POTENTIAL ANTHROPOSOL DEVELOPMENT USING PHOSPHOGYPSUM AS A SUBSTRATE WITH SOIL AND ORGANIC AMENDMENTS

by

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ABSTRACT

Phopshopgypsum is a byproduct of phosphate fertilizer production resulting from the production of phosphoric acid from phosphate rock (Rutherford et al. 1994a). Most reclamation plans for phosphogypsum stacks include a cover system that is installed over the stack; thus research in the area of phosphogypsum has been mainly related to capping depths.

Use of phosphogypsum in building anthroposols for reclamation and/or agricultural uses would require amendments to ameliorate its undesirable properties. Experiments were conducted on the potential for use of phosphogypsum as a substrate or soil building material by assessing plant performance and health, hydraulic conductivity, leachate content and select microbiological properties.

Phosphogypsum amended with topsoil, specifically clay topsoil in approximate ratios of 40 to 50 % by volume, resulted in increased plant height, health and biomass. Addition of greater than 60 % sandy soil by volume resulted in a more optimal hydraulic conductivity and reduced the concentrations of components of leachate to meet Canadian Council of Ministers of the Environment guidelines for aquatic life and agricultural use. A microbiological community was present in phosphogypsum, mainly composed of gram positive bacteria, fungi, denitrifiers and sulphate reducers. Addition of an anionic solution to phosphogypsum mixes with soil increased these numbers and addition of a sandy soil to phosphogypsum increased the number of gram negative bacteria. Thus amending phosphogypsum would be potentially useful as a soil building material or substrate.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. BACKGROUND

1. PHOSPHOGYPSUM PRODUCTION AND DISPOSAL

1.1. Phosphogypsum Production

Phosphogypsum is a byproduct of phosphate fertilizer production resulting from the production of phosphoric acid from phosphate rock (Rutherford et al. 1994a). Phosphogypsum is composed of mainly gypsum and impurities, including residual acids, soluble fluoride, trace elements and naturally occurring radionuclides (Rutherford et al. 1994b). The most common method of producing phosphoric acid is a wet process, in which phosphate rock (commonly fluorapatite) is treated with sulphuric acid and water, which results in gypsum, phosphoric acid and hydrogen fluoride (Rutherford et al. 1994a). One general equation for the reaction is $Ca_{10}(P0_4)_6F_2$ + $10H_2SO_4$ + $20H_2O$ → $10CaS0_4{\cdot}2H_2O$ + $6H_3PO_4$ + 2HF. The resulting gypsum is then filtered from the liquid, mixed with water and stored in a holding area. The processed water is recycled in production. The most common phosphoric acid production process is dihydrate which results in 28 to 30 % phosphoric acid. Other processes include the hemihydrate process which results in phosphoric acid concentrations from 35 to 52 % (Rutherford et al. 1994a).

The temperature in the processing chamber and sulphuric acid concentrations used in the production process affect the type of gypsum that is produced (Rutherford et al. 1994a, Wissa 2002). For example, in Europe, Africa and Japan, hemihydrate gypsum ($CaSO_4 \cdot ½ H_2O$) is produced with 32 to 52 % phosphoric acid. Phosphoric acid production impacts how much reagent is needed and therefore, how much of each product will be created. The ratio of phosphogypsum to phosphoric acid is usually 5:1 (Rutherford et al. 1994a, Thorne 1990), with approximately 5 tonnes of phosphogypsum produced for each tonne of phosphoric acid.

Phosphate ore source rock is a determinant of the type of phosphoric acid and phosphogypsum produced (Rutherford 1994b). Sedimentary phosphate ore, or phosphorites, characterize approximately 85 % of all phosphate rock, while the remaining 15 % is characterized by igneous or metamorphic origin. The sedimentary phosphate rock basins were formed from the material of living organisms approximately 70 million years ago (Becker 1989). Phosphorite is made of approximately 10 % quartz, 5 % muscovite, 2 % organic matter, 1 % dolomite calcitite and 1 % iron (Gulbrandsen 1967). The main mineral in the phosphate rock is apatite (Lehr and McClellan 1972); the hydroxylapatite, fluorapatite and chlorapatite have high concentrations of the hydroxyl, fluoride or chloride ions, respectively. Main components of phosphate rock include calcium oxide

(CaO), phosphorus pentoxide (P_2O_5), silicon dioxide (SiO_2), fluoride (F), carbon dioxide (CO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), magnesium oxide (MgO) and sodium oxide (Na_2O).

1.2. Phosphogypsum Disposal

At least 80 countries in the world have phosphogypsum stacks (Florida Institute for Phosphate Research 2006). Production of phosphoric acid globally reached 42.08 million tonnes in 2011, which equates to approximately 210.4 million tonnes of phosphogypsum (Heckenmüller et al. 2014). Alberta produces the only phosphogypsum in Canada, at present, with approximately 40 million tonnes of phosphogypsum stockpiled at Redwater, Alberta.

There are four widely used methods of phosphogypsum disposal; they are wet stacking, dry stacking, backfilling in mine pits and discharge into water bodies. Approximately 14 % of the phosphogypsum produced worldwide is reprocessed, 58 % is stockpiled and 28 % is dumped into existing water bodies (Rutherford et al. 1994b). Phosphogypsum can be stockpiled while it is wet or after it is dry; the stockpiling method chosen typically relates to the amount of water available (Wissa 2002).

In wet stacking, the phosphogypsum is mixed with salt or with fresh water, resulting in a slurry which is then pumped into settling ponds or holding areas on site. The fresh water can be reused in the phosphoric acid process if the solution settles; salt water can usually be discharged into a water body. Water that is reused in the phosphoric acid process can eventually reach a pH of 1.3 to 2.0. This method of stacking does not require daily construction or as much equipment and personnel as dry stacking, and is extremely common in plants that produce dihydrate gypsum.

Phosphogypsum is dry stacked where water is not readily available. In the dry stacking process, filtered phosphogypsum is transported via conveyor belts, trucks, railroad cars or barges to a disposal area by the fertilizer plant without the addition of any water. When it reaches the disposal area, machines such as dozers and conveyors spread the gypsum. These stacks can be as large as 1 million m^2 and 10 m in height (Rutherford et al. 1994a). Stacks on the coastal areas mix phosphogypsum with salt water and discharge to water bodies.

Phosphogypsum has been used in the backfilling of mine pits; however, this strategy is uncommon. In North Carolina, a phosphate ore mine used phosphogypsum mixed with phosphate clay tailings as mine fill (Wissa 2002). This method is not typically used because phosphogypsum is unstable.

2. PHOSPHOGYPSUM PROPERTIES

2.1. Chemical Properties

Phosphogypsum is typically composed of calcium sulphate dihydrate, small amounts of silica, and source phosphate rock, radium, uranium and trace elements (Wissa 2002). To understand the enrichments of trace elements in phosphorites, comparison to a common marine rock such as shale can be used (Altschuler 1980). In this comparison, phosphorites are enriched with cadmium, uranium, silver, yttrium, selenium, ytterbium, molybdenum, lanthanum, strontium, lead, zinc and all rare earth metals except cerium. Elements that are depleted in phosphorite include lithium, titanium, mercury, barium, gallium, cobalt, tin and zirconium. One theory for enrichment of cadmium, uranium, strontium, lead, zinc and yttrium in phosphorites is crystallographic spacings which substitute calcium in apatite (Gulbradsen 1966). Toxic metals present in phosphogypsum include arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, fluoride and aluminum. The concentrations of these elements depend on the source rock. The pH of the stacks can range from 2.1 to 5.5 (Rutherford et al. 1994b). The low pH of phosphogypsum can cause mobility of trace elements. Phosphogypsum contains calcium, sulphur and phosphorus which can be used in nutrient deficient soils.

2.2. Physical Properties

Phosphoric acid production can result in the dihydrate form of calcium sulphate or the hemihydrate form depending on the temperature during the reaction (Rutherford et al. 1994b). Particle size of dihydrate is approximately < 0.075 mm; crystals are silt sized and are soft in texture. General properties of phosphogypsum are naturally similar to properties of gypsum. Particle density is typically 2.27 to 2.40 Mg m^{-3}; bulk density of the material in the stacks ranges from 0.7 to 0.9 Mg m^{-3}. There is a large portion of medium to fine sized particles which can result in rapid dissolution in comparison to that of natural gypsum. The hydraulic conductivity of phosphogypsum ranges between 1 x 10^{-3} and 2 x 10^{-5} cm s^{-1} (SENES 1987). The water content of phosphogypsum after filtration ranges from 25 % to 30 % (Wissa 2002).

2.3. Radiological Properties

Phosphogypsum has radioactive properties derived from igneous and sedimentary phosphate rocks that contain higher uranium concentrations (U-238) than most other geological rock (Rutherford et al. 1994a). During phosphoric acid production, isotopes of uranium and thorium are soluble in phosphoric acid, and radium and polonium partition into phosphogypsum.

Radium (Ra-226) has the longest half life of the isotopes and is the major source of long term

radioactivity in phosphogypsum. Only radon 222 is prevalent in phosphogypsum out of the 27 isotopes of radon and is the product from the decay of radium 226 (Rutherford et al. 1994b). The half life of radon 222 is only 3.8 days and it decays into polonium 218. Although it has a short half life, radon is a health and environmental concern due to its mobility in water and because its decay products which have long half lives. Radon is considered a health concern mainly because gas inhalation is linked to lung cancer (Hanson and Laird 1988, Roessler 1990).

Thorium decreases in solution with increasing pH (Rutherford et al. 1994b). At a pH of less than 5, thorium hydrolizes and there is little effect on any further changes in pH. As pH increases, thorium adsorbs to surface particles, more so when the particle size is large.

Lead is mainly partitioned into phosphoric acid during the fertilizer production process; therefore, the lead in phosphogypsum is mainly due to the decay of radon 222. Lead decays by beta decay and therefore is not as much of a health risk as the alpha decay products, although it has a long half life of 21 years. The mobility and solubility of lead is determined by pH and Eh of the environment. The solubility of lead is low in acidic environments. Under reducing conditions lead will precipitate in solution.

Polonium is partitioned into phosphogypsum during the production of phosphoric acid. The mobility of polonium is determined by solubility of radiocolloids and is most mobile in acidic environments. Polonium is found in high amounts in ground water in Florida under mined areas.

3. PHOSPHOGYPSUM ENVIRONMENTAL HAZARDS

3.1. Fluoride

Phosphate source rock can contain approximately 4 % fluoride which reacts to form hydrogen fluoride during the phosphoric acid forming process (Rutherford et al. 1994b). Fluoride gas emissions are only a problem in operational stacks, but closed and open stacks may be concerned with the transport of dust particles that contain fluoride. The emissions of fluoride from operational pond water are approximately 0.10 kg/hectare/day (Wissa 2002).

Vegetation in close proximity to the phosphogypsum stacks have shown elevated levels of fluoride which can case fluorosis if ingested by animals (Wissa 2002). The maximum acceptable limit for fluoride in drinking water in Canada is 1.5 mg/L (Health Canada 2010). In a study conducted by Luther et al. (2006) fresh phosphogypsum leachate contained 31 mg/L of fluoride and weathered phosphogypsum contained 11 mg/L of fluoride. Both of these levels are well above the acceptable levels for drinking water in Canada. These results indicate that fluoride continues to be

problematic even after stack weathering.

3.2. Ground Water Contamination

Ground water contamination is a cause for concern through rain water leaching through stacks over time (Rutherford et al. 1994b). Alkaline soils underneath stacks can buffer the acidic leachate and reduce mobility of some heavy metals such as nickel (Ni), cobalt (Co) and copper (Cu). There are some species such as sulphate (SO_4^{2-}) and fluoride (F^-) that are not affected by the change in pH. In 1993 some jurisdictions set regulations in place that required all stacks to have a composite liner system composed of a 1.5 mm thick high density polyethylene geomembrane on top of a compacted clay layer or underneath a compacted phosphogypsum layer (Wissa 2002). Although there is a potential risk for contamination, Rutherford et al. (1994b) found in their research that only the first few rinses of phosphogypsum with water have high concentrations of a few trace elements this could likely be due to residual process water in the pores being flushed out of the stacks.

4. PHOSPHOGYPSUM IN AGRICULTURE

Properties of phosphogypsum have proven to be beneficial in agriculture (Rutherford et al. 1994b). Phosphogypsum has been used as an amendment for highly weathered soils with low cation exchange capacities, soils with high sodicity, acidic soils with high aluminum concentrations and calcareous soils. Due to its nutrient properties, phosphogypsum can be used as a source of plant nutrients for calcium, sulphur and phosphate. Phosphogypsum can also enhance the availability and uptake of other nutrients such as iron and manganese through acidification around roots of plants.

The potential for phosphogypsum use in agriculture as an amendment has been researched. Sulphur deficiencies are a problem in 45 of the United States (Rechcigl 1999). In the prairie provinces of Canada, more than 4 million ha of agricultural soils are deficient in plant available sulphur with even more areas of potential sulphur deficiency (Grant et al. 2012), limiting crop production on approximately 30 % of the 36 million ha of cultivated land (Grant et al. 2003). Sulphur, nitrogen, phosphorus and potassium are essential nutrients for plant growth. Sulphur is required for synthesis of amino acids in plants to produce protein. With insufficient sulphur, plants will be reduced in both quality and quantity. Texture may impact the amount of sulphur in soil. Coarse textured soils have a low nutrient holding capacity, resulting in less retention of sulphur (Rechcigl 1999). Many sources of sulphur such as ammonium sulphate and potassium sulphate,

commonly used to increase sulphur content in soils, are expensive. Phosphogypsum, which contains sulphur and calcium, is a more economical alternative to these sources.

Phosphogypsum increased crude protein production in *Paspalum notatum* Flugge (bahia grass) by 1 % over a 3 year period (Rechcigl 1999). It increased digestibility by up to 8 % of some forage harvested material in the first year, contributing to weight gain by livestock who would consume the crop biomass. Sulphur content had increased from 0.18 to 0.40 % in crop tissues and calcium content had increased from 0.42 to 0.60 % in crop tissues. The tissue fluoride content was not high enough to cause any harmful effects to the livestock.

Phosphogypsum may impact magnesium affected soils (Vyshpolsky et al. 2010). High concentrations of magnesium in soil can have a negative impact on soil properties such as infiltration rate, hydraulic conductivity and other physical properties which can in turn have an impact on plant growth. Phosphogypsum is a source of calcium that can be used as a soil amendment to mitigate these negative soil property values. It also adds phosphorous to soil, which is valuable for plant production.

5. PHOSPHOGYPSUM RECLAMATION

5.1. Phosphogypsum Regulations

In Canada, guidelines for the use of phosphogypsum are not defined. Its use federally is regulated under naturally occurring radioactive materials (NORM) (Health Canada 2011). Phosphogypsum falls under the category of diffuse NORM, which is a product that is large in volume with a relatively low amount of uniform radioactivity throughout the product. These products are usually stored close to their point of origin because of prohibitive transportation costs. Provincially, Alberta Environment and Sustainable Resources Development supports use of beneficial waste products through a policy document defining acceptable industry practices (Nichol 2015). A Material Safety Data Sheet (MSDS) must be produced for the waste product to be used. After the MSDS has been developed, the waste product would then be redefined as a product that can be used and sold as long as it meets criteria for the intended use.

5.2. Phosphogypsum Reclamation

In Alberta, the only requirement for phosphogypsum stack closure is that the disturbed land must be returned to equivalent land capability (Alberta Environment 2005). The nominal base case reclamation plan for the Agrium Redwater stacks is to cover with 1 m of material to revegetate

the stack (Alberta Environment 2004). This is the main reason why most research in the area of phosphogypsum is related to capping depths.

Most reclamation plans for phosphogypsum stacks include a cover system that is installed over the stack. Common materials for cover systems include high density polyethylene liners, soil, vegetation, clay and a highly compacted layer of phosphogypsum (Patel 2002). These cover systems help to prevent water from percolating through the system and prevent wind and water erosion. Due to variability in landscapes, climate and end land use there is no single closure plan for phosphogypsum stacks.

At Fort Saskatchewan Alberta, cover systems used on phosphogypsum stacks were assessed on the basis of physical, chemical and hydrologic evaluations (Hallin 2008). The researchers concluded that a 15 cm top soil cover layer provided a suitable plant growth medium including species such as *Bromus inermis* Leyss. (smooth brome), *Agropyron repens* L. Gould (quack grass), *Medicago sativa* L. (alfalfa) and *Melilotus alba* Desr. (white sweet clover) with an unlikely occurrence of erosion (Hallin et al. 2010). This cover layer met provincial and federal quality criteria, including those for gamma radiation levels and radon levels. Percolation and runoff in the capped stacks were low and runoff quality met criteria for most water quality parameters.

Another study examined the effect of capping depth on water movement at Agrium, Fort Saskatchewan on a decommissioned stack for the purpose of determining appropriate capping depth (Christensen 2013, Christensen et al. 2013). It was found that greater capping thickness increased the snowmelt infiltration, decreased runoff, soil water velocity, increased percolation and increased downward flux in the topsoil PG interface. The estimates of percolation for the capping depths less than 46 cm were less than 3 % of the annual precipitation. Spring snowmelt was identified as a dominant input to overall percolation. With the use of a bromide tracer it was found that the flux would be greater over the long term with greater capping depths (30, 46, 91 cm) than the 0, 8 and 15 cm capping depths.

At Agrium, Fort Saskatchewan soil capping depths of 0, 8, 15, 30, 46 and 91 cm were evaluated for response of five seeded grass species and hydrological movement. Five seeded grass species showed no adverse effects from rooting in 8 and 15 cm caps (Jackson 2009, Jackson et al. 2011). Soil capping depths greater than 30 cm did not have an adverse impact on water quality. Increased capping depth resulted in lower gamma emissions. No relationship was found between hydrogen fluoride gas emissions and capping depth. It was found that adding amendments such as wood shavings to phosphogypsum can aid in vegetation establishment.

At Agrium Fort Saskatchewan Turner (2013), studied various environmental parameters that would aid in developing reclamation plans for phosphogypsum stacks. Root mass accumulations were found at soil-phosphogypsum interfaces with 8, 15, 30 and 46 cm caps in 50 % of cores. Increasing capping depth resulted in increased maximum rooting depth; this however was not the case in root biomass. Capped plots were better able to sustain vegetation than uncapped plots. Vegetation on the stacks had elevated fluorine, cobalt and nickel relative to a reference control. Cap depths greater than 8 cm were associated with plants with tissue concentrations safe for animal consumption according to maximum tolerable levels (Turner 2013, United States National Research Council 2005). Thirty five species were present on site 19 years after capping and seeding the stacks.

5.3. Phosphogypsum Anthroposols

Phosphogypum may have potential in construction of soil, an increasingly scarce resource that is necessary in land reclamation. The use of phosphogypsum, a by-product that is currently only stacked and not reused in Canada, as a soil component will be beneficial in many ways including reduction of stacks on the landscape and increased soil. With increasing industrial impact, the creation of soil by humans (anthroposols) is becoming common.

Phosphogypsum has the potential to be used to create an anthroposolic soil. Anthroposols are azonal soils that have been highly modified or constructed by human activity (Naeth et al. 2012). Anthroposols have one or more horizons removed, removed and replaced, added to, or significantly modified by humans. Manufactured materials of domestic or industrial origin may be added as a layer or component of a layer. To be classified as an anthroposol, the depth of disturbance, addition or modification must be greater than or equal to 10 cm below or above the surface horizon. The anthroposol soil order was developed because soils of this classification do not fit into any order in the current Canadian System of Soil Classification and its criteria did not provide the means to describe and classify soils of this type (Soil Classification Working Group 1998). Hence the soils could not be classified and evaluated for reclamation.

Materials such as peat, mineral mixes, mine spoil and phosphogypsum are commonly used to form or develop anthroposols. Human activity causes the composition and arrangement of soil layers in an anthroposolic soil profile which means dominant soil forming processes are anthropogenic. Anthroposols may not have diagnostic horizons of other soil orders, the layers may not be similar to naturally occurring soils, and materials may be foreign to natural soil. To be classified as an anthroposol, modification of the soil or its disturbance must be evident.

A phosphogypsum anthroposol could be classified as a fusco spolic anthroposol (Naeth et al. 2012). The diagnostic feature of a spolic great group is the presence of a sufficiently deep D layer to meet the depth criterion and containing less than 17 % organic carbon. It may or may not have physical artefacts present, but if present they must constitute less than 10 % by visible chemical layers such as buried sumps or materials deposited as a slurry from human processes. It may include removed, removed and replaced, soil horizons or materials deposited in from human activities. Fusco subgroup denotes soils with a surface layer that is greater than 10 cm thick and had 2 to 17 % organic carbon. The higher amount of organic carbon would normally account for its darker colour relative to the albo subgroup.

6. KNOWLEDGE GAPS AND GENERAL RESEARCH OBJECTIVES

To successfully create phosphogypsum anthroposols, several gaps in knowledge must be addressed. Research has been conducted on effective capping depths for phosphogypsum stacks; however, research has not adequately addressed phosphogypsum as a substrate. Research is needed to determine whether phosphogypsum can be used and/or amended to provide a suitable medium for plant growth. Research is needed to evaluate how phosphogypsum reacts with different amendments, such as common organic amendments, and the ratios of amendments that would be required for optimal reclamation of phosphogypsum stacks. Some of the properties of phosphogypsum are not well understood in the context of soil amending or soil construction.

The goal of this MSc research program was to assess the potential of phosphogypsum being built into a soil though the use of amendments. This research quantifies plant response to phosphogypsum in two greenhouse studies using common reclamation plant species. The research examines important physical properties of phosphogypsum and common microbial properties of phosphogypsum.

