to poultry litter decreased ammonia (NH_3) volatilization; the volatilization of NH_3 within poultry houses can be detrimental to humans and birds. Decreases in volatilization resulted in higher total and soluble N in litter, which increased N/P ratios. High N/P ratios decreased the likelihood of excessive P runoff. Since P is considered to be the primary element of concern with respect to eutrophication of freshwater systems (Schindler, 1977), this information may benefit municipalities coping with future WTR disposal regulations.

The single most important constituent of WTR is its ability to adsorb P. Rengasamy et al. (1980) found that application of WTR at 45 Mg ha^{-1} reduced P uptake and caused yield reductions in maize (*Zea mays* L.). Tissue analysis showed tomato shoots (*Lycopersicon esculentum* L.) (Elliot and Singer, 1988) and lettuce (*Lactuca sativa* L.)(Bugbee and Frink, 1985) grown in potting media amended with WTR contained significantly lower P levels. Heil and Barbarick (1989) applied WTR at rates of 0 to 25 g kg^{-1} soil to sorghum-sudangrass (*Sorghum bicolor* (L.) Moench-*Sorghum x drummondii* (Steudel) Millsp. & Chase) grown in two soils in a greenhouse study. Phosphorus deficiencies were observed at the highest rate of WTR. By doubling the P fertilizer added to the highest WTR rate, sorghum-sudangrass produced 29% greater yield, further indicating an adsorption effect by the WTR.

The co-application of WTR and biosolids to land has not been extensively studied. Harris-Pierce et al. (1993, 1994) investigated the effects of WTR and biosolids co-application on above-ground plant biomass of four dominant shortgrass steppe species. No significant trends in the biomass or tissue concentrations of the four species (blue grama (*Bouteloua gracilis* H.B.K. Lag), western wheatgrass (*Agropyron smithii*), buffalograss (*Buchloe dactyloides*), and fringed sage (*Artemisia frigida*)) were observed in plots treated with WTR rates of 5.6 to 22.4 Mg ha^{-1}, when combined with 11.2 Mg ha^{-1} of biosolids. In a greenhouse study, Ippolito et al. (1999) co-applied variable rates of WTR with a constant biosolids rate to blue grama and western wheatgrass. They observed increased blue grama yield and decreasing P and Al plant concentrations with increasing WTR rate. They also observed a decrease in western wheatgrass Al concentration with increasing WTR rate.

My objectives were to: (1) quantify the effects of a factorial co-application of WTR and biosolids on biomass production of blue grama and western wheatgrass; and (2) determine co-application effects on P, Al, and molybdenum (Mo) plant concentrations and uptake. I considered P because of the WTR's amorphous Al hydroxide P-fixing properties, Al due to the concern for potential plant toxicity, and Mo because of the subsequent WTR interaction or dilution effect on Mo concentration in biosolids as compared to the USEPA (1993) 40 CFR Part 503 regulations.

The hypotheses I tested in this study were: increasing the factorial co-application of WTR to biosolids will: (a) decrease plant biomass production; (b) increase shoot Al concentration and Al uptake; (c) decrease shoot P concentration and P uptake, where shoot uptake is a function of concentration multiplied by dry matter yield; and (d) decrease shoot Mo concentration and uptake.

MATERIALS AND METHODS

I obtained WTR and biosolids from the city of Fort Collins, CO, drinking water and wastewater treatment facilities, respectively. I obtained soil (an Altvan sandy loam; fine-loamy over sandy or sandy-skeletal, mixed, mesic, Aridic Argiustoll; pH = 6.9) from the city of Fort Collins, CO, Meadow Springs Ranch, a parcel of land used for beneficial reuse of biosolids. I determined total elemental composition of the soil, WTR, and biosolids by a modified $HClO_4$-HNO_3-HF-HCl digestion (Table 1.1; Soltanpour et al., 1996) and analyzed the digestate using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Total N was determined by a H_2SO_4 digestion (Bremner, 1996). The NO_3-N and NH_4-N were determined using a 2 M KCl extract (Mulvaney, 1996), pH and electrical conductivity (EC) using a saturated paste extract (Thomas, 1996; Rhoades, 1996), organic matter content using the Walkley-Black procedure (Nelson and Sommers, 1996), and CEC via the Rhoades method (1982).

Blue Grama (*Bouteloua gracilis* H.B.K. Lag)

Ten blue grama plants were germinated (June 1992) in 10-cm diameter by 33-cm tall PVC pots containing 2.5 kg of the Altvan soil. Co-application rates were a factorial combination of 0, 2.5, 5, 7.5, and 10 g kg^{-1} of WTR and 0, 2.5, 5, 7.5, and 10 g kg^{-1} of biosolids. All applications were manually mixed into the top 2.5 to 5.0 cm of soil. A randomized complete block experimental design with four replications was utilized. The soil surface was kept moist by periodic misting with distilled water.

After the plants were established (approximately 8 weeks after initial planting), pots were irrigated with distilled water to field capacity (26% moisture) two to three times per week, and plants were thinned to six plants per pot. The removed plants were placed back into the pots as to not lose any material.

To promote vegetative growth, I cut seed heads off plants and placed the seed heads back into each pot. I harvested blue grama plants at a height of 2.5 cm (1 October 1992), rinsed the plants with distilled water, dried them at 70°C for at least 48 hours, and weighed. Plants were ground to pass a 20-mesh sieve. A subsample was digested in concentrated HNO_3 and analyzed for P, Al, and Mo using ICP-AES (Havlin and Soltanpour, 1980). I determined plant elemental uptake by dividing elemental concentration by dry matter yield. I performed analyses of variance on the data, assuming significant effects if the probability level (*p*) was <0.10 (Steel and Torrie, 1980).

Western Wheatgrass (*Agropyron smithii* (Rydb.) A. Love)

Co-application rates, the number of plants germinated, and experimental design were similar to blue grama. I planted 10 plants per pot on 18 January 1993.

After the plants were established (approximately 8 weeks after initial planting), pots were irrigated with distilled water to field capacity (26% moisture) two to three times per week, and plants were thinned to four plants per pot. Removed plants were placed back into the pots. Seed heads were also removed to promote vegetative growth, and placed back into pots. Plants were harvested at a height of 2.5 cm (18 May 1993) and subsequent analyses was similar to blue grama.

RESULTS AND DISCUSSION

Blue Grama

Increasing WTR rate, averaged over biosolids rates, significantly ($p<0.10$) decreased blue grama P concentration and increased Al concentration (Table 1.2). The high P adsorptive capacity of WTR (Heil and Barbarick, 1989; Ippolito et al., 1999) limited P availability even when a secondary source of P (i.e. - biosolids) was co-applied. The WTR's chemical composition [$Al_2(SO4)_3.14H_2O$] likely caused the increase in plant Al concentration. Increasing WTR rate, averaged over biosolids rates, did not affect dry matter yield, P and Al uptake, or Mo concentration and uptake.

Increasing biosolids application rate, averaged over WTR rates, affected most constituents studied due to the amount of necessary and trace elements contained in the biosolids (Table 1.2). The maximum tolerable plant levels of dietary minerals for domestic animals range from 0.8-1.5% for P, 200-1000 mg kg^{-1} for Al, and 5-100 mg kg^{-1} for Mo (NRC, 1980). The plant concentrations fell well below these tolerable levels. Also, there were no observable interaction effects between WTR and biosolids.

The effects of WTR alone (without biosolids) on dry matter yields and plant P, Al, and Mo concentrations and uptake are shown in Table 1.3. Although I do not recommend applying WTR alone due to lack of N for plant growth, I present the data to illustrate the effects. Increasing WTR rate caused an increase Al concentration and uptake ($p<0.10$). The Al content most likely increased due to WTR's chemical composition. There were no significant effects on dry matter yield, or P and Mo concentration or uptake.

Western Wheatgrass

Increasing WTR rate, averaged over biosolids rates, significantly ($p<0.10$) reduced plant P and Mo concentrations (Table 1.4). The reduction in plant P may be due to WTR's adsorption of P. Even though P concentrations decreased with increasing WTR, I did not observe any P deficiency symptoms. The decrease in Mo concentration may be due to a dilution effect or an interaction with WTR-borne Al. Water treatment residuals tend to have large quantities of amorphous Al oxides and hydroxides. And as with soils that are high in Fe and Al, especially noncrystalline Fe and Al forms on clay surfaces, the availability of Mo tends to be low (Tisdale et al., 1985). Increasing WTR rate did not affect dry matter yields, P uptake, Al concentration or uptake, or Mo uptake.

Biosolids rate, averaged over WTR rates, again affected most constituents studied (Table 1.4). This was due to addition of elements associated with biosolids application. Also, I found no significant interactions between WTR and biosolids application rates.

The effect of WTR alone (without biosolids) on dry matter yields and plant P, Al, and Mo concentrations and uptake are shown in Table 1.5. Again, applying WTR alone is not recommended due to the lack of N for plant growth. However, I present the data to illustrate WTR effects. Increasing the WTR rate caused a decrease in plant Mo concentration and uptake. The WTR rate alone did not significantly affect dry matter yields, or P and Al concentration or uptake. The decrease in both Mo concentration and uptake again may be due to a Mo interaction with WTR-borne Al.

CONCLUSIONS

I reject the hypotheses that increasing the factorial co-application of WTR to biosolids will decrease plant biomass production, increase blue grama Al uptake, increase western wheatgrass Al concentration and uptake, decrease blue grama and western wheatgrass P uptake, decrease blue grama Mo concentration and uptake, and decrease western wheatgrass Mo uptake. I accept the hypotheses that increasing the factorial co-application of WTR to biosolids will increase blue grama Al shoot concentration, decrease blue grama and western wheatgrass shoot P concentration, and decrease western wheatgrass shoot Mo concentration.

The results indicate that WTR can reduce blue grama and western wheatgrass P availability even when co-applied with biosolids which provide plant-available P. Heil and Barbarick (1989) have reported that application of WTR to soils could decrease plant available P while having little effect on trace element availability. Consequently, high application rates of WTR should be avoided due to its adverse effect on biosolids-borne P, and possible soil P availability.

In addition, increasing WTR rate, averaged over biosolids rates, produced an increase in blue grama Al concentration and a decrease in western wheatgrass Mo concentration. The increase in blue grama Al concentration is most likely due to the chemical composition of WTR used in this study. The decrease in western wheatgrass Mo concentration may be attributable to a dilution affect or Mo interaction with WTR-borne Al.

For illustrative purposes, I presented the effect of WTR alone (without biosolids application) on dry matter yields and plant P, Al, and Mo concentration and uptake. I observed an increase in blue grama Al concentration and uptake and a decrease in western wheatgrass Mo concentration and uptake. The increase in blue grama Al content was most likely due to the chemical composition and increase in WTR rate. The decrease in western wheatgrass Mo content may be due to reaction with amorphous Al hydroxides inherent to WTR.

Biosolids Mo concentration may pose a challenge for beneficial-use programs. The USEPA 40 CFR Part 503 regulations are the basis for biosolids land application and beneficial reuse. The pollutant concentration of biosolids-borne Mo limits were deleted from the 40 CFR 503 regulations pending further Mo research and investigation by the USEPA. Consequently, biosolids users currently must adhere to ceiling biosolids Mo concentrations for land application set by the USEPA. From my study it appears that WTR can reduce the plant-available Mo concentration via dilution or WTR interaction. Although I do not condone the "solution to pollution is dilution" rule, the findings are interesting in lieu of the above information.

Land application of biosolids are typically based on the N needs of the plant grown. However, agronomic biosolids N rates may oversupply P. Co-application can reduce the amount of biosolids-borne P via WTR P adsorption. This, as well as landfill avoidance, can benefit municipalities with both waste products. If high WTR application rates are necessary, supplemental P should be co-applied to offset P adsorption.

REFERENCES

AWWA Sludge Disposal Committee. Committee Report : Research Need for Alum Sludge Discharge. June 1987. J. AWWA, 79:6:99.

Bremner, J.M.. 1996. Nitrogen - total. pp.1085-1121. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Bugbee, G.J., and C.R. Frink. 1985. Alum sludge as a soil amendment : Effects on soil properties an plant growth. Conn. Agricultural Exp. Station. Bull. 823.

Cornell, D.A., and G.P Westerhoff. 1981. Management of Water Treatment Plant Sludges. *Sludge and its ultimate disposal* (J.A. borchardt et al. editors). Ann Arbor Sci. Publishers, Ann Arbor, Michigan.

Dempsey, B.A., J. DeWolfe, D. Hamilton, Y. Lee, R. Liebowitz, and H.A. Elliott. 1989. Land application of water plant sludges. Proc. 44th Purdue Indus. Waste Conf., Purdue Univ., West Lafayette, Ind.

Elliott, H.A., B.A. Dempsey, D.W. Hamilton, and J.R. DeWolfe. 1990. Land application of water treatment sludges. Final Rept. AWWARF, Denver, Colorado.

Elliott, H.A., and L.M. Singer. 1988. Effect of water treatment sludge on growth and elemental composition of tomato shoots. Commun. Soil Sci. Plant Anal. 19:345-354.

Harris-Pierce, R., K.A. Barbarick, and E.F. Redente. 1994. The effect of sewage sludge application on native rangeland soils and vegetation Fort Collins - Meadow Springs Ranch. Annual Report to the city of Fort Collins, CO.

Harris-Pierce, R., K.A. Barbarick, and E.F. Redente. 1993. The effect of sewage sludge application on native rangeland soils and vegetation Fort Collins - Meadow Springs Ranch. Annual Report to the city of Fort Collins, CO.

Havlin, H.L., and P.N. Soltanpour. 1980. A nitric acid plant tissue digest method for use with inductively coupled plasma spectrometry. Comm. Soil Sci. Plant Anal. 11:969-980.

Heil, D.M., and K.A. Barbarick. 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. J. Environ. Quality, 18:292-298.

Ippolito, J.A., K.A. Barbarick, and E.F. Redente. 1999. Co-application effects of water treatment residuals and biosolids on two range grasses. J. Environ. Quality, 28:1644-1650.

Lin, S. 1988. Effects of alum sludge application on corn and soybeans. Joint Conf. CSCEASCE, Natl. Conf. of Envir. Engrs., Vancouver, B.C..

Lucas, J.B., T.A. Dillaha, R.B. Reneau, J.T. Novak, and W.R. Knocke. 1994. Alum sludge land application and its effect on plant growth. Jour. AWWA, 86:11:75.

Moore Jr., P.A., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Effect of chemical amendments on ammonia volatilization from poultry litter. J. Environ. Qual. 24:293-300.

Mulvaney, R.L. 1996. Nitrogen - inorganic forms. pp. 1123-1184. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

National Research Council. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, Washington, D.C.

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. pp. 961-1010. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Rengasamy, P., J.M. Oades, and T.W. Hancock. 1980. Improvement of soil structure and plant growth by addition of alum sludge. Commun. Soil Sci. Plant Anal. 11:533-545.

Rhoades, J.D. 1996. Salinity: Electrical conductivity and total dissolved solids. pp. 417-435. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Rhoades, J.D. 1982. Cation exchange capacity. pp. 149-157. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Scambilis, N.A. 1977. Land disposal of chemical sludges. Ph.D. dissertation, Univ. of Missouri, Columbia.

Shreve, B.R., P.A. Moore Jr., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Reduction of Phosphorus in runoff from field-applied poultry litter using chemical amendments. J. Environ. Qual. 24:106-111.

Schindler, D.W. 1977. The evolution of phosphorus limitation in lakes. Science (Washington, DC) 195:260-262.

Soltanpour, P.N., G.W. Johnson, S.M. Workman, J.B. Jones, Jr., and R.O. Miller. 1996. Inductively coupled plasma emission spectrometry and inductively coupled plasma-mass spectrometry. pp. 91-139. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Steel, R.G.D., and J.H. Torrie. 1980. Principles and Procedures of Statistics - A Biometrical Approach. Second Ed. McGraw-Hill, Inc., USA.

Thomas, G.W. 1996. Soil pH and soil acidity. pp. 475-490. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Tisdale, S.L., W.L. Nelson, and J.D. Beaton. 1985. Soil Fertility and Fertilizers. Fourth edition. Macmillan Publishing Co. New York.

USEPA. 1993. Standards for the use or disposal of sewage sludge. Fed. Regist. 58:9248-9415.

Table 1.1. Selected chemical characteristics of soil, WTR, and biosolids used in the greenhouse experiment.

Element	**Units**	**Altvan soil**	**WTR**	**Biosolids**
Ca	g kg^{-1}	2.6	5.7	30.6
Mg	g kg^{-1}	3.8	4.5	5.2
Na	g kg^{-1}	0.1	0.2	0.6
K	g kg^{-1}	4.7	3.8	2.7
P	g kg^{-1}	0.4	0.7	22.2
Al	g kg^{-1}	16.3	74.7	9.9
Fe	g kg^{-1}	13.5	17.8	5.2
Mn	g kg^{-1}	0.3	0.8	0.1
Ti	g kg^{-1}	0.7	0.8	0.1
Cu	mg kg^{-1}	6.1	47.6	578.0
Zn	mg kg^{-1}	34.6	53.3	737.0
Ni	mg kg^{-1}	6.6	10.9	22.7
Mo	mg kg^{-1}	<0.1	<0.1	16.3
Cd	mg kg^{-1}	0.3	<0.1	4.7
Cr	mg kg^{-1}	9.2	19.1	49.0
Sr	mg kg^{-1}	22.2	31.1	315.0
B	mg kg^{-1}	46.8	91.6	34.6
Ba	mg kg^{-1}	127.0	95.2	369.0
Pb	mg kg^{-1}	7.9	<2.5	57.0
Si	mg kg^{-1}	464.0	322.0	125.0
V	mg kg^{-1}	35.6	34.3	14.9
Total N	%	0.1	0.4	5.6
NH_4-N	mg kg^{-1}	8.8	70.1	25000
NO_3-N	mg kg^{-1}	1.0	44.0	9.2
pH		6.9	6.9	7.7
EC	dS m^{-1}	0.2	0.7	11.2
O.M.	%	1.7	6.3	ND
CEC	cmol(+) kg^{-1}	11.8	39.3	ND

Table 1.2. Effects of WTR and biosolids on blue grama dry matter yields and plant P, Al, and Mo concentrations and uptake.

WTR	Biosolids	Dry matter yields	P conc.	P uptake	Al conc.	Al uptake	Mo conc.	Mo uptake
g kg^{-1}	g kg^{-1}	g pot^{-1}	g kg^{-1}	mg pot^{-1}	mg kg^{-1}	μg pot^{-1}	mg kg^{-1}	μg pot^{-1}
0	**Avg. over biosolids**	7.3	2.3	17	16	118	0.64	4.7
2.5		7.9	2.0	15	16	126	0.69	5.2
5.0		7.0	2.1	14	16	116	0.69	4.8
7.5		7.5	1.9	14	15	115	0.66	4.7
10.0		8.0	1.9	14	19	152	0.75	6.0
			ANOVA	**Probability**	**Level**	**(p)**		
WTR		0.742	*0.075*	0.136	*0.044*	0.189	0.444	0.262
Avg. over WTR	2.5	6.6	1.6	11	15	99	0.53	3.4
	5.0	8.7	1.9	15	17	146	0.59	5.1
	7.5	8.5	2.2	18	18	156	0.75	6.3
	10.0	6.4	2.6	15	16	102	0.88	5.5
			ANOVA	**Probability**	**Level**	**(p)**		
Biosolids		*0.002*	*0.000*	*0.000*	0.106	*0.000*	*0.000*	*0.000*
Interaction			**ANOVA**	**Probability**	**Level**	**(p)**		
WTR X biosolids		0.768	0.778	0.244	0.552	0.939	0.533	0.827

Table 1.3. **Effects of WTR alone (without biosolids) on blue grama dry matter yields and plant P, Al, and Mo concentrations and uptake.**

WTR	**Dry matter**	**P conc.**	**P uptake**	**Al conc.**	**Al uptake**	**Mo conc.**	**Mo uptake**
g kg^{-1}	g pot^{-1}	g kg^{-1}	mg pot^{-1}	mg kg^{-1}	μg pot^{-1}	mg kg^{-1}	μg pot^{-1}
0	1.9	1.62	3.2	14	27	2.98	4.6
2.5	1.7	1.72	2.8	21	34	0.76	1.1
5	1.9	1.72	3.2	21	37	0.58	1.1
7.5	2.4	2.02	4.7	22	56	0.42	1.0
10	2.1	1.55	3.3	25	52	0.51	1.0
		ANOVA	**Probability**	**Level**	**(p)**		
	0.271	0.821	0.442	*0.046*	*0.025*	0.129	0.164

Table 1.4. Effects of WTR and biosolids on western wheatgrass dry matter yields and plant P, Al, and Mo concentrations and uptake.

WTR	**Biosolids**	**Dry matter yields**	**P conc.**	**P uptake**	**Al conc.**	**Al uptake**	**Mo conc.**	**Mo uptake**
g kg^{-1}	g kg^{-1}	g pot^{-1}	g kg^{-1}	mg pot^{-1}	mg kg^{-1}	µg pot^{-1}	mg kg^{-1}	µg pot^{-1}
0	**Avg. over biosolids**	13.6	1.7	22	22	324	0.59	8.3
2.5		14.4	1.3	19	24	339	0.55	7.9
5.0		12.1	1.8	17	17	229	0.45	5.3
7.5		13.5	1.4	17	22	316	0.39	5.3
10.0		13.8	1.4	18	19	284	0.42	5.6
			ANOVA	**Probability**	**Level**	**(p)**		
WTR		0.760	*0.057*	0.256	0.135	0.135	*0.030*	0.135
Avg. over WTR	2.5	10.1	1.1	11	19	193	0.42	4.1
	5.0	14.9	1.3	18	23	352	0.44	6.5
	7.5	15.8	1.5	22	22	369	0.44	6.8
	10.0	13.1	2.2	25	18	280	0.62	8.4
			ANOVA	**Probability**	**Level**	**(p)**		
Biosolids		*0.003*	*0.000*	*0.000*	0.192	*0.029*	*0.008*	*0.029*
Interaction			**ANOVA**	**Probability**	**Level**	**(p)**		
WTR X biosolids		0.999	0.654	0.947	0.657	0.908	0.507	0.908

Table 1.5. **Effects of WTR alone (without biosolids) on western wheatgrass dry matter yields and plant P, Al, and Mo concentrations and uptake.**

WTR	**Dry matter**	**P conc.**	**P uptake**	**Al conc.**	**Al uptake**	**Mo conc.**	**Mo uptake**
g kg^{-1}	g pot^{-1}	g kg^{-1}	mg pot^{-1}	mg kg^{-1}	μg pot^{-1}	mg kg^{-1}	μg pot^{-1}
0	2.6	1.20	3.1	22	57	0.46	1.2
2.5	2.8	1.05	2.9	26	73	0.53	1.5
5	3.5	1.26	4.4	17	60	0.43	1.5
7.5	3.1	1.13	3.5	14	43	0.41	1.3
10	3.3	1.03	3.4	19	63	0.38	1.3
		ANOVA	**Probability**	**Level**	**(p)**		
	0.176	0.456	0.241	0.273	0.362	*0.038*	*0.050*

Chapter 2

Co-Application of WTR and Biosolids to Blue Grama and Western Wheatgrass : Randomized Complete Block Design Study and P Adsorption Isotherm Research

Published in J. Environ. Qual. 28:1644-1650 (1999).

ABSTRACT

Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is commonly used in the municipal water treatment process to destabilize colloids for subsequent flocculation and water clarification. Water treatment residuals (WTR) can be classified as a waste material from these treatment plants. Concerns over land application of WTR are due to its postulated reduction of plant available phosphorus (P) and potential plant aluminum (Al) toxicity with increasing WTR rates. Co-application of WTR with biosolids may benefit municipalities with biosolids inherently high in P concentrations and in terms of a cost savings by landfill avoidance. In a greenhouse study, I investigated the efficacy of co-application of WTR and biosolids to the native shortgrass steppe species blue grama (*Bouteloua gracilis* H.B.K. Lag) and western wheatgrass (*Pascopyrum smithii* (Rydb.) A. Love). The objectives were to quantify co-application effects on plant P and Al concentrations and uptake, biomass production, and WTR P adsorbing capacity. Co-application rates were a combination of a constant biosolids application of 5 dry g kg^{-1} soil (an agronomic rate), and varying WTR rates of 0, 10, 25, 50, 100, 150, 200, and 250 dry g kg^{-1} soil. With blue grama, I observed a positive linear relationship between increasing WTR rate and yield and a negative linear relationship with increasing WTR rate and shoot P and Al concentration (p<0.10). With western wheatgrass, increasing WTR rate produced a negative quadratic effect on shoot Al concentration (p<0.10). Some investigators have observed P deficiency symptoms associated with WTR application; however, I did not. The adsorption study indicated that co-mixing of the City of Fort Collins, CO, or the Englewood Littleton/Englewood, CO, WTR and biosolids at ratios of 8:1 will adsorb all

soluble biosolids P. Beyond this ratio the WTR could adsorb all biosolids available P and possibly some soil-borne P.

ABBREVIATIONS

AB-DTPA, ammonium-bicarbonate diethylenetriaminepentaacetic acid

DM, dry matter

EC, electrical conductivity

EPA, US Environmental Protection Agency

ICP-AES, inductively coupled plasma-atomic emission spectroscopy

p, probability level

WTR, water treatment residuals

INTRODUCTION

Alum sludge, also known as water treatment residuals (WTR), may be considered a waste material from municipal drinking water treatment plants. Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is used in the treatment process to destabilize colloids for subsequent flocculation and water clarification. Biosolids (sewage sludge) is a by-product of wastewater treatment.

In the past, the potential benefits of applying WTR to the soil have been limited. Cornwell and Westerhoff (1981) state "attempts to use coagulation sludges as soil conditioners or stabilizers have had little success." Rengasamy et al. (1980), Dempsey et al. (1989), and Lin (1988) have reported total Kjeldahl nitrogen (N) concentrations between 0.5 and 1 percent. The N may be plant available depending on the WTR mineralization rate.

The total organic carbon content of WTR is variable. A range of 0.85 to 6.5%, with typical WTR containing 3% total organic carbon content have been reported (Elliott and Dempsey, 1991; Elliott et al., 1990). Characteristic WTR organic carbon is stable and resistant to degradation, which is similar to soil organic C (Elliott et al., 1990).

Changes in soil moisture and structure properties have been documented after WTR application. Bugbee and Frink (1985) observed soil moisture retention and aeration improvements from WTR additions, and Rengasamy et al. (1980) observed increased soil aggregation accompanied by an increase in soil water holding capacity with WTR addition. Scambilis (1977) found that both alum and softening sludges modestly increased soil drainage ability and cohesion. El-Swaify and Emerson (1975) showed that precipitation of aluminum (Al) and iron (Fe) hydroxides into dispersed clay suspensions, followed by drying, increased the net bonding between clay particles.

Land application of WTR may offer disadvantages due to the potential adsorption of plant available soil phosphorus (P) by hydrous oxides of aluminum. Rengasamy et al. (1980) found that application of WTR at 45 Mg ha^{-1} reduced P uptake and yields in maize (*Zea mays* L.). Tissue analysis showed tomato shoots (*Lycopersicon esculentum* L.) (Elliott and Singer, 1988) and lettuce (*Lactuca sativa* L.) (Bugbee and Frink, 1985) grown in potting media amended with WTR had significantly lower P levels.

In a greenhouse study, Heil and Barbarick (1989) applied 0 to 25 g WTR kg^{-1} soil, with additions of 50 mL of 0.02 mol $Ca(H_2PO_4)_2$ per pot, to two soils growing sorghum-sudangrass (*Sorghum bicolor* L.). They observed P deficiencies at the highest WTR application. By doubling the P fertilizer added to the highest WTR application, sorghum-sudangrass yield increased 29 and 123% for both soils, further indicating an adsorption effect by the WTR. Lucas et al. (1994) grew fescue (*Festuca arundinaceae* Schreb.) in lime and WTR amended soil (0 to 4 percent WTR by weight) with two different P treatments (50 and 100 mg P kg^{-1} soil) in a greenhouse experiment. They observed linear decreases in yields for both P treatments. However, the higher P application resulted in higher yields over all WTR rates. Other results showed decreased P plant concentrations with increased WTR applications, indicating a P deficiency.

Peters and Basta (1996) planted Triumph 64 wheat (*Triticum* spp.) in alum-treated soils as a qualitative indicator and observed no nutrient deficiencies. However, their soils had available P levels well above the P requirement for wheat production. In a large scale field study, Geertsema et al. (1994) applied WTR at rates equal to 0, 36, and 52 dry Mg ha^{-1} to loblolly pine (*Pinus rigida* Mill.). They found no significant differences in bioavailable and total P concentrations 30 months after WTR application and concluded that soil and groundwater characteristics and pine growth were not different between amended and unamended plots.

Recent investigation into the use of alum as a poultry litter amendment have been reported. Moore et al. (1995) showed addition of alum to poultry litter decreased ammonia (NH_3) volatilization, which is an advantage because volatilization of NH_3 within poultry houses can be detrimental to humans and birds. Decreases in volatilization resulted in higher total N concentrations in poultry litter, making this material a higher quality fertilizer. In addition, alum application to poultry litter resulted in significantly lower dissolved reactive P concentrations.

Since P is considered to be the primary element of concern with respect to eutrophication of freshwater systems (Schindler, 1977), municipalities may apply WTR beneficially to soil or poultry litter to adsorb P, and subsequently reduce P waterway entry. Peters and Basta (1996) concluded that the addition of WTR reduced excessive amounts of bioavailable soil P, and by increasing the application rate one could continue to decrease the amount of bioavailable P. They further stated that potential adverse environmental impacts from salinity, pH, Al, and total and extractable metals on application of these municipal and industrial amendments should be insignificant. Shreve et al. (1995) examined the effects of adding WTR to poultry litter on P concentrations and load in runoff and evaluated the effects of amended litter on fescue (*Festuca arundinacea*

Schreb.) production. They observed decreased P runoff loss and increased forage yields with WTR-amended compared to non-amended poultry litter. Their results indicated WTR amended litter can be a poultry manure management tool for limiting P inputs into surface waters, while increasing forage yields and fertilizer value of litter, and for economically benefitting poultry producers.

In terms of waterway eutrophication, Al salts have documented use in lake rehabilitation. The Wisconsin Department of Natural Resources (1973), in conjunction with the University of Wisconsin, distributed 12.6 Mg of slurried alum in the top 60 cm of water in Horseshoe Lake, Wisconsin. Their intent was to limit plant available P and propagation of algal blooms. Their results showed a decrease in total lake P during the following summer, no large increase in total P in the hypolimnion during the following two summers, a slight increase in water transparency, and a decrease in color. Most importantly, they observed the absence of algal blooms with subsequent improvement in dissolved oxygen conditions. Narf (1985) showed that alum injection in Bullhead Lake, Wisconsin, reduced the average epilimnetic summer total and soluble reactive P by 38 and 92%, respectively. This reduction in P shifted the N:P ratio against the formation of the blue-green algae community. In its place the diatoms, green algae, flagellates, and rotifers flourished and provided a food chain base.

Land co-application of biosolids and WTR is a new concept, but co-disposal is not. Several large cities within the United States practice successful co-disposal of WTR by direct discharge of WTR to sanitary sewer systems (Cornwell and Westerhoff, 1981). This practice results in increased solids loading at the wastewater treatment facility with few operating difficulties, and this process is cost-effective for the participating municipality. Co-disposal, however, is only viable if both water and wastewater treatment facilities are in close proximity to one another, and if the WTR does not adversely affect performance or contaminate the wastewater treatment plant.

The U.S. produces an estimated 0.35 million dry Mg of WTR per year. Current environmental concerns over WTR discharge to receiving waters has resulted in this practice being discouraged in many locales (Lucas et al., 1994). Most WTR currently generated is discharged to sanitary sewers, lagooned, or dewatered and disposed of in landfills (Elliott et al., 1990). Although no federal guidelines exist for WTR, US Environmental Protection Agency (EPA) regions or individual states can prohibit direct discharge (AWWA, 1987). These issues suggest land application of WTR may be a major method of disposal in the future. Of the states that land apply WTR, many currently utilize EPA 40 CFR 503 biosolids regulations as a guideline for WTR land application, although these regulations specifically exclude WTR (Carr et al., 1996).

The Colorado Department of Public Health and Environment (1994, 1996) established guidelines regarding the land co-application of WTR and biosolids based on applicable requirements of the Colorado Biosolids Regulations, 4.9.0. They are, however, concerned with the potential reduction of plant available P due to WTR P adsorption, potential Al toxicity to plants from WTR, and additional source of trace metals added to soil from WTR application.

While application of wastewater biosolids have been extensively studied, application of WTR, either alone or in conjunction with biosolids, has been less thoroughly studied. The disposal of WTR alone would be beneficial to soils high in P, since the WTR can adsorb soluble P. Likewise, the co-application of WTR and biosolids may be advantageous to municipalities as a means of disposal of high P bearing biosolids in an environmentally sound manner. Because of WTR's ability to adsorb P, Bugbee and Frink (1985) state that WTR could play a role in the removal of P in sewage treatment plant effluent.

Harris-Pierce et al. (1993, 1994) studied the effects of WTR and biosolids co-application on above-ground plant biomass of four dominant shortgrass steppe species. No significant trends in the total biomass or plant trace element tissue concentrations of the four species (blue grama (*Bouteloua gracilis* H.B.K. Lag), western wheatgrass (*Pascopyrum smithii* (Rydb.) A. Love), buffalograss (*Buchloe dactyloides* (Nutt.) Engelm), and fringed sage (*Artemisia frigida* Willd.)) were observed in plots treated with WTR at rates of 5.6 to 22.4 Mg ha^{-1}, when combined with 11.2 Mg ha^{-1} of biosolids.

My study objectives were to: (1) quantify the effects of co-application of the City of Fort Collins, CO, WTR and biosolids on biomass production of blue grama and western wheatgrass in a greenhouse study; (2) determine co-application effects on P and Al plant concentrations and uptake, and livestock plant consumption limits (P was targeted because of the amorphous Al hydroxide P-fixing properties and Al because of potential plant toxicity); and (3) calculate the WTR P adsorbing capacity.

The hypotheses I tested in this study were: increasing the ratio of WTR to biosolids in a mixed material will (a) decrease plant biomass production; (b) increase shoot Al concentration and Al uptake; and (c) decrease shoot P concentration and P uptake, where shoot uptake is a function of concentration multiplied by dry matter yield.

MATERIALS AND METHODS

An Altvan sandy loam (fine-loamy over sandy or sandy-skeletal, mixed, mesic, Aridic Argiustoll), was air-dried and crushed using a rolling pin. The greenhouse study WTR and biosolids were obtained from the City of Fort Collins water and wastewater treatment facilities and then air-dried, crushed, and passed through a 2-mm sieve. Additional WTR and biosolids for use in P adsorption studies were obtained from the city of Englewood and Littleton/Englewood, CO's drinking water and wastewater treatment facilities, respectively.

I determined total elemental composition of soil, WTR, and biosolids by a modified $HClO_4$-HNO_3-HF-HCl digestion (Table 2.1) (Soltanpour et al., 1982) and analyzed the digestate using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Total N was measured following a concentrated H_2SO_4 digestion (Bremner and Mulvaney, 1982), and NH_4-N and NO_3-N following a 2 M KCl extraction (Keeney and Nelson, 1982). Electrical conductivity (EC) and pH were determined using a saturated paste extract (Rhoades, 1982b), organic matter using a modified Walkley-Black method (Nelson and Sommers, 1982), and cation exchange capacity was determined by the Rhoades method (1982a).

Blue Grama (*Bouteloua gracilis* H.B.K. Lag)

Ten blue grama seeds were germinated on 28 February 1994 in 20-cm diameter by 20-cm tall pots containing 2.5 kg of soil with various co-application rates. Co-application rates were a combination of a constant biosolids application of 5 dry g kg^{-1} soil (an agronomic rate), and varying WTR rates of 0, 10, 25, 50, 100, 150, 200, and 250 dry g

kg^{-1} soil. Application rates of WTR and biosolids were based on dry weights. All applications were manually mixed into the surface 2.5 to 5.0 cm of soil. The experiment was arranged as a randomized complete block design with four replications. The soil surface was kept moist by periodic misting with distilled water.

After plant establishment (approximately 8 weeks after initial planting), each pot was irrigated with distilled water to field capacity (26% moisture by weight) two to three times per week and each pot was thinned to three plants per pot. I returned thinned plants back into the pots so as to not remove any nutrients or trace elements. To promote vegetative growth, I cut seed heads off plants and placed them back into each pot.

I harvested plants at a height of 2.5 cm above the soil surface on 14 June 1994, approximately four months after initial establishment. I then rinsed plants with distilled water, dried them at 70°C for at least 48 hours, and weighed to determine dry matter yields (DM). Plants were ground to pass through a 20-mesh sieve. I digested a subsample in concentrated HNO_3 (Havlin and Soltanpour, 1980), and analyzed the digestate for P and Al using ICP-AES. Phosphorus and Al plant uptake were determined by taking the DM multiplied by the plant elemental concentration. Data were analyzed using regression analysis and analyses of variance and tested at $p = 0.10$ (Steel and Torrie, 1980).

Western Wheatgrass (*Pascopyrum smithii* (Rydb.) A. Love)

The experimental approach and statistical analyses were identical to that of blue grama. I germinated plants on 21 July 1994 and harvested on 12 December 1994. In addition, I separated roots from soil to observe possible root aluminum phosphate precipitation. Roots were rinsed in a 0.03% sodium dodecyl sulfate solution, rinsed with distilled water, and oven dried at 70°C for 72 hours. I analyzed roots for P and Al in a concentrated HNO_3 digest using ICP-AES.

Water Treatment Residuals P Adsorption Study

In an effort to calculate a "safe" co-mixing ratio of alum-containing WTR and biosolids with regards to P adsorption, I determined the biosolids-borne P adsorptive capacity of WTR in a batch study experiment. I collected both WTR and biosolids from the Fort Collins, CO, and the Englewood and Littleton/Englewood, CO, drinking water and wastewater treatment plant facilities, respectively. The WTR and biosolids were air-dried, crushed, and passed through a 2-mm sieve. The Fort Collins materials were kept separate from the Englewood and Littleton/Englewood materials throughout the subsequent methods.

Triplicate solutions of distilled-deionized (DI) H_2O and biosolids were created at a ratio of 40 mL DI:0.5g biosolids. The solutions were then shaken for various times (0.5, 1.0, 3.0, 6.0, 20, and 24 hr) to determine the maximum P released from biosolids in the shortest time span. It was determined that 16 hr were required to obtain maximum P release; for the remainder of the tests I chose a 24 hr shaking period for convenience.

Next, triplicates of various DI:biosolids dilutions were shaken to determine the lowest dilution factor of DI:biosolids with the maximum amount of P released. The Fort Collins biosolids released approximately 6900 mg P L^{-1} given a 200 fold dilution factor. The Littleton/Englewood biosolids released approximately 2200 mg P L^{-1} at a dilution of 3000.

Finally, various amounts of WTR (0 to 8.0 g dry WTR) were added to a known amount of biosolids (0.2 g dry biosolids) to obtain dry weight ratios of WTR:biosolids of 0, 1, 2, 4, 8, 12, 16, 20, 24, 28, 32, 36, and 40. I added 40 mL of DI to all Fort Collins mixtures to create a 200 fold biosolids P dilution; 450 mL of DI were added to all Littleton/Englewood mixtures to create a 3000 fold biosolids P dilution. All mixtures were triplicated. Previous work indicated that P initially contained in the WTR was not released into solution at the given WTR rates and at 200 or 3000 fold dilutions, respectively. All mixtures were shaken for 24 hours to ensure that the maximum soluble biosolids P was released. The mixtures were then centrifuged, and the decantate was filtered through Whatman No. 42 filter paper and analyzed for P using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). I plotted the observed data using an exponential rise equation:

$$Q = a[1 - e^{(-b*\text{ratio})}] \quad (1)$$

where:

Q = WTR adsorbed biosolids-borne P, expressed in mg P kg^{-1} WTR;

a = Maximum biosolids-borne P adsorbed by WTR, expressed in mg P kg^{-1} WTR;

b = Rate constant for change in WTR adsorbed P for a given change in WTR:biosolids ratio;

and ratio = WTR:biosolids ratio.

RESULTS AND DISCUSSION

Blue Grama

Increasing WTR rate, co-applied with a constant biosolids rate, significantly ($p < 0.10$) increased DM yield, and decreased P and Al shoot concentrations (Table 2.2). However, the r^2 values of regression equations for all significant effects were less than 0.50. Phosphorus deficiency or Al toxicity symptoms were not observed with increasing WTR rates.

Heil and Barbarick (1989) also observed an increase in DM and a decrease in plant P concentration with WTR application. They stated that the high adsorptive capacity of WTR, however, can limit P availability even if a secondary source of P (i.e. - biosolids) is co-applied. Bugbee and Frink (1985) noted an increase in lettuce yield with a mixture of 33% perlite, 33% peat, and 33% WTR as a potting media as compared to other mixtures of the above three constituents and soil. They explained improvements in growth possibly due to increased aeration and water holding capacity, which overcame the adverse effects of P deficiency. Similarly, Cornell et al. (1995) observed an increase in canopy cover on native rangeland vegetation as compared to lower co-application ratios three years after co-application of 5 dry tons biosolids A^{-1} with 10 dry tons WTR A^{-1}. My DM results are similar; the biosolids may have acted as a bioavailable P source, overcoming the WTR's P adsorptive capacity, while the WTR increased aeration and water holding capacity.

McLaughlin et al. (1981) showed a one-month aged amorphous Al gel sorbed approximately 35 times more P than a crystalline gibbsite. They hypothesized P surface adsorption of short-range order hydrous oxides in soils will behave similarly to that of aged Al gels. When applied to soils, the WTR may act similarly to these short-range order hydrous oxides, resulting in decreases in plant shoot Al and P concentrations.

From the nearly neutral soil and waste mixture pH (Table 2.1) it could be hypothesized that plant Al concentrations would decrease due to possible crystalline $Al(OH)_3$ formation. However, due to soil versus WTR ammonium-bicarbonate diethylenetriaminepentaacetic acid (AB-DTPA) extractable Al (0.65 and 8.17 mg Al kg^{-1} material, respectively) and WTR's chemical composition (amorphous aluminum hydroxide as determined by x-ray diffraction analyses; similar to x-ray diffraction studies by Rengasamy et al., 1980) I anticipated a plant Al content increase with increasing WTR rate.

The AB-DTPA extraction is a qualitative indicator of certain plant available metals found in sludge-amended soils (Barbarick and Workman, 1987; Barbarick et al., 1997). Amorphous aluminum hydroxide has a solubility approximately an order of magnitude greater than gibbsite (Lindsay, 1979) which could lead to slightly higher plant available soil Al concentrations immediately after WTR application. More importantly, soil addition of amorphous Al materials (e.g. - WTR) at neutral pH may lead to polynuclear hydroxyl Al species formation. These species are intermediates in the precipitation of solid $Al(OH)_3$, and may or may not be toxic to plants (Marschner, 1995).

Based on the above inferences and the observed decrease in shoot Al and P concentrations, I hypothesize the Al and P was sorbed by roots and not significantly translocated to shoots; this issue will be addressed in the discussion of western wheatgrass.

The maximum tolerable levels of dietary P and Al for domestic animals range from 0.8-1.5% and 200-1000 mg kg^{-1}, respectively (National Research Council, 1980). The plant concentrations fell well below these tolerable levels (Table 2.2).

Western Wheatgrass

Increasing WTR rate, co-applied with a constant biosolids rate, significantly (p <0.10) affected plant Al concentration (Table 2.3); the trend being decreasing plant Al concentration with increasing WTR rate. The r^2 value of the regression equation was 0.62. Again, no P deficiency or Al toxicity symptoms were noted, and the concentrations of both elements were well below those considered harmful to domestic animals.

Root P and Al concentrations were not affected by increasing co-applications of these materials (Table 2.4). The ratio of root P to Al was approximately 1:1. Although I cannot distinguish which root portion contained these elements, Millard et al. (1990) used x-ray photoelectron spectroscopy and observed a similar ratio for PO_4 to Al on the root surface of two barley strains (*Hordeum vulgare* Dayton and Kearney) grown at pH 4.5. They hypothesized that Al resistant plants may precipitate $AlPO_4$ at the root surface, acting as a barrier and reducing Al transport into the root. Other researchers (Fageria et al., 1988; Taylor, 1991) have suggested, in addition to precipitation, Al chelation, immobilization in non-sensitive sites of cells, or other metabolic exclusion mechanisms as a means of Al resistance.

Phosphorus shoot and root concentrations were correlated ($r = 0.71$) with relatively equal concentrations found in both plant fractions. This emphasizes the fact that P is easily translocated from roots to shoots, thus negating the proposed hypothesis of root P adsorption with decreased shoot translocation. Shoot Al concentrations, however, were negatively correlated with root concentrations ($r = -0.47$; shoot:root ≈ 1:35). This supports the contention that translocation of Al from roots to shoots is low. This also supports the hypothesis relative to blue grama that Al was sorbed by the roots and not significantly translocated to the shoots.

The effects of Al on plant growth tend to be limited to the roots (as with my study), with subsequent impacts on water and nutrient uptake (Pearson, 1966). McLean and Gilbert (1927) demonstrated the injurious effects of Al on root growth with restricted Al transport to the shoots of rye (*Secale cereale* Rosen). Similar results have been shown by Jan and Pettersson (1989) with the growth of Al-tolerant upland rice (*Oryza sativa* BG35).

Water Treatment Residual P Adsorption Study

Based on the Fort Collins and Englewood and Littleton/Englewood experimental data, a maximum of 6910 and 2180 mg biosolids-borne P kg^{-1} WTR was adsorbed at a ratio of WTR:biosolids of 8:1 or greater, respectively (Figures 2.1 and 2.2).