II. POTENTIAL OF PHOSPHOGYPSUM AMENDED WITH MANURE AND TOPSOIL AS A PLANT SUBSTRATE

1. INTRODUCTION

Phopshopgypsum is a byproduct from phosphate fertilizer production when phosphoric acid is produced from phosphate rock (Rutherford et al. 1994). Phosphogypsum is composed of mainly gypsum and impurities, including residual acids, soluble fluoride, trace elements and naturally occurring radionuclides (Rutherford et al. 1995b). The most common method of producing phosphoric acid is a wet process, where phosphate rock is treated with sulphuric acid and water which results in gypsum, phosphoric acid and hydrogen fluoride (Rutherford et al. 1994). Phosphogypsum is usually stacked in the vicinity of its production site, which will eventually require closure and reclamation.

There are environmental issues associated with phosphogypsum production, stacking and use. Phosphate source rock can contain fluorine which forms hydrogen fluoride during phosphoric acid production (Rutherford et al. 1994a). Fluoride gas emissions are a problem in operational stacks; closed and open stacks may have to be concerned with transported dust particles containing fluoride. Fluoride emissions from operational pond water are approximately 0.10 kg/ha/day (Wissa 2002). Vegetation close to phosphogypsum stacks can have elevated concentrations of fluoride which can cause fluorosis if ingested by animals. Luther et al. (2006) found that fresh phosphogypsum leachate contained 31 mg/L of fluoride and weathered phosphogypsum contained 11 mg/L, well above the maximum acceptable limit of 1.5 mg/L for fluoride in drinking water in Canada (Health Canada 2010). Ground water may be contaminated through rain water leaching through stacks over time (Rutherford et al. 1994a) although Rutherford et al. (1994b) found only the first few rinses of phosphogypsum with water had high concentrations of trace elements. Thus regulations in Florida require stacks to have a composite liner system of a 1.5 mm thick high density polyethylene geomembrane on top a compacted clay layer or underneath a compacted phosphogypsum layer (Wissa 2002).

Phosphogypsum can be beneficial for use in agriculture (Rutherford et al. 1994a). It has been used to amend highly weathered soils with low cation exchange capacity, high sodicity soils, acidic soils with high aluminum concentrations and calcareous soils. Phosphogypsum can be a source of calcium, sulphur and phosphate and can increase availability and uptake of other nutrients such as iron and manganese through acidification around plant roots. Phosphogypum

may have potential in anthroposol building for land reclamation. The use of phosphogypsum, a product that is currently stocked and not resused, as a soil component could be beneficial in many ways including the reduction of stacks on the landscape, reduced stack reclamation and increased soil. With increasing industrialization and associated reclamation, soil building by humans is becoming common.

If phosphogypsum was to be used in building anthroposols for reclamation and/or agricultural uses it would need to be amended to ameliorate its negative properties. It would also need to be amended if it were to be reclaimed without capping. Amendment with topsoil and manure, two commonly used amendments in agriculture and in reclamation which are readily available in large quantities, could ameliorate the lack of organic matter and lack of some major plant nutrients and very fine texture to make phosphogypsum more hospitable for plant growth and plant community development.

Manure increases the organic matter content in soil and contributes various plant nutrients such as nitrogen and available phosphorous, which are especially beneficial to plants (Land Resources Network 1993). Manure is used as a soil amendment to increase water stable aggregates, decrease bulk density and aids in many water characteristics that affect plant growth (Land Resources Network 1993). The addition of manure to soil can increase pore size and volume which positively affects infiltration capacity and soil water retention properties, which can be especially significant in areas of drought (Bayu, 2004, Land Resources Network 1993). Root penetration is improved with manure, especially in fine textured soils (Land Resources Network 1993).

Top soil contains organic matter which is important for long term soil fertility and tilth as it improves physical, biological and chemical properties of the substrate to which topsoil is added (Diacono and Montemurro 2010). Top soil consists of various important soil nutrients, it increases water holding capacity and provides a good quality seed bed for vegetation (Thurber Consultants et al 1990).

2. RESEARCH OBJECTIVES

The objective of this research was to determine whether phosphogypsum had potential as a soil building material for anthroposols. Specific research objectives were to determine whether amending phosphogypsum with topsoil and manure affected the resulting mix capacity to support plant growth as assessed by plant performance and health.

3. MATERIALS AND METHODS

3.1. Treatments and Experimental Design

The substrate treatments were mixes of phosphogypsum, loamy topsoil and partially decomposed dairy cattle manure. Phosphogypsum was sourced from Agrium at Fort Saskatchewan, Alberta, manure from the University of Alberta research farm and topsoil from a local garden shop. The phosphogypsum was derived from Florida phosphate rock (Nichol 2006) and has been characterized in several other research projects that have used it (Hallin 2007, Jackson 2008, Christensen 2013, Turner 2013). Amendments were applied to phosphogypsum at four rates of 5, 10, 20 and 40 %, by volume (hereafter referred to as mixes).

Three plant species, *Hordeum vulgare* L. (barley) and *Agropyron trachycaulum* H.F. Lewis (slender wheat grass) and *Agropyron elongatum* P. Beauv (tall wheat grass) were used to assess plant response to the substrate treatments. These plant species was selected for the research as they are commonly used in land reclamation in Alberta and have been used successfully in a variety of greenhouse experiments. Barley is a common agricultural crop used in Alberta. The two *Agropyron* species were planted as a grass mix in the same pot and the barley was planted in pots as a monoculture.

Each treatment was replicated 10 times. The treatments were phosphogypsum x 2 amendments (manure, topsoil) x 4 rates of amendments (5, 10, 20 and 40 %) x 2 vegetation treatments (*Agropyron* species mix, *Hordeum*) x 10 replicates = 160 pots plus a control of phosphogypsum alone x 2 vegetation treatments x 10 replicates = 20 pots. This provided for a total of 180 pots for the experiment.

3.2. Greenhouse Procedures

The greenhouse experiment was conducted at the University of Alberta and ran for 8 weeks in August 2013. The greenhouse temperature was set at 20 to 21 °C with 18 hours of daylight to provide a desirable growing environment for plants.

Prior to seeding, seeds were counted by hand and checked for general viability using a light table in the laboratory. Germination tests were then conducted. For each species, 10 seeds were placed into each of 10 petri dishes on a damp paper towel and placed on a window sill for optimal sun exposure. Germination was recorded daily until it ceased. The petri dishes were watered daily, as required if they were dry. After two weeks germination had ceased and the number of germinated seeds was converted to a percent germination for each species. Germination was 84

% for *Hordeum vulgare*, 92 % for *Agropyron elongatum* and 96 % for *Agropyron trachycaulum*.

Amendments were mixed with phosphogypsum in a large tub at a laboratory at the University of Alberta. The manure and topsoil were thoroughly mixed by hand with the phosphogypsum in ratios of 5, 10, 20 and 40 % by volume. Large pieces of phosphogypsum, top soil and manure were broken up by hand to provide a homogeneous mixture. All of the mixes were stored in labelled buckets and transported to the greenhouse for potting.

Greenhouse pots were 15.24 cm in diameter and 10.16 cm deep. Each pot had 4 holes in the bottom for drainage. The bottoms of the pots were covered with two pieces of landscape fabric cut in 15.24 cm diameter circles. The phosphogypsum mixes were scooped up with garden trowels from the labeled buckets into the pots. The pots were placed into greenhouse trays and set up in blocks (replicates) in the greenhouse to account for environmental conditions such as ventilation, sun exposure and temperature heterogeneity. The positions of the pots in each block in the greenhouse were determined randomly, with each pot given a treatment and replicate number. In the final placement of pots in the greenhouse, there was one replicate of each treatment in each block.

Each pot was seeded with 15 seeds for *Hordeum vulgare* and 15 seeds each of *Agropyron trachycaulum* and *Agropyron elongatum* for a total of 30 seeds in the grass mix pots. Seeds were evenly distributed on the pot surface by hand, then gently pressed under the surface of the substrate with fingers. The seeds were covered with no more than 1 cm for optimal germination for these species.

Three pots from each mix were used to determine field capacity, the water content that would be approximated for each watering of the pots. These pots were watered to saturation, by pouring water slowly and evenly over the substrate surface. Approximately 1.5 L were added to each pot so that it dripped out of the holes and the pots were consistent in the amount of water added. These pots were monitored every 12 hours for qualitative water content. Field capacity was considered reached when water no longer dripped from the bottom and the top of the substrate was damp to the touch. Pot weights were taken before water was added and 12 and 24 hours after water was added. Individual pot weights of the same ratio were averaged. Field capacity water content and mass of water to be added at watering point were then calculated based on these data. The pots were watered every 2 days to approximate field capacity with approximately 100 to 200 mL of water depending on environmental factors such as temperature and greenhouse ventilation.

3.3. Plant Measurements

To assess emergence and survival, plant density in each pot was recorded weekly. After 4 weeks *Hordeum vulgare* plants were thinned to 5 plants per pot, and the grass mix was thinned to 6 plants per pot (3 plants of each *Agropyron* species). Plants were thinned in each consecutive week to these numbers if new plants emerged.

Plant height was measured after 4, 6 and 8 weeks. Measurements were made with a ruler from the substrate base to the top of the plant with the tallest stem stretched to its maximum height for each of the plants.

Plant health was evaluated after 4, 6 and 8 weeks using a 5 point scale (Naeth 2013). A value of 5 was assigned to necrotic plants (< 10 % live material); 4 assigned to plants exhibiting some unhealthy symptoms such as chlorosis or wilting (< 25 % live material); 3 assigned to a half dying plant (> 50 % live material); 2 assigned to a mostly healthy plant with little chlorosis (> 75 % green); and 1 assigned to a healthy green plant (> 90 % live plant material). Each pot was assigned an average plant heath value generally representative of all plants in the pot.

At the end of the 8 week experiment a final vegetation assessment was conducted in addition to the above measurements. Leaves were counted for each plant in each pot. Plants that reached the inflorescence stage were counted. Above ground biomass was determined by clipping plants at the soil surface using scissors. Fresh biomass was weighed, placed in paper bags and labelled. These samples were then oven dried at 80 °C for 48 hours, then weighed again to determine oven dry biomass. After clipping above ground biomass, the remaining contents of each pot were individually dumped into a pan and large chunks of substrate without imbedded roots were taken out by hand. Roots with residual substrate material attached to them were put in a sieve and rinsed with tap water to remove all substrate materials from the roots. The roots were placed on paper towels to air dry for a short time, then weighed and put into labelled paper bags. Roots were then oven dried and weighed following the same procedure as that used for above ground biomass.

3.4. Laboratory Analyses

Three samples from each of the phosphogypsum and the dairy cattle manure and topsoil amendments and one mixture of phosphogypsum with 20 % topsoil from the greenhouse experiment were analyzed at Exova laboratories in Edmonton, Alberta. The samples were oven dried at the University of Alberta laboratory at 80 ^{o}C for two days before sending to the laboratory for analyses.

Each sample was analyzed for the following properties. Ammonium and nitrate concentrations were determined using potassium chloride extraction (Maynard et al 2008), available phosphorous and available potassium by modified Kelowna extraction (Ashworth and Mrazek 1995) and available sulphate by calcium chloride extraction (Byers 1981). Total organic carbon was determined by dry combustion (Nelson and Sommers 1996). The micro nutrients zinc, copper, manganese and iron, were determined by diethylenetriamine pentacetic acid extraction (Byers 1981). The soluble ions calcium, magnesium, sodium and potassium were determined by saturated paste and inductively coupled plasma atomic emission spectroscopy (Miller and Curtin 2008). Cation exchange capacity was determined by ammonium acetate displacement and macro Kjeldahl distillation (Chapman, 1981), pH by calcium chloride solution and pH meter (Peech 1981) and electrical conductivity by saturated paste and electrical conductivity meter.

3.5. Statistical Analyses

All of the analyses for this experiment were conducted using base R software (R Core Team 2014). The required assumptions for a two way analysis of variance (ANOVA) were conducted using the Shapiro-Wilkes test for normality and the Bartlett's test for equal variances. A permutational test (package lmperm) was used to run the ANOVA for soil height and biomass for each individual plant species, since the data did not fit a normal distribution with equal variances. This ANOVA test was then followed by Tukey's HSD post-hoc for those comparisons that were showing significance.

4.0 RESULTS

4.1. Plant Response To Treatments

Plant emergence (presented as plant density at an assessment date) for *Agropyron* species and *Hordeum vulgare* followed a similar trend for all substrates with plants continuing to emerge until just over a month (Figures 2.1, 2.2). Although values were similar, greatest emergence of *Agropyron* was in treatments with topsoil 10 % and 20 % and manure 20 %; lowest emergence was in topsoil 5 % and pure phosphogypsum (Figure 2.1). *Hordeum vulgare* emergence was also similar among treatments with greatest emergence in pure phosphogypsum and lowest in manure 40 % (Figure 2.2).

Plant health followed a similar trend for all species in all substrates, being generally good in week 4, declining by week 6, then declining again by week 8 (Figures 2.3, 2.4, 2.5). Health of *Agropyron trachycaulum* was similar in all treatments in week 4 (Figure 2.3). In week 6, plants in topsoil

treatments were generally in better health than those in manure mixtures and pure phosphogypsum, with healthiest plants in topsoil 40 % and 20 % and manure 40 %. By week 8, decreased plant health was most noticeable in pure phosphogypsum, topsoil 40 % and manure 20 % and 5 %. Health of *Agropyron elongatum* was similar in all treatments in week 4 except for poor health in topsoil 5 % (Figure 2.4). In week 6 least healthy plants were in pure phosphogypsum, manure 5 % and 10 % and topsoil 5%, with heathiest plants in topsoil 40 % and manure 40 % and 20 %. In week 8 declining plant health was most noticeable in pure phosphogypsum and manure 5 %. Health of *Hordeum vulgare* was greatest in topsoil treatments and manure 20 % and 40 % in all weeks (Figure 2.5).

Plant height generally increased with time for all species (Figures 2.5, 2.6, 2.7). In weeks 4, 6 and 8 treatments had a significant effect on height of *Agropyron trachycaulum* and *Hordeum vulgare* but not *Agropyron elongatum* (Table 2.1). In week 4, *Agropyron trachycaulum* was significantly shorter in pure phosphogypsum and manure 5 % and 10 % than in topsoil treatments and manure 40 % (Figure 2.6, Table 2.2). In week 6, plants were significantly shorter in pure phosphogypsum, manure 5 %, 10 % and 20 % and topsoil 5 % than in topsoil 10 %, 20 % and 40 % (Figure 2.6, Table 2.3). In week 8 plants were significantly shorter in pure phosphogypsum and manure 5 % and 10 % than in topsoil 10 %, 20 % and 40 % (Figure 2.6, Table 2.4). There were no significant treatment effects for *Agropyron elongatum* although visual trends were for shorter plants in manure 5 % and 10 % and pure phosphogypsum (Figure 2.8). In week 4 *Hordeum vulgare* in pure phosphogypsum and manure 5 % and 10 % was significantly shorter than in topsoil treatments and manure 20 % and 40 % (Figure 2.8, Table 2.5). In week 6 plants in pure phosphogypsum and manure 5 % and 10 % were significantly shorter than in manure 20 % and 40 % and topsoil 10 %, 20 % and 40 % (Figure 2.8, Table 2.6). In week 8 plants were significantly shorter in pure phosphogypsum and manure 5 % than in other treatments (Figure 2.8, Table 2.7).

Treatment had a significant effect on above and below ground biomass for all plant species evaluated (Table 2.8), being greater in topsoil than in manure (Table 2.9). *Agropyron* species biomass was significantly lower in pure phosphogypsum and manure 5 % than in the other treatments (Figure 2.9, Table 2.10). Below ground biomass was significantly lower in the pure phosphogypsum, manure 5 %, 10 % and 20 % and topsoil 5 % than in the other treatments (Figure 2.9, Table 2.11). *Hordeum vulgare* above ground biomass was significantly lower in pure phosphogypsum and manure 5 % and 10 % than in the other treatments (Figure 2.10, Table 2.12). Below ground biomass was significantly lower in manure 5 % and 10 % than in the other treatments (Figure 2.10, Table 2.13).

4.2. Chemical Properties Of Substrates And Plant Tissue

Topsoil, manure and phosphogypsum had considerably different chemical properties (Table 2.14). Phosphogypsum had higher available ammonium than manure and topsoil. Topsoil had higher iron, potassium and cation exchange capacity than manure and phosphogypsum. Manure had higher nitrate and phosphorous than topsoil and phosphogypsum. Phosphogypsum had a much lower potassium concentration than manure and topsoil. Topsoil pH was near neutral, that of manure was alkaline at approximately 9 and pH of phosphogypsum was acidic at approximately 5. Topsoil had a much lower electrical conductivity and nitrate concentration than manure and phosphogypsum. Addition of 20 % topsoil by volume to phosphogypsum had little impact on chemical properties of the resulting mix.

5. DISCUSSION

General trends in plant health performance were as expected. In week 4 and 6 plants were healthier than in week 8 due to typical greenhouse plant response which may be associated with low pot volume for root growth and low water holding capacity which cannot meet the plant water requirements. Lowest plant health was associated with the least favourable growing conditions, like pure phosphogypsum and lower ratios of manure mixes. The healthier plants found in higher ratios of topsoil mixes and manure mixtures were likely due to higher organic matter content, available nutrients and higher water retention.

Highest emergence of *Agropyron* species in treatments with the highest topsoil ratios may be due to higher organic matter content, higher water holding capacity and higher nutrient adsorption and release which improved conditions for plants to grow in. Treatments with lower seedling emergence had high manure contents which could have led to high salinity and basic pH affecting plant response. *Hordeum vulgare* treatments with highest germination were in phosphogypsum. This result was unexpected and not readily explained. It could be due to the high concentrations of nitrate, phosphorous, potassium and manganese that the phosphogypsum provides, and also to the barley being better able to perform under poorer soil conditions, as it is a relatively easy to grow cereal crop.

Finding the shortest plants and the lowest biomasses in manure and pure phosphpgypsum and the tallest plants in mixes with the highest rates of topsoil was as expected. Topsoil is simply a better substrate with higher organic matter content, higher water holding capacity and greater nutrient concentrations than phosphogypsum with its low pH, low cation exchange capacity and

high electrical conductivity.

For use in reclamation in Alberta, substrates must meet specific soil quality criteria (Soil Quality Criteria Working Group 1987). Requirements differ for three regions in Alberta, the plains region, the northern forest region and the eastern slopes region, and whether the material will be purposed for topsoil or subsoil.

In the plains region pure phosphogypsum for topsoil and subsoil would be categorized as poor for organic carbon, pH and electrical conductivity and categorized as good for sodium absorption ratio. For the northern forest region for topsoil and subsoil phosphogypsum would be categorized as good for sodium adsorption ratio. Based on pH it would be categorized as fair and based on electrical conductivity it would be categorized as poor. For the eastern slopes region for root zone substrate, pH and sodium adsorption ratio would be characterized as fair, electrical conductivity would be categorized as poor.

In the plains region, the phosphogypsum 80 % soil 20 % mix for would be categorized as poor for organic carbon, pH and electrical conductivity, and categorized fair for sodium absorption ratio in both the topsoil and subsoil categories. For the northern forest region, for topsoil and subsoil, the mix would be categorized as good for sodium adsorption ratio, fair for pH and poor for electrical conductivity. For the eastern slopes region, for root zone substrate, for pH and electrical conductivity it would be categorized as poor and for sodium adsorption ratio it would be categorized as good. Thus the categorization is often good for reclamation consideration.

In general phosphogypsum has an acidic pH and high electrical conductivity which make it a generally poor substrate material for Alberta regions if it were to be used unamended. Amending phosphogypsum with manure and topsoil could ameliorate these properties sufficiently for it to be used in anthroposol building. Topsoil has a low electrical conductivity and neutral pH. The mixture analyzed of 80 % phosphogypsum and 20 % topsoil shows that the electrical conductivity of phsophogypsum can be lowered with a small amount of topsoil added. However a higher ratio of topsoil would need to be added to get pH closer to neutral in a phosphogypsum dominated mix. Other chemical amendments could assist with that as well. Manure could be considered as an amendment to aid in pH neutralization due to its normally basic pH. These amendments could also be appropriate to use if phosphogypsum were to be reclaimed rather than capped, as is the current practice.

6. CONCLUSIONS

Phosphogypsum may have potential for use in anthroposol building if it is amended. Amendment of phosphogypsum with manure and topsoil generally enhanced plant response as assessed through emergence, height, health and above and below ground biomass. Generally topsoil was a better amendment for phosphogypsum than manure.

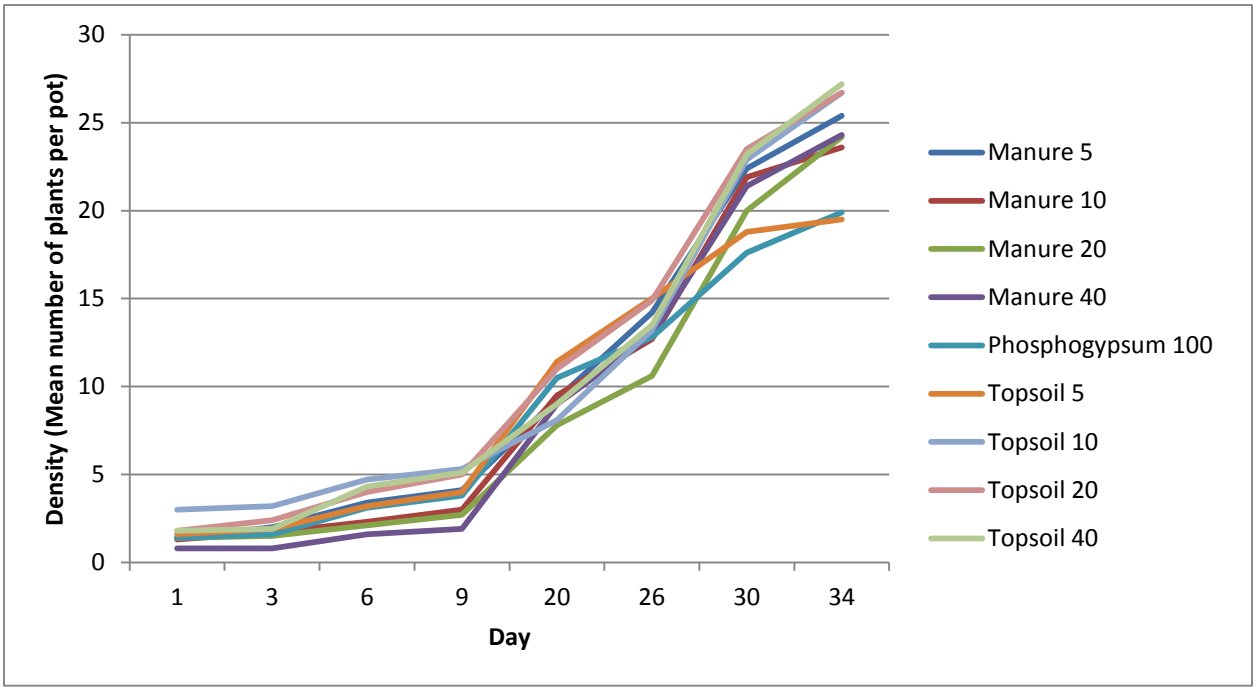

Figure 2.1. Mean plant density over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron* species.

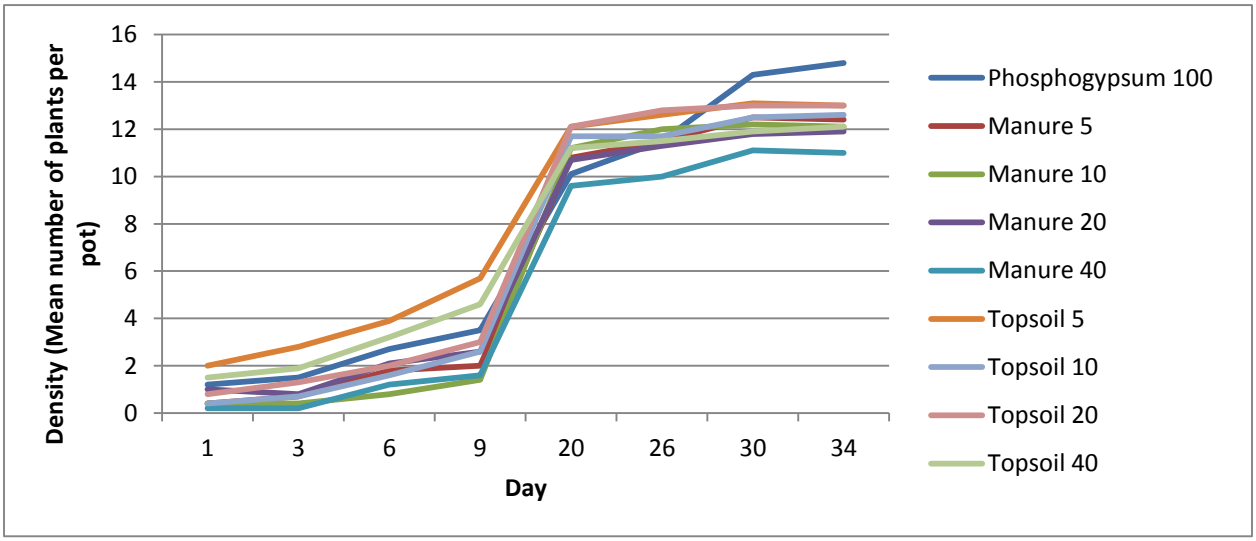

Figure 2.2. Mean plant density over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Hordeum vulgare*.

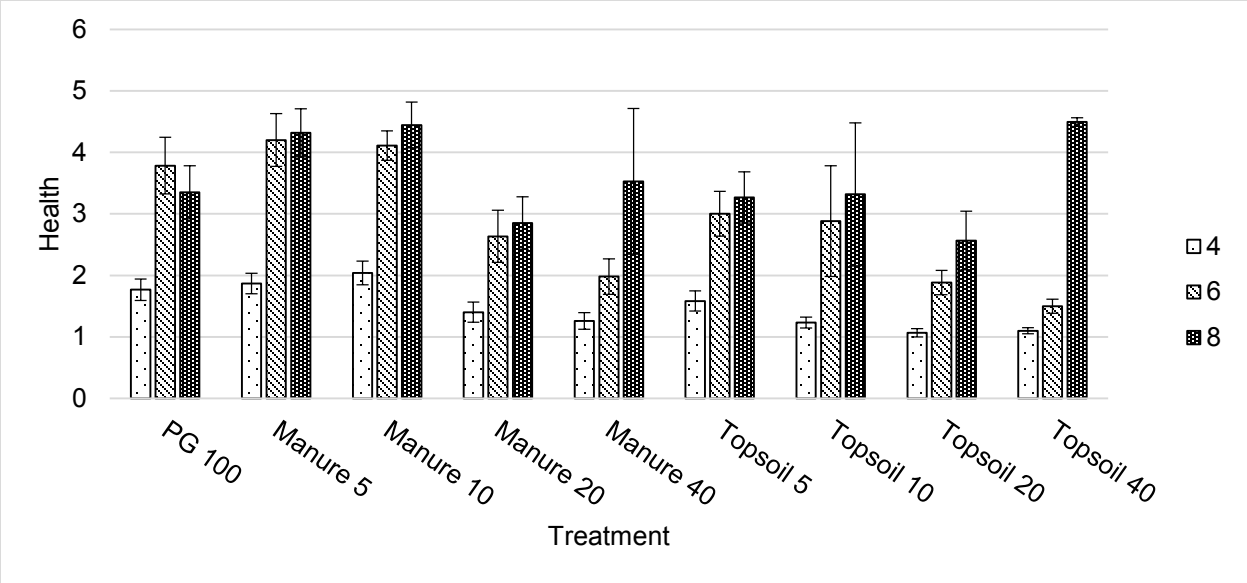

Figure 2.3. Mean plant health over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron trachycaulum*.

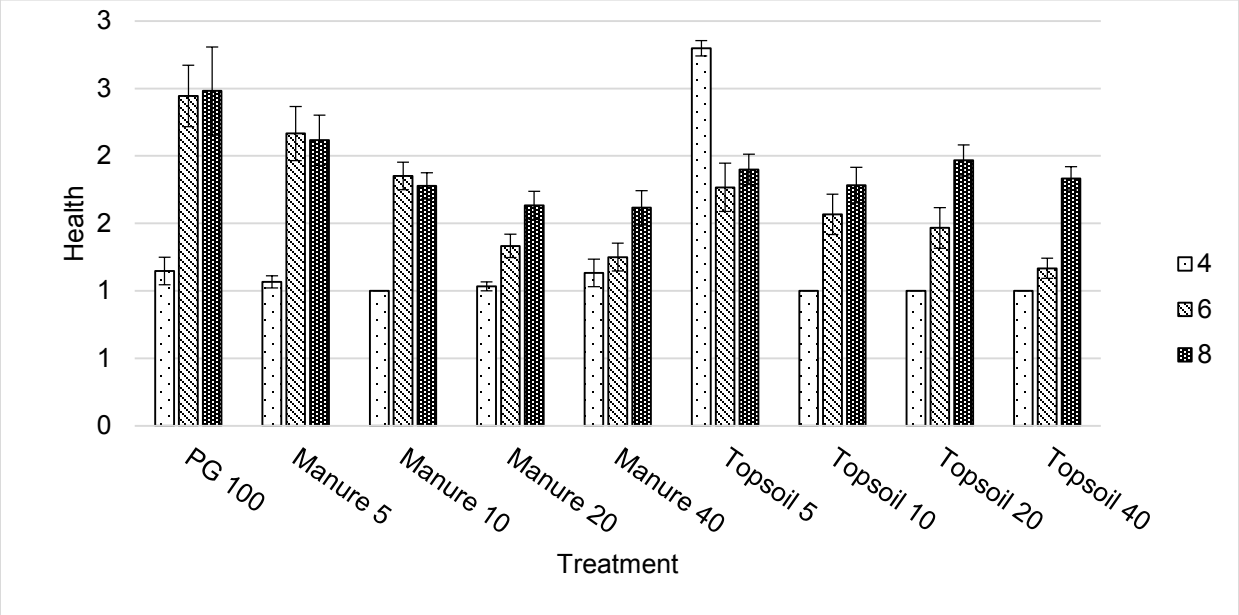

Figure 2.4. Mean plant health over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron elongatum*.

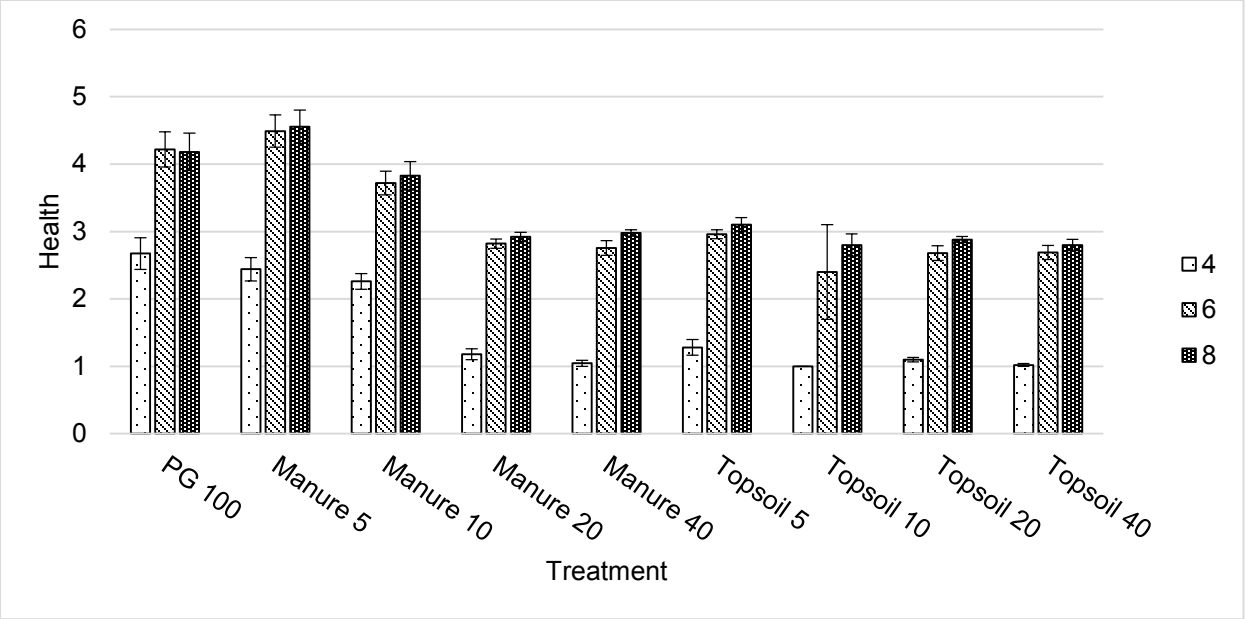

Figure 2.5. Mean plant health over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Hordeum vulgare*.

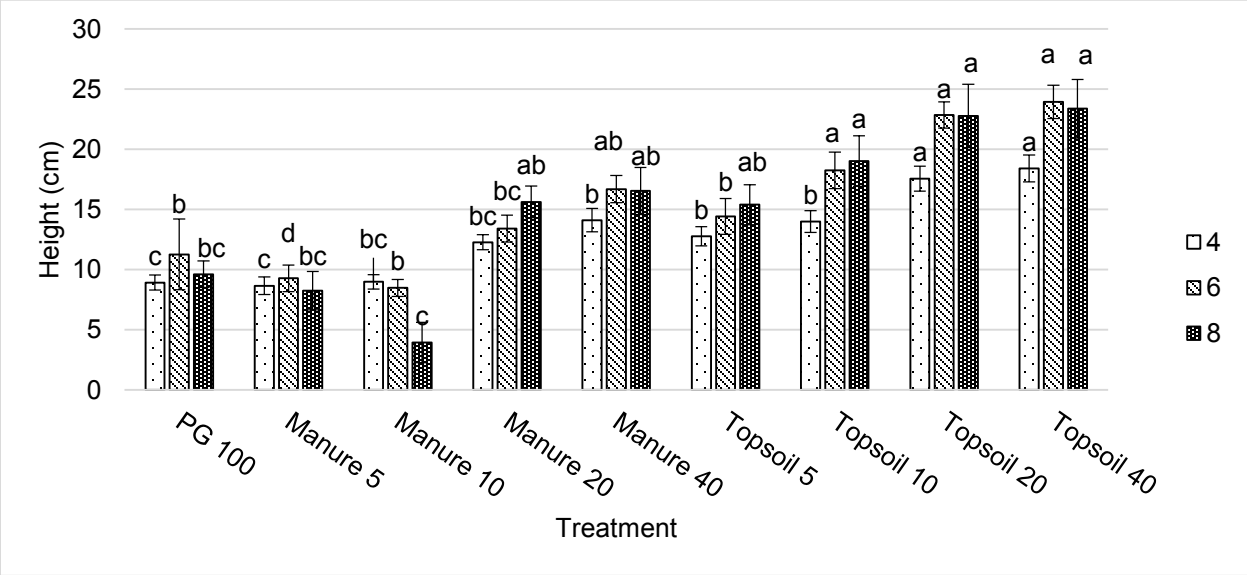

Figure 2.6. Mean plant height over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron trachycaulum*. Letters indicate significant differences within weeks.

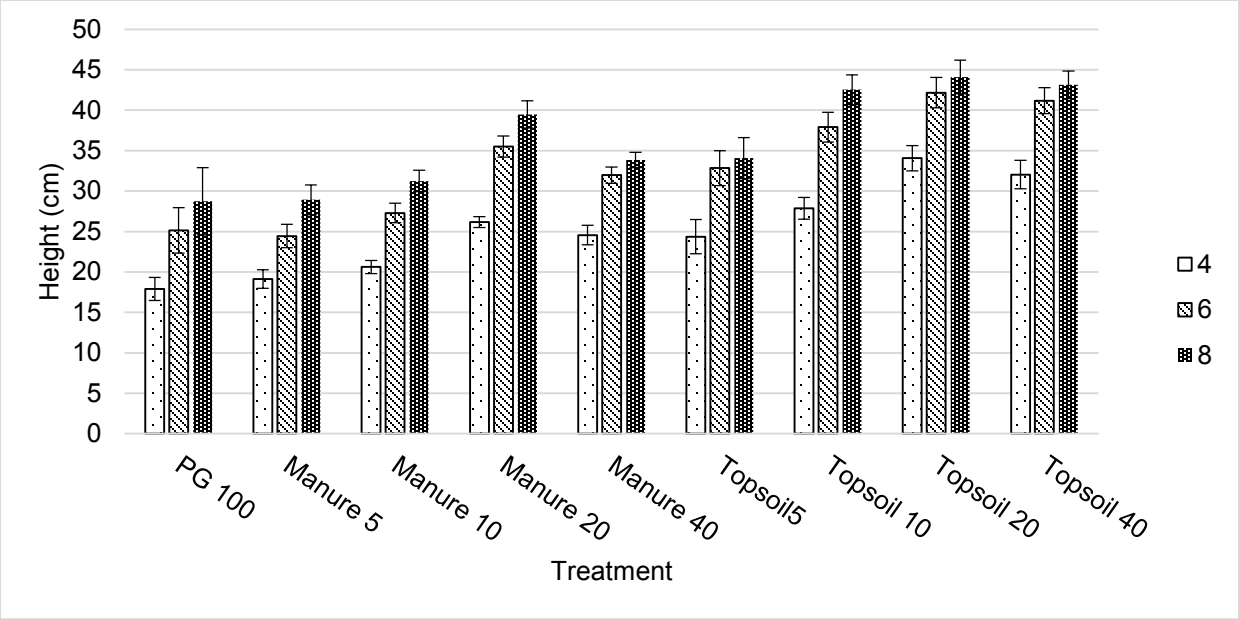

Figure 2.7. Mean plant height over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron elongatum*.

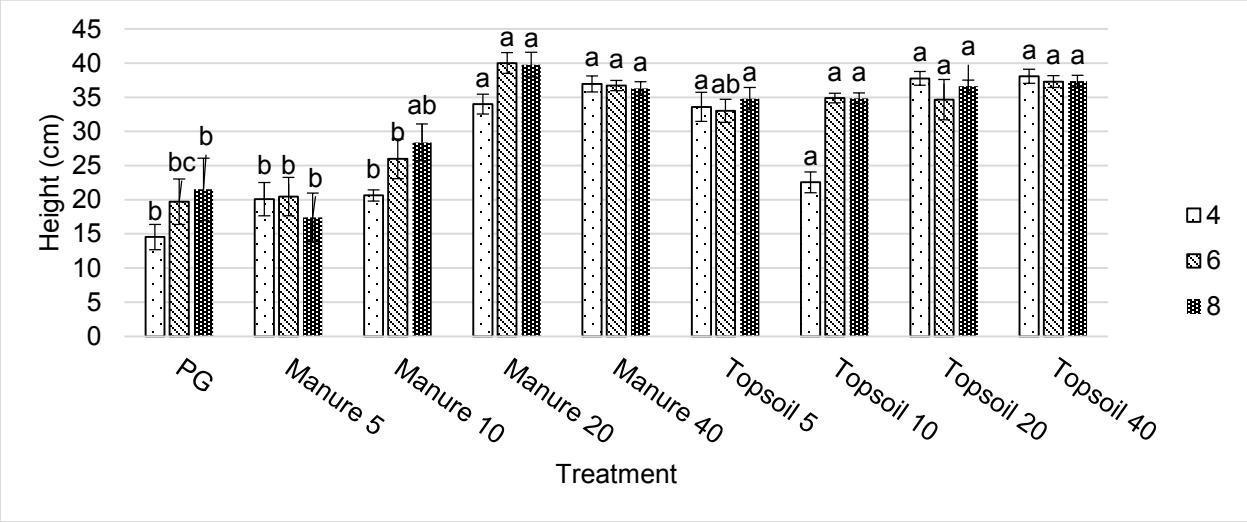

Figure 2.8. Mean plant height over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Hordeum vulgare*. Letters indicate significant differences within weeks.

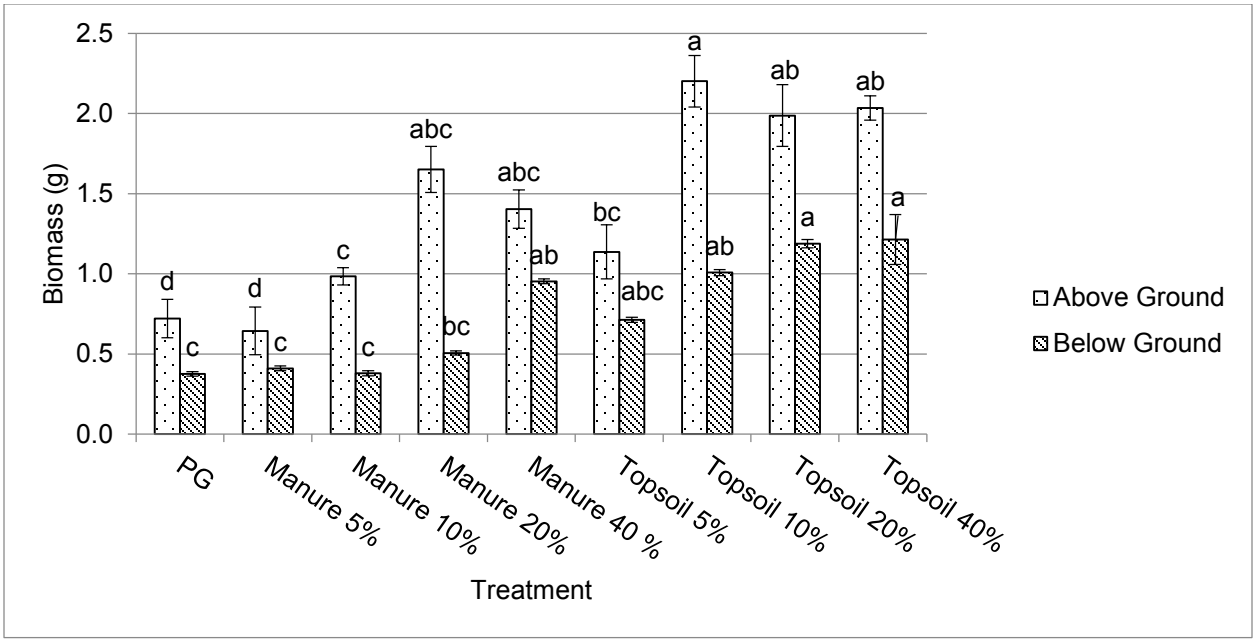

Figure 2.9. Mean plant biomass over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Agropyron* mix. Letters indicate significant differences within below or above ground biomass.