The equation describing the Fort Collins WTR:Biosolids curve (Figure 1) is:

$$\text{WTR Adsorbed P (mg kg}^{-1}\text{)} = 6910[1\text{-}e^{(-0.635*\text{ratio})}] \quad (2)$$

The equation describing the Englewood and Littleton/Englewood WTR:biosolids curve (Figure 2) is:

$$\text{WTR Adsorbed P (mg kg}^{-1}\text{)} = 2180[1\text{-e}^{(-0.580*\text{ratio})}] \quad (3)$$

where ratio = the ratio of WTR:biosolids.

Heil and Barbarick (1989) observed WTR P adsorption capacity ranges between 737 to 3570 mg P kg^{-1} WTR; my values are very similar. They additionally stated that P adsorptive capacity of WTR is a function of a number of factors, including WTR age, pH, particle-size fraction, surface area, and the availability of P. It is interesting to note that the P adsorption sites on both cities WTRs were maximized at a WTR:biosolids ratio of 8:1. This is most probably due to the similarity of the two WTR and biosolids utilized, and especially true for the P and Al content of all materials (see Table 2.1).

Some considerations should be taken into account if the two materials are co-applied to soil: the initial biosolids and soil P, the P adsorption capacity of WTR, the amount or ratio of mixture applied, and the depth of mixture incorporation. All of these factors will determine the amount of soil P adsorbed.

CONCLUSIONS

I reject the hypotheses that increasing the ratio of WTR to biosolids in a mixed material will decrease plant biomass production, increase shoot Al concentration and uptake, and decrease shoot P uptake; I accept the hypothesis that increasing the ratio of WTR to biosolids in a mixed material will decrease shoot P concentration in blue grama.

The blue grama experiment showed that increased WTR rates increased dry matter yields, decreased P and Al shoot concentrations, and had no effect on P or Al shoot uptake. With western wheatgrass, increased WTR rates only affected shoot Al concentration in a decreasing trend. Unlike the findings with blue grama, I did not observe an increase in western wheatgrass dry matter yield. This may be due to the time of year both studies were performed in the greenhouse or differences in plant species. In both studies P deficiency or Al toxicity symptoms were not observed. Plant shoot Al concentrations decreased with increasing WTR rates, and western wheatgrass shoot Al concentrations were negatively correlated with root concentrations. This supports the contention that translocation of Al from roots to shoots is low. This also supports the hypothesis relative to blue grama that Al was sorbed by the roots but not significantly translocated to the shoots.

Data from the adsorption study suggests when co-mixing and applying WTR and biosolids at ratios of 8:1 or larger, over 99% of the immediately soluble biosolids P will be adsorbed. If co-applying WTR and biosolids to soil at ratios greater than 8:1, all biosolids available P, as well as some plant-available soil P, could be adsorbed by the WTR. The amount of plant-available P adsorbed will be determined by the initial biosolids and soil P present, the amount of mixture added to soil, and the depth of mixture incorporation. When co-applying these sludges it is important to observe the 8:1 mixing ratio.

Water treatment residual's innate capacity to adsorb P makes it a useful product for application to high P containing materials or soils that are potential polluters. This would be especially true for soils in locales where waterway eutrophication due to P is a concern. Elliott et al. (1990) summed it up well, stating:

> "The application of water treatment sludge to high P soils may be a very good opportunity for farmers and water utilities to reconcile several problems. Many farmers are being pressured to reduce the pollution impact of their traditional fertilization practices. By land applying water treatment sludge to high P containing soils, these traditional practices are less threatened. Additionally, farmers would receive payment for receiving water treatment sludge or have fields plowed during the disposal process. Water utilities could have a more economic and labor conservative disposal method than the more common methods of water treatment sludge disposal, such as landfilling, sewage disposal and coagulant recovery."

As landfill space becomes less available, municipalities must look towards alternative methods of WTR waste disposal. Co-application of WTR and biosolids may benefit municipalities in terms of a cost savings by landfill avoidance and potential reduction of bioavailable P in high P containing biosolids. Land application of WTR alone will also benefit high P containing soils by adsorbing excess P and reducing the risk of non-point source pollution losses of P.

If these materials are to be co-applied to land, the co-application should first be based on the agronomic N needs of the crop. Since biosolids contain much higher N levels than WTR, the biosolids application rate should be determined first, then applied.

The application of WTR could then take place based on adsorption research and the amount of P an applicator may wish to adsorb. Another alternative would be to co-mix the two agents, determine the N concentration, and then land apply according to the N needs of the crop. As with all material applications, soil testing and material analyses must be conducted to ensure optimum crop yields along with environmental protection.

REFERENCES

AWWA Sludge Disposal Committee. June 1987. Committee Report : Research Need for Alum Sludge Discharge. J. AWWA. 79:6:99.

Barbarick, K.A., and S.M. Workman. 1987. Ammonium bicarbonate-DTPA and DTPA extractions of sludge-amended soils. J. Environ. Qual. 16:125-130.

Barbarick, K.A., J.A. Ippolito, and D.G. Westfall. 1997. Sewage biosolids cumulative effects on extractable-soil and grain elemental concentrations. J. Environ. Qual. 26:1696-1702.

Bremner, J.M., and C.S. Mulvaney. 1982. Nitrogen - total. p. 595-624. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison,WI.

Bugbee, G.J., and C.R. Frink. 1985. Alum sludge as a soil amendment : Effects on soil properties an plant growth. Conn. Agricultural Exp. Station. Bull. 823.

Carr, S., J.E. Smith Jr., S.I. McMillan, N.E. McTigue, A. Rubin, and R. Southworth. 1996. Regulatory issues concerning management of water treatment plant residuals. p. 6-16. *In* Technology transfer handbook: Management of water treatment plant residuals. ASCE and AWWA. New York, New York and Denver, CO.

Colorado Department Public Health and Environment. 1996. Revised Biosolids Regulation 4.9.0. Denver, CO.

Colorado Department Public Health and Environment. 1994. Beneficial use of water treatment sludge and fees applicable to the beneficial use of sludges. 5 CCR 1003-7. Denver, CO.

Cornell, E.S, E.F. Redente, and K.A. Barbarick. 1995. Annual Report - The effect of sewage sludge application on native rangeland vegetation. Fort Collins - Meadow Springs Ranch.

Cornwell, D.A., and G.P. Westerhoff. 1981. Management of Water Treatment Plant Sludges. *Sludge and its ultimate disposal* (J.A. borchardt et al, editors). Ann Arbor Sci. Publishers, Ann Arbor, Michigan.

Dempsey, B.A., J. DeWolfe, D. Hamilton, Y. Lee, R. Liebowitz, and H.A. Elliott. 1989. Land application of water plant sludges. Proc. 44th Purdue Indus. Waste Conf., Purdue Univ., West Lafayette, Ind.

Elliott, H.A., and B.A. Dempsey. 1991. Agronomic effects of land application of water treatment sludges. J. AWWA. 83:4:126.

Elliott, H.A., B.A. Dempsey, D.W. Hamilton, and J.R. DeWolfe. 1990. Land application of water treatment sludges: Impact and Management. AWWARF, Denver, Colorado.

Elliott, H.A., and L.M. Singer. 1988. Effect of water treatment sludge on growth and elemental composition of tomato shoots. Commun. Soil Sci. Plant Anal. 19:345-354.

El-Swaify, S.A., and W.W. Emerson. 1975. Changes in the physical properties of soil clays due to precipitated aluminum and iron hydroxides: I. Swelling and aggregate stability after drying. Soil Sci. Soc. Amer. Proc., 39:1056-1063.

Fageria, N.K., V.C. Baligar, and R.J. Wright. 1988. Aluminum toxicity in crop plants. J. Plant Nutr. 11:303-319.

Geertsema, W.S., W.R. Knocke, J.T. Novak, and D. Dove. 1994. Long-term effects of sludge application to land. J. AWWA. 86:11:64.

Harris-Pierce, R., K.A. Barbarick, and E.F. Redente. 1993. The effect of sewage sludge application on native rangeland soils and vegetation Fort Collins - Meadow Springs Ranch. Annual Report to the city of Fort Collins, CO.

Harris-Pierce, R., K.A. Barbarick, and E.F. Redente. 1994. The effect of sewage sludge application on native rangeland soils and vegetation Fort Collins - Meadow Springs Ranch. Annual Report to the city of Fort Collins, CO.

Havlin, H.L., and P.N. Soltanpour. 1980. A nitric acid plant tissue digest method for use with inductively coupled plasma spectrometry. Comm. Soil Sci. Plant Anal. 11:969-980.

Heil, D.M., and K.A. Barbarick. 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. J. Environ. Qual. 18:292-298.

Jan, F., and S. Pettersson. 1989. Varietal diversity of upland rice in sensitivity to aluminum. J. Plant Nutr. 12:973-993.

Keeney, D.R., and D.W. Nelson. 1982. Nitrogen - inorganic forms. p. 648-659. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Lin, S. 1988. Effects of alum sludge application on corn and soybeans. Joint Conf. CSCEASCE, Natl. Conf. of Envir. Engrs. Vancouver, B.C..

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley and Sons, New York.

Lucas, J.B., T.A. Dillaha, R.B. Reneau, J.T. Novak, and W.R. Knocke. Nov. 1994. Alum Sludge Land Application and its Effect on Plant Growth. J. AWWA. 86:11:75.

Marschner, H. 1995. Mineral Nutrition of Higher Plants. Second edition. Academic Press, Inc. San Diego, CA.

McLaughlin, J.R., J.C. Ryden, and J.K. Syers. 1981. Sorption of inorganic phosphate by iron- and aluminum- containing components. J. Soil Sci. 32:365-377.

McLean, F.T., and B.E. Gilbert. 1927. Aluminum tolerance of crop plants. J. Soil Sci. 24:165-176.

Millard, M.M., C.D. Foy, C.A. Coradetti, and M.D. Reinsel. 1990. X-ray photoelectron spectroscopy surface analysis of aluminum ion stress in barley roots. J. Plant Physiol. 93:578-583.

Moore Jr., P.A., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Effect of chemical amendments on ammonia volatilization from poultry litter. J. Environ. Qual. 24:293-300.

Narf, R.P. 1985. Impact of phosphorus reduction via metalimnetic alum injection in Bullhead Lake, Wisconsin. TB153. Dep. Nat. Res. Madison, WI.

National Research Council. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, Washington, D.C. 577pp.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 570-573. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Pearson, R.W. 1966. Soil environment and root development. p. 95-126. *In* W.H. Pierre, D. Kirkham, J. Pesek, and R. Shaw (eds.). Plant Environment and Efficient Water Use. American Society of Agronomy and Soil Science Society of America. Madison, WI.

Peters, J.M., and N.T. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. J. Environ. Qual. 25:1236-1241.

Rengasamy, P., J.M. Oades, and T.W. Hancock. 1980. Improvement of soil structure and plant growth by addition of alum sludge. Commun. Soil Sci. Plant Anal. 11:533-545.

Rhoades, J.D. 1982a. Cation exchange capacity. p. 149-157. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. 1982 American Society of Agronomy. Madison, WI.

Rhoades, J.D. 1982b. Soluble salts. p. 167-180. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Scambilis, N.A. 1977. Land disposal of chemical sludges. Ph.D. dissertation, Univ. of Missouri, Columbia.

Schindler, D.W. 1977. The evolution of phosphorus limitation in lakes. Science (Washington, DC) 195:260-262.

Shreve, B.R., P.A. Moore Jr., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Reduction of Phosphorus in runoff from field-applied poultry litter using chemical amendments. J. Environ. Qual. 24:106-111.

Soltanpour, P.N., J.B. Jones Jr., S.M. Workman. 1982. p. 55-57. Optical emission spectrometry. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Steel, R.G.D., and J.H. Torrie. 1980. Principles and Procedures of Statistics - A Biometrical Approach. Second Ed. McGraw-Hill, Inc., USA.

Taylor, G.J. 1991. Current views of the aluminum stress response; The physiological basis of tolerance. p. 57-93. *In* Current topics in plant biochemistry and physiology, 1991: Proceedings of the tenth annual Plant Biochemistry and Physiology Symposium. University of Missouri. Columbia, MO.

Wisconsin Department of Natural Resources. 1973. Eutrophication control. Nutrient inactivation by chemical precipitation at Horseshoe Lake, Wisconsin. TB62. Dep. Nat. Res. Madison, WI.

Table 2.1. Selected chemical characteristics of soil, WTR, and biosolids.

Element	Units	Altvan Soil	Fort Collins WTR	Fort Collins Biosolids	Englewood WTR	Littleton/ Englewood Biosolids
Ca	g kg^{-1}	2.6	5.7	30.6	20.3	42.4
Mg	g kg^{-1}	3.8	4.5	5.2	6.2	6.0
Na	g kg^{-1}	0.06	0.21	0.63	0.56	1.1
K	g kg^{-1}	4.7	3.8	2.7	6.1	2.9
P	g kg^{-1}	0.4	0.7	22.2	2.0	23.0
Al	g kg^{-1}	16.3	74.7	9.9	72.6	19.3
Fe	g kg^{-1}	13.5	17.8	5.2	28.2	17.0
Mn	g kg^{-1}	0.28	0.82	0.10	2.4	0.29
Ti	g kg^{-1}	0.73	0.79	0.10	0.88	0.86
Total N	g kg^{-1}	ND[†]	ND	55.9	6.9	21.0
NH_4-N	g kg^{-1}	ND	ND	24.7	0.03	8.6
NO_3-N	mg kg^{-1}	1.0	44.0	9.2	1220	8.7
Cu	mg kg^{-1}	6.1	47.6	578	5010	657
Zn	mg kg^{-1}	34.6	53.3	737	146	652
Ni	mg kg^{-1}	6.6	10.9	22.7	18.6	51.7
Mo	mg kg^{-1}	<0.1	<0.1	16.3	4.6	24.4
Cd	mg kg^{-1}	0.3	<0.1	4.7	<0.2	6.1
Cr	mg kg^{-1}	9.3	19.1	49.0	34.8	59.4
Sr	mg kg^{-1}	22.2	31.1	315	190	443
B	mg kg^{-1}	46.8	91.6	34.6	92.3	59.4
Ba	mg kg^{-1}	127.0	95.2	369	278	144
Pb	mg kg^{-1}	7.9	<2.5	57.0	24.9	27.0
Si	mg kg^{-1}	464	322	125	ND	ND
V	mg kg^{-1}	35.6	34.3	14.9	61.8	30.3
pH		6.9	6.9	7.7	7.4	8.0
EC	dS m^{-1}	0.2	0.7	11.2	4.8	21.6
O.M.	g kg^{-1}	1.7	6.3	ND	23.2	ND
CEC	cmol(+) kg^{-1}	11.8	39.3	ND	40.7	ND

[†] = Not determined.

Table 2.2. **Effects of WTR and biosolids co-applications on blue grama dry matter yields and P and Al shoot concentrations and uptake.**

WTR	Biosolids	Dry Matter Yields	Shoot P	P uptake	Shoot Al	Al uptake
g kg^{-1}	g kg^{-1}	g pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	µg pot^{-1}
0	5	6.9	2180	14.9	36.1	248
10	"	4.2	2010	8.5	32.0	135
25	"	6.2	1340	8.3	33.0	204
50	"	6.8	1760	11.9	27.7	187
100	"	4.7	1520	7.2	25.4	120
150	"	10.8	1520	16.4	24.4	265
200	"	11.3	1610	18.2	30.8	349
250	"	8.6	1320	11.4	23.6	203
			Prob.	Level	(*p*)	
	<u>regression f-test</u>					
	Linear	0.050	0.091	0.327	0.053	0.301
	Quad	0.166	0.217	0.644	0.086	0.616
	LSD$_{0.10}$	2.8	350	—	4.8	—

Table 2.3. **Effects of WTR and biosolids co-applications on western wheatgrass dry matter yields and P and Al shoot concentrations and uptake.**

WTR	Biosolids	Dry Matter Yields	Shoot P	P uptake	Shoot Al	Al uptake
g kg^{-1}	g kg^{-1}	g pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	µg pot^{-1}
0	5	9.7	2790	27.2	52.2	508
10	"	10.4	1750	18.1	51.8	536
25	"	10.1	1520	15.4	38.8	392
50	"	11.0	1310	14.4	40.7	448
100	"	9.2	1620	14.9	44.7	412
150	"	14.2	1490	21.2	44.0	626
200	"	12.1	1470	17.8	43.0	520
250	"	7.4	1810	13.3	58.4	430
			Prob.	Level	(*p*)	
	regression f-test					
	Linear	0.956	0.440	0.376	0.535	0.836
	Quad	0.278	0.196	0.628	0.087	0.787
	$\text{LSD}_{0.10}$	----	----	----	7.0	----

Table 2.4. **Effects of WTR and biosolids co-applications on western wheatgrass root P and Al concentrations.**

WTR	Biosolids	Root P	Root Al
g kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
0	5	2100	1030
10	"	1450	1390
25	"	1070	1650
50	"	1040	1600
100	"	1370	1750
150	"	1150	1210
200	"	1020	1340
250	"	1490	1240
		Prob. Level (*p*)	
	regression f-test		
	Linear	0.475	0.656
	Quad	0.749	0.442
	$LSD_{0.10}$	----	----

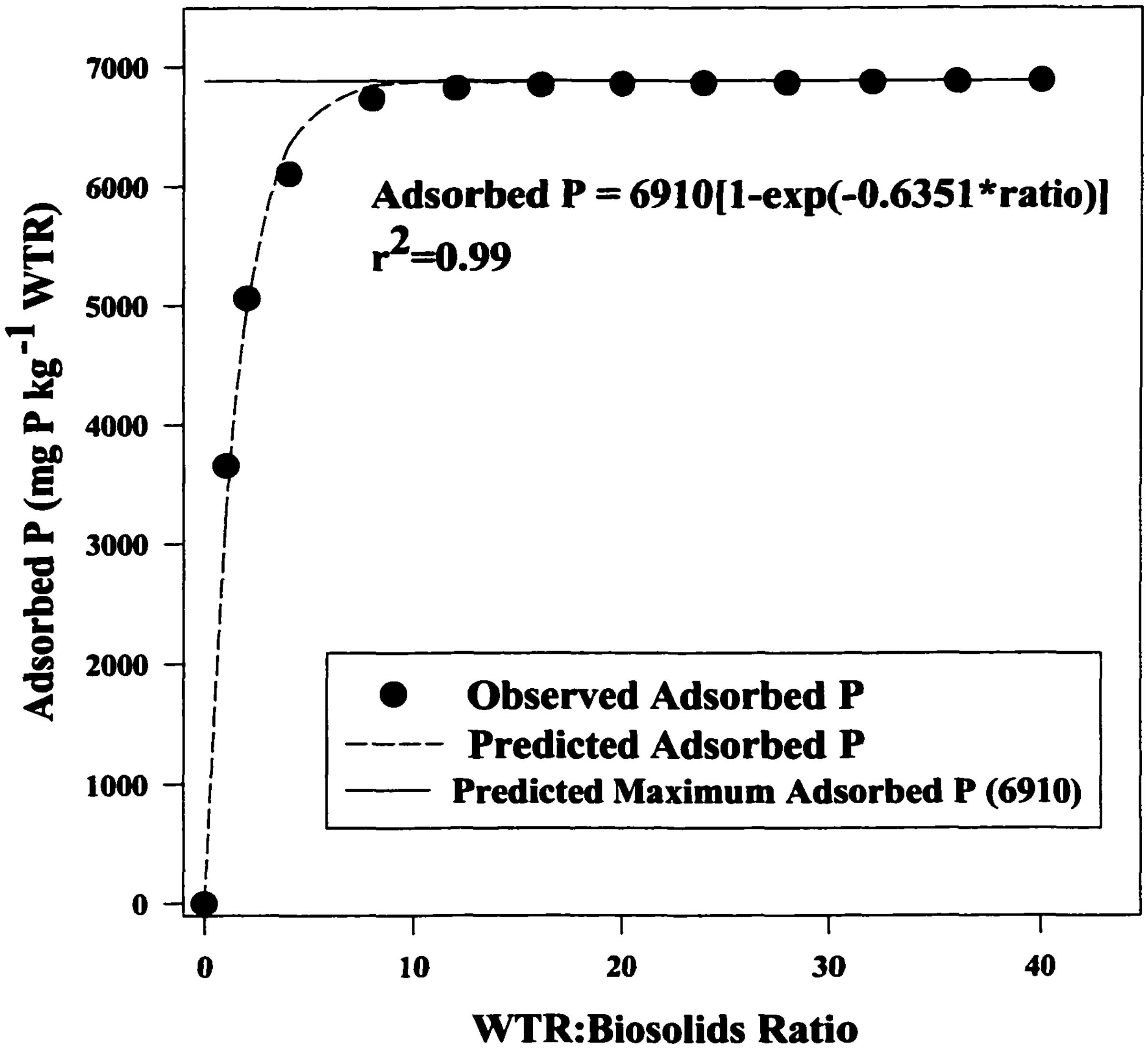


Figure 2.1. Adsorbed P vs WTR:Biosolids Ratio - Fort Collins, CO.

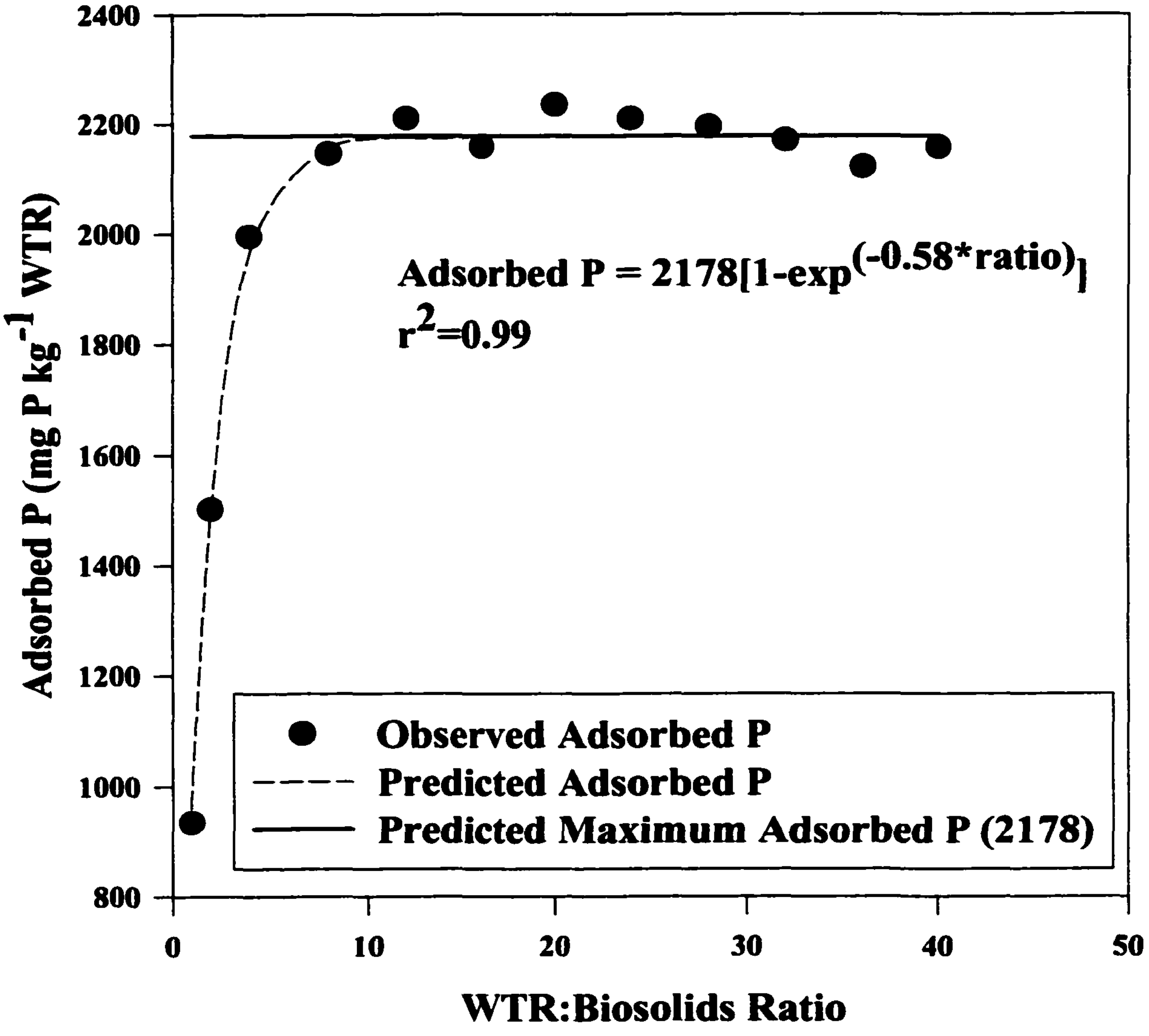


Figure 2.2. Adsorbed P vs WTR:Biosolids Ratio - Littleton/Englewood, CO.

Chapter 3

Phosphorus Adsorptive Mechanisms of Water Treatment Residuals

ABSTRACT

Water treatment residuals (WTR) are a by-product of municipal drinking water treatment plants and are created during the water clarification process. Depending on the inherent nature of the WTR, they can have the capacity to adsorb tremendous amounts of P. Understanding the initial process of WTR P adsorption is important for discerning where and how strongly P is being adsorbed. I studied the P adsorbing mechanism of an alum-containing [$Al_2(SO_4)_3 \bullet 14H_2O$] WTR from Englewood, CO. My previous research indicated that the WTR from Englewood, CO, is a strong adsorber of available P (see Chapter 2). In a laboratory study, I investigated the efficacy of Al, Ca, and P desorption and pH changes from WTR. I shook mixtures of P-loaded WTR in 0.01 M $CaCl_2$ for 1, 2, 4, 7, 14, 28, 84, and 211 days followed by solution pH analysis, and desorbed Ca, Al, and P analysis via inductively coupled plasma atomic emission spectroscopy (ICP-AES). After shaking periods, I also examined the solids fraction using x-ray diffraction (XRD) and electron microprobe analysis using wavelength dispersive spectroscopy (EMPA-WDS). The shaking results indicated an increase in pH from 7.2 to 8.2, an increase in desorbed Ca and Al concentrations, and a decrease in desorbed P concentration. The pH and Ca concentration increases suggested that $CaCO_3$ controlled Ca availability in my systems. The Al concentration increase may be due to WTR's amorphous $Al(OH)_3$ content forming the $Al(OH)_4^-$ solution species. The decrease in P content, in conjunction with the increase in pH, is consistent with calcium phosphate formation or precipitation. The system appeared to be undersaturated with respect to dicalcium phosphate (DCP; $CaHPO_4$) and supersaturated with respect to octacalcium phosphate (OCP;

$Ca_4H(PO_4)_3 \bullet 2.5H_2O$). The Ca and Al increases, as well as OCP formation were supported by MINTEQA2 modeling. The XRD and EMPA-WDS results for all shaking times, however, suggested surface P chemisorption as an amorphous Al-P mineral phase might occur.

ABBREVIATIONS

DCP, dicalcium phosphate ($CaHPO_4$)

EC, electrical conductivity

EMPA-WDS, electron microprobe analysis using wavelength dispersive spectroscopy

ICP-AES, inductively coupled plasma-atomic emission spectroscopy

LSD, least significant difference

OCP, octacalcium phosphate ($Ca_4H(PO_4)_3 \bullet 2.5H_2O$)

p, probability level

TCP, tricalcium phosphate ($Ca_3(PO_4)_2$)

WTR, water treatment residuals

XRD, x-ray diffraction

INTRODUCTION

Water treatment plant residuals (WTR) are a waste product of drinking water treatment facilities. Alum [$Al_2(SO_4)_3 \bullet 14H_2O$] is commonly used in the treatment process for particulate flocculation and water clarification. Disposal of this waste material in landfills is common practice. However, municipalities must look toward beneficial reuse of WTR as landfill space becomes less available and more costly to utilize. One method of recycling WTR is application to land.

The potential benefits of WTR land application are increased plant available N and total organic C (Rengasamy et al., 1980; Lin, 1988; Dempsey et al., 1989; Elliott et al., 1990; Elliott and Dempsey, 1991), and increased aggregate stability, water retention, aeration, and drainage capacity (El-Swaify and Emerson, 1975; Scambilis, 1977; Rengasamy et al., 1980; Bugbee and Frink, 1985). Heil and Barbarick (1989) noted Fe deficiencies in sorghum-sudangrass (*Sorghum bicolor* (L.) Moench *Sorghum* X *drummondii* (Steudel) Millsp. & Chase) grown in a calcareous soil. However, addition of WTR increased dry matter production and eliminated deficiency symptoms by increasing plant available Fe. The amorphous hydrous oxides in WTR may benefit coarse soils by increasing the cation exchange capacity (American Society of Civil Engineers et al., 1996). Water treatment residuals with neutral to basic pH may also be used as a liming agent in soils that require pH adjustment.

Potential disadvantages of WTR land application due to the WTR's water source and treatment include increases in each of the following characteristics: soil trace element concentration; salinity; pH; and soil consistence. The metals content, salinity, and pH of

WTR is important for potential impacts on beneficial reuse based on state regulations. The total levels of Cd, Cu, Cr, Ni, Pb, and Zn in WTR are generally 10 to 35 % of the corresponding values for biosolids (American Society of Civil Engineers et al., 1996). In a greenhouse study, Heil (1988) studied effects of increased WTR addition on plant elemental concentrations. The plant concentrations of Al, Cu, Mn, Ni, and Pb were not high enough to decrease plant growth. However, with his highest WTR application rate, some Cd and Mn concentrations were above levels considered a threat to livestock consumption (NRC, 1980).

Peters and Basta (1996) observed increasing pH with increasing addition of two different WTRs to soil. Each WTR acted as a liming agent because the pH of the soil was 5.3 and the WTRs were 7.0 and 7.6, respectively. They did not observe any salinity increases with WTR addition. The consistency of WTR is generally that of very fine soils, and when overapplied can increase the amount of dust generated from its dry form (American Society of Civil Engineers et al., 1996). It can, however, be used as a suitable landfill material, aiding in neutralization of low pH refuse effluent (Cornwell and Westerhoff, 1981).

The single most important disadvantage of WTR land application is its adsorption of plant available soil P. Heil and Barbarick (1989) noted severe P-deficiency symptoms associated with an excessive rate of WTR addition. However, they were able to increase sorghum-sudangrass production by increasing P fertilizer addition. Ippolito et al. (1999) observed decreasing P concentrations in blue grama (*Bouteloua gracilis*) with increasing WTR rates. Rengasamy et al. (1980) observed reduced P uptake in maize (*Zea mays* L.)

with WTR addition. Elliott and Singer (1988) and Bugbee and Frink (1985) showed reduced P concentrations in tomato (*Lycopersicon esculentum* L.) and lettuce (*Lactuca sativa* L.) grown in WTR-amended potting media.

The negative connotation associated with land application of WTR, however, can be eliminated if WTR is applied to high P-bearing materials or soils. Hyde and Morris (2000) and Haustein et al. (2000) showed marked decreases in Mehlich-3 soil P concentrations following WTR addition. Application of WTR to soils that contain excess poultry litter-borne P have been shown to drastically reduce the amount of water soluble, Bray and Kurtz no. 1-extractable P, and bioavailable P (Codling et al., 2000; Peters and Basta, 1996). Ippolito et al. (1999) used two WTRs to adsorb biosolids-borne P. They found that, at ratios > 8:1 (WTR:biosolids), the WTR would adsorb all biosolids-borne P and possibly soil-borne P. Butkus et al. (1998) suggested adding P to WTR as a pretreatment so as to convert WTR from a P consumer to a P supplier.

Basic data concerning fundamental P reactions with alum-containing WTR is incomplete. One hypothesis indicates that P adsorption occurs at the WTR's hydrous aluminum oxide interface. Phosphate replaces singly coordinated OH^- groups and then reorganizes into a very stable binuclear bridge between cations (Bohn et al., 1985). This chemiadsorption process is coupled with the release of OH^- ions, thus the process is favored by low pH values (Stumm, 1987). Cox et al. (1997) studied low-pH WTR addition to acid soil. They observed P immobilization and associated that with phosphate-bound Al. van Riemsdijk et al. (1975) reported aluminum phosphate precipitation from mixing a phosphate solution with amorphous $Al(OH)_3$ at pH 5. Other potential P reactions may be surface adsorption or precipitation, or precipitation of new solid mineral phases.

My research objectives were to investigate the efficacy of P adsorption to a slightly basic, alum-containing WTR, the efficacy of P removal from a P-loaded WTR, monitor long-term changes with respect to pH, Ca, Al, and P concentrations, and to examine long-term chemical phase changes utilizing x-ray diffraction (XRD) and electron microprobe analysis using wavelength dispersive spectroscopy (EMPA-WDS).

The hypotheses I tested in this study were: (a) WTR will have a high P adsorption capacity; (b) P-loaded WTR will readily desorb P to solution; and (c) long-term chemical phase changes will show an association of P with the Ca fraction of WTR, precipitating solid calcium phosphate mineral phases.

MATERIALS AND METHODS

The WTR used in this study was obtained from the Englewood, CO, water treatment facility. The water inflow supply typically has a pH between 7.5 and 8.0. The water treatment facility routinely adds an anionic polymer for conditioning prior to belt pressing.

I determined total elemental composition of the WTR by a modified $HClO_4$-HNO_3-HF-HCl digestion (Table 3.1; Soltanpour et al., 1982) and analyzed the digestate using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). I determined total N via LECO-1000 analysis (Miller et al., 1998), NH_4-N and NO_3-N following a 2 M KCl extraction (Mulvaney, 1996), and organic N via subtraction of inorganic from total. The pH and electrical conductivity (EC) were determined using a saturated paste extract (Rhoades, 1982b) and CEC via the Rhoades method (1982a). Amorphous and crystalline Al hydroxides were determined using an ammonium oxalate extraction and a citrate-bicarbonate-dithionite extraction, respectively (Loeppert and Inskeep, 1996).

I air dried the WTR and then separated the 0.1- to 0.3-mm size fraction to use for this as well as future experiments. In several 1000-mL nalgene bottles I added 20 g WTR (dry weight basis) and 800 mL of 0.1 M KCl containing 300 mg kg^{-1} P. They were placed on a reciprocating shaker for 24 hours, decanted, and the decantate was saved. I then added 800 mL DI to the WTR, shook vigorously, let sit overnight, decanted, saved the decantate, and analyzed both decantates for P using ICP-AES. The P adsorbed was calculated from the difference between initial and final concentrations. I saved the P-loaded WTR for further analysis.

The P-loaded WTR was air dried, then triplicate 4-g (dry weight basis) subsamples were weighed into 50-mL centrifuge tubes. I added 20 mL of 0.01 M $CaCl_2$ solution and shook the tubes for 1, 2, 4, 7, 14, 28, 84, and 211 days. After the appropriate shaking period, I decanted the liquid and analyzed it for pH and Ca, Al, and P using ICP-AES. I converted solution concentrations (mg L^{-1}) from ICP-AES to a weight basis (mg kg^{-1} WTR) using a dilution factor of five (4g WTR per 20 mL 0.01 M $CaCl_2$) to express the amount of Ca, Al, or P desorbed from a given quantity of WTR.

To verify that Ca interferences were not occurring with addition of the 0.01 M $CaCl_2$ ionic strength buffer solution, I weighed out triplicate 4 g WTR subsamples into 50-mL centrifuge tubes and added 20 mL of 0.02 M KCl. They were placed on a reciprocating shaker for 1 day and 1 week, filtered through Whatman No. 42 filter paper, and analyzed the decantate for the same constituents.

I calculated activities of the Ca and Al based on day 211 desorbed values, and potential calcium phosphate species based on individual shaking period pH values and desorbed values for Ca and P. I also calculated the CO_2 partial pressure for use in determining which carbonate minerals were potentially present. I compared these activities to activities calculated from equilibrium constants found in Lindsay (1979). In addition, I utilized the equilibrium speciation model MINTEQA2 (Allison et al., 1991) to verify the results. I utilized the observed activities data from day 211, entered a fixed pH of 8.15, entered amorphous $Al(OH)_3$ and calcite as finite solids, and excluded all crystalline Al hydroxide species as well as hydroxyapatite for MINTEQA2 input. These will subsequently be labeled "observed", "calculated", or "MINTEQA2" in the results section.

Data were analyzed using regression analysis and analyses of variance and tested at a probability level (p) = 0.10 (Steel and Torrie, 1980). I additionally calculated a least significant difference (LSD) in order to predict reaction completion.

After the various shaking periods I examined the solids fraction using XRD and EMPA-WDS. I utilized two or all three replicates from the 1, 28, 84, and 211 d samples for XRD and EMPA-WDS analysis, respectively. For XRD analysis, the samples were ground with a porcelain mortar and pestle before placing them in the XRD holder. The samples were packed into the 2.54-cm diameter by 0.32-cm deep holders as packed dry powder mounts. The samples were then analyzed from 5°2 theta to 55°2 theta. The XRD (SCINTAG Model XDS 2000 XGEN-4000, Thermo ARL, Switzerland) had a copper target. Box car smoothing was used and K-α2 stripping was performed using K-α1 and K-α2 as 1.540562 and 1.544390, respectively.

For EMPA-WDS analysis, samples were placed in a monolayer in the bottoms of individual 0.7-cm by 1.6-cm by 1-cm deep plastic boats. I gently poured Acrylimet epoxy (South Bay Technology, Inc., San Clemente, CA) over the samples and let them cure for 24 h at room temperature and 138 kPa of pressure. After curing, the epoxy-coated samples were removed from the plastic boats and wet wheel-polished with an Exakt automated microgrinder using 800 and then 1200-grit polishing paper to remove approximately 0.15 mm of material. The amount of material removed was approximately equal to half the diameter of the sample particles. The samples were carbon coated in a vacuum evaporator (Kinney vacuum evaporator Model KDTG-3P). Samples were analyzed using a JEOL JXA-8900 Electron Microprobe analyzer (JEOL USA, Inc., Peabody, MA) at an accelerating voltage of 15 keV and a magnification between 300x and 550x. I used backscattered electrons for collecting images of the specimen surface and wavelength dispersive spectroscopy to generate dot maps of P, Al, and Ca.

RESULTS AND DISCUSSION

Initial WTR P Loading

My initial WTR P loading experiment indicated that 250 mg P L^{-1} was adsorbed. This equated to 12,500 mg P adsorbed kg^{-1} WTR, or 1.25%. My previous research (Chapter 2) indicated an adsorption capacity of 2178 mg P adsorbed kg^{-1} of Englewood, CO, WTR. However, my previous study was a WTR and biosolids co-mixing study, where the WTR was not fractionated, and the biosolids rate, and thus the rate of bioavailable P, was held constant. I expected to observe higher adsorption capacities with smaller WTR size fractions due to greater specific surface area and because all of the P was available for adsorption in this study.

Shaking Period Results

When I compared the 1 d to 1 wk solution Ca, Al, and P concentrations, the 0.02 M KCl ionic strength buffer solution showed similar trends to that of the 0.01 M $CaCl_2$ solution. I also used MINTEQA2 to compare the two solutions and found <0.01% difference between the final solution compositions. Therefore, I assumed the $CaCl_2$ solution did not significantly interfere with the overall results.

As shaking time increased, the solution pH increased to a maximum of 8.15 (Figure 3.1). The equation describing the curve is:

$$\text{pH} = 7.22 + 0.93\,[1 - e^{(-0.04 \cdot \text{days})}] \qquad (1)$$

The predicted curve agreed with the observed values with $r^2 = 0.93$ and $p = 0.001$. The LSD = 0.15, which indicated no change in pH from day 84 to day 211. This suggests a solid phase species controlling pH at the latter time periods.

The desorbed Ca concentration increased to 1680 mg kg^{-1} WTR with increased shaking (Figure 3.2). The equation describing the curve is:

$$\text{Ca (mg kg}^{-1}\text{ WTR)} = 1080 + 11.22\ \text{days}^{(0.74)} \qquad (2)$$

The predicted curve agreed with the observed values with $r^2 = 0.99$ and $p < 0.001$. The LSD = 43, which indicated desorbed Ca concentration was increasing even after 211 d of shaking.

The observed and calculated Ca concentration at 211 d, when converted to activity, equaled $10^{-2.43}$ and $10^{-2.93}$, respectively. MINTEQA2 results also showed a Ca activity equal to $10^{-2.98}$, further supporting the findings.

A pH of 8.15, along with the above Ca results, support the hypothesis of $CaCO_3$ controlling Ca availability at a partial pressure of CO_2 slightly less than atmospheric (0.0002 versus 0.0003 atm). Based on the observed data, I calculated a CO_2 partial pressure equal to 0.00023 atm. This slight decrease in atmospheric CO_2 could have occurred due to $CaCO_3$ precipitation and to the centrifuge tubes systems being closed. It is interesting to note that lime was not added during the water treatment process, which could have influenced $CaCO_3$ formation. However, the incoming drinking water treatment plant water tends to have a pH of approximately 7.5 to 8.0, while the WTR Ca content is 25.9 g kg^{-1}. This suggests that the water is in equilibrium with a Ca species, possibly $CaCO_3$.

The desorbed Al concentration increased with increased shaking time (Figure 3.3). The equation describing the curve is:

$$\text{Al (mg kg}^{-1}\text{ WTR)} = 0.11\ e^{(0.02\text{days})} \qquad (3)$$

The predicted curve agreed with the observed values with $r^2 = 0.99$ and $p < 0.001$. The LSD = 0.31, which indicated solution Al concentration was increasing drastically from day 84 to day 211. This may be explained by amorphous $Al(OH)_3$ forming the solution species $Al(OH)_4^-$, and is supported by comparing the Al activity from the observed and calculated results and to MINTEQA2 results ($10^{-4.91}$, $10^{-5.47}$, and $10^{-4.89}$, respectively). I expected to observe an increase in desorbed Al content since Al undergoes hydrolysis with increasing pH, and hydroxy Al complexes dominate above pH 7. Schecher and Driscoll (1988) noted the distribution of Al species was mainly $Al(OH)_4^-$ above pH 5.5. The slight discrepancy in the activity values may be explained by variation in the thermodynamic equilibrium constants. Schecher and Driscoll (1987) presented Al species equilibrium constants, their standard deviations, and a measure of uncertainty. Their paper supports the contention that the thermodynamic equilibrium constants contain uncertainty.

The desorbed P concentration decreased with increased shaking time, indicating a further adsorption effect (Figure 3.4). The equation describing the curve is:

$$P\ (\mathrm{mg\ kg^{-1}\ WTR}) = 5.37 + 11.79\ e^{(-0.03\mathrm{days})} \qquad (4)$$

The predicted curve agreed with the observed values with $r^2 = 0.98$ and $p < 0.001$. The LSD = 0.59, which indicated that P concentration was decreasing even at 211 d. This decrease may be due to P finding more reactive sites in micro-pores, becoming more strongly chemiadsorbed at individual surface sites, layered surface precipitation, or the formation of calcium phosphate precipitates. Griffin and Jurinak (1973) studied P adsorption on calcite. They speculated that P adsorption occurs, in part, as a multilayer phenomenon on specific sites on the calcite surface. They interpreted their data as the onset of heterogeneous nucleation of calcium phosphate crystallites on the calcite surface.

Castro and Torrent (1998) studied P sorption by calcareous soils. They described sorption as a two-step process; an initial linear region associated with P adsorption on variable charge surfaces and a latter linear region corresponding to the precipitation of calcium phosphates. The two linear regions from the study may correspond to Castro and Torrent's (1998) findings, with the gradual transformation in the latter linear region due to conversion from more to less soluble calcium phosphate minerals.

Figure 3.5 shows the solubility isotherms for several P minerals. The system appears to be undersaturated with respect to dicalcium phosphate (DCP; $CaHPO_4$) and trending towards the formation of octacalcium phosphate (OCP; $Ca_4H(PO_4)_3 \bullet 2.5H_2O$). MINTEQA2 output also suggests the formation of OCP. Considering this, as well as the possibility of Ca being controlled by the presence of $CaCO_3$, Griffin and Jurinak's (1973) findings may be credible to the results. In addition, according to these results the system appears to be progressing from a more to a less soluble mineral form, from slightly less soluble than DCP to equilibrium with OCP, as is suggested by Castro and Torrent (1998). The data point at day 211 is slightly less soluble that of OCP, which may suggest an additional transformation from OCP to tricalcium phosphate (TCP; $Ca_3(PO_4)_2$).

The P findings are interesting in light of Butkus et al.'s (1998) suggestion of adding P to WTR as a pretreatment so as to convert WTR from a phosphate consumer to a P supplier. The results indicate that P is not easily desorbed. To the contrary, it is either being further chemiadsorbed to the WTR or Ca fraction or is precipitating as OCP, as suggested by the above findings.

Others have studied P solubility in soils. Lindsay (1979) suggested a pH of 6 to 6.5 where several phosphate minerals, such as variscite, DCP, and OCP, can coexist. Below this pH range the Al species variscite would control P availability. Above this pH range, and as suggested with my study, the calcium phosphate minerals would control P availability. Pierzynski et al. (1990a) showed soil sample supernatants with pH values >6.8 exhibited solubility relationships between that of OCP, TCP, and hydroxyapatite. Fixen and Ludwick (1982) verified the presence of P minerals in the solubility range between that of OCP, TCP, and hydroxyapatite in several calcareous soils. O'Connor et al. (1986) confirmed evidence of β-TCP controlling P availability in a calcareous soil with a history of P fertilization.

XRD Analysis and EMPA-WDS Results

The XRD results are presented in Figures 3.6 through 3.13. I did not detect any major differences between any of the samples. For all samples, many 1:1 and 2:1-type clays, and quartz are present which are indicative of the flocculation and drinking water clarification process. In addition, I did verify the presence of calcite, $CaCO_3$, as was suggested by my shaking experiment. I did not identify, however, the presence of any phosphate mineral phases. This is not to say they are not present, however. The XRD detection limits for most mineral phases is ~1% and my samples contained 1.25% P.

The EMPA-WDS results are presented in Figures 3.14 through 3.25. Again, I did not detect any major differences between any of the samples. It is clear from the Ca and

P dot maps that there is no visible association between these elements. This is evident by the black areas on the P dot map closely associated with the white areas from the Ca dot map. For all samples it appears that P is more closely associated with the Al fraction of the WTR. Furthermore, P is associated with Al throughout the particle and not strictly occurring as a particle surface coating. I can infer this because I polished the samples essentially in half. This would suggest, in light of finding no Ca or Al phosphate mineral species using XRD, that P surface chemiadsorption is occurring and no calcium phosphate mineral phases are present. This method, however, also has detection limits near ~1% and my samples contained 1.25% P.