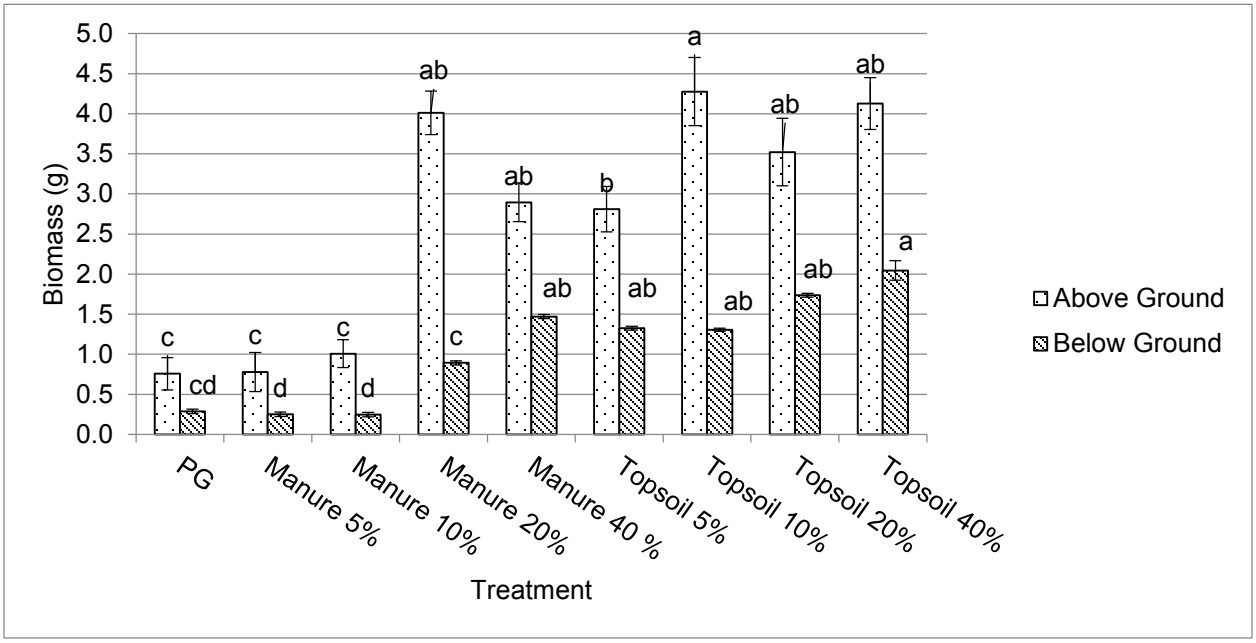

Figure 2.10. Mean plant biomass over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with topsoil and manure for *Hordeum vulgare*. Letters indicate significant differences within below or above ground biomass.

Table 2.1. ANOVA output for weeks 4, 6 and 8 plant height.

	Species	Parameter	Degrees Of Freedom	P Value
Week 4	*Agropyron trachycaulum*	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	0.169
		Amendment:Ratio	9	0.015
		Residuals	79	
	Agropyron elongatum	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	0.146
		Amendment:Ratio	9	0.184
		Residuals	78	
	Hordeum vulgare	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	4e-04
		Amendment:Ratio	9	<2e-16
		Residuals	80	
Week 6	*Agropyron trachycaulum*	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	0.041
		Amendment:Ratio	9	0.015
		Residuals	79	
	Agropyron elongatum	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	0.662
		Amendment:Ratio	9	0.098
		Residuals	78	
	Hordeum vulgare	Amendment	1.25	<2e-16
		Ratio	1.25	<2e-16
		Block		0.002
		Amendment:Ratio		<2e-16
		Residuals		
Week 8	*Agropyron trachycaulum*	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Block	4	0.404
		Amendment:Ratio	9	0.001
		Residuals	79	
	Agropyron elongatum	Amendment	1	0.002
		Ratio	4	<2e-16
		Block	4	0.226
		Amendment:Ratio	9	0.080
		Residuals	77	
	Hordeum vulgare	Amendment	1	0.001
		Ratio	4	<2e-16
		Block	4	0.038
		Amendment:Ratio	9	0.001
		Residuals	80	

Table 2.2. Height interactions in week 4 for *Agropyron trachycaulum*.

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum 100	3.8500	0.031113
Topsoil 10 : Phosphogypsum 100	5.0800	0.000855
Topsoil 20 : Phosphogypsum 100	8.6400	0.000000
Manure 40 : Phosphogypsum 100	5.1800	0.000967
Topsoil 40 : Phosphogypsum 100	9.4900	0.000000
Topsoil 5 : Topsoil 0	3.8500	0.031113
Topsoil 10 : Topsoil 0	5.0800	0.000855
Topsoil 20 : Topsoil 0	8.6400	0.000000
Manure 40 : Topsoil 0	5.1800	0.000967
Topsoil 40 : Topsoil 0	9.4900	0.000000
Topsoil 5 : Manure 5	4.1100	0.015656
Topsoil 10 : Manure 5	5.3400	0.000364
Manure 20 : Manure 5	3.6200	0.054896
Topsoil 20 : Manure 5	8.9000	0.000000
Manure 40 : Manure 5	5.4400	0.000423
Topsoil 40 : Manure 5	9.7500	0.000000
Manure 10 : Topsoil 5	-3.7811	0.047489
Topsoil 20 : Topsoil 5	4.7900	0.002144
Topsoil 40 : Topsoil 5	5.6400	0.000131
Topsoil 10 : Manure 10	5.0111	0.001631
Topsoil 20 : Manure 10	8.5711	0.000000
Manure 40 : Manure 10	5.1111	0.001785
Topsoil 40 : Manure 10	9.4211	0.000000
Topsoil 20 : Topsoil 10	3.5600	0.063242
Topsoil 40 : Topsoil 10	4.4100	0.006722
Topsoil 20 : Manure 20	5.2800	0.000444
Topsoil 40 : Manure 20	6.1300	2.34E-05
Manure 40 : Topsoil 20	-3.4600	0.097597
Topsoil 40 : Manure 40	4.3100	0.012387

Table 2.3. Height interactions in week 6 for *Agropyron trachycaulum*.

Treatments	Mean Difference	P Value
Topsoil 20 : Phosphogypsum	11.57	0.000136
Topsoil 40 : Phosphogypsum	12.67	2.05E-05
Topsoil 10 : Manure 5	8.98	0.007539
Topsoil 20 : Manure 5	13.58	4.1E-06
Topsoil 40 : Manure 5	14.68	5E-07
Topsoil 20 : Topsoil 5	8.44	0.015760
Topsoil 40 : Topsoil 5	9.54	0.003366
Topsoil 10 : Manure 10	9.76	0.003566
Topsoil 20 : Manure 10	14.36	0.000002
Manure 40 : Manure 10	8.20	0.036583
Topsoil 40 : Manure 10	15.46	3E-07
Topsoil 20 : Manure 20	9.44	0.003899
Topsoil 40 : Manure 20	10.54	0.000728

Table 2.4. Height interactions in week 8 for *Agropyron trachycaulum*.

Treatments	Mean Difference	P Value
Topsoil 10 : Phosphogypsum 100	9.37	0.013668
Topsoil 20 : Phosphogypsum 100	13.14	6.71E-05
Topsoil 40 : Phosphogypsum 100	13.74	2.61E-05
Topsoil 10 : Topsoil 0	9.37	0.013668
Topsoil 20 : Topsoil 0	13.14	6.71E-05
Topsoil 40 : Topsoil 0	13.74	2.61E-05
Topsoil 10 : Manure 5	10.75	0.002266
Topsoil 20 : Manure 5	14.52	7.4E-06
Topsoil 40 : Manure 5	15.12	2.8E-06
Manure 10 : Topsoil 5	-11.47	0.001281
Topsoil 10 : Manure 10	15.07	5.9E-06
Manure 20 : Manure 10	11.71	0.000919
Topsoil 20 : Manure 10	18.84	0.000000
Manure 40 : Manure 10	12.59	0.000413
Topsoil 40 : Manure 10	19.44	0.000000

Table 2.5. Height interactions in week 4 for *Hordeum vulgare*.

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum100	18.75	0.000000
Topsoil 10 : Phosphogypsum100	17.96	0.000000
Manure 20 : Phosphogypsum100	19.16	0.000000
Topsoil 20 : Phosphogypsum100	22.95	0.000000
Manure 40 : Phosphogypsum100	22.15	0.000000
Topsoil 40 : Phosphogypsum100	23.26	0.000000
Topsoil 5 : Topsoil 0	18.75	0.000000
Topsoil 10 : Topsoil 0	17.96	0.000000
Manure 20 : Topsoil 0	19.16	0.000000
Topsoil 20 : Topsoil 0	22.95	0.000000
Manure 40 : Topsoil 0	22.15	0.000000
Topsoil 40 : Topsoil 0	23.26	0.000000
Topsoil 5 : Manure 5	13.48	0.000001
Topsoil 10 : Manure 5	12.69	0.000004
Manure 20 : Manure 5	13.89	0.000000
Topsoil 20 : Manure 5	17.68	0.000000
Manure 40 : Manure 5	16.88	0.000000
Topsoil 40 : Manure 5	17.99	0.000000
Manure 10 : Topsoil 5	-12.95	0.000002
Topsoil 10 : Manure 10	12.16	0.000010
Manure 20 : Manure 10	13.36	0.000001
Topsoil 20 : Manure 10	17.15	0.000000
Manure 40 : Manure 10	16.35	0.000000
Topsoil 40 : Manure 10	17.46	0.000000

Table 2.6. Height interactions in week 6 for *Hordeum vulgare.*

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum	12.56	0.004526
Topsoil 10 : Phosphogypsum	18.91	1.7E-06
Manure 20 : Phosphogypsum	19.56	7E-07
Topsoil 20 : Phosphogypsum	14.19	0.000715
Manure 40 : Phosphogypsum	16.25	9.79E-05
Topsoil 40 : Phosphogypsum	16.83	2.68E-05
Topsoil 5 : Topsoil 0	12.56	0.004526
Topsoil 10 : Topsoil 0	18.91	1.7E-06
Manure 20 : Topsoil 0	19.56	7E-07
Topsoil 20 : Topsoil 0	14.19	0.000715
Manure 40 : Topsoil 0	16.25	9.79E-05
Topsoil 40 : Topsoil 0	16.83	2.68E-05
Topsoil 5 : Manure 5	12.55	0.004575
Manure 10 : Manure 5	5.51	0.74979
Topsoil 10 : Manure 5	18.90	1.7E-06
Manure 20 : Manure 5	19.55	7E-07
Topsoil 20 : Manure 5	14.18	0.000724
Manure 40 : Manure 5	16.24	9.91E-05
Topsoil 40 : Manure 5	16.82	2.71E-05
Topsoil 10 : Manure 10	13.39	0.001805
Manure 20 : Manure 10	14.04	0.000853
Topsoil 20 : Manure 10	8.67	0.157852
Manure 40 : Manure 10	10.73	0.037289
Topsoil 40 : Manure 10	11.31	0.016459

Table 2.7. Height interactions week 8 *Hordeum vulgare*.

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum	12.38	0.049293
Topsoil 10 : Phosphogypsum	17.01	0.000981
Manure 20 : Phosphogypsum	17.37	0.000694
Manure 40 : Phosphogypsum	13.87	0.021267
Topsoil 40 : Phosphogypsum	14.93	0.006517
Topsoil 10 : Topsoil 0	17.01	0.000981
Manure 20 : Topsoil 0	17.37	0.000694
Topsoil 20 : Topsoil 0	14.23	0.011779
Manure 40 : Topsoil 0	13.87	0.021267
Topsoil 40 : Topsoil 0	14.93	0.006517
Topsoil 5 : Manure 5	17.39	0.000681
Topsoil 10 : Manure 5	22.02	5.6E-06
Manure 20 : Manure 5	22.38	3.7E-06
Topsoil 20 : Manure 5	19.24	0.000107
Manure 40 : Manure 5	18.88	0.000258
Topsoil 40 : Manure 5	19.94	5.18E-05

Table 2.8. ANOVA output for above and below ground biomass.

Biomass	Species	Parameter	Degrees Of Freedom	P Value
Above Ground	*Agropyron* species	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Amendment:Ratio	9	<2e-16
		Residuals	79	
	Hordeum vulgare	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Amendment:Ratio	9	<2e-16
		Residuals	78	
Below Ground	*Agropyron* species	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Amendment:Ratio	9	0.08662
		Residuals	79	
	Hordeum vulgare	Amendment	1	<2e-16
		Ratio	4	<2e-16
		Amendment:Ratio	9	0.002
		Residuals	78	

Table 2.9. ANOVA output for above and below ground biomass.

Biomass	Species	Parameter	Mean Difference
Above Ground	*Agropyron* species	Phosphogypsum : Topsoil	0.5775988
		Phosphogypsum : Manure	
	Hordeum vulgare	Phosphogypsum : Topsoil	1.237487
		Phosphogypsum : Manure	
Below Ground	*Agropyron* species	Phosphogypsum : Topsoil	0.4008163
		Phosphogypsum : Manure	
	Hordeum vulgare	Phosphogypsum : Topsoil	0.7313265
		Phosphogypsum : Manure	

Table 2.10. Above ground biomass interactions for *Agropyron* mix.

Treatments	Mean Difference	P Value
Topsoil 10 : Phosphogypsum 100	1.28	0.000000
Manure 20 : Phosphogypsum 100	0.68	0.020043
Topsoil 20 : Phosphogypsum 100	1.32	0.000000
Manure 40 : Phosphogypsum 100	0.63	0.034392
Topsoil 40 : Phosphogypsum 100	1.58	0.000000
Topsoil 5 : Manure 5	1.01	0.000044
Topsoil 10 : Manure 5	1.36	0.000000
Manure 20 : Manure 5	0.76	0.005549
Topsoil 20 : Manure 5	1.40	0.000000
Manure 40 : Manure 5	0.95	0.000154
Topsoil 40 : Manure 5	0.73	0.006527
Topsoil 10 : Topsoil 5	0.77	0.003095
Topsoil 20 : Topsoil 5	1.24	5E-07
Topsoil 40 : Topsoil 5	0.67	0.033115
Topsoil 10 : Manure 10	1.02	3.37E-05

Table 2.11. Below ground biomass interactions for *Agropyron* mix.

Treatments	Mean Difference	P Value
Topsoil 20 : Phosphogypsum 100	0.81	0.005141
Topsoil 40 : Phosphogypsum 100	0.89	0.001443
Topsoil 20 : Manure 5	0.78	0.008935
Topsoil 40 : Manure 5	0.85	0.002615
Topsoil 10 : Manure 10	0.67	0.073890
Topsoil 20 : Manure 10	0.89	0.001959
Manure 40 : Manure 10	0.66	0.066257
Topsoil 40 : Manure 10	0.97	0.000535
Topsoil 20 : Manure 20	0.68	0.037631
Topsoil 40 : Manure 20	0.76	0.012631

Table 2.12. Above ground biomass interactions for *Hordeum vulgare*.

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum 100	2.055	0.000140
Topsoil 10 : Phosphogypsum 100	3.52	0.000000
Manure 20 : Phosphogypsum 100	3.255	0.000000
Topsoil 20 : Phosphogypsum 100	2.766	1E-07
Manure 40 : Phosphogypsum 100	2.13775	0.000203
Topsoil 40 : Phosphogypsum 100	3.3715	0.000000
Topsoil 5 : Manure 5	2.033222	0.000285
Topsoil 10 : Manure 5	3.498222	0.000000
Manure 20 : Manure 5	3.233222	0.000000
Topsoil 20 : Manure 5	2.744222	3E-07
Manure 40 : Manure 5	2.115972	0.000382
Topsoil 40 : Manure 5	3.349722	0.000000
Manure 10 : Topsoil 5	-1.80464	0.000945
Topsoil 10 : Topsoil 5	1.465	0.021178
Topsoil 40 : Topsoil 5	1.3165	0.094187
Topsoil 10 : Manure 10	3.269636	0.000000
Manure 20 : Manure 10	3.004636	0.000000
Topsoil 20 : Manure 10	2.515636	7E-07
Manure 40 : Manure 10	1.887386	0.001238
Topsoil 40 : Manure 10	3.121136	0.000000
Manure 40 : Topsoil 10	-1.38225	0.064151

Table 2.13. Below ground biomass interactions for *Hordeum vulgare*.

Treatments	Mean Difference	P Value
Topsoil 5 : Phosphogypsum 100	0.903	0.000742
Topsoil 10 : Phosphogypsum 100	1.017	8.06E-05
Topsoil 20 : Phosphogypsum 100	1.448	0.000000
Manure 40 : Phosphogypsum 100	1.180889	5.1E-06
Topsoil 40 : Phosphogypsum 100	1.757	0.000000
Topsoil 5 : Manure 5	0.94	0.000368
Topsoil 10 : Manure 5	1.054	3.79E-05
Manure 20 : Manure 5	0.641	0.054432
Topsoil 20 : Manure 5	1.485	0.000000
Manure 40 : Manure 5	1.217889	2.3E-06
Topsoil 40 : Manure 5	1.794	0.000000
Manure 10 : Topsoil 5	-0.94373	0.000222
Topsoil 40 : Topsoil 5	0.854	0.001823
Topsoil 10 : Manure 10	1.057727	2.09E-05
Manure 20 : Manure 10	0.644727	0.041909
Topsoil 20 : Manure 10	1.488727	0.000000
Manure 40 : Manure 10	1.221616	1.2E-06
Topsoil 40 : Manure 10	1.797727	0.000000
Topsoil 40 : Topsoil 10	0.74	0.012603
Topsoil 20 : Manure 20	0.844	0.002180
Topsoil 40 : Manure 20	1.153	4.7E-06

Table 2.14. Mean chemical properties of substrates.

(mg/kg)	Topsoil	Manure	Phosphogypsum	Mix
Ammonium	9.3 (0.5)	17.3 (1.2)	411.0 (51.2)	381.5 (3.5)
Carbon (total organic % dry weight)	27.4 (0.7)	36.2 (1.6)	0.3 (0.4)	0.4 (0.4)
Copper	3.0 (0.6)	13.3 (1.2)	10.0 (1.7)	9.0 (0.4)
Iron	306.7 (26.6)	40.0 (4.0)	6.7 (0.2)	6.7 (0.2)
Manganese	15.0 (1.0)	27.4 (2.2)	7.0 (1.1)	6.34 (0.2)
Zinc	20.8 (0.5)	88.5 (6.9)	6.8 (1.2)	6.1 (0.4)
Nitrate	2.0 (0.0)	266.7 (25.2)	33.0 (1.0)	32.5 (0.7)
Phosphorus	123.3 (5.8)	4000.0 (100.0)	196.7 (11.6)	190.0 (0.0)
Potassium	1943.3 (63.5)	1803.3 (665.8)	56.3 (2.3)	57.0 (2.8)
Sulphate	1116.7 (89.6)	433.3 (12.5)	1356.7 (55.1)	1325.0 (7.1)
Cation Exchange Capacity	103.3 (5.8)	89.3 (4.6)	6.5 (1.1)	5.9 (0.2)
Electrical Conductivity (dS/m)	3.0 (0.1)	6.2 (0.3)	6.6 (0.4)	6.4 (0.1)
Hydrogen Ions (pH)	7.4 (0.0)	9.2 (0.0)	4.7 (0.0)	4.7 (0.0)

All units are in mg/kg unless otherwise indicated. Mix is 80 % phosphogypsum 20 % topsoil.
Numbers are means followed by standard deviations in brackets.

III. POTENTIAL OF PHOSPHOGYPSUM AMENDED WITH CLAY AND SAND TEXTURED SOILS AS A PLANT SUBSTRATE

1. INTRODUCTION

Phopshopgypsum is a byproduct from phosphate fertilizer production when phosphoric acid is produced from phosphate rock (Rutherford et al. 1994). Phosphogypsum is composed of mainly gypsum and impurities, including residual acids, soluble fluoride, trace elements and naturally occurring radionuclides (Rutherford et al. 1995b). The most common method of producing phosphoric acid is a wet process, where phosphate rock is treated with sulphuric acid and water which results in gypsum, phosphoric acid and hydrogen fluoride (Rutherford et al. 1994). Phosphogypsum is usually stacked in the vicinity of its production site, which will eventually require closure and reclamation.

There are environmental issues associated with phosphogypsum production, stacking and use. Phosphate source rock can contain fluorine which forms hydrogen fluoride during phosphoric acid production (Rutherford et al. 1994a). Fluoride gas emissions are a problem in operational stacks; closed and open stacks have to be concerned with transported dust particles containing fluoride. Fluoride emissions from operational pond water are approximately 0.10 kg/ha/day (Wissa 2002). Vegetation close to phosphogypsum stacks can have elevated concentrations of fluoride which can cause fluorosis if ingested by animals. Luther et al. (2006) found that fresh phosphogypsum leachate contained 31 mg/L of fluoride and weathered phosphogypsum contained 11 mg/L, well above the maximum acceptable limit of 1.5 mg/L for fluoride in drinking water in Canada (Health Canada 2010). Ground water may be contaminated through rain water leaching through stacks over time (Rutherford et al. 1994a) although Rutherford et al. (1994b) found only the first few rinses of phosphogypsum with water have very high concentrations of trace elements. Thus regulations require stacks to have a composite liner system of a 1.5 mm thick high density polyethylene geomembrane on top a compacted clay layer or underneath a compacted phosphogypsum layer (Wissa 2002).