Galarneau and Gehr (1997) examined P removal from wastewaters using WTR. They concluded that the minimum residual orthophosphate concentration required would be 2244 mg P L^{-1}, at pH 7, in order for solution to be in equilibrium with $Al(PO_4)$. My final P concentration was much lower than this value, suggesting other mechanisms of P sorption.

Samadi and Gilkes (1999) studied P transformations in calcareous soils using scanning electron microscopy in conjunction with energy dispersive spectroscopy. They found no evidence of P association with other soil elements. However, Sawhney (1973) used electron microprobe analysis and found P associated with Al, Fe, and Si throughout particles from Connecticut soils. Castro and Torrent (1995) studied P availability in calcareous soils. They noted that soils containing a higher ratio of clays and Fe oxides may occlude P. Holford and Mattingly (1975) noted high-energy P adsorption in calcareous soils appeared to be mainly associated with surfaces of Fe compounds or perhaps, more generally, with all the hydrous oxides present.

Pierzynski et al. (1990b) studied P chemistry in excessively fertilized soils. They concluded that the elemental makeup of P-rich particles probably contained several cations in association with P, and that Al was the predominant cation association regardless of soil pH. In a follow-up study, Pierzynski et al. (1990c) studied the P-rich particles using scanning transmission electron microscopy equipped with an energy dispersive x-ray analyzer. They concluded that the P-rich particles were an amorphous mix of Al, Si, and P, and they made an analogy between the particles to an amorphous analog of variscite and allophane.

It is possible that surface chemiadsorption is occurring. Phosphorus may initially be adsorbed as an outer sphere complex or found in the diffuse ion swarm near individual particles. As time progresses, P may become more strongly adsorbed as an inner sphere complex on to WTR, forming amorphous variscite. The MINTEQA2 results, from the shaking experiment, indicated that the system was undersaturated with respect to crystalline variscite. The version of MINTEQA2 I used did not, unfortunately, contain equilibrium constants for amorphous variscite, and therefore I can not verify its presence.

It is also possible that calcium phosphate mineral phases were controlling P availability in my system. These minerals may found in very low quantities as a surface precipitate on calcite, and EMPA-WDS cannot detect these phases due to detection limits and the resolution at which I sampled.

CONCLUSIONS

I accept the hypothesis that WTR will have a high P adsorption capacity. I loaded a WTR with P, and the results indicated that the Englewood, CO, WTR's P adsorptive capacity was approximately 12,500 mg P kg^{-1} WTR. I separated and used the 0.1- to 0.3-mm size fraction for this determination. Therefore, one might expect less adsorption of P with a non-fractionated source due to less reactive surface area.

I researched the influence of shaking period on pH and the desorption of Ca, Al, and P species from the P-loaded WTR. The results indicated an increase in pH from 7.2 to 8.2 and an increase in desorbed Ca concentration from 410 to 1680 mg kg^{-1} WTR. The final pH, along with the observed and calculated Ca activity levels, suggest the system was in equilibrium with $CaCO_3$.

The desorbed Al concentration also increased, from 0.3 to 10.3 mg kg^{-1} WTR, which suggest that amorphous $Al(OH)_3$ inherent in WTR is forming the solution species $Al(OH)_4^-$. I expected to see such an increase due to Al undergoing hydrolysis with increasing pH, and above pH 7 hydroxy Al complexes, such as $Al(OH)_4^-$, dominate.

I reject the hypothesis that P-loaded WTR will readily release P to solution. I observed a decrease in soluble P concentration with increased shaking time, from 17.3 to 4.7 mg kg^{-1} WTR. This decrease could be caused by P finding more occluded surface sites to react with, becoming more strongly sorbed at individual surface sites, layered surface precipitation, or the formation of calcium phosphate precipitates. It has been hypothesized that P adsorption occurs at the WTR's hydrous aluminum oxide interface, where phosphate replaces singly coordinated OH^- groups and then reorganizes into a very stable binuclear bridge between cations (Bohn et al., 1985).

The shaking experiment results support the contention of P adsorption by Ca with subsequent calcium phosphate precipitation. Specifically, I observed evidence of transformation from a more to less soluble calcium phosphate mineral species; from DCP to OCP. It also is possible that the system is showing evidence of an additional transformation, from that of OCP to TCP. MINTEQA2 results supported these findings. This supports the hypothesis that long-term chemical phase changes will show an association of P with the Ca fraction of WTR.

I further researched possible mineral phases and P associations using XRD and EMPA-WDS. Results from both studies did not verify the presence of calcium or aluminum phosphate mineral precipitates, although they may be contained in amounts less than detection limits or in an amorphous mineral form. The XRD results displayed a lack of any P mineral phase, but revealed the presence of mainly 1:1 and 2:1 type clays as well as quartz. The EMPA-WDS results showed that P is associated with the Al fraction of the WTR. This association is most likely due to surface P chemiadsorption, from a less to more stable form, or precipitation of amorphous variscite. Based on this information, I cannot accept my hypothesis with regards to a P-Ca association.

REFERENCES

Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems. EPA/600/3-91/021. US Environmental Protection Agency, National Exposure Research Laboratory, Athens, GA.

American Society of Civil Engineers, American Water Works Association, and the United States Environmental Protection Agency. 1996. Technology transfer handbook: Management of water treatment plant residuals. ASCE and AWWA. New York, New York and Denver, CO.

Bohn, H., B. McNeal, and G. O'Connor. 1985. Soil Chemistry. 2nd ed. John Wiley and Sons, New York.

Bugbee, G.J., and C.R. Frink. 1985. Alum sludge as a soil amendment : Effects on soil properties and plant growth. Conn. Agricultural Exp. Station. Bull. 823.

Butkus, M.A., D. Grasso, C.P. Schulthess, and H. Wijnja. 1998. Surface complexation modeling of phosphate adsorption by water treatment residual. J. Environ. Qual. 27:1055-1063.

Castro, B., and J. Torrent. 1998. Phosphate sorption by calcareous vertisols and inceptisols as evaluated from extended P-sorption curves. Eur. J. Soil Sci. 49:661-667.

Castro, B., and J. Torrent. 1995. Phosphate availability in calcareous Vertisols and Inceptisols in relation to fertilizer type and soil properties. Fert. Res. 40:109-119.

Codling, E.E. R.L. Chaney, and C.L. Mulchi. 2000. Use of aluminum- and iron-rich residues to immobilize phosphorus in poultry litter and litter-amended soils. J. Environ. Qual. 29:1924-1931.

Cornwell, D.A., and G.P Westerhoff. 1981. Management of Water Treatment Plant Sludges. *In* Sludge and its ultimate disposal (J.A. Borchardt et al, eds.). Ann Arbor Sci. Publishers, Ann Arbor, Michigan.

Cox, A.E., J.J. Camberato, and B.R. Smith. 1997. Phosphate availability and inorganic transformation in an alum sludge-affected soil. J. Environ. Qual. 26:1393-1398.

Dempsey, B.A., J. DeWolfe, D. Hamilton, Y. Lee, R. Liebowitz, and H.A. Elliott. 1989. Land application of water plant sludges. Proc. 44th Purdue Indus. Waste Conf., Purdue Univ., West Lafayette, Ind.

Elliott, H.A., and B.A. Dempsey. 1991. Agronomic effects of land application of water treatment sludges. J. AWWA. 83:4:126-131.

Elliott, H.A., B.A. Dempsey, D.W. Hamilton, and J.R. DeWolfe. 1990. Land application of water treatment sludges: Impact and Management. AWWARF, Denver, Colorado.

Elliott, H.A., and L.M. Singer. 1988. Effect of water treatment sludge on growth and elemental composition of tomato shoots. Commun. Soil Sci. Plant Anal. 19:345-354.

El-Swaify, S.A., and W.W. Emerson. 1975. Changes in the physical properties of soil clays due to precipitated aluminum and iron hydroxides: I. Swelling and aggregate stability after drying. Soil Sci. Soc. Amer. Proc., 39:1056-1063.

Fixen, P.E., and A.E. Ludwick. 1982. Residual available phosphorus in near-neutral and alkaline soils: I. Solubility and capacity relationships. Soil Sci. Soc. Amer J. 46:332-334.

Galarneau, E., and R. Gehr. 1997. Phosphorus removal from wastewaters: experimental and theoretical support for alternative mechanisms. Wat. Res. 31:328-338.

Griffin, R.A., and J.J. Jurinak. 1973. The interaction of phosphate with calcite. Soil Sci. Soc. Amer. Proc. 37:847-850.

Haustein, G.K., T.C. Daniel, D.M. Miller, P.A. Moore, Jr., and R.W. McNew. 2000. Aluminum-containing residuals influence high-phosphorus soils and runoff water quality. J. Environ. Qual. 29:1954-1959.

Heil, D.M. 1988. The influence of water treatment sludge on the growth of sorghum-sudangrass. Master's thesis. Colorado State University, Fort Collins.

Heil, D.M., and K.A. Barbarick. 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. J. Environ. Qual. 18:292-298.

Holford, I.C.R., and G.E.G. Mattingly. 1975. The high and low-energy phosphate adsorbing surfaces in calcareous soils. J. Soil Sci. 26:407-417.

Hyde, J.E., and T.F. Morris. 2000. Phosphorus availability in soils amended with dewatered water treatment residual and metal concentration with time in residual. J. Environ. Qual. 29:1896-1904.

Ippolito, J.A., K.A. Barbarick, and E.F. Redente. 1999. Co-application effects of water treatment residuals and biosolids on two range grasses. J. Environ. Qual. 28:1644-1650.

Lin, S. 1988. Effects of alum sludge application on corn and soybeans. Joint Conf. CSCEASCE, Natl. Conf. of Envir. Engrs. Vancouver, B.C..

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley and Sons, New York.

Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639-664. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

Miller, R.O., J. Kotuby-Amacher, and J.B. Rodriguez. 1998. Western States Laboratory Proficiency Testing Program Soil and Plant Analytical Methods. Ver. 4.10.

Mulvaney, R.L. 1996. Nitrogen - inorganic forms. p. 1123-1184. *In* D.L. Sparks (ed.). Methods of Soil Analysis, Part 3 - Chemical Methods. Soil Science Society of America. Madison, WI.

National Research Council. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, Washington, DC.

O'Connor, G.A., K.L. Knudtsen, and G.A. Connell. 1986. Phosphorus solubility in sludge-amended calcareous soils. J. Environ. Qual. 15:308-312.

Peters, J.M., and N.T. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. J. Environ. Qual. 25:1236-1241.

Pierzynski, G.M., T.J. Logan, and S.J. Traina. 1990a. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibria. Soil Sci. Soc. Am. J. 54:1589-1595.

Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990b. Phosphorus chemistry and mineralogy in excessively fertilized soils: Quantitative analysis of phosphorus-rich particles. Soil Sci. Soc. Am. J. 54:1576-1583.

Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990c. Phosphorus chemistry and mineralogy in excessively fertilized soils: Descriptions of phosphorus-rich particles. Soil Sci. Soc. Am. J. 54:1583-1589.

Rengasamy, P., J.M. Oades, and T.W. Hancock. 1980. Improvement of soil structure and plant growth by addition of alum sludge. Commun. Soil Sci. Plant Anal. 11:533-545.

Rhoades, J.D. 1982a. Soluble salts. p. 149-157. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Rhoades, J.D. 1982b. Soluble salts. p. 167-180. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Samadi, A., and R.J. Gilkes. 1999. Phosphorus transformations and their relationships with calcareous soil properties of southern western Australia. Soil Sci. Soc. Am. J. 63:809-815.

Sawhney, B.L. 1973. Electron microprobe analysis of phosphates in soils and sediments. Soil Sci. Soc. Am. Proc. 37:658-660.

Scambilis, N.A. 1977. Land disposal of chemical sludges. Ph.D. dissertation, Univ. of Missouri, Columbia.

Schecher, W.D., and C.T. Driscoll. 1987. An evaluation of uncertainty associated with Al equilibrium calculations. Water Resour. Res., 23:525-534.

Schecher, W.D., and C.T. Driscoll. 1988. An evaluation of the equilibrium calculations within acidification models: The effect of uncertainty in measured chemical components. Water Resour. Res., 24:533-540.

Soltanpour, P.N., J.B. Jones Jr., and S.M. Workman. 1982. p. 55-57. Optical emission spectrometry. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of Soil Analysis, Part 2. Chemical and Biological Properties. 2nd ed. American Society of Agronomy. Madison, WI.

Steel, R.G.D., and J.H. Torrie. 1980. Principles and Procedures of Statistics - A Biometrical Approach. Second Ed. McGraw-Hill, Inc., USA.

Stumm, W. 1987. Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface. John Wiley and Sons. New York.

van Riemsdijk, W.H., F.A. Weststrate, and G.H. Bolt. 1975. Evidence for a new aluminum phosphate phase from reaction rate of phosphate with aluminum hydroxide. Nature. 257:473-474.

Table 3.1. Elemental composition of the Englewood, CO, WTR.

Element	Units	WTR
Ca	g kg^{-1}	31.4
K	g kg^{-1}	3.7
P	g kg^{-1}	2.5
Al	g kg^{-1}	72.6
Amorphous Al	g kg^{-1}	49.9
Crystalline Al	g kg^{-1}	24.1
Fe	g kg^{-1}	19.8
Total N	g kg^{-1}	8.3
Organic N	g kg^{-1}	7.7
NH_4-N	mg kg^{-1}	3.8
NO_3-N	mg kg^{-1}	554
Cu	mg kg^{-1}	5080
Zn	mg kg^{-1}	106
Ni	mg kg^{-1}	15.6
Mo	mg kg^{-1}	3.2
Cd	mg kg^{-1}	0.03
Cr	mg kg^{-1}	19.1
Pb	mg kg^{-1}	27.0
As	mg kg^{-1}	11.1
Se	mg kg^{-1}	0.46
Hg	mg kg^{-1}	<0.05
pH		7.4
EC	dS m^{-1}	4.8
CEC	cmol(+) kg^{-1}	40.7

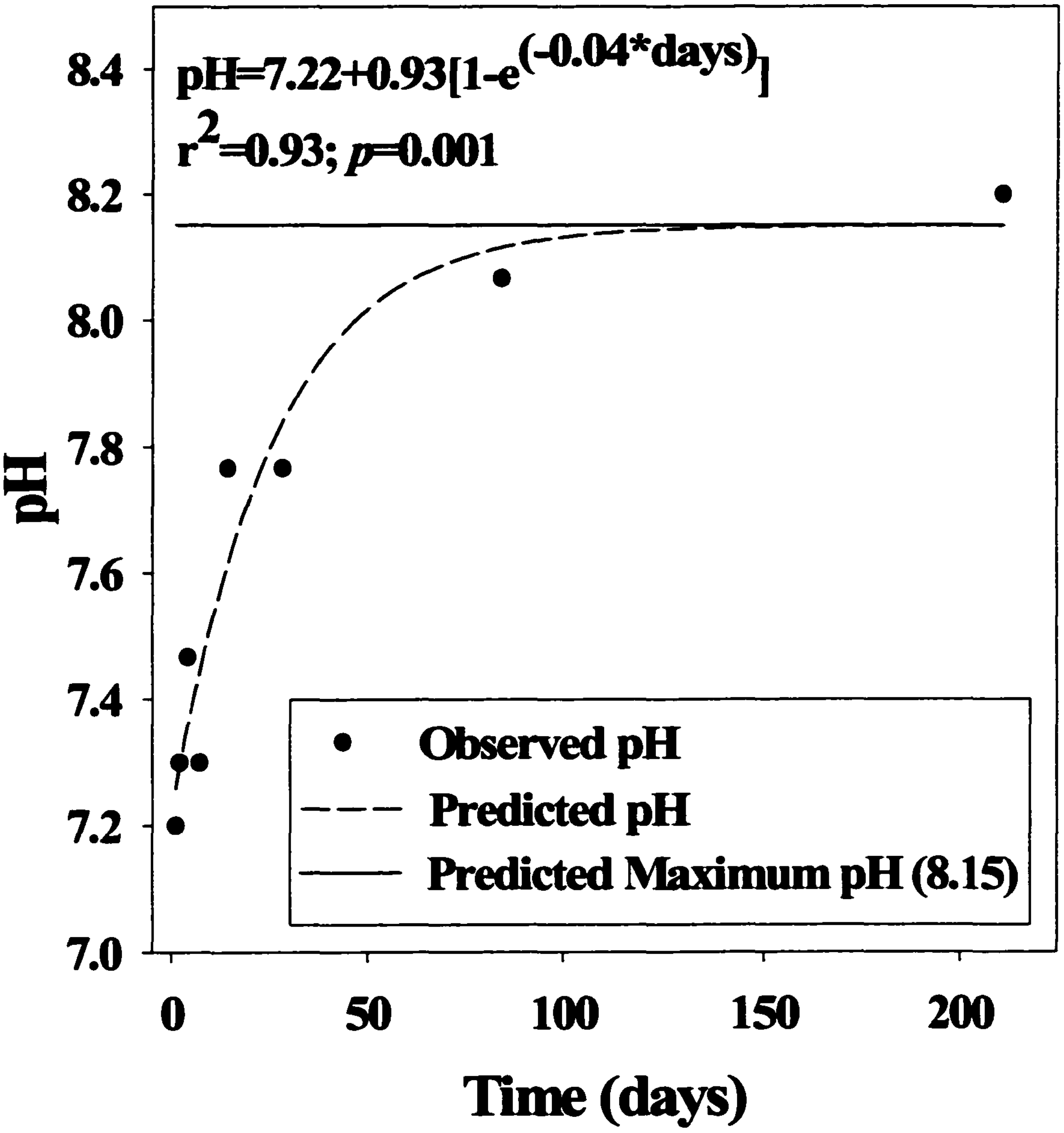


Figure 3.1. The influence of shaking time on solution pH.

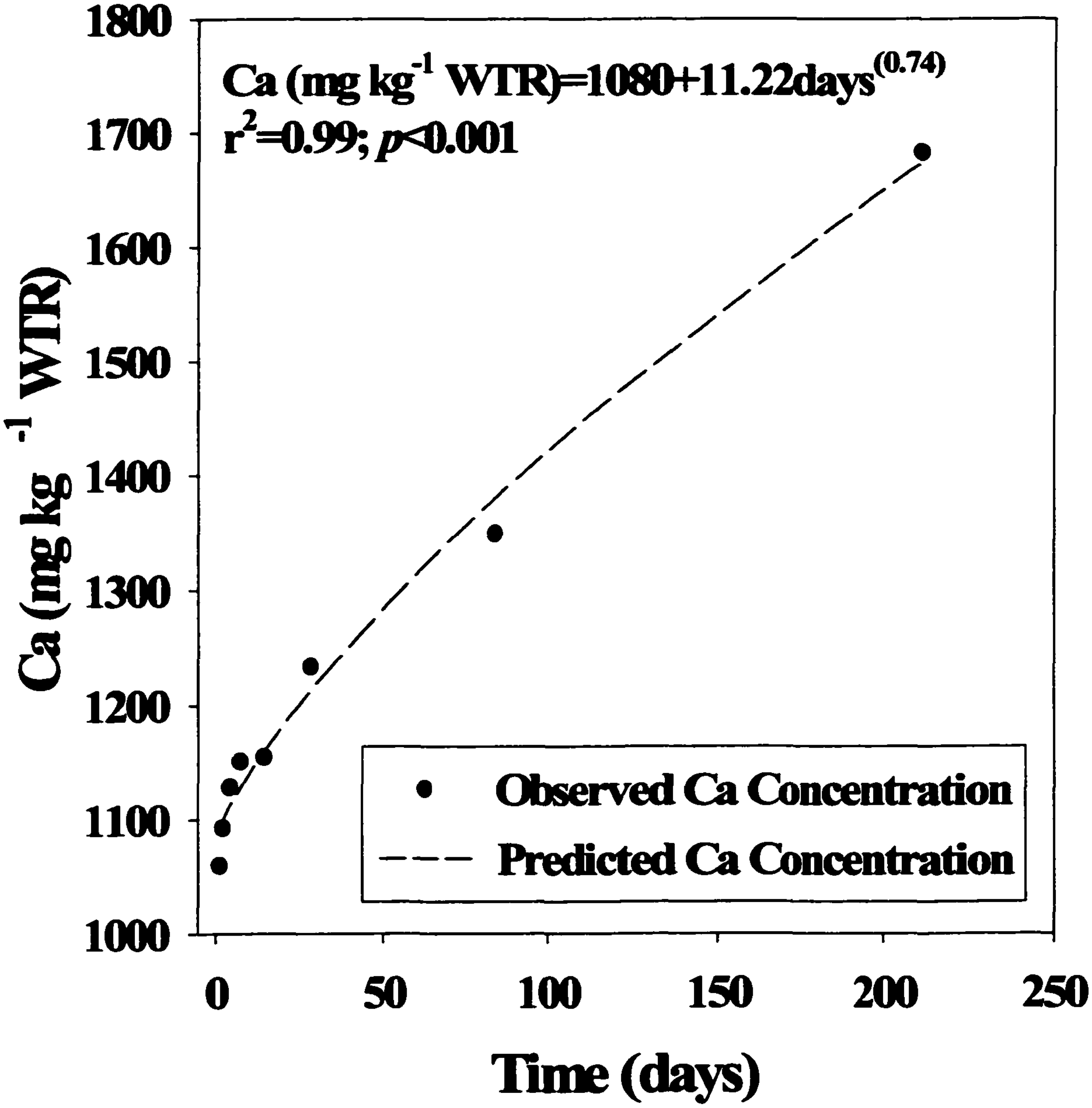


Figure 3.2. The influence of shaking time on Ca desorption from WTR.

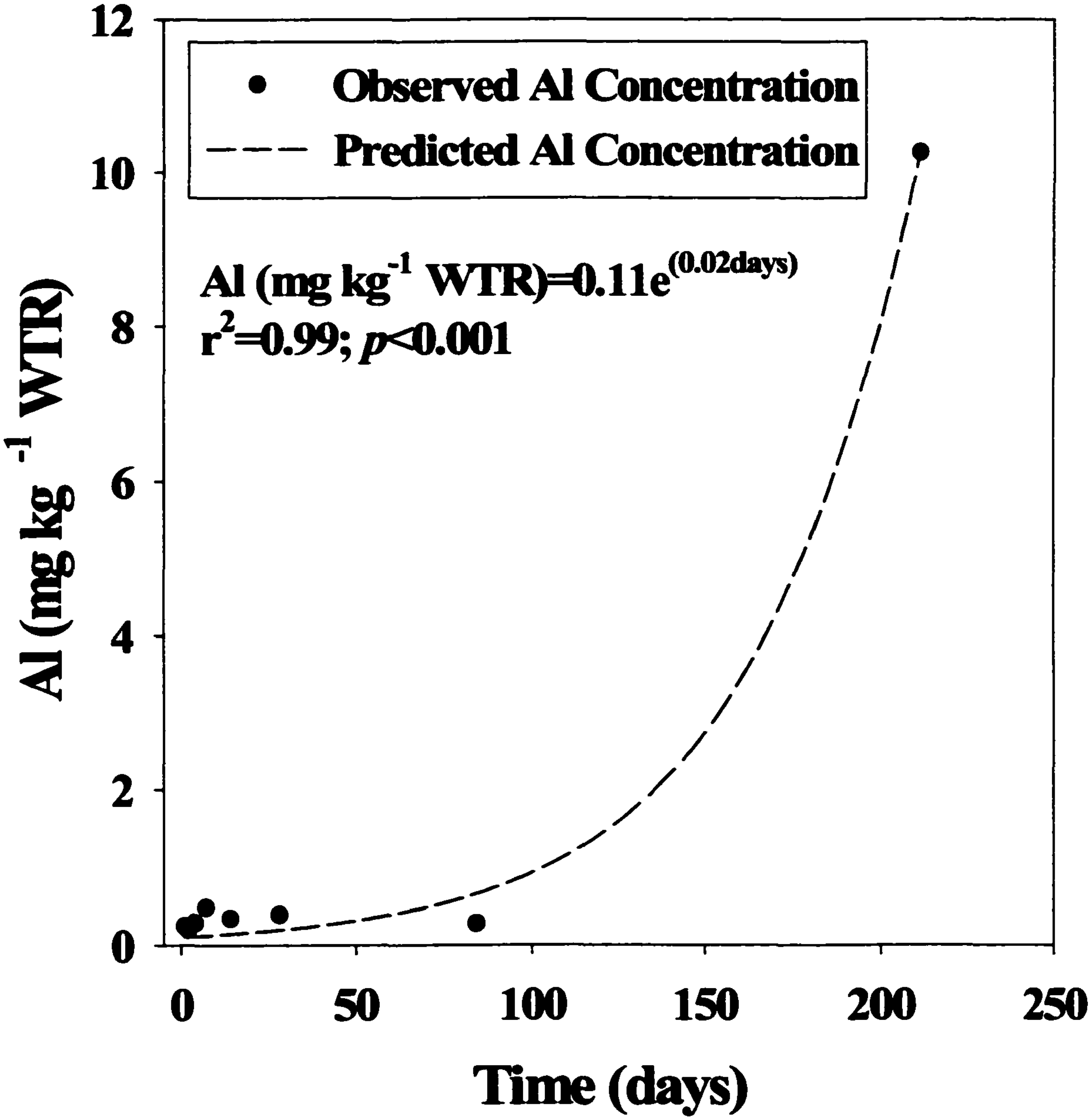


Figure 3.3. The influence of shaking time on Al desorption from WTR.

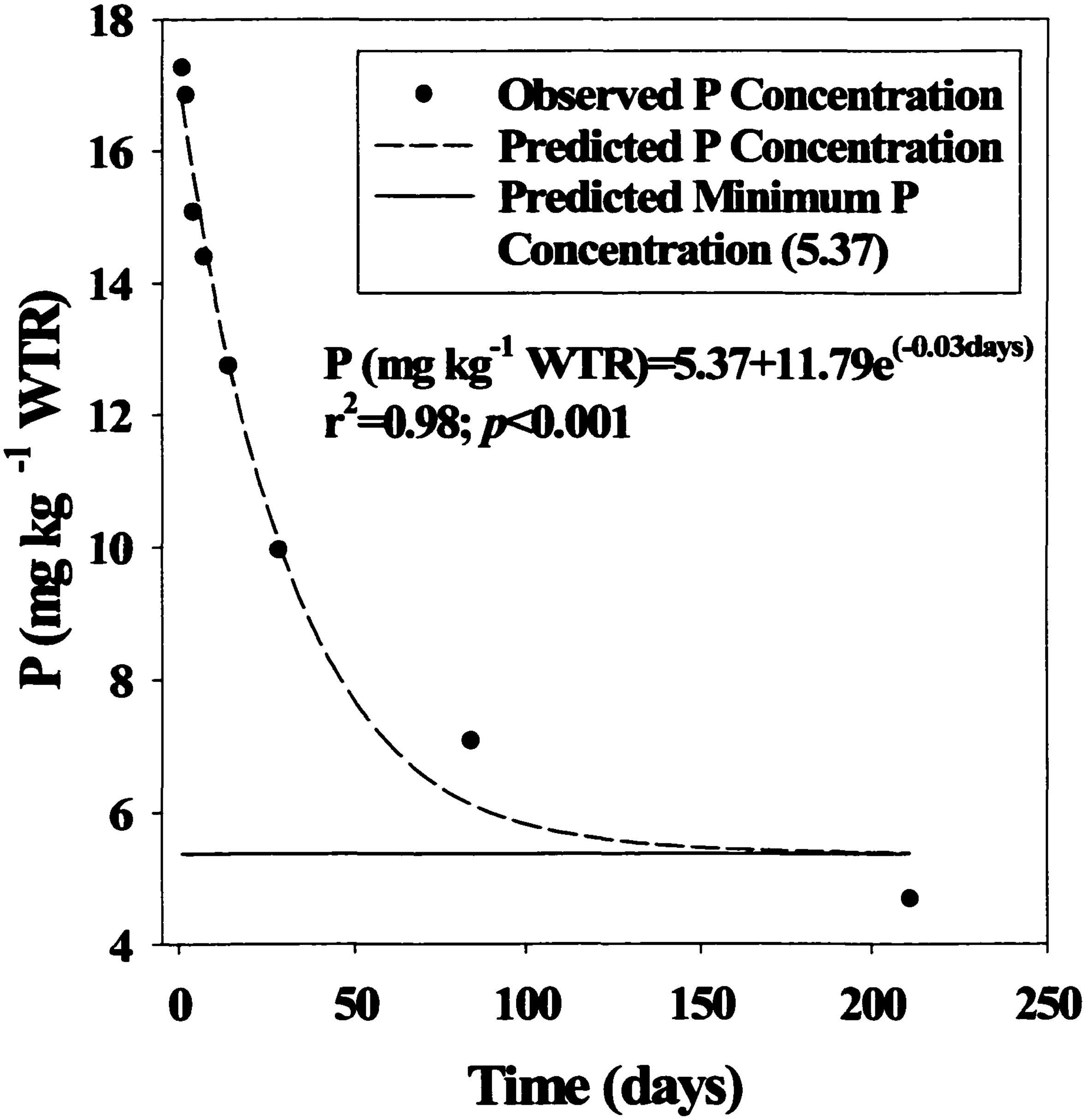


Figure 3.4. The influence of shaking time on P desorption from WTR.

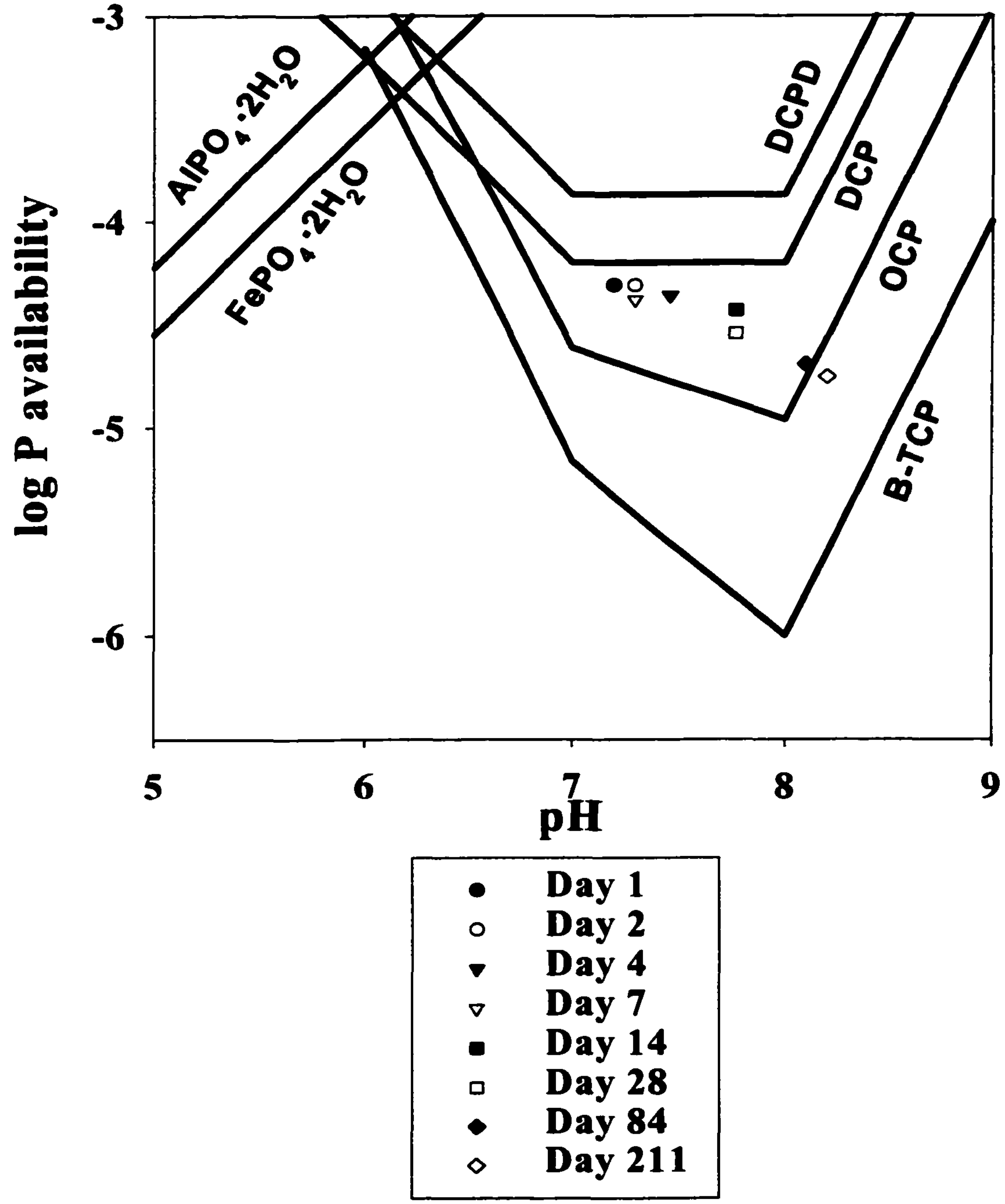


Figure 3.5. The influence of shaking time on P mineral solubility.

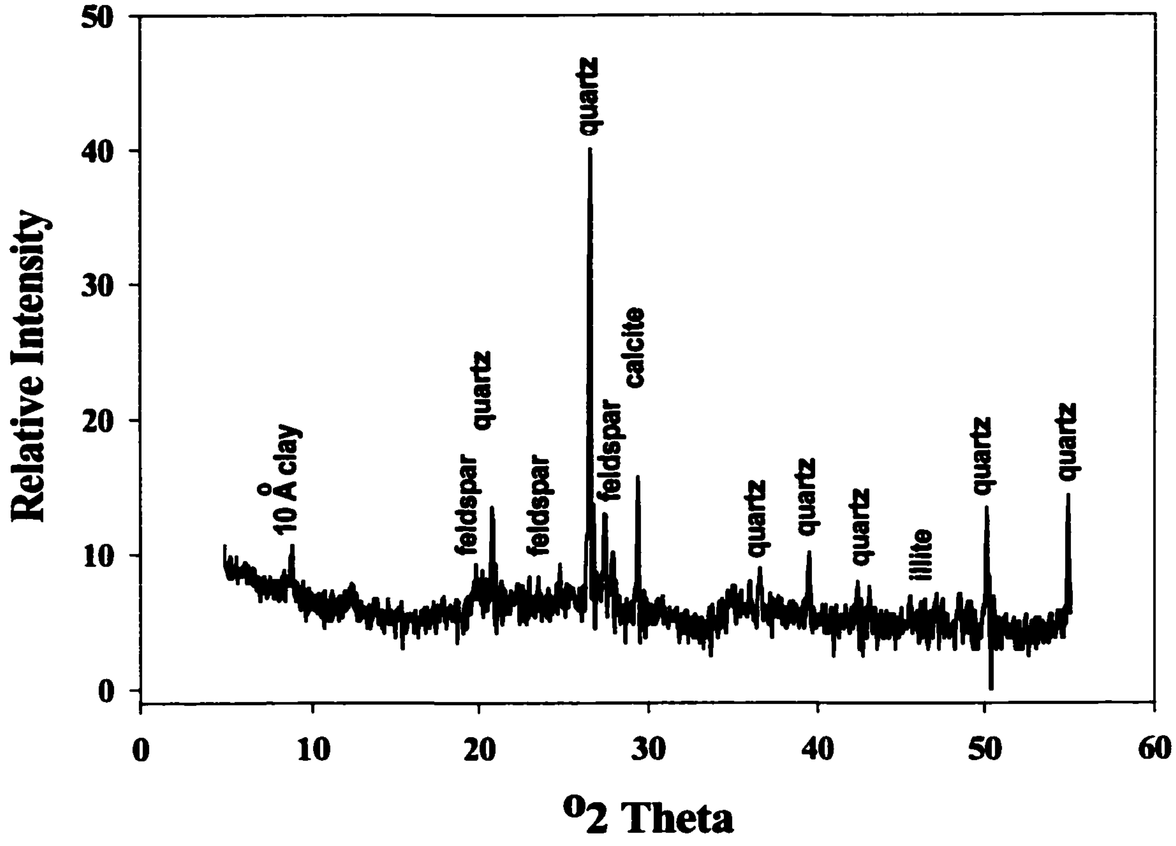


Figure 3.6. XRD analysis of sample Day 1, Replicate 1.

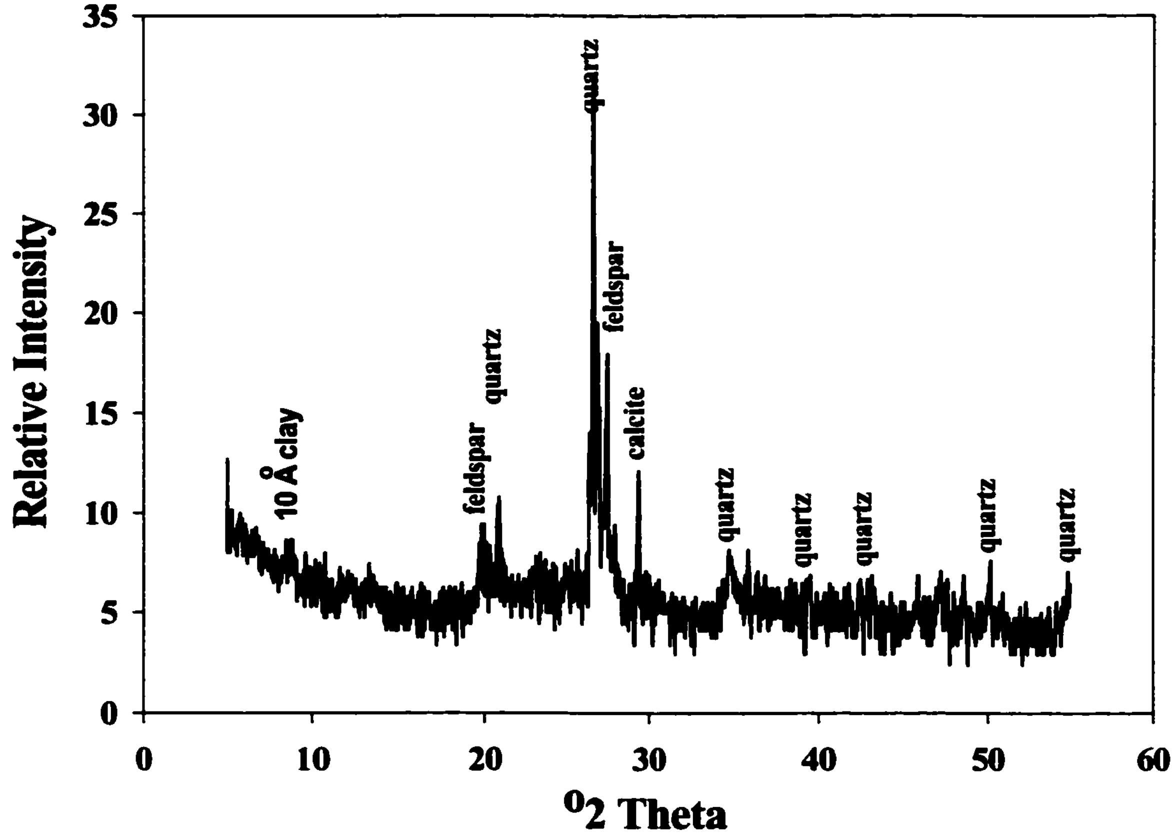


Figure 3.7. XRD analysis of sample Day 1, Replicate 2.

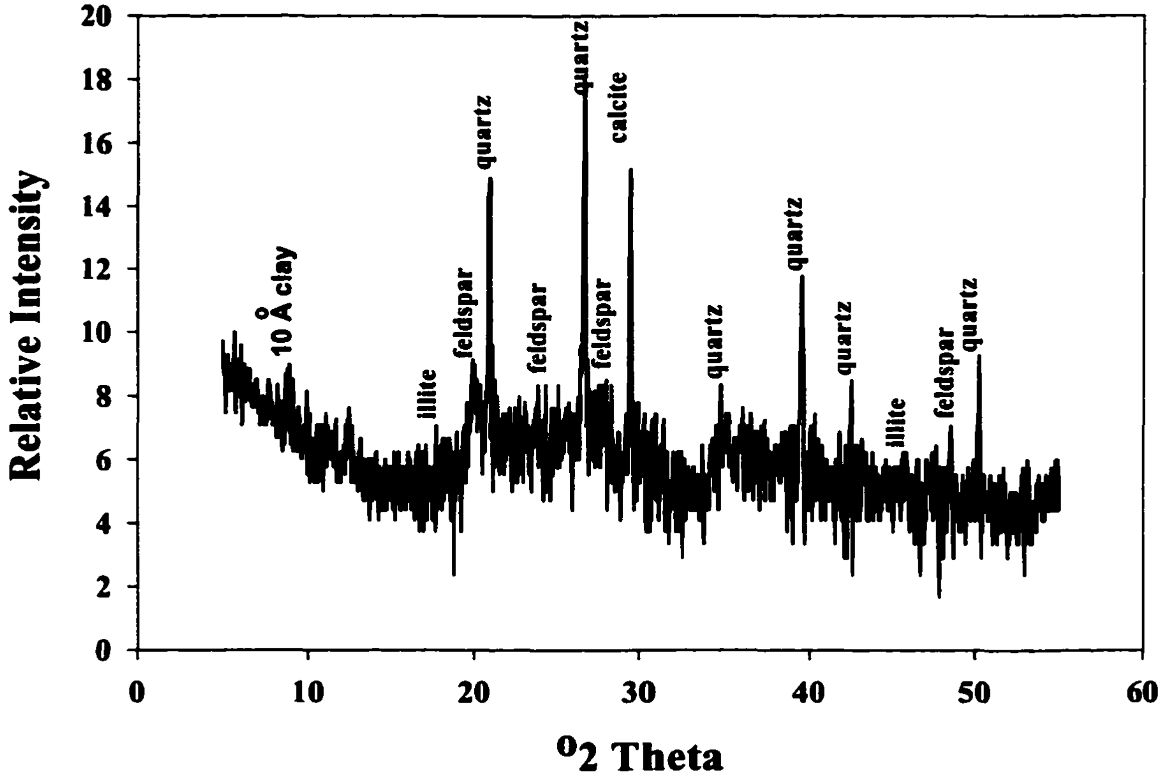


Figure 3.8. XRD analysis of sample Day 28, Replicate 1.

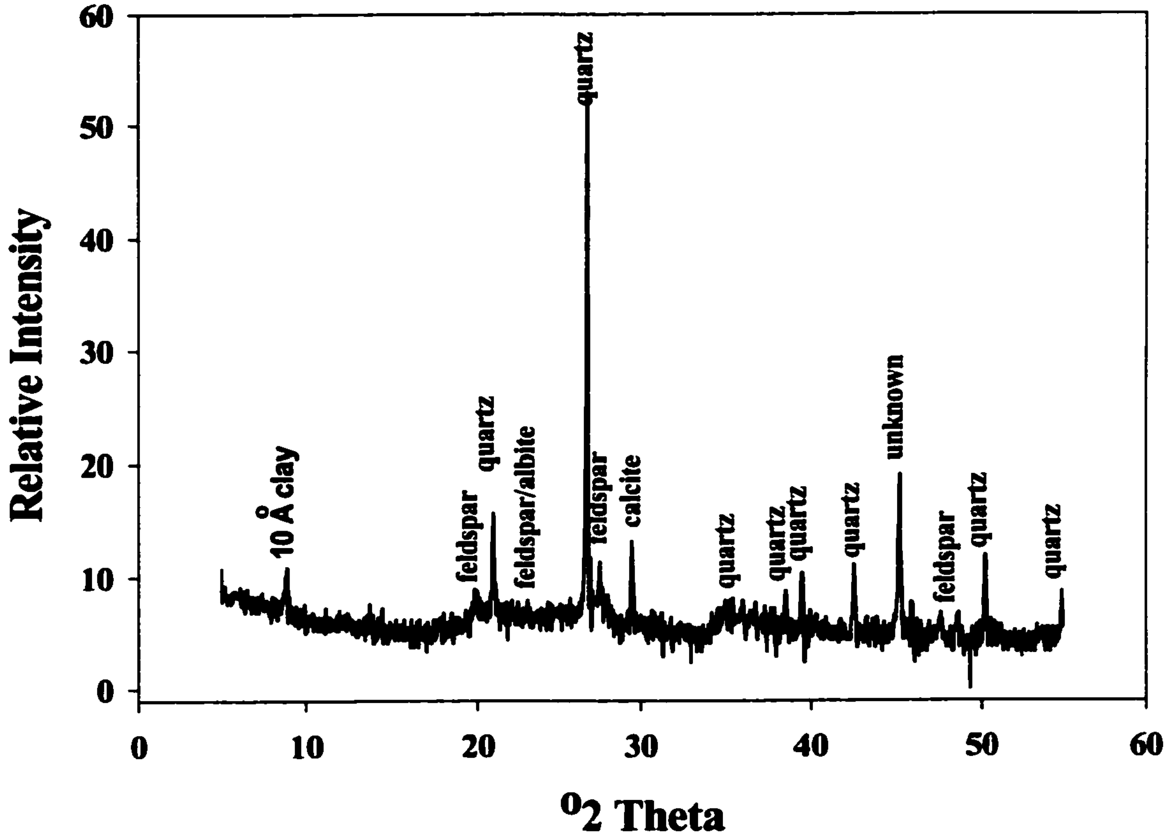


Figure 3.9. XRD analysis of sample Day 28, Replicate 2.