Phosphogypsum can be beneficial for use in agriculture (Rutherford et al. 1994a). It has been used to amend highly weathered soils with low cation exchange capacity, high sodicity soils, acidic soils with high aluminum concentrations and calcareous soils. Phosphogypsum can be a source of calcium, sulphur and phosphate and can increase availability and uptake of other nutrients such as iron and manganese through acidification around plant roots. Phosphogypum

may have potential in anthroposol building for land reclamation. The use of phosphogypsum, a product that is currently treated as waste, as a soil component could be beneficial in many ways including reduction of waste, reduction of stacks on the landscape, reduced stack reclamation and increased soil. With increasing industrialization and associated reclamation, soil building by humans is becoming common.

If phosphogypsum was to be used in building anthroposols for reclamation and/or agricultural uses it would need to be amended to reduce its negative properties. Amendment with soil of various textures could ameliorate the lack of organic matter, lack of some of the major plant nutrients, fine texture and high electrical conductivity of phosphogypsum to make it more hospitable for plant growth and development.

Sand textured soil has large pore spaces and particles that do not have a strong affinity for each other and do not form aggregates readily (Gardner et al. 1999). Sand textured soil has high drainage and aeration due to the large pore spaces. Clay textured soil has a higher tendency to form aggregates.

2. RESEARCH OBJECTIVES

The objective of this research was to determine whether phosphogypsum had potential as a soil building material for anthroposols. Specific research objectives were to determine whether amending phosphogypsum with sand and clay textured soil affected the resulting mix capacity to support plant growth as assessed by plant performance and health.

3. MATERIALS AND METHODS

3.1. Treatments and Experimental Design

The substrate treatments were mixes of phosphogypsum and sandy and clay textured soils. Phosphogypsum and a sandy soil were sourced from Agrium at Fort Saskatchewan, Alberta, and a clay textured soil from a University of Alberta research station near Ellerslie, Alberta. The phosphogypsum was derived from Florida phosphate rock (Nichol 2006) and has been characterized in several other research projects that have used it (Hallin 2007, Jackson 2008, Christensen 2013, Turner 2013). Mixes were 0, 20, 40, 50, 60, 80, 100 % phosphogypsum amended with corresponding percentages of each of the soils. These amendment percentages were designed to determine the ratio at which phosphogypsum could be potentially detrimental to plant growth and development in an anthroposol.

One plant species, *Agropyron elongatum* P. Beauv (tall wheat grass) was used to assess plant response to the substrates. This plant species was selected for the research as it is a native grass commonly used in land reclamation in Alberta and has been used successfully in a variety of greenhouse experiments.

Each treatment was replicated and set up as a complete randomized block in the greenhouse. There were 140 pots with phosphogypsum substrate x 2 amendments (sandy soil, clay soil) x 7 ratios of soil and phosphogypsum x 1 plant species x 10 replicates.

3.2. Greenhouse Procedures

The greenhouse experiment was conducted in a University of Alberta greenhouse and ran for 8 weeks starting in June 2014. The greenhouse temperature was set at 20 to 21 °C with 18 hours of daylight to provide a desirable growing environment for plants.

Prior to seeding, seeds were manually counted and checked for apparent viability using a light table. Germination tests were then conducted. Ten seeds were placed into each of 10 petri dishes on a damp paper towel and put on a window sill for optimal sun exposure. Germination was recorded daily until it ceased. Petri dishes were watered daily as required if dry. After 2 weeks when germination had ceased, the number of germinated seeds was converted to percent. Germination for *Agropyron elongatum* was 92 %.

Phosphogypsum and soils were mixed in a large tub at a laboratory at the University of Alberta in ratios by volume. Large pieces of phosphogypsum were broken up by hand before mixing into the mix to provide a generally homogeneous mixture. All of the mixes were stored in labelled buckets and transported to the greenhouse for potting.

Greenhouse pots were 15.24 cm in diameter and 10.16 cm deep. Each pot had 4 holes in the bottom to provide for drainage. The bottoms of the pots were covered with 2 pieces of landscape fabric cut in 15.24 cm diameter circles to keep material from falling out the bottom. The phosphogypsum mixes were scooped with small garden trowels from the labeled buckets into the labeled pots. The pots were tapped onto the counter to settle the substrates as the pots were filled to within a few cm from the top. The pots were then placed into greenhouse trays and set up in blocks (replicates) in the greenhouse. The blocking was to account for environmental conditions such as ventilation, sun exposure and temperature heterogeneity that was known to occur. The position of pots in each block in the greenhouse was determined randomly, with each pot given a treatment and replicate number. In the final placement of pots, there was one replicate of each treatment in each of the blocks.

Each pot was seeded with 15 seeds. Seeds were evenly distributed on the pot surface by hand, then gently pressed under the surface of the soil with fingers and covered no more than 1 cm deep for optimal germination for that species.

Three pots from each mixture were used to determine field capacity, the water content that would be approximated for each watering of the pots. These pots were watered to saturation, by pouring water slowly and evenly over the soil surface. Approximately 1.5 liters were added to each pot so that it dripped out of the holes and the pots were consistent in the amount of water added. These pots were monitored every 12 hours for qualitative water content. Field capacity was considered reached when water no longer dripped from the bottom and the top of the substrate was damp to the touch. Pot weights were taken before water was added and 12 and 24 hours after water was added. Individual pot weights of the same ratio were averaged. Field capacity water content and mass of water to be added at watering point were then calculated based on these data. The pots were watered every 2 days to approximate field capacity with 100 to 200 mL of water depending on environmental factors such as temperature and greenhouse ventilation.

3.3. Plant Measurements

Plant emergence in each pot was assessed weekly. After 4 weeks, plants were thinned to 6 plants per pot so that they would not become root bound during the experiment. Plants were thinned to 6 plants in each consecutive week if new plants emerged. Plant emergence data reported in results is the total number of plants that emerged over the course of the experiment, which includes total live and dead plants.

Plant height was measured after 4, 6 and 8 weeks. Measurements were made with a ruler from the substrate base to the top of the plant with the tallest stem stretched to its maximum height for each of the plants.

Plant health was evaluated after 4, 6 and 8 weeks using a 5 point scale (Naeth 2013). A value of 5 was assigned to necrotic plants (< 10 % live material); 4 assigned to plants exhibiting some unhealthy symptoms such as chlorosis or wilting (< 25 % live material); 3 assigned to a half dying plant (> 50 % live material); 2 assigned to a mostly healthy plant with little chlorosis (> 75 % green); and 1 assigned to a healthy green plant (> 90 % live plant material). Each pot was assigned an average plant heath value generally representative of all plants in the pot.

At the end of the 8 week experiment a final vegetation assessment was conducted in addition to the above measurements. Leaves were counted for each plant in each pot. The plants that reached the stage of inflorescence were counted. Above ground biomass was determined by

clipping plants at the substrate surface using scissors. Fresh above ground biomass was weighed, placed in paper bags and labelled with the treatment, replicate and species. These samples were taken to the laboratory and oven dried at 80 °C for 48 hours and then weighed again to determine oven dry biomass. After clipping above ground biomass, the remaining contents of each pot were individually dumped into a pan and large chunks of substrate without imbedded roots were taken out by hand, leaving the roots. The roots with residual substrate attached were put in a sieve and rinsed with tap water to remove all substrate materials from the roots. The roots were placed on paper towels to air dry for a short time, then weighed and put into labelled paper bags. Roots were then oven dried and weighed following the same procedure as for above ground biomass.

3.4. Substrate And Plant Tissue Laboratory Analyses

Three samples of each substrate mix were analyzed at Exova laboratories in Edmonton, Alberta using American Public Health Association (APHA) and United States Environmental Protection Agency standard methods. The samples were oven dried at the University of Alberta laboratories at 80 ^{o}C for two days before sending to the laboratory.

Each sample was analyzed for the following properties. Ammonium and nitrate concentrations were determined by potassium chloride extraction (Maynard et al 2008). Available phosphorous and available potassium were determined by the modified Kelowna extraction (Ashworth and Mrazek 1995) and available sulphate was determined by calcium chloride extraction (Byers 1981). Total organic carbon was determined by dry combustion (Nelson and Sommers 1996). The micro nutrients zinc, copper, manganese and iron were determined by diethylenetriamine pentacetic acid extraction (Byers 1981). The soluble ions, calcium, magnesium, sodium, potassium were determined by saturated paste and inductively coupled plasma atomic emission spectroscopy (Miller and Curtin 2008). Cation exchange capacity was determined by ammonium acetate displacement and macro Kjeldahl distillation (Chapman, 1981). The pH was determined by calcium chloride solution and pH meter (Peech, 1981) and electrical conductivity by saturated paste and the electronic conductivity meter.

The oven dried above ground plant tissue was composited for each treatment and analyzed at Maxxam laboratories in Edmonton, Alberta. Fluoride concentration was determined by ion selective electrode method according to standard methods for the examination of water and wastewater (Standard Methods 2006).

3.5. Statistical Analyses

All of the statistical analyses were conducted using base R software (R Core Team 2014). The required assumptions for a two way analysis of variance (ANOVA) were tested by conducting the Shapiro-Wilkes test for normality and the Bartlett's test for equal variances. The two way ANOVA was conducted by soil type and phosphogypsum:soil ratios for plant height and followed with a Tukey's HSD post-hoc test for those comparisons showing significance. A permutational test (package lmperm) was used to run the ANOVA for soil type and phosphogypsum:soil ratio impact on above and below ground biomass since the data did not fit a normal distribution. ANOVA was followed by Tukey's HSD post-hoc test for those comparisons showing significance.

4. RESULTS

4.1. Plant Response To Treatments

Mean plant emergence followed a similar trend for all substrate treatments with exponential growth occurring on day 1 to day 7 of the experiment, then tapering off by day 19 (Figure 3.1). Treatments with the highest plant emergence were sandy soil 20 %, 100 %, 40 % and 80 %. Treatments with the lowest plant emergence were phosphogypsum 100 % and clay soil 20 %, 40 % and 100 %.

Mean plant health was similar at each assessment date for all treatments (Figure 3.2). Plants were generally healthy into week 6. By week 8, plant health was decreasing in all treatments, most noticeably with 100 % and 80 % sandy soil, 100 % clay soil and 100 % phosphogypsum. Healthiest plants were in 50 % clay soil and 40 % and 50 % sandy soil. By week 8 plants with the least favourable growing conditions, like PG and sandy soil treatments were least healthy.

Visual trends showed mean plant height increased with time in all treatments, with treatment differences of only a few cm (Figure 3.3). The main effects of substrate type and ratio of soil to phosphogypsum had statistical significance; however, their interaction, or the treatment that included ratio and soil type together, was not significant (Table 3.1). Although no statistically significant differences were found between these interaction (ratio) treatments, trends were visible (Figure 3.3). At all assessments, plant height was numerically greatest in the mid mixtures of each soil treatment. Plants were initially shorter in sandy than clay soil treatments. In week 6, pure phosphogypsum, 20 % sandy or clay soil, and 100 % clay soil had the shortest plants, with tallest plants in clay soil 50 % and 80 % and sandy soil 100 %. By the end of the experiment the shortest plants were in phosphogypsum 100 % and clay soil 100 %. Most amendments resulted in plants

that were taller than those in pure phosphogypsum.

Soil type, ratio and the interaction between these two main factors all had a significant effect on both above and below ground plant biomass (Figure 3.4, Table 3.1). Above and below ground biomass were significantly higher in clay soil and phosphogypsum mixes than in sandy soil and phosphogypsum mixes (Figure 3.4, Table 3.2). Any rate of sand added to phosphogypsum increased below ground biomass relative to pure phosphogypsum (Figure 3.4). Mixtures of clay and phosphogypsum increased below ground biomass relative to pure phosphogypsum and pure clay soil and clay 80 % (Figure 3.4). Interactions between treatments in above ground biomass show that all ratios of clay except for pure clay were significantly higher than all other treatments (Figure 3.4, Table 3.3). Interactions between below ground biomass show that pure clay soil and pure phosphogypsum were significantly lower than all other clay mixes, sandy soil 50 % and sandy soil 20 % (Figure 3.4, Table 3.4).

With further investigation of treatment interaction effects on above ground biomass, pure clay soil substrate significantly reduced biomass relative to all other clay mixes except clay 80 % (Figure 3.4, Table 3.3). Pure phosphogypsum had significantly less above ground biomass than clay 60 %, 40 % and 20 %. Significant differences were also found in below ground biomass between pure clay and all other clay mixes, where the pure clay had a significantly lower biomass (Figure 3.4, Table 3.4). Pure clay biomass was significantly lower than that of sandy soil 20 % and 50 %.

4.2. Chemical Properties Of Substrates And Plant Tissue

Plant tissue grown in clay soil substrates had the lowest concentrations of fluoride and those that were grown in phosphogypsum had the highest concentrations of fluoride (Table 3.5). The highest amounts of phosphogypsum in substrate mixtures were associated with the highest fluoride concentrations in plant tissue. Soil concentrations of fluoride were lowest in pure soil, whether sandy or clay textured, and these concentrations increased considerably with any amount of phosphogypsum.

Phosphogypsum mixes had higher concentrations of phosphorous, sulphate, copper, calcium, sodium and potassium than pure sandy and clay soils (Table 3.6). Electrical conductivity and pH of phosphogypsum was higher than pure sand and clay soils. Mixes of phosphogypsum and clay soil and phosphogypsum and sandy soil were similar to each other in properties.

5. DISCUSSION

Plant performance in the greenhouse was as expected for the species under controlled

conditions. Regular watering and the fertilizer application in week 6 likely helped to keep the plants healthy throughout most of the experiment, regardless of substrate. By week 8, the greatest declines in plant health were associated with the least favourable growing conditions, like pure phosphogypsum and sandy soils. By this time health will normally decrease in greenhouse plants and may be associated with reduced pot volume for root growth and low water holding capacity which cannot meet the plant water requirements.

Plant response to substrate clearly showed the beneficial effects of adding sandy and clay soils to phosphogypsum to create a substrate. This is likely due to plants receiving maximum benefits from both phosphogypsum and the clay or sandy soil. Phosphogypsum would provide more nutrients but would have lower water holding capacity and other benefits associated with organic matter in a substrate.

The lowest emergence in pure phosphogypsum may have been affected by the small crust that formed on the phosphogypsum surface, creating a hard cement like layer, which may have impeded seed germination and seedling emergence. Sand could provide higher porosity and thus better root growing conditions if water stress was not an issue. Clay could provide more nutrient adsorption and release, as well as higher water holding capacity. Tallest plants in mixtures with approximately 50 % of each substrate may be due to the plants receiving maximum benefits from both substrates. The higher biomass in clay soil than sandy soil mixes are likely due to nutrient adsorption, water holding capacity, electrical conductivity and cation exchange capacity differences.

For use in reclamation in Alberta, substrates must meet specific soil quality criteria (Soil Quality Criteria Working Group, 1987). Requirements differ for three regions in Alberta, the plains region, the northern forest region and the eastern slopes region, and whether the material will be purposed for topsoil or subsoil.

For the plains region, pH of any of the sandy soil mixes except for sand 80 % would be categorized as good for suitable topsoil (Table 3.6). Clay 80 and sand 80 % would be categorized as fair, while the rest of the mixes would be categorized as poor. Based on electrical conductivity only sand 80 % would be categorized as good; the rest of the treatments would be categorized as fair. Based on sodium adsorption ratio all of the treatments would be categorized as good. For subsoil in the plains region, pH would be categorized the same as that discussed for topsoil. Based on electrical conductivity and sodium absorption ratio all treatments would be categorized as good.

For the northern forest region of the province for topsoil, all clay soil mixes and clay soil and

phosphogypsum alone would be categorized as good based on pH. All sand mixes except for sand 80 % would be classified as fair, and sand 80 % would be classified as poor. Based on electrical conductivity only sand 80 % would be classified as good, and the rest of the phosphogypsum soil mix treatments would be categorized as fair. Based on sodium adsorption ratio all of the treatments would be categorized as good. For subsoil in the northern forest region, based on pH all clay mixes, pure clay soil, pure phosphogypsum and sand 50 % would be categorized as good, all other mixes would be categorized as fair. Based on electrical conductivity and sodium adsorption ratio all treatments would be categorized as good for reclamation uses.

For the eastern slopes region for root zone substrate, all clay soil mixes, clay soil and phosphogypsum alone would be categorized as good based on pH; all sand mixes except for sand 80 % would be categorized as fair, and sand 80 % would be categorized as poor. Based on electrical conductivity only sand 80 % would be categorized as good and the rest of the treatments would be categorized as fair. Based on sodium adsorption ratio all of the treatments would be categorized as good.

Overall, sandy soil mixes would work well in the plains region. In the northern plains region clay soil mixes and pure phosphogypsum would be a good substrate for use. Clay mixes would be best in the eastern slopes region but most sand mixes would work as well.

The Canadian Council of Ministers of the Environment (CCME) soil guidelines for the protection of human and environmental health allows for a maximum of 200 mg/L of fluoride for agricultural use and 400 mg/L for residential use. Based on fluoride, all mixes except for pure sandy soil would not be acceptable for agricultural use and only pure sandy soil and pure clay soil would be acceptable for residential use.

6. CONCLUSIONS

Phosphogypsum may have potential for use in anthroposol building if it is amended. Adding clay and sandy textured soils to phosphogypsum improved plant response of above and below ground biomass relative to pure phosphogypsum and pure soil. Clay soil mixes with phosphogypsum resulted in higher above and below ground biomass than sandy soil mixes with phosphogypsum. Although no statistically significant effect was found on height by the treatments, visual trends showed that mid range mixtures of both soil types resulted in greatest height of plants.

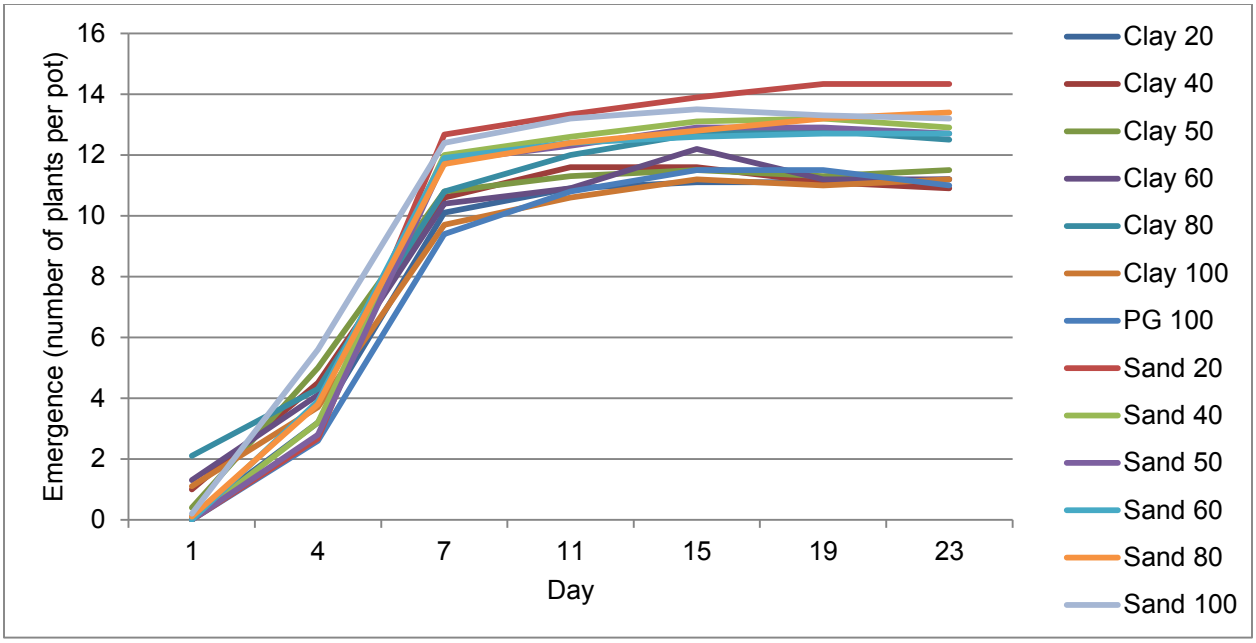

Figure 3.1. Mean plant emergence over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with clay and sand textured soils.

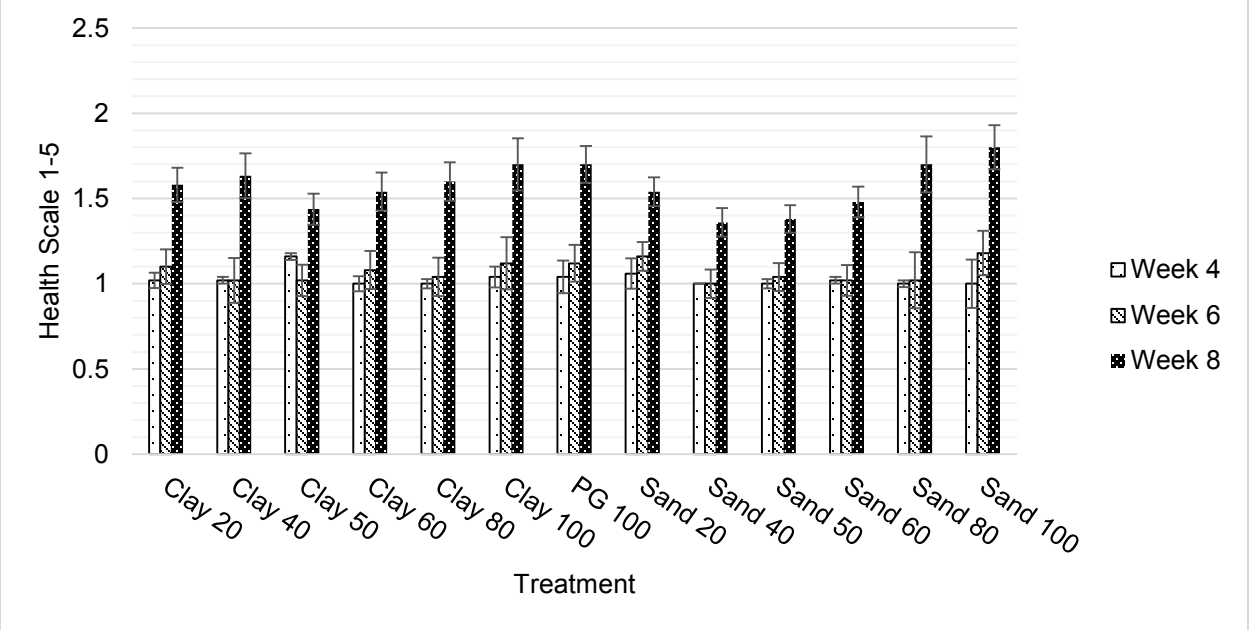

Figure 3.2. Mean plant health over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with clay and sand textured soils.

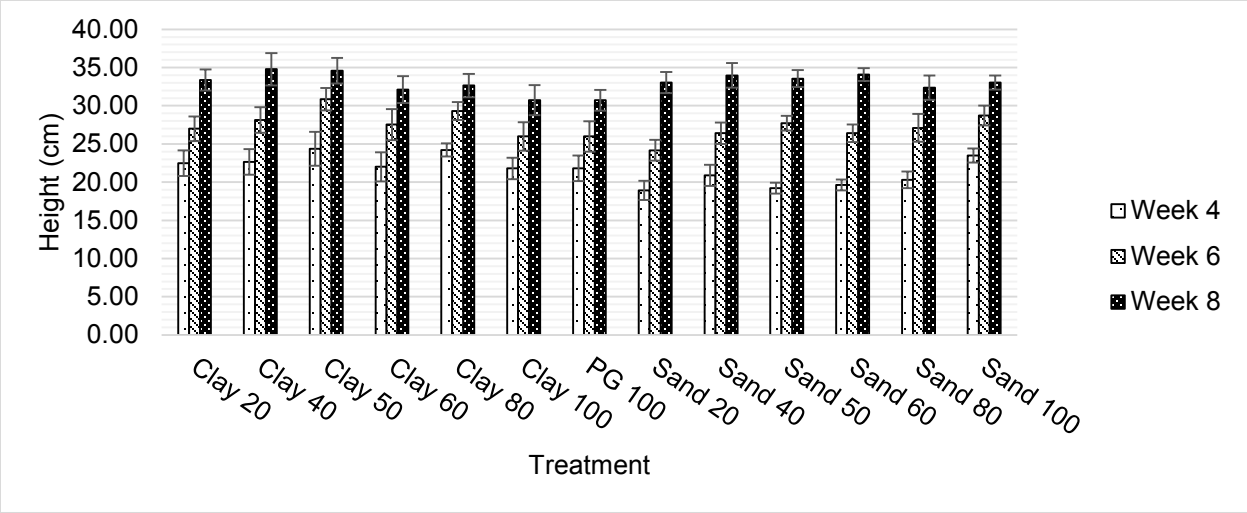

Figure 3.3. Mean plant height over 8 weeks in treatments of volumetric ratios (%) of phosphogypsum (PG) with clay and sand textured soils.

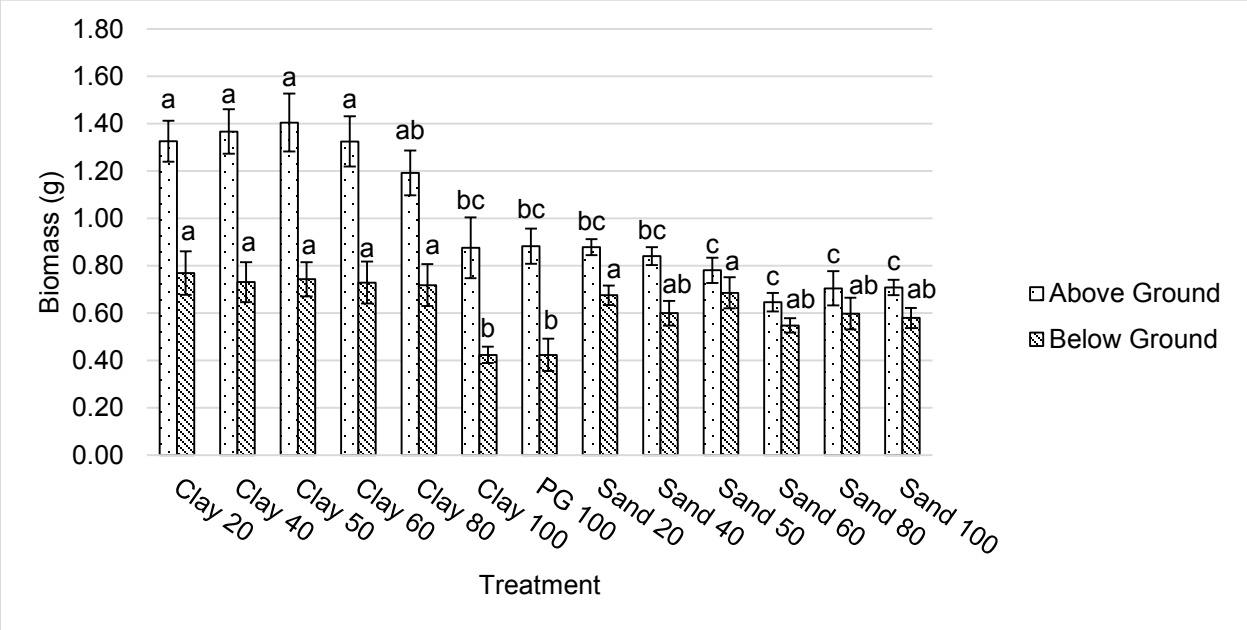

Figure 3.4. Mean above and below ground biomass dry weight at week 8 in treatments of volumetric ratios (%) of phosphogypsum (PG) with clay and sand textured soils. Letters indicate significant differences within weeks.

Table 3.1. ANOVA output for weeks 4, 6 and 8 plant height and below and above ground biomass for week 8.

	Parameter	Degrees Of Freedom	P Value
Height Week 4	Soil	1	0.000561
	Ratio	6	0.000464
	Block	9	0.000000
	Soil:Ratio	6	0.237300
	Residuals	117	1.250000
Height Week 6	Soil	1	0.041300
	Ratio	6	0.000011
	Block	9	0.000000
	Soil:Ratio	6	0.276300
Height Week 8	Soil	1	0.611000
	Ratio	6	0.147000
	Block	9	0.000000
	Soil:Ratio	6	0.320000
	Residuals	117	
Above Ground Biomass	Soil	1	<2e-16
	Ratio	6	<2e-16
	Block	9	0.219000
	Soil:Ratio	6	<2e-16
	Residuals	117	
Below Ground Biomass	Soil	1	0.02003
	Ratio	6	<2e-16
	Block	9	<2e-16
	Soil:Ratio	6	0.00840
	Residuals	117	

Table 3.2. ANOVA output for biomass.

Biomass	Parameter	Mean Difference
Above Ground	Phosphogypsum-Sand : Phosphogypsum-Clay	-0.416428
Below Ground	Phosphogypsum-Sand : Phosphogypsum-Clay	-0.060857

Table 3.3. Statistical details for above ground biomass interactions.

Treatments	Mean Difference	P Value
Clay 60 : Clay 100	0.472182	0.002300
Clay 50 : Clay 100	0.529	0.000464
Clay 40 : Clay 100	0.467333	0.005835
Clay 20 : Clay 100	0.45	0.006808
Clay 80 : Sand 100	0.484	0.002245
Clay 60 : Sand 100	0.640182	3.3E-06
Clay 50 : Sand 100	0.697	6E-07
Clay 40 : Sand 100	0.635333	0.000015
Clay 20 : Sand 100	0.618	1.52E-05
Sand 80 : Clay 80	-0.487	0.002029
Sand 60 : Clay 80	-0.53	0.000448
Sand 50 : Clay 80	-0.411	0.021987
Clay 60 : Sand 80	0.643182	2.9E-06
Clay 50 : Sand 80	0.7	5E-07
Clay 40 : Sand 80	0.638333	1.33E-05
Clay 20 : Sand 80	0.621	1.35E-05
Sand 60 :Clay 60	-0.68618	4E-07
Sand 50 : Clay 60	-0.56718	6.71E-05
Sand 40 : Clay 60	-0.50718	0.000663
Sand 20 : Clay 60	-0.46918	0.002549
Phosphogypsum 100 : Clay 60	-0.46518	0.002922
Clay 50 : Sand 60	0.743	1E-07
Clay 40 : Sand 60	0.681333	2.4E-06
Clay 20 : Clay 60	0.664	2.3E-06
Sand 50 : Clay 50	-0.624	0.000012
Sand 40 : Clay 50	-0.564	0.000127
Sand 20 : Clay 50	-0.526	0.000518
Phosphogypsum 100 : Clay 50	-0.522	0.000598
Clay 40 : Sand 50	0.562333	0.000237
Clay 20 : Sand 50	0.545	0.000258
Sand 40 : Clay 40	-0.50233	0.001900
Sand 20 : Clay 40	-0.46433	0.006402
Phosphogypsum 100 : Clay 40	-0.46033	0.007237
Clay 20 : Sand 40	0.485	0.002171
Sand 20 : Clay 20	-0.447	0.007480
Phosphogypsum 100 : Clay 20	-0.443	0.008472

Table 3.4. Statistical details for below ground biomass interactions.

Treatments	Mean Difference	P Value
Clay 80 : Clay 100	0.294	0.002872
Clay 60 : Clay 100	0.292	0.002160
Clay 50 : Clay 100	0.319	0.000710
Sand 50 : Clay 100	0.262	0.014727
Clay 40 : Clay 100	0.323	0.000943
Clay 20 : Clay 100	0.345	0.000151
Sand 20 : Clay 100	0.252	0.023571

Table 3.5. Mean total fluoride concentrations in plant tissue and soil treatments.

Treatment	Fluoride Plant (mg/kg)	Fluoride Soil (mg/kg)
Sand 100	24	140
Sand 80	25	1200
Sand 60	25	2500
Sand 50	23	2300
Sand 40	21	1900
Sand 20	28	1200
Phosphogypsum 100	31	2500
Clay 100	<20	250
Clay 80	<20	1100
Clay 60	20	3600
Clay 50	<20	2400
Clay 40	22	1600
Clay 20	23	1500

Table 3.6. Mean chemical properties of substrates.

Concentration (mg/kg)	PG 100	Sand 20	Sand 40	Sand 50	Sand 60	Sand 80	Sand 100	Clay 20	Clay 40	Clay 60	Clay 80	Clay 100
Nitrate	19	20	24	27	25	21	23	25	48	54	46	52
Phosphorus	100	100	110	110	120	160	10	90	120	100	90	140
Potassium	<25	<25	27	31	39	48	59	42	73	93	123	154
Sulphate	905	914	920	926	939	949	14	929	963	975	984	998
Copper	1.9	1.2	1.0	0.7	0.8	0.6	0.4	1.3	0.7	1.0	1.0	0.4
Iron	9.1	11.0	17.0	16.0	24.0	25.5	41.3	24.7	45.2	51.3	62.2	26.6
Manganese	1.5	1.6	1.9	1.1	2.4	1.5	4.3	2.7	4.7	4.9	6.8	1.9
Zinc	<0.5	<0.5	0.7	0.7	0.9	0.7	1.4	1.2	2.5	3.1	3.5	1.0
Ammonium	5.6	6.2	5.1	2.6	4.2	3.0	1.2	5.6	3.7	3.9	4.6	6.1
Hydrogen Ions (pH)	5.2	6.8	7.1	7.0	7.1	7.2	7.6	5.4	5.3	5.5	5.4	5.4
Electrical Conductivity (dS/m)	2.56	2.55	2.62	2.66	2.69	2.64	0.79	2.62	2.83	2.86	2.84	2.83
Sodium Adsorption Ratio	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.3	0.3	0.3	0.3	0.2

All units are in mg/kg unless otherwise indicated.
All nutrients are available.
PG = phosphogypsum.

IV. HYDRAULIC CONDUCTIVITY AND LEACHATE CHEMICAL PROPERTIES OF PHOSPHOGYPSUM AMENDED WITH SANDY SOIL

1. INTRODUCTION

Phopshopgypsum is a byproduct from phosphate fertilizer production when phosphoric acid is produced from phosphate rock (Rutherford et al. 1994). Phosphogypsum is composed of mainly gypsum and impurities, including residual acids, soluble fluoride, trace elements and naturally occurring radionuclides (Rutherford et al. 1995b). The most common method of producing phosphoric acid is a wet process, where phosphate rock is treated with sulphuric acid and water which results in gypsum, phosphoric acid and hydrogen fluoride (Rutherford et al. 1994). Phosphogypsum is usually stacked in the vicinity of its production site, which will eventually require closure and reclamation.

There are environmental issues associated with phosphogypsum production, stacking and use. Phosphate source rock can contain fluorine which forms hydrogen fluoride during phosphoric acid production (Rutherford et al. 1994a). Fluoride gas emissions are a problem in operational stacks; closed and open stacks have to be concerned with transported dust particles containing fluoride. Fluoride emissions from operational pond water are approximately 0.10 kg/ha/day (Wissa 2002). Vegetation close to active phosphogypsum stacks can have elevated concentrations of fluoride which can cause fluorosis if ingested by animals. Luther et al. (2006) found that fresh phosphogypsum leachate contained 31 mg/L of fluoride and weathered phosphogypsum contained 11 mg/L, well above the maximum acceptable limit of 1.5 mg/L for fluoride in drinking water in Canada (Health Canada 2010). Ground water may be contaminated through rain water leaching through stacks over time (Rutherford et al. 1994a) although Rutherford et al. (1994b) found only the first few rinses of phosphogypsum with water have very high concentrations of trace elements. Thus some jurisdictions have regulation that require stacks to have a composite liner system of a 1.5 mm thick high density polyethylene geomembrane on top a compacted clay layer or underneath a compacted phosphogypsum layer (Wissa 2002).

Phosphogypsum can be beneficial for use in agriculture (Rutherford et al. 1994a). It has been used to amend highly weathered soils with low cation exchange capacity, high sodicity soils, acidic soils with high aluminum concentrations and calcareous soils. Phosphogypsum can be a source of calcium, sulphur and phosphate and can increase availability and uptake of other nutrients such as iron and manganese through acidification around plant roots. Phosphogypum

may have potential in anthroposol building for land reclamation. The use of phosphogypsum, a product that is currently treated as waste, as a soil component could be beneficial in many ways including reduction of waste, reduction of stacks on the landscape, reduced stack reclamation and increased soil. With increasing industrialization and associated reclamation, soil building by humans is becoming common.

Hydraulic functions in soil are important because they have potential to significantly impact plant growth and development. Research is needed to understand the water properties of phosphogypsum relative to soil so that phsophogypsum stacks can be vegetated or for the use of phosphogypsum in reclamation. Hydraulic conductivity is defined as the ability of soil to transmit water (Klute and Dirksen 1986). Soil texture is a determinant of hydraulic conductivity since large pores result in higher saturated hydraulic conductivity and that is often related to a coarser textured soil (Jury et al 2004).

Use of phosphogypsum in building anthroposols for reclamation and/or agricultural uses would require its amendment to reduce its undesirable properties. Hydrologic properties of concern would be the low hydraulic conductivity of phosphogypsum and the chemical properties of the leachate. Leachate properties would be expected to meet relevant regulatory criteria for the land use and jurisdiction in which it occurs.

2. RESEARCH OBJECTIVES

The objective of this research was to determine whether phosphogypsum had potential as a soil building material for anthroposols. Specific research objectives were to determine whether amending phosphogypsum with a sand textured soil affected hydraulic conductivity of the resulting mix and chemical properties of the leachate from the mixes.

3. MATERIALS AND METHODS

3.1. Treatments and Experimental Design

A column experiment to evaluate hydraulic conductivity was conducted at a University of Alberta laboratory in January 2015, set up as a complete randomized design with 4 replicates of each of 7 substrate treatments. Treatments were mixes of phosphogypsum and sandy soil, sourced from Agrium, Fort Saskatchewan. Treatment mixes were 0, 20, 40, 50, 60, 80, 100 % phosphogypsum amended with corresponding percentages of sandy soil (hereafter mixes).

3.2. Hydraulic Conductivity and Leachate Collection Procedures

Hydraulic conductivity was determined by the falling head method (Reynolds 2008). The phosphogypsum and sandy soil were put through a 2 mm sieve separately to create homogeneous sized samples. Transparent acrylic columns, 10 cm in diameter and 40 cm in height, were used for the experiment. Screens were secured to the bottom of each column using cable ties to prevent loss of material out the bottom. Clean, sterilized sand was poured into the bottom 2 cm of each column to prevent smaller sized materials from running through the screen at the bottom of the columns. A funnel with plastic tubing attached was used to fill the columns, starting by placing the tubing at the bottom of the column on top the sand and rotating the tubing around the circumference of the column until it was filled with the mix. The tubing was then moved up the column gradually to create even compaction and material distribution within each column. The columns were filled up to 20 cm above the clean sand surface, then shaken slightly to even out the surface of the substrate on the surface of the column.

Columns were saturated from the top down. A large stand with a ring clamp attached was used to hold the columns up. A funnel attached to a plastic tube was placed on the top of the column with the tube reaching just above the surface. Distilled water was poured through the funnel to fill the column 5 cm above the surface of the mix. This was repeated until the entire column was visibly saturated with water. All of the water leaching through the column was collected for leachate analyses in beakers below the columns.

After saturation, the columns were filled with distilled water to 10 cm above the surface of the mix using the funnel and tubing in the same method previously described. The height was recorded at time zero when the water was poured into the column. Starting at time zero and for every 2 cm that the water surface fell in the column, the time was noted and recorded. When the water level reached the surface of the mix in the column, the time notations were stopped. During this process, the leachate was collected from the bottom of the column until it stopped dripping. Collection of leachate took approximately 10 minutes for the sandy soil and 2 to 3 hours for pure phosphogypsum.

Hydraulic conductivity was calculated using the equation: $K= [L(t_1-t_0) \times \ln [(L+H_0)/(L+H_1)]$; where t_0 is the is the start time (s), t_1 is the recording time (s), L is the sample thickness (cm), H_0 is height of water over substrate sample at t_0 (cm), H_1 is height of water over substrate sample at t_1 (cm) (Hillel, 1971). Each 2 cm drop resulted in a hydraulic conductivity value, for each replicate there were a total of 5 values. These hydraulic conductivities were averaged resulting in one hydraulic conductivity value for each replicate.

3.3. Leachate Laboratory Analyses

Leachate analyses were conducted at a commercial laboratory, Exova Laboratories in Edmonton, Alberta on 3 samples that were randomly selected from among the 4 samples collected during the experiment. American Public Health Association (APHA) 1992 and United States Environmental Protection Agency (USEPA) standard methods were followed for analyses. The samples were sent to the laboratory before a maximum recommended time of 48 hours had elapsed since collection.

Aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, chromium, cobalt, copper, lead, lithium, molybdenum, nickel, selenium, silver, strontium, thallium, tin, titanium, uranium, vanadium and zinc concentrations were determined by inductively coupled plasma mass spectrometry (APHA 3125B, 3120B, EPA 200.2, 200.8). Sulphur, silicone, calcium, magnesium, sodium, potassium, iron and manganese were determined by inductively coupled plasma emission spectroscopy (APHA 3120B). Fluoride was determined by ion chromatography with chemical suppression of eluent conductivity (APHA 4110B). Chloride was determined by automated spectrophotometer ferricyanide method (APHA 4500-Cl-E) and mercury by cold vapour atomic absorption spectrometry (APHA 3112B). Nitrate, nitrite and sulphate were determined by chemical suppression of eluent conductivity (APHA 4110B) and hydroxide, carbonate and bicarbonate were determined by ethylenediaminetetraacetic acid titration (APHA 2320B). Alkalinity was determined by titration (APHA 2320B), pH by electromagnetic method (APHA 4500-H+B) and electrical conductivity by conductivity meter (APHA 2510B).

3.4. Statistical Analyses

Statistical analyses for this experiment were conducted using base R software (R Core Team 2014). The required assumptions for a one way analysis of variance (ANOVA) were conducted using the Shapiro-Wilkes test for normality and the Bartlett's test for equal variances. A permutational test (package lmperm) was used to run the ANOVA for hydraulic conductivity since the data did not fit a normal distribution with equal variances. This test was followed by Tukey's HSD post-hoc of 95 % significance.

4. RESULTS

4.1. Hydraulic Conductivity Response to Treatments

In general as the percent of sandy soil added to phosphogypsum by volume increased, hydraulic conductivity also increased (Figure 4.1, Table 4.1). Highest hydraulic conductivity was in 100 %

soil with a mean of approximately 2.0 x 10^{-2} cm s^{-1}; lowest hydraulic conductivity was in 80 % phosphogypsum at approximately 9.0 x 10^{-4} cm s^{-1}.

The ratio of soil to phosphogypsum in the mixes had a significant effect on hydraulic conductivity (Table 4.2). Adding up to 50 % sand, did not significantly alter hydraulic conductivity; yet adding another 10 % did. Adding even more sand increased hydraulic conductivity even more, and significantly. Phosphogypsum 40 %, 20 % and 0 % had significantly higher hydraulic conductivities than the other treatments, and were also significantly different form each other (Figure 4.1, Table 4.3). Hydraulic conductivity of phosphogypsum 80 % was significantly lower than phosphogypsum 60 %.