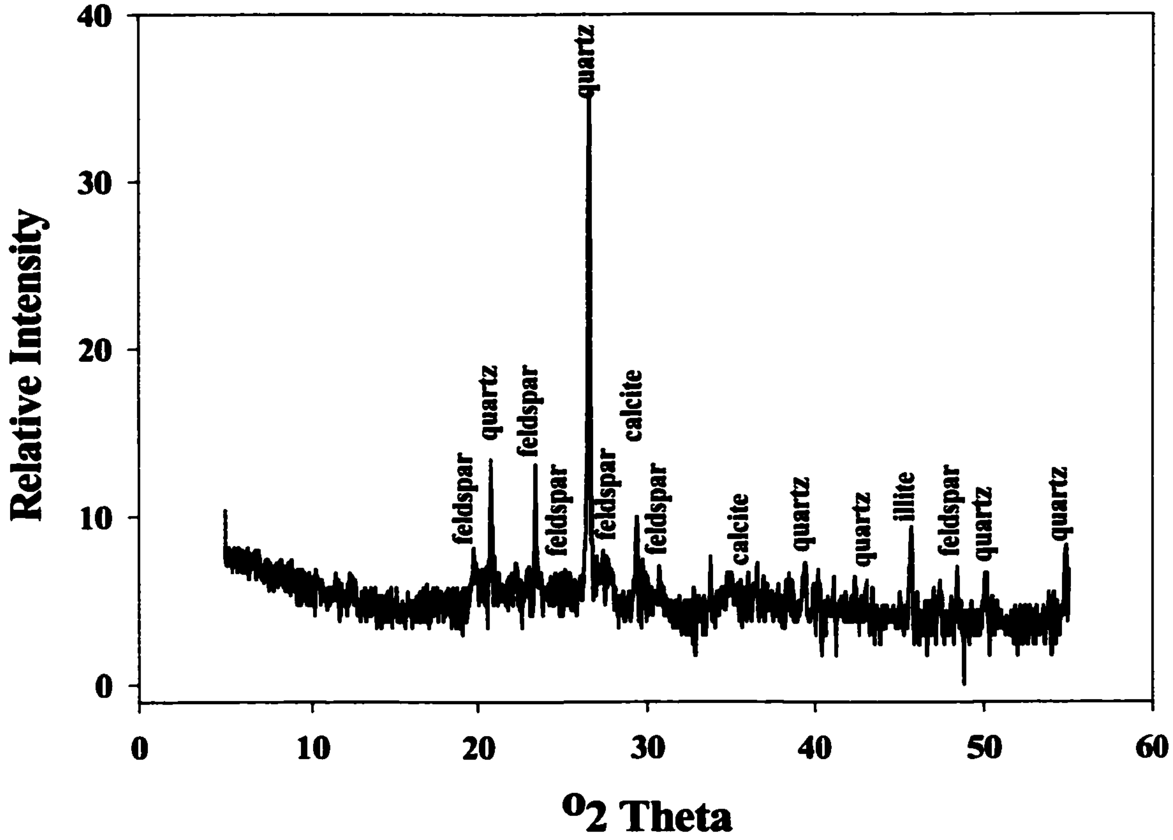


Figure 3.10. XRD analysis of sample Day 84, Replicate 1.

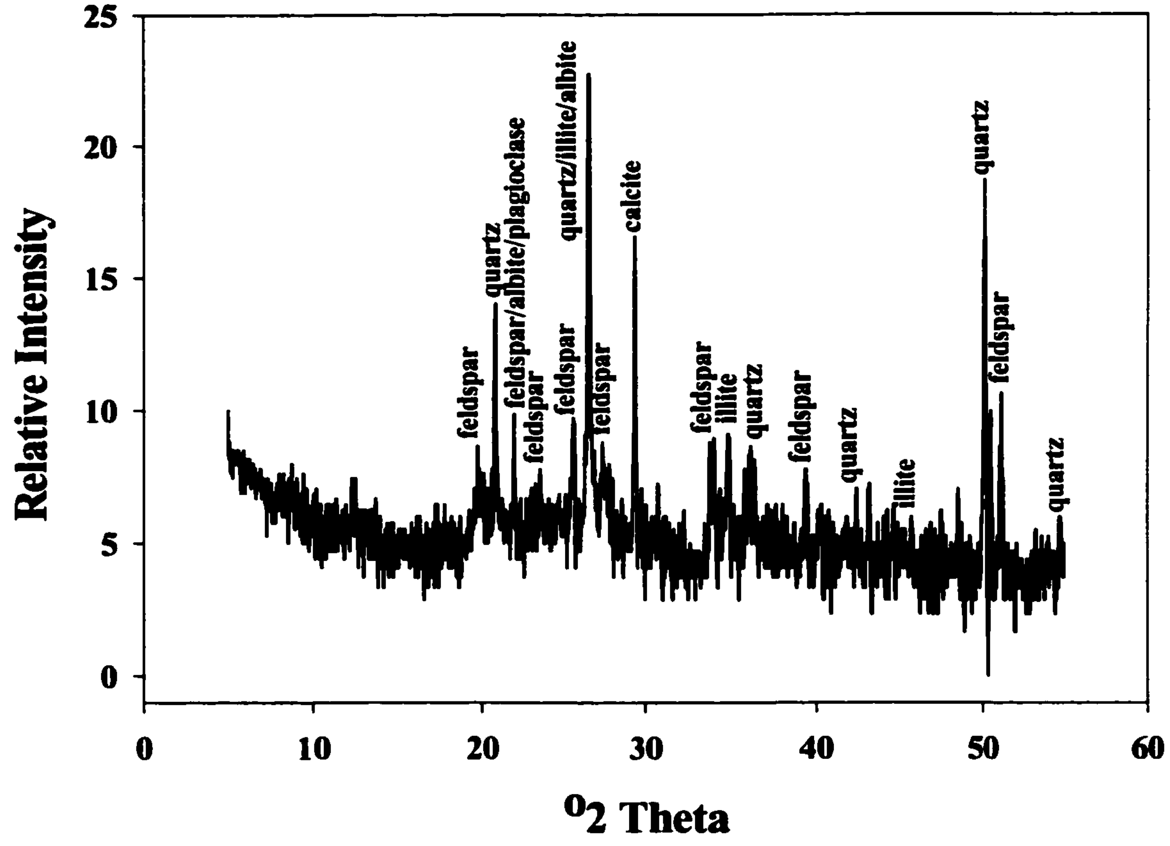


Figure 3.11. XRD analysis of sample Day 84, Replicate 2.

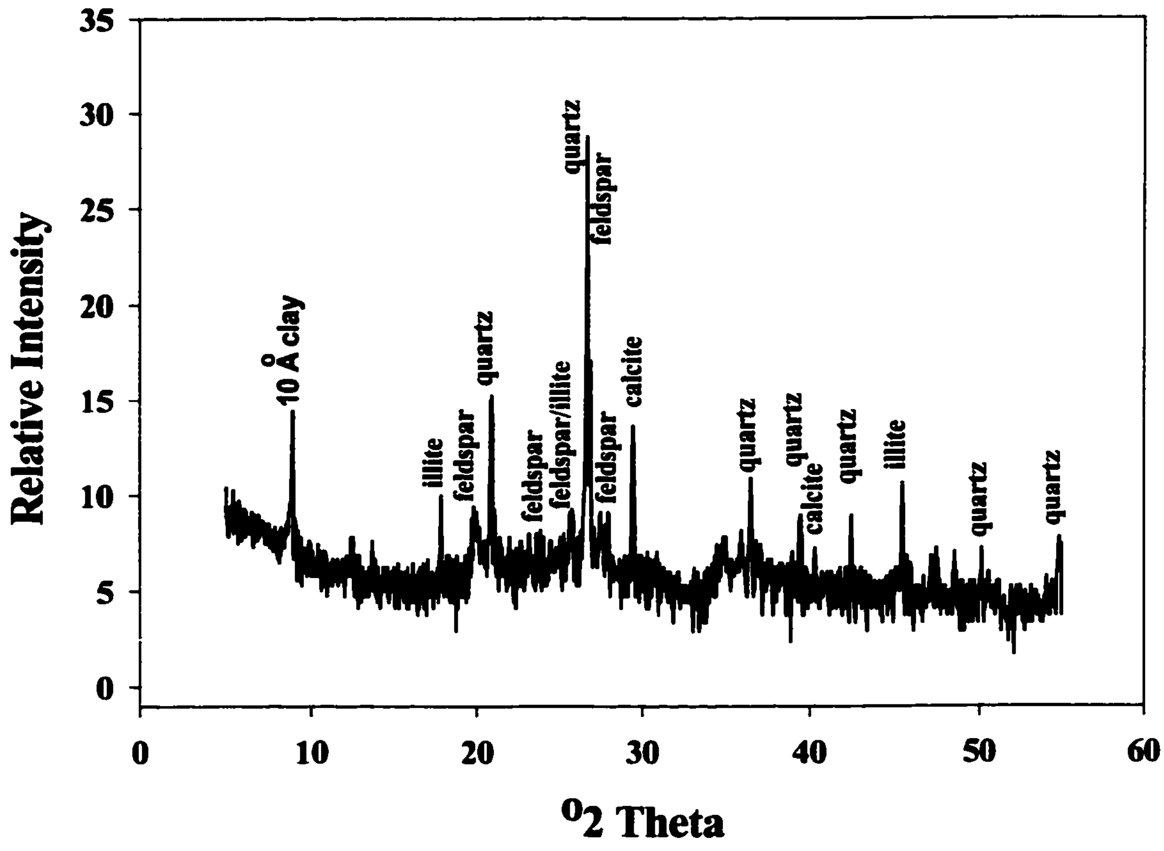


Figure 3.12. XRD analysis of sample Day 211, Replicate 1.

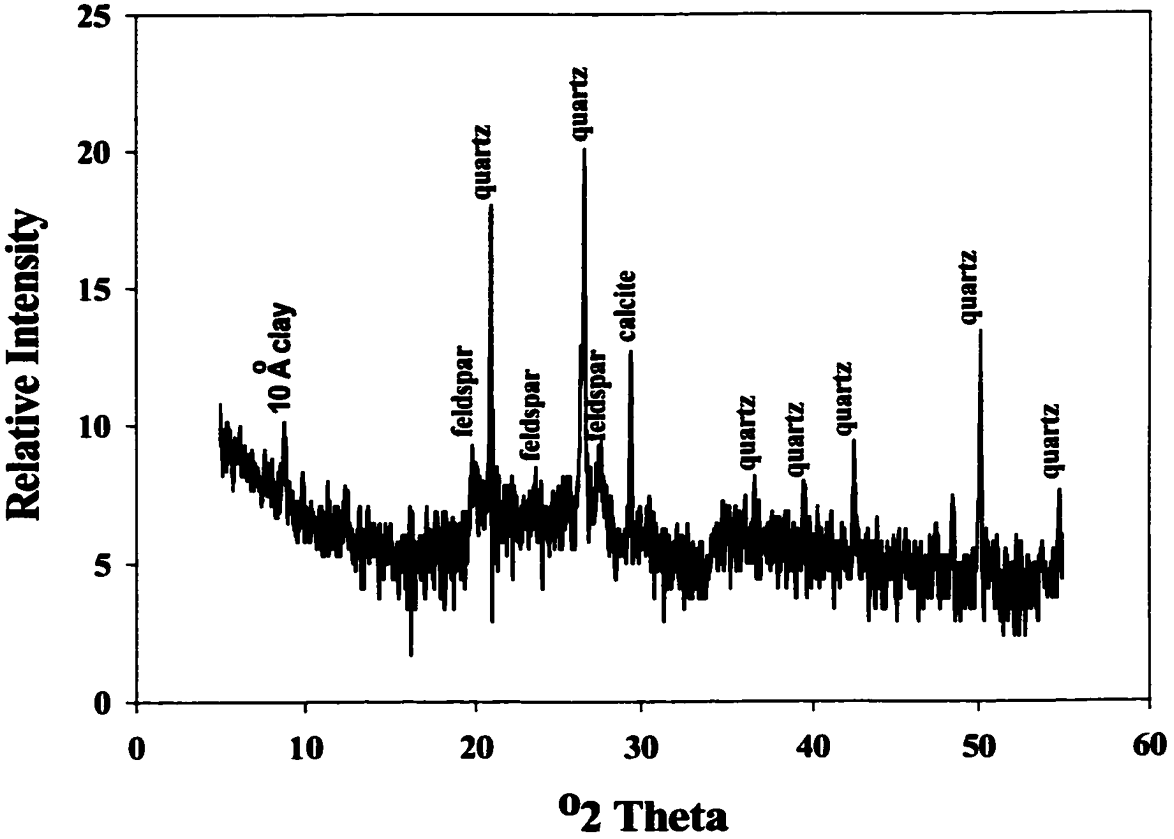
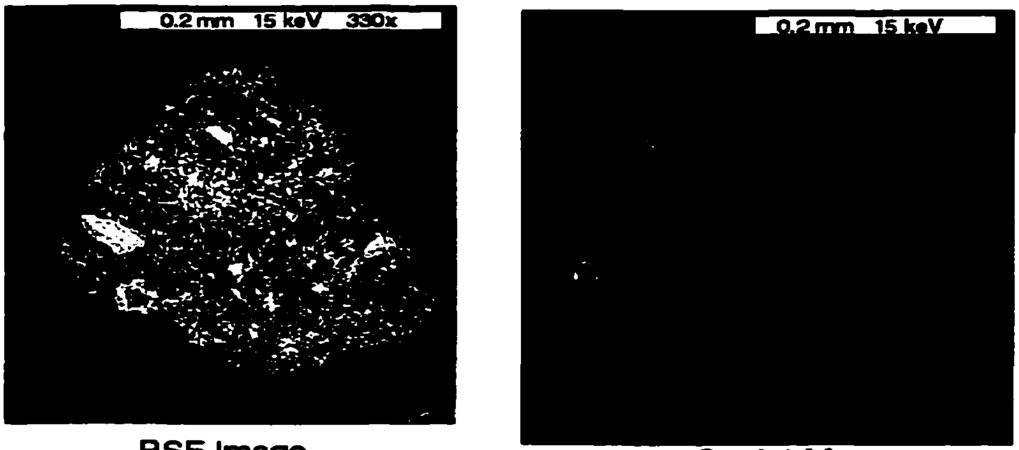
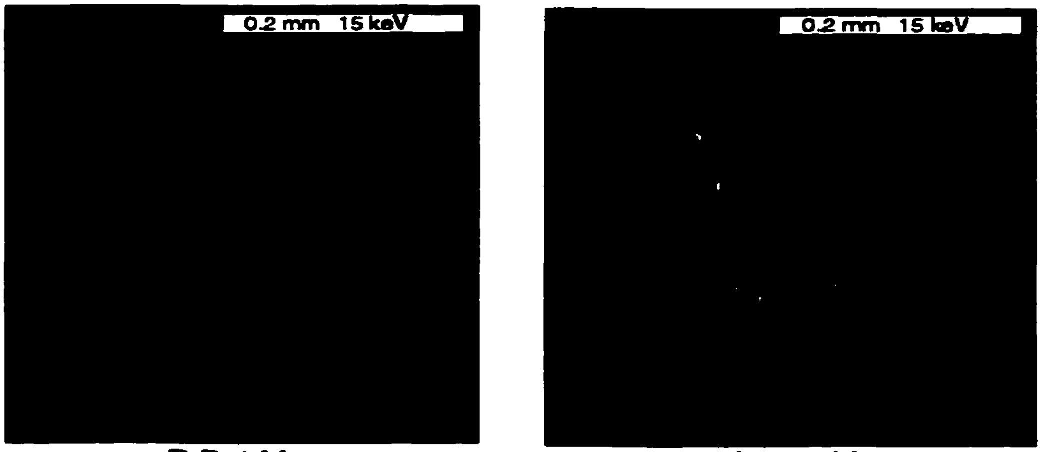


Figure 3.13. XRD analysis of sample Day 211, Replicate 2.



BSE Image

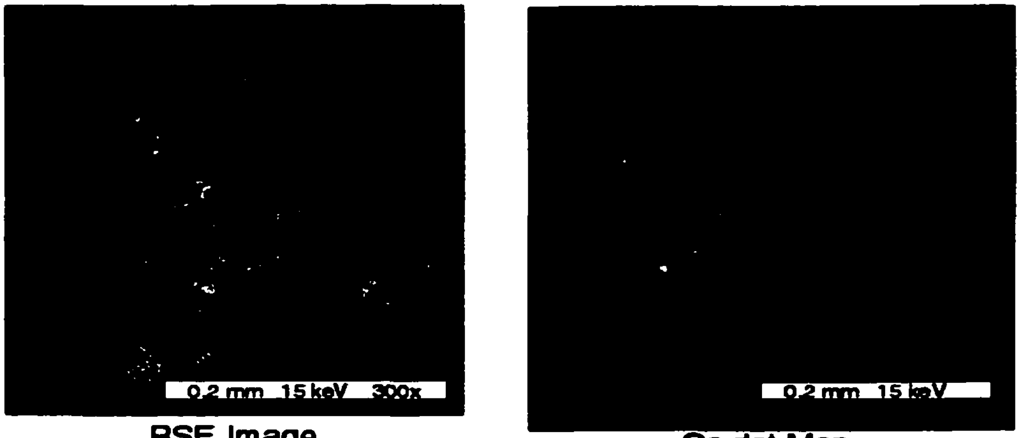
Ca dot Map



P Dot Map

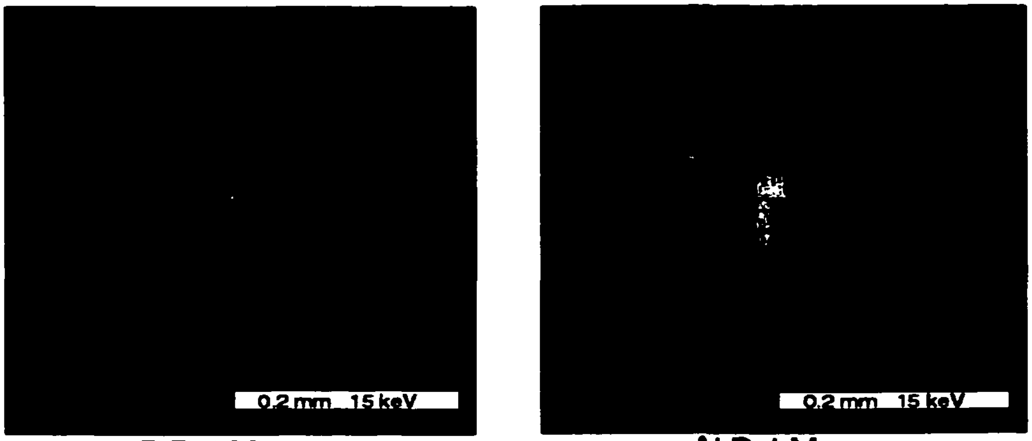
Al Dot Map

Figure 3.14. Backscattered electron image and dot maps of Ca, P, and Al; Day 1, Replicate 1.



BSE Image

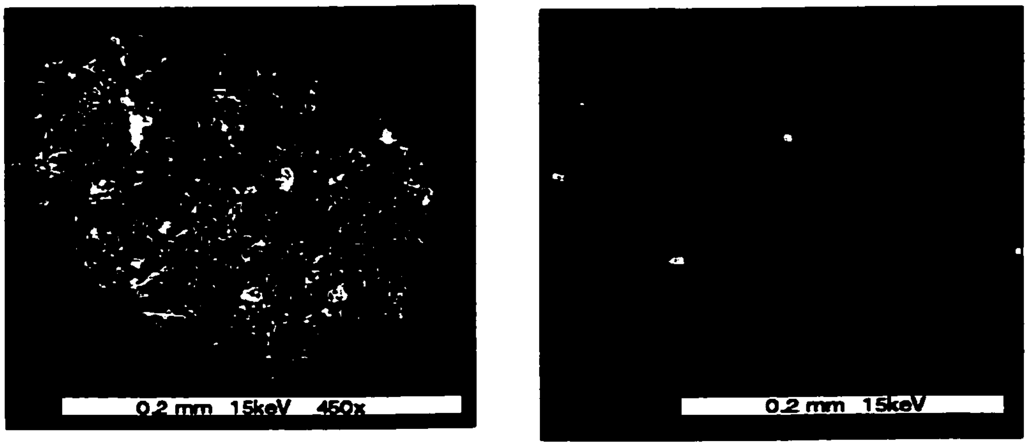
Ca dot Map



P Dot Map

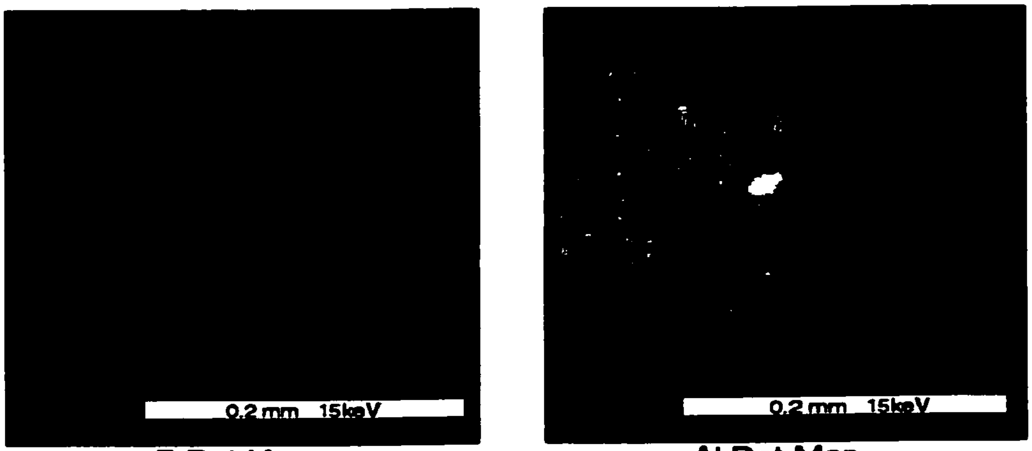
Al Dot Map

Figure 3.15. Backscattered electron image and dot maps of Ca, P, and Al; Day 1, Replicate 2.



BSE Image

Ca dot Map



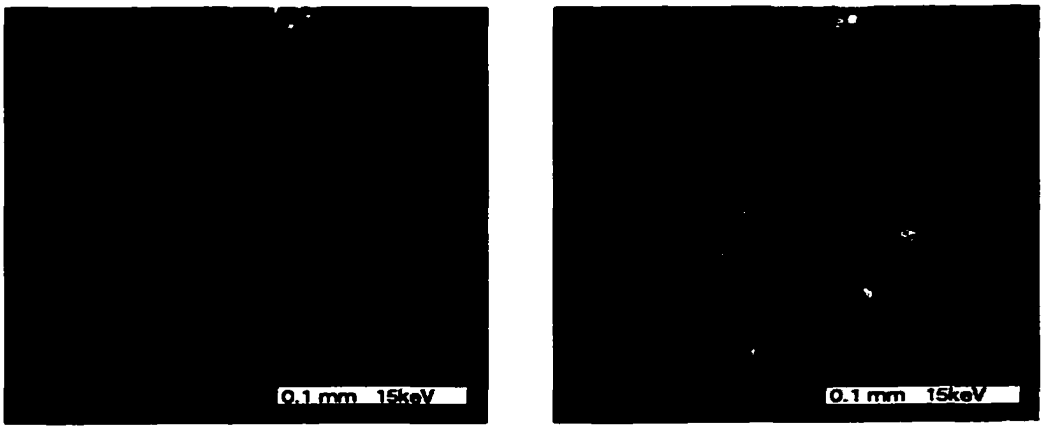
P Dot Map

Al Dot Map

Figure 3.16. Backscattered electron image and dot maps of Ca, P, and Al; Day 1, Replicate 3.