4.2. Chemical Properties Of Leachate

Approximately a liter of leachate was collected from each of the treatments. Leachate from mixes with high amounts of phosphogypsum had higher concentrations of aluminum, arsenic, calcium, cobalt, fluoride, manganese, nickel, sodium, sulphate, sulphur, dissolved solids, vanadium, zinc and electrical conductivity than from mixes that had higher amounts of soil (Tables 4.4, 4.5). Phosphogypsum leachate had a pH of approximately 5.6 which generally increased with increasing amounts of soil, and leachate from pure soil was approximately 7.8.

5. DISCUSSION

Phosphogypsum had a fine texture which would result in a low hydraulic conductivity relative to sandy soil. Although the hydraulic conductivity of phosphogypsum is approximately 7 times lower than the sandy soil, it is not different from the hydraulic conductivity of a typical clay soil which ranges from 1.4 x 10^{-4} to approximately 4.0 x 10^{-5} cm s^{-1} (USDA 2015). Adding more than 20 % sandy soil to the phosphogypsum could increase hydraulic conductivity likely by changing the texture of the mix. The hydraulic conductivity of phosphogypsum could be potentially altered by adding different amounts of sandy soil if the anthroposol was going to be used as a reclamation substrate. The sandy soil used in this experiment has a higher hydraulic conductivity than a very fine textured material such as phosphogypsum. Addition of a coarser textured soil to phosphogypsum should increase the hydraulic conductivity; data from this experiment supported that. Adding 60 % soil by volume to pure phosphogypsum would approximately increase the hydraulic conductivity 5 times. The sandy soil used in this experiment would result in the most dramatic effects in hydraulic conductivity of PG mixes, and other textures of soil would be likely to produce different results.

In other parts of this experiment it was noted that a crust formed on the surface of pure phosphogypsum (Chapter III). Adding sandy soil or other coarse textured soils may reduce this characteristic and enhance water entry and movement.

The nickel concentration in phosphogypsum leachate of approximately 15 mg/L is considerably higher than the Canadian Council of Ministers of the Environment (CCME 2014) guideline for nickel concentration for irrigation (0.2 mg/L) and livestock (1.0 mg/L). These high nickel concentrations in this phosphogypsum are due to its inherent properties or most likely from airborne drift from adjacent industries (Turner 2013). Based on the analysis of leachate from the mixes, theoretically mixing phosphogypsum with 60 % sandy soil would reduce the concentration to acceptable levels for livestock, and mixing with 80 % soil would reduce the concentration to approximately acceptable irrigation concentrations.

The 16.6 mg/L of fluoride in pure phosphogypsum leachate is higher than the allowable concentrations of fluoride in fresh water aquatic systems (0.12 mg/L) and irrigation systems (1.0 mg/L) according to CCME (2014). Mixes of phosphogypsum with soil did not result in concentrations below the requirements of the CCME. The 0.67 mg/L in of fluoride in pure soil is below the requirements of irrigation systems but not below those of fresh water aquatic systems. In previous work with phosphogypsum soil mixes (Chapter III) high concentrations of fluoride in phosphogypsum did not result in high concentrations of fluoride taken up by plants and found in plant tissue. Hence there should be little concern with using plants grown on these mixes for forages.

Concentrations of arsenic in leachate from the mixes with high amounts of phosphogypsum were above the allowable limits for aquatic fresh water, aquatic marine and livestock according to CCME (2014); however, they were below criteria for irrigation (1.0 mg/L). Theoretically mixing phosphogypsum with more than 40 % sandy soil would result in the concentration being lowered to below all criteria except for aquatic fresh water.

Based on CCME (2014) criteria for cadmium, neither pure phosphogypsum nor soil leachates would meet the requirements for aquatic life. Pure soil leachate would meet the requirements for irrigation and livestock. Theoretically mixing phosphogypsum with more than 40 % soil would result in a concentration that would meet requirements for irrigation and livestock. Although concentrations of molybdenum were higher in phosphogypsum leachate than soil leachate, all concentrations met the requirements for aquatic life and livestock. Concentrations of zinc in phosphogypsum leachate would not be low enough for aquatic fresh water systems but would meet requirements for livestock. Leachate from soil used would meet requirements for both.

Although the hydraulic conductivity in pure phosphogypsum would be suitable for use as a substrate and the addition of soil to it could increase the hydraulic conductivity to a level suitable for the use, consideration of the leachate component must be addressed and makes the issue more complex. Many of the chemical properties of pure phosphogypsum leachate do not meet CCME (2014) guidelines, however the addition of soil may bring these concentrations below the requirements. From this experiment it is apparent that any addition of more than 40 % soil would reduce most chemical components to below the requirements and would bring the hydraulic conductivity to a more desirable and appropriate rate for use in reclamation.

In general phosphogypsum has an acidic pH and high electrical conductivity which make it a generally poor substrate material for Alberta regions if it were to be used unamended. Amending phosphogypsum with soil could ameliorate these properties sufficiently for it to be used in anthroposol building. Other chemical and organic amendments, such as manure and topsoil discussed in the previous chapter could assist with that as well. These amendments could also be appropriate to use if phosphogypsum were to be reclaimed rather than capped, as is the current practice.

6. CONCLUSIONS

Phosphogypsum may have potential for use in anthroposol building if it is amended with soil. Hydraulic conductivity of phosphogypsum was lower than a sandy soil, although it was within the range of a typical clay or silty soil. Addition of 40 % sandy soil by volume to phosphogypsum increased hydraulic conductivity of the mix compared to pure phosphogypsum, significantly so at 60 % soil amendment. Leachate from pure phosphogypsum had concentrations of nickel, fluoride, arsenic, cadmium, sulphate, nitrate, cobalt, thallium, manganese, selenium, and zinc that were higher than allowable limits for agriculture and aquatic life according to the CCME guidelines. Generally, it appears that the addition of greater than 60 % sandy soil by volume would reduce these concentrations to acceptable levels.

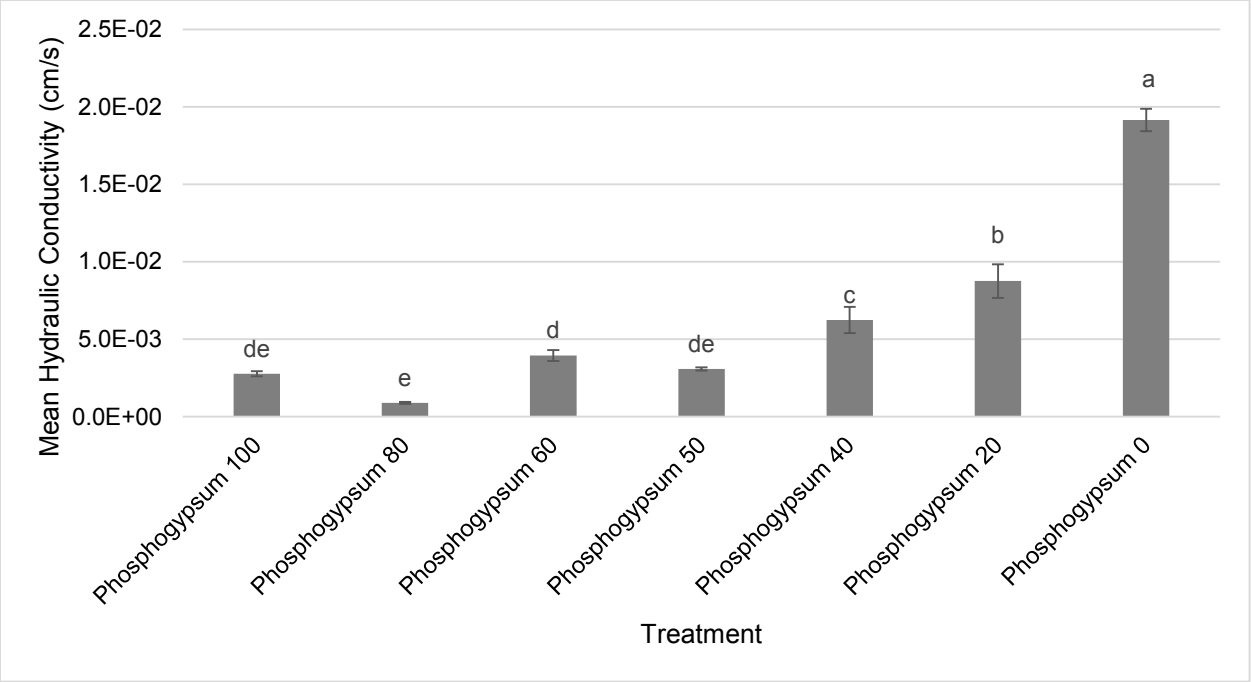

Figure 4.1. Mean hydraulic conductivity in treatments of volumetric ratios (%) of phosphogypsum (PG) with sandy soil. Letters indicate significant differences.

Table 4.1. Mean hydraulic conductivity (x 10^{-3} cm/s) of phosphogypsum:sand mixes.

Treatments	Mean	Standard Deviation
Phosphogypsum 100	2.78	3.27
Phosphogypsum 80	8.95	1.24
Phosphogypsum 60	3.95	7.15
Phosphogypsum 50	3.08	2.06
Phosphogypsum 40	6.25	8.43
Phosphogypsum 20	8.76	2.16
Phosphogypsum 0	19.10	1.46

N = 4

Table 4.2. ANOVA output for hydraulic conductivity.

Parameter	Degrees of Freedom	P Value
Ratio	6	2e-16
Replicate	3	0.6019
Residuals	18	

N = 4

Table 4.3. Statistical details for hydraulic conductivity interactions.

Ratio	Mean Difference	P Value
Phosphogypsum 40 : Phosphogypsum 100	0.003465	0.002820
Phosphogypsum 20 : Phosphogypsum 100	0.005963	0.000002
Phosphogypsum 0 : Phosphogypsum 100	0.01637	0.000000
Phosphogypsum 60 : Phosphogypsum 80	0.003059	0.009475
Phosphogypsum 40 : Phosphogypsum 80	0.005351	0.000011
Phosphogypsum 20 : Phosphogypsum 80	0.007849	0.000000
Phosphogypsum 0 : Phosphogypsum 80	0.018256	0.000000
Phosphogypsum 20 : Phosphogypsum 60	0.00479	0.000055
Phosphogypsum 0 : Phosphogypsum 60	0.015198	0.000000
Phosphogypsum 40 : Phosphogypsum 50	0.003165	0.006913
Phosphogypsum 20 : Phosphogypsum 50	0.005663	0.000005
Phosphogypsum 0 : Phosphogypsum 50	0.01607	0.000000
Phosphogypsum 20 : Phosphogypsum 40	0.002498	0.047115
Phosphogyosum 0 : Phosphogypsum 40	0.012905	0.000000
Phosphogyosum 0 : Phosphogypsum 20	0.010408	0.000000

Table 4.4. Mean chemical properties of phosphogypsum leachate below CCME guidelines.

	Phosphogypsum (%)						
(mg/kg)	100	80	60	50	40	20	0
Antimony	0.002 (0.000)	0.002 (0.000)	0.001 (0.001)	0.001 (0.000)	0.001 (0.000)	0.001 (0.000)	0.001 (0.000)
Barium	0.12 (0.00)	1.70 (0.34)	0.50 (0.11)	1.00 (0.36)	0.30 (0.06)	0.80 (0.07)	0.30 (0.02)
Beryllium	0.001 (0.000)	0.001 (0.000)	0.000 (0.000)	0.001 (0.000)	0.000 (0.000)	0.000 (0.000)	0 (0.000)
Bicarbonate	22.3 (3.2)	45.3 (5.0)	59.3 (26.2)	68.0 (21.2)	78.0 (24.3)	120.0 (12.1)	223.7 (8.1)
Bismuth	0.001 (0.000)	0.005 (0.000)	0.001 (0.001)	0.002 (0.000)	0.001 (0.000)	0.001 (0.000)	0.001 (0.000)
Boron	0.13 (0.00)	0.43 (0.03)	0.23 (0.02)	0.22 (0.04)	0.22 (0.02)	0.10 (0.01)	0.06 (0.00)
Calcium	669.3 (2.1)	2993.3 (46.2)	1049.7 (184.2)	1526.7 (259.3)	760.3 (9.8)	707.3 (14.6)	242.3 (25.9)
Carbonate	6.0 (0.0)	6.0 (0.0)	6.0 (0.000)	6.0 (0.0)	6.0 (0.0)	6.0 (0.0)	6.0 (0.0)
Chloride	1.5 (0.2)	33.7 (0.9)	5.5 (1.9)	12.0 (2.7)	2.8 (0.4)	2.9 (0.4)	4.0 (0.3)
Chromium	0.002 (0.000)	0.005 (0.000)	0.002 (0.001)	0.002 (0.000)	0.001 (0.000)	0.001 (0.000)	0.001 (0.000)
Copper	0.07 (0.01)	0.08 (0.02)	0.03 (0.01)	0.04 (0.00)	0.03 (0.01)	0.02 (0.01)	0.03 (0.02)
Hydroxide	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)	5.0 (0.0)
Iron	0.02 (0.00)	0.10 (0.00)	0.04 (0.02)	0.05 (0.00)	0.02 (0.00)	0.1 (0.06)	0.04 (0.01)
Lead	0.000 (0.000)	0.001 (0.000)	0.000 (0.0002)	0.001 (0.000)	0.000 (0.000)	0.000 (0.000)	0.000 (0.000)
Lithium	0.050 (0.002)	0.060 (0.006)	0.030 (0.006)	0.030 (0.010)	0.020 (0.006)	0.010 (0.006)	0.007 (0.001)
Magnesium	64.5 (5.0)	1146.7 (25.2)	180.7 (54.2)	331.0 (99.7)	75.2 (4.2)	84.4 (5.1)	29.3 (3.0)
Mercury	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Molybdenum	0.01 (0.00)	0.03 (0.00)	0.02 (0.00)	0.02 (0.00)	0.01 (0.01)	0.01 (0.00)	0.00 (0.00)
Nitrite	0.02 (0.00)	0.20 (0.09)	0.04 (0.08)	0.17 (0.01)	0.99 (0.96)	6.00 (0.84)	0.42 (0.08)
Potassium	2.9 (0.3)	42.7 (1.2)	5.4 (1.6)	11.8 (3.0)	3.5 (0.9)	5.2 (0.3)	4.5 (0.4)
Silicon	8.4 (0.6)	12.7 (0.8)	10.9 (1.9)	9.6 (1.0)	13.8 (2.9)	8.0 (1.0)	6.0 (0.2)
Silver	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Sodium	41.2 (2.0)	240.3 (6.0)	39.0 (7.9)	69.5 (19.7)	20.7 (1.7)	14.7 (2.1)	8.7 (0.6)
Strontium	3.0 (0.02)	19.1 (0.2)	3.9 (0.8)	6.4 (1.7)	2.5 (0.08)	1.8 (0.1)	0.6 (0.1)
Sulphur	586.7 (20.5)	719.3 (28.4)	550.3 (30.0)	570.0 (17.3)	609.7 (4.5)	535.0 (12.8)	85.3 (14.8)
Tin	0.002 (0.000)	0.010 (0.000)	0.004 (0.002)	0.005 (0.000)	0.002 (0.000)	0.002 (0.000)	0.001 (0.000)
Titanium	0.001 (0.0)	0.005 (0.0)	0.002 (0.0006)	0.002 (0.0006)	0.001 (0.0)	0.001 (0.0)	0.001 (0.0001)
Uranium	0.001 (0.000)	0.005 (0.000)	0.002 (0.001)	0.002 (0.000)	0.001 (0.000)	0.001 (0.000)	0.004 (0.000)
Vanadium	0.022 (0.000)	0.013 (0.001)	0.008 (0.001)	0.006 (0.000)	0.007 (0.001)	0.003 (0.000)	0.002 (0.000)
EC	2.43 (30.6)	17.2 (346.4)	5.0 (9.0)	6.67 (1329.2)	3.2 (125.8)	2.5 (85.1)	1.2 (102.1)

All units are in mg/kg unless otherwise stated. EC = electrical conductivity in dS/m.
Numbers are means followed by standard deviations in brackets.

Table 4.5. Mean chemical properties of phosphogypsum leachate above CCME guidelines.

	Phosphogypsum (%)						
(mg/kg)	100	80	60	50	40	20	0
Arsenic	0.1 (0.007)	0.03 (0.002)	0.01 (0.001)	0.01 (0.001)	0.008 (0.001)	0.004 (0.0)	0.003 (0.0)
Cadmium	0.01 (0.0)	0.008 (0.002)	0.01 (0.02)	0.01 (0.02)	0.01 (0.02)	0.001 (0.0)	0.005 (0.007)
Cobalt	3.2 (0.2)	5.3 (0.8)	0.2 (0.08)	0.2 (0.07)	0.04 (0.01)	0.04 (0.0)	0.002 (0.001)
Fluoride	16.6 (0.1)	22.7 (1.1)	14.3 (2.4)	18.1 (5.2)	13.2 (0.5)	4.8 (0.3)	0.7 (0.07)
Nickel	14.6 (0.8)	30.2 (3.4)	1.4 (0.04)	1.8 (0.5)	0.3 (0.04)	0.2 (0.006)	0.03 (0.003)
Nitrate	40.5 (6.3)	2890.0 (115.)	506.3 (244.7)	998.3 (324.3)	119.0 (15.5)	68.1 (9.8)	74.7 (5.01)
Selenium	0.004 (0.0002)	0.01 (0.001)	0.003 (0.001)	0.005 (0.0009)	0.002 (0.0)	0.002 (0.0001)	0.003 (0.0001)
Sulphate	1760 (62.45)	2156.67 (83.27)	1650 (91.652)	1706.7 (51.32)	1830 (10)	1603.3 (40.4)	255.67 (43.9)
Thallium	0.0 (0.0)	0.005 (0.0004)	0.0 (0.0001)	0 (0.0001)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Hydrogen ions (pH)	5.6 (0.05)	6.6 (0.04)	6.9 (0.1)	7.2 (0.05)	7.0 (0.05)	7.1 (0.04)	7.8 (0.05)
Zinc	1.5 (0.08)	0.1 (0.03)	0.06 (0.02)	0.03 (0.01)	0.03 (0.02)	0.01 (0.0)	0.01 (0.01)
Manganese	2.4 (0.24)	1.6 (0.5)	0.3 (0.1)	0.3 (0.08)	0.1 (0.05)	0.1 (0.01)	0.05 (0.009)

All units are in mg/kg unless otherwise stated.
Numbers are means followed by standard deviations in brackets.

V. MICROBIAL EXPLORATION OF PHOSPHOGYPSUM AMENDED WITH SANDY SOIL

1. INTRODUCTION

Phopshopgypsum is a byproduct from phosphate fertilizer production when phosphoric acid is produced from phosphate rock (Rutherford et al. 1994). Phosphogypsum is composed of mainly gypsum (calcium sulphate) and impurities including residual acids, soluble fluoride, trace elements and naturally occurring radionuclides (Rutherford et al. 1995b). The most common method of producing phosphoric acid is a wet process, where phosphate rock is treated with sulphuric acid and water which results in gypsum, phosphoric acid and hydrogen fluoride (Rutherford et al. 1994). Phosphogypsum is usually stacked in the vicinity of its production site, which will eventually require closure and reclamation.

There are environmental issues associated with phosphogypsum production, stacking and use. Phosphate source rock can contain fluorine which forms hydrogen fluoride during phosphoric acid production (Rutherford et al. 1994a). Fluorine gas emissions are a problem in operational stacks; closed and open stacks have to be concerned with transported dust particles containing fluoride. Fluoride emissions from operational pond water are approximately 0.10 kg/ha/day (Wissa 2002). Vegetation close to phosphogypsum stacks can have elevated concentrations of fluoride which can cause fluorosis if ingested by animals. Luther et al. (2006) found that fresh phosphogypsum leachate contained 31 mg/L of fluoride and weathered phosphogypsum contained 11 mg/L, well above the maximum acceptable limit of 1.5 mg/L for fluoride in drinking water in Canada (Health Canada 2010). Ground water may be contaminated through rain water leaching through stacks over time (Rutherford et al. 1994a) although Rutherford et al. (1994b) found only the first few rinses of phosphogypsum with water have very high concentrations of trace elements. Thus some jurisdictions have regulations that require stacks to have a composite liner system of a 1.5 mm thick high density polyethylene geomembrane on top a compacted clay layer or underneath a compacted phosphogypsum layer (Wissa 2002).

Phosphogypsum can be beneficial for use in agriculture (Rutherford et al. 1994a). It has been used to amend highly weathered soils with low cation exchange capacity high sodicity soils, acidic soils with high aluminum concentrations and calcareous soils. Phosphogypsum can be a source of calcium, sulphur and phosphate and can increase availability and uptake of other nutrients such as iron and manganese through acidification around plant roots. Phosphogypum may have potential in anthroposol building for land reclamation. The use of phosphogypsum, a product that

is currently treated as waste, as a soil component could be beneficial in many ways including reduction of waste, reduction of stacks on the landscape, reduced stack reclamation and increased soil. With increasing industrialization and associated reclamation, soil building by humans is becoming common.

Use of phosphogypsum in building anthroposols for reclamation and/or agricultural uses would require its amendment to reduce its undesirable properties and enhance its desirable properties. It is not known whether phosphogypsum will affect the microbial composition of soil, a critical element for biological and ecological processes such as element cycling and organic matter production. Very little research has been conducted on the microbiological properties of phosphogypsum. Only one study by Castillo et al. (2012) was found, indicating that sulphate reducing bacteria were found on phosphogypsum stacks on Tinto River and focused on their use in bioremediation. Hence an exploratory assessment would be needed as a starting point to assess microbiological support capabilities of phosphogypsum and its mixes.

2. RESEARCH OBJECTIVES

The objective of this research was to determine whether phosphogypsum had potential as a soil building material for anthroposols. Specific research objectives were to explore the type of microbial community that was present in phosphogypsum and phosphogypsum amended with sandy soil, as assessed by most probable numbers of iron reducing, sulphate reducing, and denitrifying bacteria and fungal and bacterial viable dilution plate count numbers.

3. MATERIALS AND METHODS

3.1. Treatments And Experimental Design

A microbiology experiment was conducted at the University of Alberta laboratories in winter 2015. The experiment was established as a complete randomized design with 6 treatments and 3 replicates. The treatments consisted of phosphogypsum mixed with sandy soil, both collected from Agrium Inc. at Fort Saskatchewan, in ratios of 0, 25, 50, 75 and 100 % by volume.

One 50 % mixture had an added anionic solution (5 % by weight linoleic acid derivative) and a non-ionic (5 % by weight N91-8, linear alcohol ethoxylate surfactant) detergent mixture adjusted to pH 7.0 before application. The anionic solution was used to aid in water infiltration as infiltration was visually hampered by the phosphogypsum and the samples needed to be hydrated for incubation.

3.2. Plate Count And Species Identification Procedure

Phosphogypsum and sandy textured soil were both sourced from Agrium Inc. at Fort Saskatchewan. Substrates were hand mixed at 0, 25, 50, 75 and 100 % by volume of phosphogypsum amended with corresponding percentages of sandy soil. Large pieces of phosphogypsum and soil were broken up by hand to provide a generally homogeneous mixture. Each treatment was measured to fill half a 9 litre tub and maintained to approximate field capacity which was determined visually. The detergent treatment was initially brought to field capacity with distilled water and maintained thereafter with the detergent amended water.

For 3 months prior to the experiment, tubs were incubated in a University of Alberta laboratory. All treatments were incubated with the lids on the tubs, except for during watering. This incubation period was necessary for the phosphogypsum mixes to reach an equilibrium of microbial populations capable of being supported by the mix.

Five boring cores were taken from each tub, one from the center and one from each of the four corners. These cores were mixed to create one composite sample to be researched. This sampling was replicated three times for each treatment. The samples were then put through a 2 mm sieve and 10 g of each sample was added to a 90 mL phosphate buffer dilution blank and shaken for 20 minutes. After the samples were shaken, a dilution series was created by pipetting 10 mL of the shaken solution into a new 90 ml dilution blank; this solution was shaken 10 times and the series was replicated until 5 serial dilutions were achieved. Five grams of each soil sample were set aside and put into the oven for 24 hours at 80 ^{o}C to determine soil water content (Table 5.1).

Plate count agar was made by mixing 23.5 g of Difco plate count agar with 1000 mL of distilled water, autoclaved and poured into petri dishes. Rose bengal agar was created by mixing 17 g of laboratory standard agar, 10 g of malt extract and 10 mL of 1:10,000 dilution rose bengal to 1000 mL of water; the solution was autoclaved and poured into petri dishes. Recipes were according to Difco Laboratories (1984)

Four plates each of rose bengal agar and plate count agar were pipetted with 0.1 mL volumes of each dilution. The plates were rotated and spread with glass spreaders that were sterilized after each plate. Each replicate quartet of dilution inoculated plates were secured with an elastic band and incubated with the cover plates downward in sealed ziploc bags for 14 days.

After two weeks, the dilution from each treatment replicate that contained between 30 and 300 colonies was selected for counting. Each of these plates was assessed for the total number of

bacterial or fungal colonies, and morphologically distinct isolates were chosen from the same counting dilution and circled for later comparison.

After colony assessment, the plates were put back into their air tight containers and two weeks later the morphologically distinct isolates were gram stained. Gram staining was done according to standard procedure by streaking each morphologically distinct bacteria colony on a separate plate and allowing it to grow for one week. One distinct colony was then selected on a sterilized loop and spread onto a microscope slide containing one drop of distilled water. The colony was spread vigorously until dry. The slide was sealed with a few passes over a flame and placed on a tray for the next stage. The slide was then soaked with crystal violet, left for 30 seconds then rinsed with distilled water. Iodine stabilized solution was then dropped onto the slide to completely cover it, left for 30 seconds, then rinsed with a decolorizer (alcohol solution) for 5 seconds followed by distilled water rinsing. Saphranine was then used to counterstain by covering the slide, letting it sit for 30 seconds, then rinsing with distilled water. The slides were air dried and then isolates were viewed with a light microscope using immersion oil on the slide with a 970 times magnification

The gram negative species were further assessed to determine species using the Biomerieux API 20 NE strip, a standardized system for the identification of non-fastidious, non-enteric gram negative rods, combining 8 conventional tests, 12 assimilation tests and a database (Biomerieux Canada Inc 2015). The strip consists of 20 microtubes containing dehydrated substrates. The conventional tests are inoculated with a saline bacterial suspension which reconstitutes the media. During incubation, metabolism produces colour changes that are either spontaneous or revealed by the addition of reagents. The assimilation tests were inoculated with a minimal medium and the bacteria will grow if they are capable of utilizing the corresponding substrate. The reactions were read according to the reading table and the identification was obtained by referring to the analytical profile index or using the identification software provided with the strips.

One to 4 colonies were selected from each isolate plate and mixed with 5 mL of a 0.85 % solution of sodium chloride (NaCl). After the colony was well distributed into the solution, it was pipetted into the first half of the species identification strip. Mineral oil was added on top of the solution for D-glucose (GLU), urea (URE) and L-arginine (ADH). The rest of the solution was poured into the ampule of the main ammonium suphate based agar (AUX) media and mixed using a pipette, that was then used to fill the rest of the wells on the strip. The strips were left for one week and then read using the strip result indicator colours.

3.3. Most Probable Number Procedure

Numbers of culturable sulphate reducing, denitrifying and iron reducing bacteria were determined using most probable number dilutions (Cochrane 1950). Sulphate reducing bacteria were enumerated using a medium of 1 L deionized water with 0.5 g of dipotassium phosphate (K_2HPO_4), less than 1 g of ammonium (NH_4), 2.0 g of sodium sulphate (Na_2SO_4), 1.5 ml of sodium lactate (60%) and 1.0 g of yeast extract with pH 7.1 to 7.2 (Butlin et al. 1949). Denitrifying bacteria cultural media was prepared by dissolving 5 g of potassium nitrate (KNO_3) and peptone into 1 L deionized water with pH 7, excluding the agar in the original formula (Aaronson 1970). Iron reducing bacteria growth media was prepared by dissolving 0.5 g of ammonium sulphate (NH_4SO_4), 0.5 g of sodium sulphate (Na_2SO_4), 0.1 g of dipotassium phosphate (K_2HPO_4), 1.0 g of magnesium sulphate heptahydrate ($MgSO_4.7H_2O$), 5 g of ferric ammonium phosphate and 5 g of nutrient broth into 1 L deionized water (Aaronson 1970). The media were heated over a hot plate and mixed using a magnetic stirrer for complete dissolution. Sodium hydroxide (NaOH) was added to the iron reducing medium to ensure the pH was approximately 7; the other media were already pH balanced. Each of the 3 media were dispensed into 16 x 150 mmm culture tubes (15 mL). The tubed media were autoclaved to sterilize prior to use and capped to prevent contamination. Two small metal nails were added to the sulphate reducing tubes to achieve poising, and a small durham tube was added to the denitrifier tubes open side down.

Eighteen trays of 50 tubes each were prepared. One mL of each of the solutions from the soil dilution series were pipetted into the media tubes. These tubes were incubated or 3 weeks at room temperature and then assessed. The denitrifiers were positive if gas bubbles formed in the small glass tubes; the iron reducers were positive if the clear ferric solution was precipitated as ferrous salts; and sulphate reducers were positive if black sediment formed in the bottom of the tubes around the iron nails.

4. RESULTS

4.1. Plate Counts And Species Identification

The number of bacterial colonies was highest in the 50 % phosphogypsum 50 % sandy soil mix treatment supplemented with the anionic solution (Table 4.2). It was approximately four times the number of the second highest bacterial count which was in phosphogypsum 0 %. Phosphogypsum 100 % and phosphogypsum 25 % had the next highest number of bacterial colonies. Phosphogypsum 75 % and phosphogypsum 50 % had the lowest number of bacterial

colonies. The number of morphologically distinct bacterial isolates was highest in phosphogypsum 75 % and 0 %. However, these treatments only had a mean of one more bacterial isolate than the next highest treatment, phosphogypsum 50 % of both treatments. The treatment that resulted in the lowest number of morphologically distinct isolates (probable bacteria species) was phosphogypsum 100 %.

The number of fungal colonies was highest in the phosphogypsum 50 % with anionic solution treatment (Table 5.2). It was only 1.6 times higher than the next highest treatment, which was phosphogypsum 25 %. The rest of the treatments had much lower fungal colonization than these two treatments, with phosphogypsum 0 % having no fungal colonies present.

The percent of gram positive bacteria was highest in phosphogypsum 100 % (Table 5.3). The amount of gram positive bacteria was higher in the phosphogypsum 50 % mix with the anionic solution than without it. Phosphogypsum 0 % had 40 % gram positive bacteria.

Microbial species present in phosphogypsum 0 % included *Chryseobacterium indologenes* and *Pseudomonas aeruginosa* (Table 5.4). In phosphogypsum 50 % the microbial species found were *Brevundimonas vesicularis*, *Chryseobacterium indologenes* and *Burkholderia* species. In the 50 % phosphogypsum with anionic solution species included *Photobacterium damselae* and *Chryseobacterium indologenes*.

4.2. Most Probable Number

The most probable number for iron reducing bacteria was highest in 50 % phosphogypsum with the anionic solution added (Table 5.5). It was 1.3 times higher than phosphogypsum 50 %, the second highest treatment. The treatment with the lowest number of iron reducers was phosphogypsum 100 %.

The most probable number for denitrifying bacteria was highest in 70 % phosphogypsum. This amount was over 3 times more than the other treatments, except for phosphogypsum 50 % which was lowest. Phosphogypsum 100 %, 25 %, 0 % and 50 % with anionic solution were all similar in number.

The highest most probable number for sulphate reducing bacteria was in phosphogypsum with anionic solution which was approximately 7 times higher than the next highest treatment, phosphogypsum 25 %. The next highest treatment was phosphogypsum 50 %, and the lowest treatment was phosphogypsum 0 %.

5. DISCUSSION

The highest number of bacteria, fungal colonies, iron reducers and sulphate reducers found in Phosphogypsum 50 % with anionic solution was likely due to the anionic solution. This anionic solution is a carbon source, is water soluble and helped water infiltrate into the mix and thus the bacteria and fungi could grow more rapidly in it. The bacteria and fungi that could reproduce the fastest in soil would consume the anionic solution, which is usually gram negative bacteria.

The higher bacterial counts in phosphogypsum 0 % than phosphogypsum 100 % and and the fact that phosphogypsum 100 % bacteria were all gram positive bacteria suggests that the microbial community is less diverse and lower in number than that in soil. However, a community is present nonetheless. Addition of soil up to 75 % by volume did not have a noticeable impact on the number of bacteria present, but it did impact the percent of gram negative bacteria which increased with addition of soil. Depending on the use of the phosphogypsum, the microbial community could be manipulated with the addition of soil.

Interestingly soil had no culturable fungi present in it. This is highly unusual and could be due to the origin or treatment of the soil. The focus of the study however, is that phosphogypsum had a fungal community present in in it, and when soil was added the number did not increase the community. This may have been due to the fact that the soil had no fungi present in it, and if another soil was added that did contain a fungal community results could be different.

In the process of phosphoric acid production, iron would be extracted, leaving phosphogypsum with little iron in it. Therefore, there would not be many iron reducing bacteria evolving in it. This is likely why there was a low iron reducing bacteria count in phosphogypsum. Denitrifying bacteria were present in phosphogypsum and mixes high in phosphogypsum likely because there are many different species of bacteria that can function as aerobes, and when oxygen is not present they will switch to anaerobic and use other terminal electron acceptors. Sulphate reducing bacteria would be present since there is sulphate already in phosphogypsum in the form of calcium sulphate.

The species identified in the mixes were all gram negative due to the procedure used. Therefore no species could be identified from the pure phosphogypsum since the bacteria were all gram positive. In the mixes that species were identified from, *Chryseobacterium indologenes* was present in all of them. This is a yellow bacteria filamentous, non-motile rod that is found naturally in soil and plants. It is a facultative anaerobic chemo-organotroph. In anaerobic conditions, it can use nitrate as the terminal electron acceptor. A species present in 50 % phosphogypsum only was *Brevundimonas vesicularis*, which was not present in soil alone. This is gram negative, motile bacilli. *Pseudomonas aeruginosa* was only present in pure soil. It is gram negative, rod shaped,

asporogenous and monoflagellated. It can respire with wide versatility using many different electron acceptors. It is often found in soil and water.

6. CONCLUSIONS

Phosphogypsum had a microbial community comprised primarily of gram positive bacteria, and fungi. The bacterial population had components that demonstrated both anaerobic denitrification and sulphate reduction. The anionic solution increased the number of bacteria, fungi, iron reducers, sulphate reducers and denitrifiers in the phosphogypsym 50 % mix. The addition of soil to phosphogypsum did increase bacteria counts. If it was added in excess of 75 %, it increased the number of iron reducers and sulphate reducers, and did not increase the number of fungi or denitrifiers.

Table 5.1. Calculations for water content of phosphogypsum soil mixes.

Treatment	Replicate	Wet Weight (g)	Dry Weight (g)	Water Content
Phosphogypsum 100	1	5.5	4.7	0.83
Phosphogypsum 100	2	5.5	4.5	0.78
Phosphogypsum 100	3	5.5	4.5	0.78
Phosphogypsum 75	1	5.5	5.1	0.92
Phosphogypsum 75	2	5.5	5.1	0.92
Phosphogypsum 75	3	5.5	5.1	0.92
Phosphogypsum 50	1	5.5	4.8	0.85
Phosphogypsum 50	2	5.5	4.8	0.85
Phosphogypsum 50	3	5.5	4.8	0.85
Phosphogypsum 25	1	5.5	4.6	0.80
Phosphogypsum 25	2	5.5	4.6	0.80
Phosphogypsum 25	3	5.5	4.6	0.80
Phosphogypsum 0	1	5.5	5.3	0.96
Phosphogypsum 0	2	5.5	5.0	0.90
Phosphogypsum 0	3	5.5	5.0	0.90
Phosphogypsum 50 A	1	5.5	4.8	0.85
Phosphogypsum 50 A	2	5.5	4.7	0.83
Phosphogypsum 50 A	3	5.5	4.7	0.83

A = Anonic solution.

Table 5.2. Mean number of bacterial and fungal colonies in 1 gram of dry soil and morphologically distinct isolates in bacterial plates from treatments of phosphogypsum sandy soil by volume.

Treatment		Mean Colonies	Standard Deviation	Mean isolates
Phosphogypsum 100	Bacteria	1.30×10^7	1.51×10^7	4
	Fungi	3.31×10^4	1.73×10^4	
Phosphogypsum 75	Bacteria	6.49×10^6	2.20×10^6	8
	Fungi	8.28×10^3	4.29×10^3	
Phosphogypsum 50	Bacteria	6.27×10^6	2.93×10^6	7
	Fungi	1.32×10^4	3.17×10^3	
Phosphogypsum 25	Bacteria	1.22×10^7	7.50×10^6	6
	Fungi	1.49×10^5	4.63×10^4	
Phosphogypsum 0	Bacteria	2.77×10^7	3.92×10^7	8
	Fungi	4.83×10^3	2.25×10^3	
Phosphogypsum 50 A	Bacteria	1.05×10^8	7.85×10^7	7
	Fungi	1.78×10^5	7.40×10^4	

A = Anionic solution.

Table 5.3. Mean percent of gram positive bacteria in phosphogypsum:soil treatments.

Treatment	% Gram Positive
Phosphogypsum 100	100
Phospogypsum 50	26
Phosphogypsum 0	40
Phosphogypsum 50 A	55

A = Anonic solution.

Table 5.4. Microbial species identified from phosphogypsum:soil treatments.

Treatment	Species
Phosphogypsum 0	*Chryseobacterium indologenes* *Pseudomonas aeruginosa*
Phosphogypsum 50	*Chryseobacterium indologenes* *Burkholderia* *Brevundimonas vesicularis*
Phosphogyspum 50 A	*Photobacterium damselae* *Chryseobacterium indologenes*

A = Anionic solution.

Table 5.5. Mean most probable number of iron reducers, denitrifiers and sulphate reducers in treatments of phosphogypsum and sandy soil by volume.

Treatment	Bacteria Type	Mean	Standard Deviation
Phosphogypsum 100	Iron reducers	1.20×10^2	3.78×10^1
	Denitrifiers	1.17×10^2	9.92×10^1
	Sulphate reducers	2.83×10^1	1.52×10^1
Phospogypsum 75	Iron reducers	6.17×10^2	4.85×10^2
	Denitrifiers	3.70×10^2	1.11×10^2
	Sulphate reducers	2.00×10^1	7.26×10^0
Phosphogypsum 50	Iron reducers	2.00×10^3	4.32×10^2
	Denitrifiers	2.83×10^1	1.81×10^1
	Sulphate reducers	4.90×10^1	0.00×10^0
Phosphogypsum 25	Iron reducers	3.27×10^2	1.86 x 102
	Denitrifiers	1.17×10^2	1.03×10^2
	Sulphate reducers	1.96×10^2	1.09×10^2
Phosphogypsum 0	Iron reducers	2.78×10^2	3.62×10^2
	Denitrifiers	9.43×10^1	6.69×10^1
	Sulphate reducers	1.01×10^1	5.52×10^0
Phosphogypsum 50 A	Iron reducers	2.70×10^3	1.13×10^3
	Denitrifiers	1.19×10^2	7.40×10^1
	Sulphate reducers	1.45×10^3	1.77×10^3

A = Anionic solution.

VI. SUMMARY, APPLICATIONS AND FUTURE RESEARCH

1. RESEARCH SUMMARY

This research showed a high potential for use of phosphogypsum as a substrate when amended with soil. To vegetate phosphogypsum, some qualities require amelioration. Each experiment was designed to explore the effects of amending phosphogypsum with different amendments in various ratios for optimization of its properties.

Since phosphogypsum has such a fine texture, has little organic matter and lacks some main nutrients required for plant growth, topsoil was the amendment that worked best to enhance or ameliorate the necessary properties, specifically the clay topsoil in ratios from 40 to 60 % by volume. The fine texture of phosphogypsum results in a low hydraulic conductivity which may be problematic for plant growth and water infiltration. Addition of more than 60 % sandy soil resulted in a significant increase in hydraulic conductivity which could be beneficial to water properties and plant growth. Addition of 60 % sandy soil positively impacted the leachate chemistry of phosphogypsum, reducing elevated elements below Canadian Council of Ministers of the environment (CCME 2014) guidelines. Results showed that microbial communities were present in pure phosphogypsum. With the addition of more than 75 % sandy soil, the percentages of gram negative bacteria, sulphur reducers and iron reducers increased. Addition of an anionic solution to the 50 % phosphogypsum and soil mix resulted in numerically higher values for all microbiological components of the community.

2. APPLICATIONS FOR RECLAMATION

It is clear from the research results presented in this thesis that phosphogypsum has good potential to be used as a reclamation soil component when amended with natural soil. Phosphogypsum had properties that improved plant growth, including specific nutrients such as phosphate, sulphate and calcium, which acted as a fertilizer. Phosphogypsum may aid in neutralizing undesirable properties from soils including soils with low cation exchange capacities, calcareous soils and soils low in sulphur or high in magnesium. It may help to ameliorate soils with a very coarse texture. Phosphogypsum has been used as an amendment in agriculture where it has already proven to be effective. This new research shows that there may be further applications in using phosphogypsum as a main substrate material for reclamation and the building of anthroposols. Although not explicitly researched, the research results from this study

support the reclamation of phosphogypsum through use of amendments rather than the current practice of capping. This warrants further investigation.

3. STUDY LIMITATIONS

Main limitations of this study are the amount and types of amendments that could be included in the experiments, given the time frame and budget for the research. The focus was on soils of two textures, clay and sand, although there are many other types of amendments and soil textures that could potentially be evaluated. There were limitations with the number of plant species that could be used in experiments. Native grass species were used in these experiments however there are many other types of plants such as forbs and shrubs or other grass species that count have been used. Microbial assessments were very general, and although they proved that phosphogypsum had microbial communities, the number and types of individual organisms evaluated were limited. Thus the potential for increasing the breadth of uses for phosphogypsum in agricultural and reclamation contexts was only explored on a preliminary basis.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

Future studies may be conducted in the field which would provide a less controlled setting to monitor the implications of variability on the areas of study. More research may be done on the uptake of fluoride in plants from phosphogypsum. The findings in this study show that there was not a lot of plant uptake from the phosphogypsum and soil mixes, but the analysis was done at the end of an 8 week study and more monitoring periods may be necessary. There would be value in evaluating different textures of soil in the column and microbiological studies which had only been conducted with sandy soil in this research. Clay soil would be interesting to study further since it showed optimal results in the greenhouse studies.

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