BSE Image

Ca dot Map



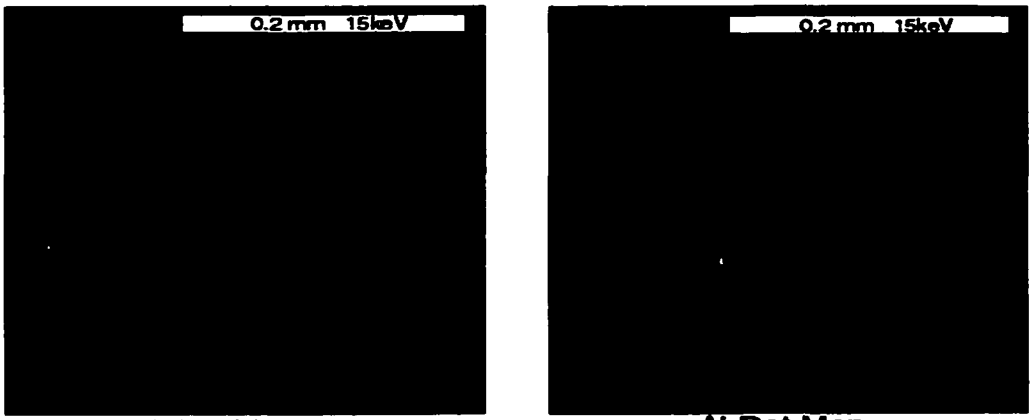
P Dot Map

Al Dot Map

Figure 3.17. Backscattered electron image and dot maps of Ca, P, and Al; Day 28, Replicate 1.

BSE Image

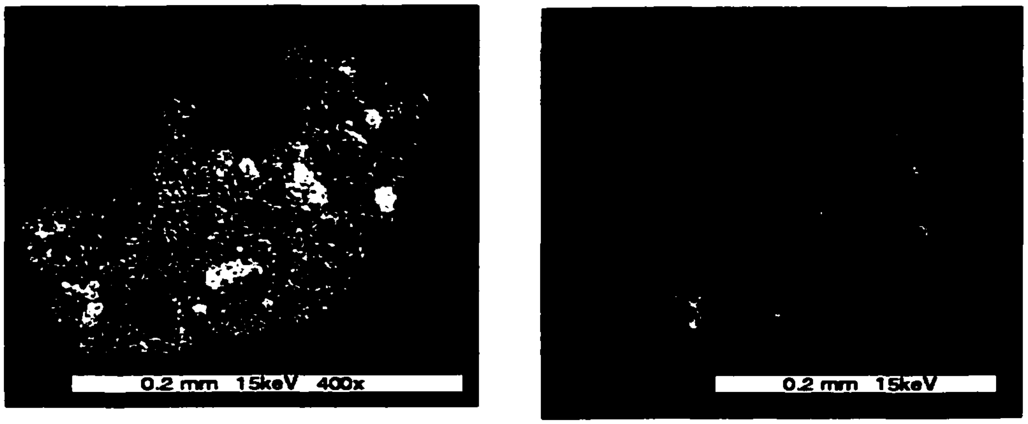
Ca dot Map



P Dot Map

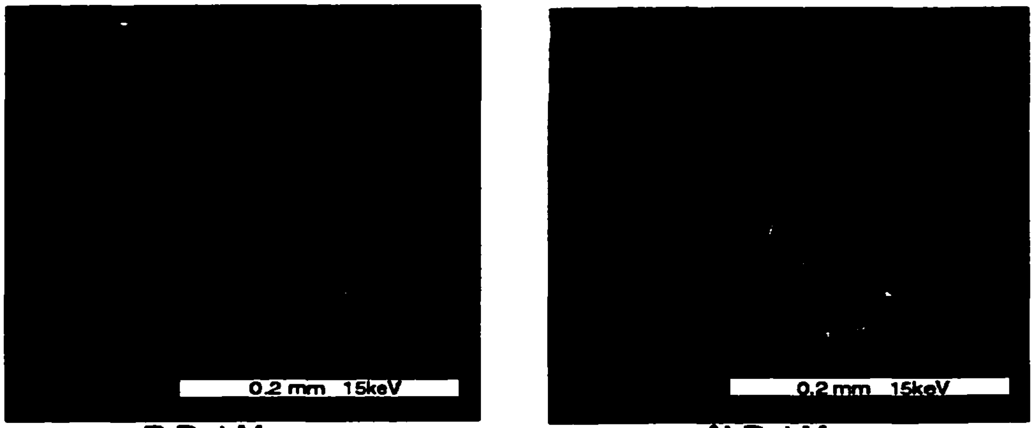
Al Dot Map

Figure 3.18. Backscattered electron image and dot maps of Ca, P, and Al; Day 28, Replicate 2.



BSE Image

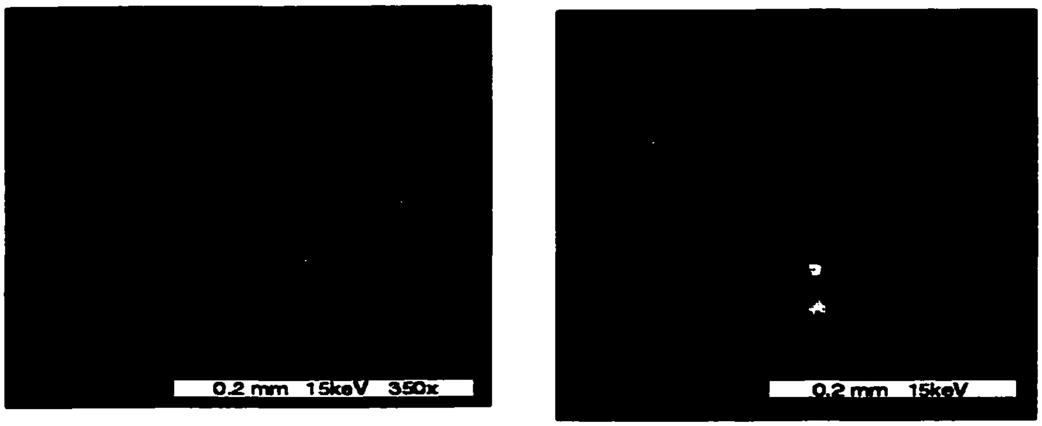
Ca dot Map



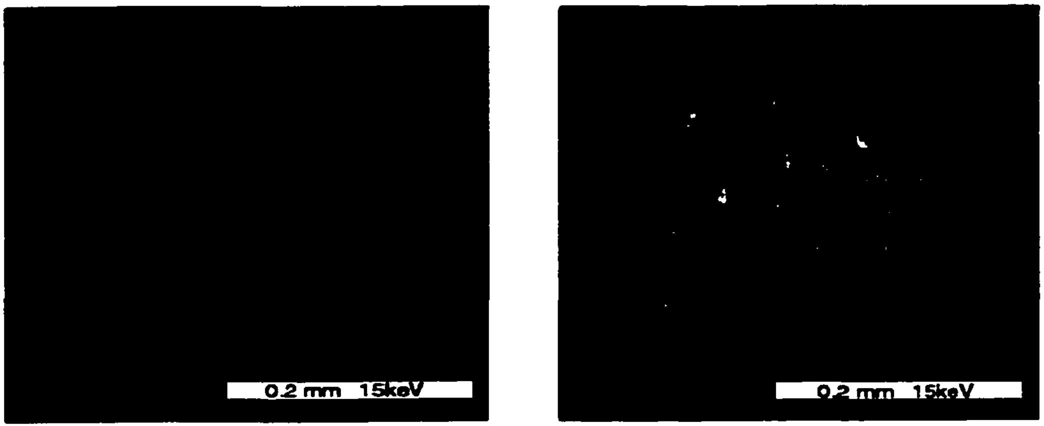
P Dot Map

Al Dot Map

Figure 3.19. Backscattered electron image and dot maps of Ca, P, and Al; Day 28, Replicate 3.



BSE Image Ca dot Map

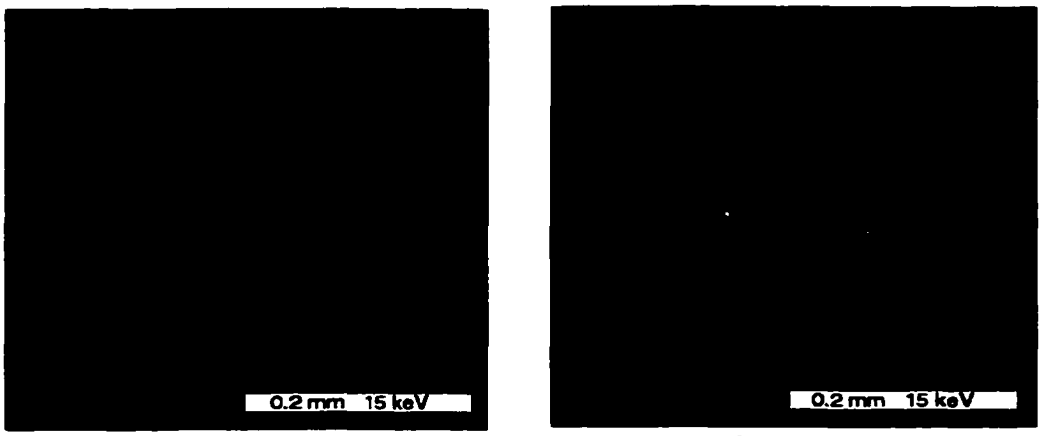


P Dot Map Al Dot Map

Figure 3.20. Backscattered electron image and dot maps of Ca, P, and Al; Day 84, Replicate 1.

BSE Image

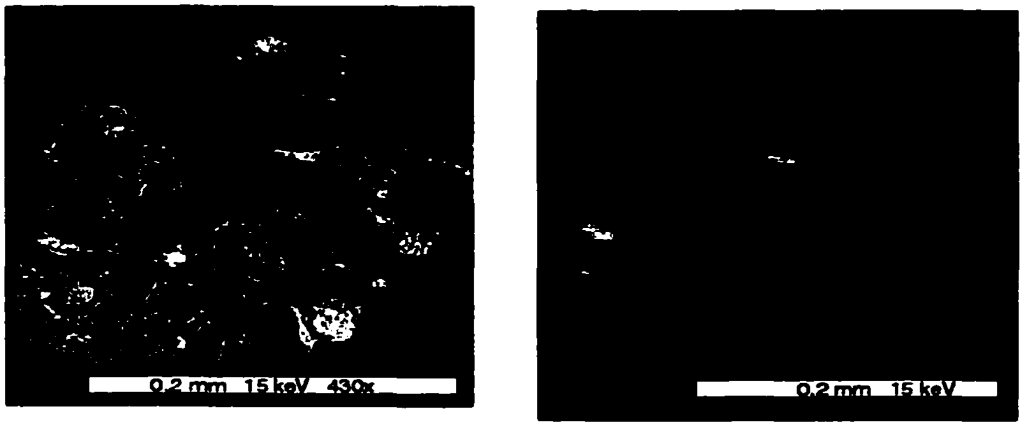
Ca dot Map



P Dot Map

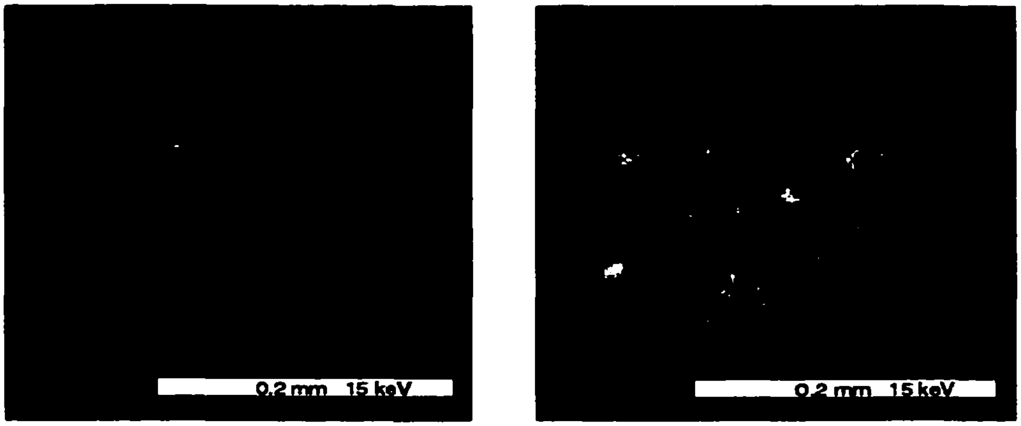
Al Dot Map

Figure 3.21. **Backscattered electron image and dot maps of Ca, P, and Al; Day 84, Replicate 2.**



BSE Image

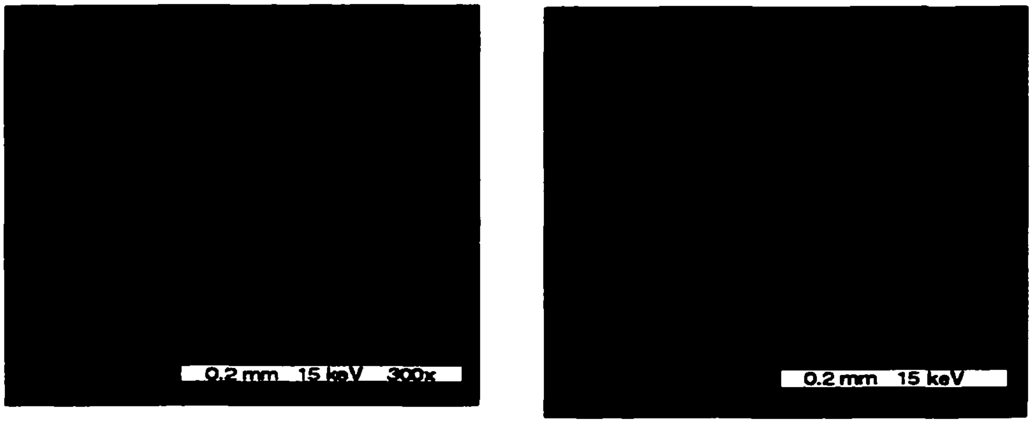
Ca dot Map



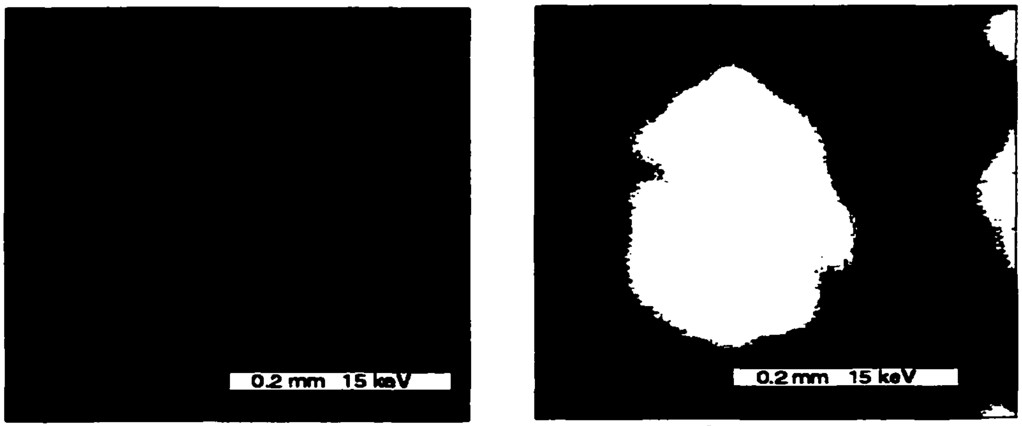
P Dot Map

Al Dot Map

Figure 3.22. Backscattered electron image and dot maps of Ca, P, and Al; Day 84, Replicate 3.

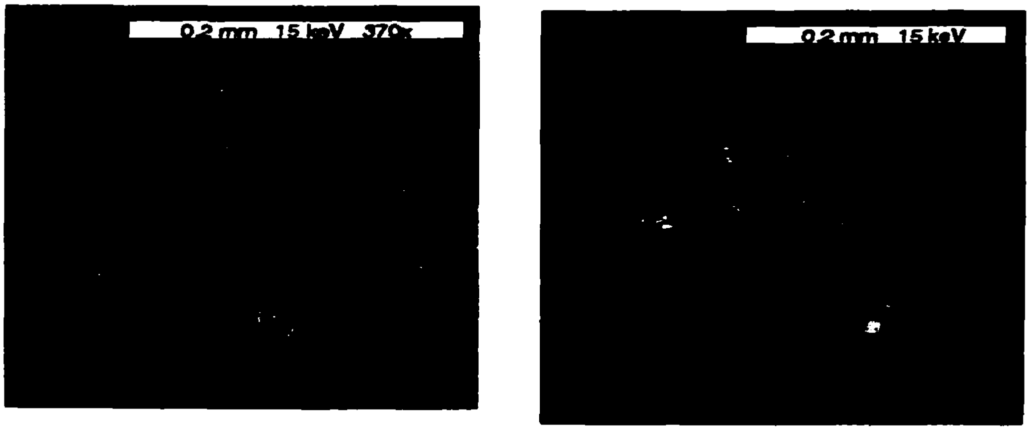


BSE Image **Ca dot Map**



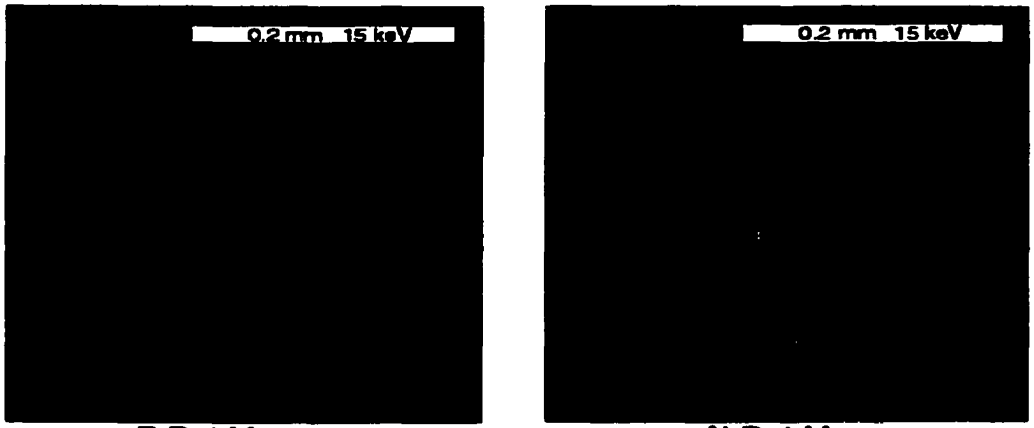
P Dot Map **Al Dot Map**

Figure 3.23. **Backscattered electron image and dot maps of Ca, P, and Al; Day 211, Replicate 1.**



BSE Image

Ca dot Map

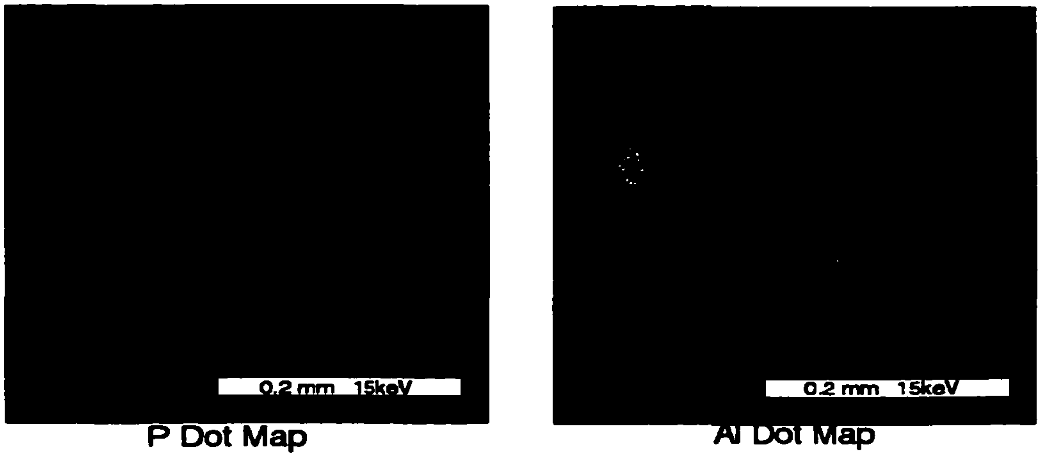


P Dot Map

Al Dot Map

Figure 3.24. Backscattered electron image and dot maps of Ca, P, and Al; Day 211, Replicate 2.

BSE Image Ca dot Map



P Dot Map Al Dot Map

Figure 3.25. Backscattered electron image and dot maps of Ca, P, and Al; Day 211, Replicate 3.

SUMMARY

The factorial co-application of WTR and biosolids to blue grama and western wheatgrass study showed that: (1) increasing WTR rate, averaged over biosolids rates, decreased blue grama shoot P concentration and increased Al concentration, and reduced western wheatgrass shoot P and Mo concentrations; (2) increasing biosolids application rate, averaged over WTR rates, affected most constituents studied for both grasses; and (3) increasing the WTR rate alone caused an increase in blue grama shoot Al concentration and uptake, and a decrease in western wheatgrass plant Mo concentration and uptake. I did not observe any P deficiency or Al toxicity symptoms with blue grama or western wheatgrass.

The randomized complete block co-application of WTR and biosolids to blue grama and western wheatgrass study showed that: (1) increasing WTR rate, co-applied with a constant biosolids rate, increased blue grama DM yield, and decreased P and Al shoot concentrations; (2) decreased western wheatgrass shoot Al concentration; and (3) western wheatgrass root P and Al concentrations were not affected by increasing co-applications. Again, I did not observe any P deficiency or Al toxicity symptoms with blue grama or western wheatgrass.

The WTR/biosolids P adsorption batch study showed that: co-mixing of both municipalities' WTR and biosolids at ratios of 8:1 will adsorb most soluble biosolids-borne P. Ratios mixed beyond 8:1 may have the ability to adsorb additional soil- borne P.

The WTR P adsorption mechanism study showed that: (1) at day 211, the pH (8.15), in conjunction with the Ca ion activity, infer the presence of $CaCO_3$ controlling Ca. This was verified by XRD analysis; (2) the desorbed P concentration decreased, indicating greater chemiadsorption (outer sphere or diffuse ion swarm to inner sphere complexation); (3) the data, plotted on the P mineral solubility diagram suggested solid OCP had formed and may be trending towards *B*-TCP. XRD and EMPA-WDS did not verify the presence of any Ca-P mineral species; and (4) the EMPA-WDS results show P most closely associated with Al from WTR.

The U.S. produces an estimated 0.35 million dry Mg of WTR per year. Environmental concerns over WTR discharge to receiving waters have resulted in this practice being discouraged. Most WTR currently generated is discharged to sanitary sewers, lagooned, or disposed of in landfills. Although no federal guidelines exist for WTR, US Environmental Protection Agency regions or individual states can prohibit direct discharge. These issues suggest land application of WTR may be a major method of disposal in the future.

My research could aid in planning for WTR land application, either alone or in conjunction with biosolids. I recommend that soil testing, WTR and biosolids analyses, and setting appropriate crop yield goals must be used with any program to ensure environmental protection.